CHARACTERIZATION OF BIMETAL AND MONO-METAL MONOLAYER PROTECTED CLUSTERS

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A dissertation submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry (Analytical Chemistry).

Chapel Hill, 2007

Approved by:

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ABSTRACT
Alicia D. Douglas: Characterization of Bimetal and Mono-metal Monolayer Protected Clusters
(Under the Direction of Dr. Royce W. Murray)

Chapter One is an introduction to bimetal and mono-metal Monolayer Protected Clusters (MPCs) covering their synthesis, optical properties, electrochemistry, purification, and fractionation.

Chapter Two describes stable AgAu bimetal monolayer protected clusters (MPCs) that have been synthesized via two routes; the core metal galvanic exchange reaction and a modified Brust synthesis. These routes lend themselves to a wide degree of versatility in core metal composition, monolayers, and tunable properties. Luminescence spectroscopy, UV-vis spectroscopy, electrochemistry, transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDX) were used to characterize the MPCs.

Chapter Three describes stable PdAu bimetal monolayer protected clusters (MPCs) that have been synthesized via two routes; the core metal galvanic exchange reaction and a modified Brust synthesis. These routes lend themselves to a wide degree of versatility in core metal composition, monolayers, and tunable properties. Luminescence spectroscopy, UV-vis spectroscopy, electrochemistry, transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDX) were used to characterize the MPCs.
Chapter Four investigates the roles of Ir and Au in the core metal galvanic exchange reaction. The properties observed from reactions between Au MPCs and Ir thiolate, and the reverse Ir MPCs with Au thiolate are discussed. The production of Au nanoparticles from an aged solution of Au(I) thiolate and how they are effecting the core metal galvanic exchange reaction is also investigated. Luminescence spectroscopy, UV-vis spectroscopy, and transmission electron microscopy (TEM) were used to characterize the products.

Chapter Five describes the chromatographic separation of bimetal and mono-metal Tiopronin MPCs with reverse phase ion-pair HPLC. Ag, AgAu, Pd, an PdAu Tiopronin MPCs were separated using both isocratic and gradient elution on a octadecylsilyl (C₁₈) column with tetrabutylammonium fluoride (Bu₄N⁺F⁻) as the ion-pair reagent in methanol/water phosphate buffer solutions. Chromatographic peaks were detected by both absorbance and fluorescence detectors.

Chapter Six investigates the acid/base properties of Au Tiopronin MPCs. Even in a homogenous monolayer, collective effects are observed, which differ from those of individual ligands. Such a system, which exhibits collective effects, is a Au Tiopronin MPC which has a monolayer composed of carboxylic acid terminated ligands. These effects are studied by determining dependence of the Au Tiopronin acid dissociation constant on core size and amount of electrolyte present in solution.
ACKNOWLEDGEMENTS

I would like to thank my research advisor, Dr. Royce W. Murray for the unlimited knowledge and guidance he provided me through my graduate study at the University of North Carolina at Chapel Hill. He is a true inspiration with a great passion for science, and I am honored to have been a member of his lab. I will forever be grateful for all his support, understanding, and patience throughout my graduate career.

I would like to thank both the present and past Murray group members I have had the pleasure of working with though the years. They were always there when needed, and would never hesitate to help. I have created lasting friendships with wonderful people who truly value science.

Finally, I would like to thank my family and friends whom without I would have never made it to where I am today. They believed in me when I could not, and for that I will forever be grateful.
# Table of Contents

List of Figures .............................................................................................................. x
List of Abbreviations and Symbols ............................................................................. xiv

Chapter I. **AN INTRODUCTION TO MONOLAYER PROTECTED CLUSTERS**... 1

1.1 MPC SYNTHESIS.................................................................................................... 1

   1.1.1 Modified Brust Synthesis ............................................................................. 1

   1.1.2 Core Metal Galvanic Exchange Reaction .................................................. 2

1.2 BIMETAL MPCs .................................................................................................... 5

1.3 WATER SOLUBLE MPCs .................................................................................... 6

1.4 OPTICAL PROPERTIES OF BIMETAL MPCs ..................................................... 7

1.5 ELECTROCHEMISTRY OF MPCs ......................................................................... 9

1.6 PURIFICATION AND FRACTIONATION OF MPCs ........................................... 10

1.7 REFERENCES ...................................................................................................... 12

Chapter II. **CHARACTERIZATION OF TIOPRIN-CoATED Ag-Au BIMETAL MONOLAYER PROTECTED CLUSTERS** ................. 18

2.1 INTRODUCTION .................................................................................................. 18

2.2 EXPERIMENTAL .................................................................................................. 22

   2.2.1 Chemicals .................................................................................................... 22

   2.2.2 Synthesis of MPCs ...................................................................................... 22

   2.2.3 Core Metal Galvanic Exchange Reaction ................................................... 23

   2.2.4 Spectroscopic Measurements .................................................................... 23

   2.2.5 Transmission Electron Microscopy (TEM) ................................................. 23
Chapter III. CHARACTERIZATION OF TIOPRONIN-COATED Pd-Au MONOLAYER PROTECTED CLUSTERS

3.1 INTRODUCTION

3.2 EXPERIMENTAL

3.2.1 Chemicals

3.2.2 Synthesis of MPCs

3.2.3 Core Metal Galvanic Exchange Reaction

3.2.4 Spectroscopic Measurements

3.2.5 Transmission Electron Microscopy (TEM)

3.2.6 X-ray Photoelectron Spectroscopy (XPS)

3.2.7 Electrochemistry

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis of Tiopronin MPCs

3.3.2 Core Metal Galvanic Exchange Reaction

2.2.6 X-ray Photoelectron Spectroscopy (XPS)

2.2.7 Electrochemistry

2.3 RESULTS AND DISCUSSION

2.3.1 Spectra of Alloy AgAu Tiopronin MPCs

2.3.2 Solvent Dependence of Alloy AgAu Tiopronin MPC Emission

2.3.3 Core Metal Galvanic Exchange Reaction

2.3.4 Transmission Electron Microscopy

2.3.5 X-ray Photoelectron Spectroscopy

2.3.6 Electrochemistry

2.3.7 Conclusion

2.4 REFERENCES
Chapter IV. CHARTERIZATION OF Ir CONTAINING BIMETAL MONOLAYER PROTECTED CLUSTERS AND AN AGED SOLUTION OF Au(I)[p-SCH₂(C₆H₄)C(CH₃)₃]……………………………………………………... 88

4.1 INTRODUCTION…………………………………………………………………. 88
4.2 EXPERIMENTAL…………………………………………………………………. 89
  4.2.1 Chemicals…………………………………………………………………... 89
  4.2.2 Synthesis of MPCs…………………………………………………………. 89
  4.2.3 Core Metal Galvanic Exchange Reaction………………………………… 90
  4.2.4 Spectroscopic Measurements………………………………………………. 90
  4.2.5 Transmission Electron Microscopy (TEM).………………………………... 91

4.3 RESULTS AND DISCUSSION…………………………………………………. 91
  4.3.1 Au(I) Thiolate……………………………………………………………… 91
  4.3.2 Core Metal Galvanic Exchange Reaction………………………………… 102
  4.3.3 Conclusions……………………………………………………………….. 105

4.4 REFERENCES…………………………………………………………………… 106

Chapter V. REVERSED PHASE ION-PAIR CHROMATOGRAPHY OF TIOPRONIN-COATED MONOLAYER PROTECTED CLUSTERS. 108

5.1 INTRODUCTION………………………………………………………………... 108
5.2 EXPERIMENTAL………………………………………………………………... 109
  5.2.1 Chemicals…………………………………………………………………. 109
  5.2.2 Synthesis of MPCs………………………………………………………... 110
  5.2.3 Reversed Phase Ion-Pair HPLC………………………………………….. 111

5.3 RESULTS AND DISCUSSION…………………………………..…………….. 112
LIST OF FIGURES

Figure 1.1  A cartoon representation of the structure of an MPC. The three regions where
the composition of the MPCs can be modified are marked with asterisks…… 3

Figure 2.1  Structure of tiopronin (a), and a cartoon representing a tiopronin-coated MPC
(b)…………………………………………………………………………………………………… 20

Figure 2.2  Luminescence spectrum (excited at 400 nm), with an expanded view of the
visible region (a), and UV-vis spectrum (b) of 1 µM alloy AgAu Tiopronin
MPCs in H2O………………………………………………………………………………………….. 25

Figure 2.3  Luminescence spectra (excited at 400 nm), with an expanded view of the
visible region, of 1 µM alloy AgAu Tiopronin MPCs in H2O with 0, 40, and
70% ethanol………………………………………………………………………………………… 28

Figure 2.4  Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 µM
galvanic exchanged AgAu MPCs in CH2Cl2 as a function of time. Samples
were prepared from diluted aliquots taken from the reaction mixture
(concentrations were based off the known concentration of Ag Tiopronin
MPCs initially present)…………………………………………………………………………….. 32

Figure 2.5  Luminescence spectra (excited at 400 nm) of 1 µM galvanic exchanged AgAu
MPCs in toluene/ethanol (50:50) and ethanol and upon the addition of Au (I)
thiolate complex to the solution mixture (concentrations were based off the
known concentration of Ag Tiopronin MPCs initially present). Insert shows
an expanded view of the visible region………………………………………………………….. 35

Figure 2.6  Schematic representation of the possible core formations of the bimetal
MPCs……………………………………………………………………………………………. 37

Figure 2.7  Transmission electron micrographs and size histograms of alloy AgAu
Tiopronin MPCs (a) and galvanic exchanged AgAu MPCs (b). HRTEM of
single MPCs are shown in the inserts…………………………………………………………….. 39

Figure 2.8  Energy dispersive spectrum of the AgAu Tiopronin MPCs taken on the TEM
grid from which the image in Figure 2.7a was obtained………………………………. 42

Figure 2.9  High resolution transmission electron micrographs of aged galvanic
exchanged AgAu MPCs taken at two different sites on the TEM grid. Two
compositions were observed, one with large Ag content (a), and one with
large Au content (b)……………………………………………………………………………….. 44

Figure 2.10  X-ray photoelectron spectra of AgAu Tiopronin MPCs of Au4f (a) and Ag3d
(b). The Au 4f peaks are found at 84.2 and 88 eV and the Ag 3d peaks are
found at 368 and 374 eV. From the peak intensities the metals were found to
be at 1:1 ratio……………………………………………………………………………………… 46
Figure 2.11  Cyclic voltammograms of 1 mM Ag Tiopronin MPCs and AgAu Tiopronin MPCs in 0.5 M KOH. The reduction of the thiolate ligands from the metal core occurs for Ag Tiopronin MPCs occurs at -1175 mV, and for AgAu Tiopronin MPCs at -1400 mV.  

Figure 3.1  UV-vis spectra of 1 µM Pd Tiopronin and PdAu Tiopronin MPCs in H2O. 

Figure 3.2  Transmission electron micrographs and size histograms of Pd Tiopronin (a) and PdAu Tiopronin MPCs (b). 

Figure 3.3  X-ray photoelectron spectrum of PdAu Tiopronin MPCs of Au 4d and Pd 3d. The Au 4d peaks are found at 335 and 351 eV and the Ag 3d peaks are found at 335 and 341 eV. From the peak intensities the metals were found to be at 1:1 ratio. 

Figure 3.4  Cyclic voltammograms of 1 mM Pd, Ag, and Au tiopronin MPCs in 5 mL of 0.5 M KOH. The working electrode was a 3mm glassy carbon electrode, the counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl (aqueous) electrode. 

Figure 3.5  Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 µM core metal galvanic exchanged PdAu dodecanethiol MPCs in CH2Cl2 after both 2 min and 4 days of reaction. 

Figure 3.6  Transmission electron micrograph (a) and size histogram (b) of core metal galvanic exchanged PdAu dodecanethiol MPCs. A HRTEM image of a single MPC is shown in the insert. 

Figure 3.7  Energy dispersive spectrum of the core metal galvanic exchanged PdAu dodecanethiol MPCs taken on the TEM grid from which the image in Figure 3.6 was obtained. 

Figure 3.8  Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 µM core metal galvanic exchanged PdAu tiopronin MPCs in CH2Cl2 after both 2 min and 4 days of reaction.

Figure 3.9  Luminescence spectrum (excited at 400 nm) of 1µM Au Tiopronin MPCs. 

Figure 3.10  Transmission electron micrograph (a) and size histogram (b) of core metal galvanic exchanged PdAu tiopronin MPCs. 

Figure 3.11  X-ray photoelectron spectrum of core metal galvanic exchanged PdAu tiopronin MPCs of Au 4d and Pd 3d. The Au 4d peaks are found at 335 and 351 eV and the Ag 3d peaks are found at 335 and 340 eV. From the peak intensities the metals were found to be at 1:1 ratio.
Figure 4.1  Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 μM CH₂Cl₂ solutions from the core metal galvanic exchange reaction between Ir MPCs and Au(I) thiolate after 2 min and 1 month of reaction time……….. 92

Figure 4.2  Luminescence spectrum (excited at 400 nm) (a), and UV-vis spectrum (b) of a 1 month old 1 μM CH₂Cl₂ solution of Au(I) [SCH₂(C₆H₄)C(CH₃)₃] that was not exposed to light before measurements……………………………….. 95

Figure 4.3  High resolution transmission electron micrograph of 1 month old solution of Au(I) [SCH₂(C₆H₄)C(CH₃)₃] in CH₂Cl₂. An enlarged view of a single MPC is shown in the insert…………………………………………………………. 98

Figure 4.4  Luminescence spectrum (excited at 400 nm) of a 1 µM CH₂Cl₂ solution of Au(I) [SCH₂(C₆H₄)C(CH₃)₃] 1 hour after the addition of excess AgNO₃ to the solution mixture………………………………………………………….. 100

Figure 4.5  Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 µM solution in CH₂Cl₂ of core metal galvanic exchanged AuIr tiopronin MPCs after 2 min, 1 hour, and 1 day of reaction time. A magnified view of the visible luminescence spectra is shown……………………………………. 103

Figure 5.1  Isocratic elution of Ag Tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 90% MeOH and 10% water, pH 4.5 phosphate buffer: (a) chromatogram from PMT detector and (b) absorbance spectrum extracted from chromatographic peak at 9 min……………………………………… 113

Figure 5.2  Gradient elution of Ag Tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 100% water to 100% MeOH, pH 4.5 phosphate buffer: (a) chromatograms from PMT (red) and FL (blue) detectors, (b) absorbance spectra, and (c) fluorescence spectra (excited at 400 nm) extracted from labeled chromatographic peaks at 17.5 and 22.5 min respectively………….. 116

Figure 5.3  Chromatogram from PMT detector of gradient elution of Ag Tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 100% water to 100% MeOH, pH 4.5 phosphate buffer. Gradient was repeated; however no further injections were made………………………………………………………………… 118

Figure 5.4  Gradient elution of AgAu tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 65% water to 65% MeOH, pH 4.5 phosphate buffer: (a) chromatograms from PMT (red) and FL (blue) detectors, (b) absorbance spectra extracted from labeled chromatographic peaks at 24, 29, 33, and 42 min respectively…………………………………………………………... 121

Figure 5.5  Isocratic elution of Pd tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 65% MeOH and 35% water, pH 4.5 phosphate buffer: (a) chromatogram from PMT detector and (b) absorbance spectrum extracted from chromatographic peak at 6 min. The absorbance was not found to change at different locations throughout the peak…………………………….. 124
Figure 5.6  Isocratic elution of PdAu tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 65% MeOH and 35% water, pH 4.5 phosphate buffer: (a) chromatogram from PMT detector and (b) absorbance spectrum extracted from chromatographic peak at 17 min………………………………………. 127

Figure 6.1  Titration curves of 1 µM Au Tiopronin MPCs, at different electrolyte concentrations, with 0.01 M NaOH,. The pKₐ values were extrapolated from the curves and found to be 6.1, 5.6, 5.4 and 5.3 with no electrolyte, 0.01 M, 0.05 M, 0.1 M NaNO₃ respectively………………………………………. 135

Figure 6.2  Luminescence spectrum (excited at 400 nm) (a) and UV-vis spectrum (b) of 1µM Au Tiopronin MPCs………………………………………………… 138

Figure 6.3  Titration curves for 1 µM (a ) and 1 mM (b) tiopronin with 0.01 M NaOH (pKₐ=3.5 was extrapolated from both curves)……………………………. 140

Figure 6.4  UV-vis spectra from 1 µM Au Tiopronin MPCs separated by gel electrophoresis, cuts 1 and 8………………………………………………. 143

Figure 6.5  Titration curves of 1 µM Au Tiopronin MPCs, separated by gel electrophoresis (cuts 2, 4, and 6), with 0.01 M NaOH. The pKₐ values were extrapolated from the curves and found to be 5.8, 5.4, and 5.2 for cuts 2, 4, and 6 respectively………………………………………. 145
### LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<td>Silver-silver ion non-aqueous reference electrode</td>
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<td>Bu₄NClO₄</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<td>HPLC</td>
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<td>SAM</td>
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Chapter I

AN INTRODUCTION TO MONOLAYER PROTECTED CLUSTERS

The properties and applications of nanometer size materials and devices have been the subject of intense research for over a decade. Materials such as metal nanoparticles are of considerable interest because they have different chemical, optical, and physical properties than metals at the molecular level and in the bulk. Monolayer protected clusters (MPCs) are nanoparticles composed of a metal core coated with a monolayer of ligands. Gold alkanethiol protected clusters are the most extensively studied MPCs, however there have been reports of MPCs with a variety of other metal cores as well as protection ligands. These MPCs are very robust, where they can be dissolved, dried, and re-dissolved without aggregation and remain stable over time. The properties of the MPCs depend upon their size and composition. In this chapter, the preparation, composition, and properties of mono-metal and bimetal MPCs will be discussed.

1.1 MPC SYNTHESIS

1.1.1 Modified Brust Synthesis. The Brust synthesis was developed in 1994, where a two-phase synthesis yielded stable gold MPCs with a relatively controlled core diameter size of a few nanometers. The general synthetic pathway is believed to be a nucleation, growth, and passivation process, however the intimate details of the mechanism are not fully understood. The synthesis is briefly described; where the gold salt is phase transferred into the organic phase. The addition of thiol leads to the formation of a Au(I) thiolate polymer. A reducing agent is then added, reducing Au(I) to Au°. Au cores are formed from the nucleation of Au°
and the thiols eventually stop growth by passivating the core. The MPCs are washed to remove impurities, and the final product is a fine powder that can be easily handled and functionalized. The structure of a MPC is represented in Figure 1.1. This structure offers three main regions that can be modified; the core, protecting monolayer, and head group of the ligands.

The Brust synthesis is very versatile, and minor modifications can lead to varying different average core sizes, metal cores, and protecting ligands. The general synthesis of various MPCs, encompassing all the minor modifications, has been coined the modified Brust synthesis. The average core size of the MPCs has been found to be dependent upon the thiol ligand to metal mole ratio, solution temperature, addition rate, and quenching time. Smaller average core sizes result from larger thiol ligand to metal mole ratios, colder solution temperatures, faster mixing rates, and shorter reaction times. MPCs consisting of a number of different metal cores including Au, Ag, Pd, Ir, Pt, and Cu, as well as various bimetal combinations of these metals have been characterized. The synthesis of MPCs with protecting ligands varying from non-polar thiols to polar thiols has been achieved. The ligand does not necessarily have to be a thiol, MPCs with ligands such as phosphines have also been synthesized. The solubility of the ligand used will have a direct effect on the solubility of the MPCs. The MPCs ligand coverage can be modified by the ligand place-exchange reaction by which various degrees of mixed monolayers can be obtained. The ligands composing the monolayer can also be functionalized for specific applications.

1.1.2 Core Metal Galvanic Exchange Reaction. Bimetal MPCs can be synthesized by many different synthetic routes including the modified Brust synthesis discussed above, and the core metal galvanic exchange reaction. The core metal galvanic exchange reaction takes place
Figure 1.1 A cartoon representation of the structure of an MPC. The three regions where the composition of the MPCs can be modified are marked with asterisks.
Head Group

Metal Core

Monolayer
between a metal nanoparticle and a salt of a more noble metal. The exact mechanism is not fully understood, however the general concept is that during this reaction the metal within the core of the nanoparticle is replaced with the more noble metal. Since gold is known as the most noble metal, running the reaction with a Au salt is advantageous, however due to the instability of many Au salts, the selection of applicable Au salts is limited. \(\text{Au(I)[p-SCH}_2\text{(C}_6\text{H}_4\text{)C(CH}_3\text{)}_3]}\) is often the Au salt of choice since it is stable and is soluble in a number of organic solvents. This reaction appears to occur as strictly a metal and not a ligand exchange. The existing ligands on the original metal nanoparticles used in the reaction remain. The initial average core size of the metal nanoparticles used in the reaction is also maintained.

The core metal galvanic exchange reaction has been used to yield bimetal nanoparticles encapsulated in dendrimers, bimetal sulfides, bimetal core-shell nanoparticles, and bimetal MPCs. This reaction was first used to yield bimetal AgAu, PdAu, AgPd, and CuAu alkanethiol MPCs by Shon and coworkers. Our lab has also reported the synthesis of AgAu Tiopronin MPCs (tiopronin is N-(2-mercaptopropionyl) glycine) by the use of this reaction. These bimetal MPCs are analogous to those synthesized by the modified Brust synthesis and can be easily handled and functionalized.

1.2 BIMETAL MPCs. Bimetal nanoparticles have been the subject of intense research in recent years. These nanoparticles are of such interest because they are distinctly different from their related mono-metal nanoparticles, where they exhibit different physical, optical and catalytic properties. Among the most common bimetal combinations are AgAu and PdAu. For these metal combinations the most extensively studied properties are the optical and catalytic properties. Nanoparticles containing noble metals such as gold and silver have a surface plasmon band which will be affected by the metal composition of the core and size of
Gold and palladium containing bimetal nanoparticles have been found to enhance catalytic activity. Monolayer protected colloidal bimetal AgAu and PdAu nanoparticles are MPCs that offer a broad range of properties to probe. The properties of these bimetal MPCs are highly dependent upon the composition and size of the MPCs which are largely dependent upon the synthetic procedure. There are numerous different synthetic procedures that yield bimetal MPCs, where two of the most common are the simultaneous reduction of a mixture of metal salts, and the seed mediated growth method. The simultaneous reduction of salts is essentially a modified Brust synthesis, where two different metal salts are used at the beginning of the reaction and various different reducing agents can be employed. The seed mediated growth method consists of the addition of metal ions to metallic seeds. Depending upon the exact synthetic conditions, the size, ligand coverage, and core composition of the MPCs vary. The core structures are of a core/shell or alloy formation, and the solubility of the MPCs is largely determined by the ligand coverage.

### 1.3 WATER SOLUBLE MPCs.

The use of polar ligands as the protecting monolayer on the MPC leads to water-soluble MPCs. There is great interest in water soluble MPCs because they make use of the nanoparticles in biological applications more feasible. These MPCs provide the possible advantages of chemical functionalities such as selectivity and reactivity, and they are also physiologically compatible. MPCs with biologically important ligands such as tiopronin, glutathione, N-acetyel-L-cysteine, N,N,N-trimethyl(mercaptoundecyl) ammonium (TMA), mercaptosuccinic acid, and polyethylene glycol (PEG) thiols have been synthesized and characterized. Various MPCs with different metal cores, including Au, Ag, Pd, and Pt protected by these ligands have been studied. These water soluble MPCs have been functionalized to be used in biological applications such as DNA.
and antibody binding.\textsuperscript{59} Phase transfer of the MPCs can also be achieved by functionalizing the protecting ligands with more non-polar groups.\textsuperscript{60,61} The MPCs stability, distribution, and size remain constant after being phase transferred into the organic phase.

Tiopronin MPCs have been the most extensively studied of the water soluble MPCs. Tiopronin is of particular interest due to its biological importance, where it has been used as a drug for rheumatoid arthritis.\textsuperscript{62} Water soluble tiopronin MPCs have been reported for metal cores consisting of Au,\textsuperscript{14} Ag,\textsuperscript{6} and Pt.\textsuperscript{11} There have been reports of the physical, optical and catalytic properties,\textsuperscript{6,11,63} fractionalization towards use in biological applications,\textsuperscript{58} and modeling of these MPCs.\textsuperscript{64} Furthermore, the terminal carboxylic acid groups on the tiopronin ligand can be used to study the acid/base properties of the MPCs.

1.4 OPTICAL PROPERTIES OF MPCs. The absorbance and luminescence of MPCs are dependent upon their core size, core composition, and ligand coverage. These optical properties are important because they provide some information on the electronic structure of the MPCs. Within the nanometer size range, the smallest MPCs will exhibit molecular like optical properties, with spectral fine structure, whereas the larger MPCs behave more like bulk metals. Furthermore, the optical properties of the various sizes of MPCs will differ depending upon whether the protecting ligand is electron withdrawing or electron donating.\textsuperscript{65}

Large colloidal gold and silver nanoparticles have been shown to display surface plasmon absorption in the visible region that originates from the coherent oscillation of the surface conduction electrons in response to the incident light. For gold MPCs with an average core size greater than 2 nm, a surface plasmon band at 520 nm is observed.\textsuperscript{15} A featureless exponential-like decay, from short to long wavelengths, is observed for Au MPCs with an average core size of 1.6 nm.\textsuperscript{15} For Au MPCs of an even smaller average core size of 1.1 nm, step-like fine structure is observed that is characteristic of molecular like behavior.\textsuperscript{13,66,67} A
surface plasmon band at 480 nm can be observed for Ag MPCs with an average core size of 1.6 nm,\(^6\) meanwhile Pd MPCs do not exhibit a surface plasmon band in the visible region.\(^{48}\) A surface plasmon band is observed for alloy AgAu bimetal MPCs with average core sizes greater than 2 nm, and the location of the band will depend on the Ag to Au ratio.\(^{35}\) For alloy PdAu bimetal MPCs the intensity of the observed surface plasmon band at 520 nm will depend upon the percentage of Au in the MPC.\(^{43}\) Bimetal MPCs in a core-shell formation will behave according to the metal composing the shell of the MPCs.\(^{68}\)

The luminescent properties of MPCs are dependent upon size and surface characteristics. In general luminescence is not favored for metals, due to the lack of an energy band gap. For MPCs with small core sizes a HOMO-LUMO energy gap exists, making luminescence more favorable. More recently, it has been proposed that luminescence can also result from localized electronic surface states,\(^{63}\) where it has been shown that the luminescence intensity is additionally affected by different electronic polarization of the bonds between the core atoms and the thiolate ligands.\(^{65}\) The metal present on the surface of the core and the bonded ligand thus both influence the observed luminescence. The origin of luminescence from the various MPCs is quite complicated. For any given MPC, the size of the core, metal composition of the core, and ligands attached will all affect the observed luminescence emission.

Gold MPCs with cores containing a specific number of atoms such as, Au\(_{11}\),\(^{29,69}\) Au\(_{25}\),\(^{67}\) and Au\(_{75}\),\(^{70}\) and protected with various different ligands have a clear HOMO-LUMO band gap and are more highly luminescent. For those MPCs that have an average core size small enough for a HOMO-LUMO band gap to be observed, the general trend of higher emission energy and quantum efficiency with decreasing core sizes is followed.\(^{71}\) Luminescence is also observed for the larger core sizes, where no HOMO-LUMO band gap is present, of Au\(^{63,72}\) and Ag tiopronin,\(^6\) and Au TMA MPCs.\(^{63}\) The emission intensity is dependent upon the metal core
and the ligands attached, where more polar or charged ligands yield higher emission intensity.\textsuperscript{63,65} The emission energy of these larger MPCs is comparable to that of the smaller core size MPCs and is believed to be controlled by localized core surface states. For both small Au\textsubscript{25} and larger Au\textsubscript{140} MPCs, luminescence can be induced upon running a ligand place-exchange reaction with more polar or charged ligands.\textsuperscript{65} Luminescence from MPCs can also be obtained by functionalizing the MPCs with fluorophores.\textsuperscript{73,74}

1.5 ELECTROCHEMISTRY OF MPCs. The electrochemical properties of MPCs are dependent upon core size, metal composition, and attached ligands of the MPCs. When a MPC is small enough, a single-electron transition can be observed. This is possible because at this small size range the capacitance of the MPC diminishes to a point where the thermal disturbance is less than the energy required to remove one electron. Single electron transfers can be seen in voltammograms of MPCs, where multiple, evenly spaced charging peaks corresponding to single electron transfers are observed.\textsuperscript{75-77} This phenomenon is called quantized double layer (QDL) charging. The MPC can be viewed as a spherical capacitor since the metal core is surrounded by a dielectric medium. Using the capacitor model, the size of the MPC can be estimated. QDL charging has been observed for Au\textsubscript{140}\textsuperscript{75} and Au\textsubscript{225} MPCs.\textsuperscript{78} For smaller core sizes such as Au\textsubscript{25}\textsuperscript{66,67} and Au\textsubscript{75}\textsuperscript{70} the electrochemistry shows a clear HOMO-LUMO band gap, where a smaller electrical band gap is observed for the larger core size.

Electrochemistry can also be used to look at the reductive desorption of the monolayer on the MPC in order to determine the surface coverage of the thiolate. In alkaline solutions the electrochemical reduction of the thiolate ligands from the metal core occurs at negative potentials. This process can be viewed as two capacitors in series including the thiolate head group and hydrocarbon phase. This phenomenon has been observed for thiol self assembled
monolayers (SAM) on Au(111) surfaces, where the less densely packed layers desorb at less negative potentials.79

1.6 PURIFICATION AND FRACTIONATION OF MPCs. The initial product obtained after synthesizing MPCs via the modified Brust synthesis will contain some impurities and can be quite polydisperse in nature.15 Any impurities present will affect the observed properties of the MPCs and therefore must be removed. The core size dispersity of the MPCs will depend upon the exact synthetic conditions, however in all cases some extent of size dispersity is present.1,15 The properties of these MPCs are size dependant even amongst a nanometer difference. The size fractionation of these MPCs is therefore of great importance.

The removal of impurities through the use of solvents in which the impurities are soluble, and the MPCs are not, is the most commonly used method.66,75 This method is limited by the solubility of the MPCs and it is not always possible to find optimal solvents. Dialysis is employed to help in the purification of water soluble MPCs,6 where the use of different solvents is not as applicable. Centrifugation80 and filtration81 are useful in the purification of both organic and water soluble MPCs. Often combinations of the methods are used to obtain the most pure samples possible. Each of these methods lead to some extent of size fractionation as well.

Some synthetic techniques have been aimed at obtaining more monodisperse samples. Etching of the MPCs has been used to decrease the core size82 and annealing of the MPCs have lead to a greater degree of monodispersity,75,76 however these techniques lack control and reproducibility. Other techniques such as heating83 and vapor treatment84,85 have similar limitations. Electrophoretic and chromatographic separations have lead to greater success in the separation and isolation of monodisperse MPCs. These methods include: gel electrophoresis,53,86 capillary electrophoresis,87-90 continuous free-flow electrophoresis,91 size
Exclusion chromatography, reversed phase chromatography, ion exchange chromatography and reversed phase ion-pair chromatography. Depending upon the MPC characteristics, different detection methods are used such as, photodiode array (PDA), electrochemical, and fluorescence detection. These methods can be applied to MPCs with differences in composition of their protecting ligands and metal cores, and span from organic soluble to water soluble MPCs.

The electrophoretic techniques are most commonly used and are most applicable for water soluble MPCs, where they have been used to separate tiopronin and glutathione MPCs. Reversed phase ion-pair chromatography has led to successful separation of water soluble tiopronin and N-acetyl-L-cysteine MPCs. Reversed phase chromatography is most often used to separate organic soluble MPCs with an average core size less than 2 nm, where size exclusion chromatography is often used for MPCs of larger core sizes. All of these separation methods have their advantages and disadvantages, and in general they are complicated and are affected by many factors including core metal, core size, and the characteristics of the ligand coverage.
1.7 REFERENCES


(29) Yang, Y. Y.; Chen, S. W. Nano Letters 2003, 3, 75-79.


2.1 INTRODUCTION

Bimetal nanoparticles, especially those containing either gold or silver, have been the subject of extensive research in recent years. These nanoparticles are of such interest due to their unique optical and catalytic properties. More specifically, nanoparticles containing noble metals such as gold and silver have a surface plasmon band which is affected by the metal composition of the core and size of the core. Gold-containing bimetal nanoparticles have been found to enhance catalytic activity. Furthermore, bimetal nanoparticles are distinctly different from their related mono-metal nanoparticles.

The structure of the core of bimetal nanoparticles can exist in two forms: alloy and core/shell. Many synthetic routes can yield bimetal nanoparticles. Most commonly, alloy nanoparticles are synthesized by the simultaneous reduction of a mixture of metal salts and core/shell nanoparticles by the seed mediated growth method. This is not to say that these methods will respectively always yield alloy or core/shell nanoparticles. There are reports of both core/shell and alloy nanoparticles that are synthesized via the same method. Furthermore, there has also been a report of bimetal nanoparticles that spontaneously change from core/shell to alloy nanoparticles. Bimetal nanoparticles can also be obtained via a core metal galvanic exchange reaction. In this method, presumably
yielding core-shell structure, a mono-metal nanoparticle is reacted with a salt of a more noble metal.

While AgAu bimetal nanoparticles have been widely studied, there are few reports of nanoparticles that have an average core diameter of less than 3 nm.\textsuperscript{2,11,13} The research on mono-metal monolayer protected clusters (MPCs) is well known in the size range of 1-3 nm.\textsuperscript{9,16,17} Not only are these MPCs very small but they also can be isolated and re-dissolved, maintaining their stability. Reported here are two AgAu bimetal MPCs with average core diameters of 2-3 nm. Two different routes to bimetal MPCs were explored: a simultaneous reduction of a mixture of salts, producing presumably alloy MPCs, and a core metal galvanic exchange reaction, producing presumably core/shell MPCs.

The AgAu bimetal MPCs reported here have tiopronin as their protecting ligand. The structure of tiopronin and a cartoon representing a tiopronin-coated MPC can be seen in Figure 2.1. Tiopronin is of particular interest due to its biological importance where it has been used as a drug for rheumatoid arthritis.\textsuperscript{18} Tiopronin MPCs are also water soluble which allows for potential biological applications. Ag and Au Tiopronin MPCs studied to date have been found to both be luminescent.\textsuperscript{19,20} The interesting properties of the mono-metal MPCs lead us to study the bimetal combination of these metals. The AgAu Tiopronin MPCs discussed in this chapter exhibit some unique properties attributed to bimetal nanoparticles. Luminescence spectroscopy and UV-vis spectroscopy were used to study the optical properties of the MPCs, and transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDX), and electrochemistry to further characterize the MPCs.
Figure 2.1 Structure of tiopronin (a), and a cartoon representing a tiopronin-coated MPC (b).
(a)

\[
\text{HS} - \text{CON} - \text{COOH}
\]

Tiopronin

(b)

Tiopronin-coated MPC
2.2 EXPERIMENTAL

2.2.1 Chemicals. HAuCl₄ₓH₂O,⁴¹ triethylammonium monomethyl polyethylene glycol (MePEG-350) hydroxide¹⁰ and Au(I)[p-SCH₂(C₆H₄)C(CH₃)₃]¹⁰ were synthesized according to literature. Silver nitrate (AgNO₃, 99%), N-(2-mercaptopropionyl)glycine (tiopronin, 99%), sodium borohydride (NaBH₄, 99%), tetra-n-butylammonium perchlorate (Bu₄NClO₄, 99%), and tetra-n-butylammonium hydroxide (Bu₄NOH, 99%) were purchased from Aldrich. Methylene chloride (HPLC grade), toluene (HPLC grade), and ethanol (HPLC grade) were purchased from Fisher and used as received. House-distilled water was purified on a Barnstead NANOpure system (≥ 18MΩ).

2.2.2 Synthesis of MPCs. Ag Tiopronin MPCs were synthesized as reported previously.¹⁰ Briefly, AgNO₃ (1.0 g, 5.89 mmol) in 50mL H₂O, N-(2-mercaptotropionyl)glycine (2.8 g, 17.6 mmol) in 20 mL of H₂O, and NaBH₄ (0.6 g, 15.9 mmol) in 15 mL of H₂O were all cooled to 0 °C. All solutions were mixed simultaneously, resulting in a black solution, which was stirred for 30 min. The Ag MPCs were precipitated with 300 mL of methanol, then filtered and washed with methanol, ethanol and acetone. The black powder product was dissolved in 25 mL of H₂O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.

For AgAu Tiopronin MPCs a similar procedure was followed; AgNO₃ (0.06 g, 0.35 mmol) in 10 mL of H₂O and tetrachloroauric acid (0.12 g, 0.35 mmol) in 10 mL of H₂O were cooled to 0 °C, then mixed. To the salt solutions 5 mL of N-(2-mercaptotropionyl)glycine (0.15 g, 0.92 mmol) in 10 mL of H₂O (cooled to 0 °C) was added. The salt solutions were combined and NaBH₄ (0.13g, 3.4 mmol) in 5 mL of H₂O (cooled to 0 °C) was added. The resulting solution was stirred for 30 min. The AgAu MPCs were precipitated with 50 mL of methanol, then filtered and washed with methanol, ethanol and acetone. The black powder
product was dissolved in 25 mL of H$_2$O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.

2.2.3 Core Metal Galvanic Exchange Reaction. Triethylammonium monomethyl polyethylene glycol (MePEG-350) hydroxide was added drop-wise to a 10 mM H$_2$O solution of Ag Tiopronin MPCs until a pH of 8. The water was removed under vacuum and the Ag MPCs were dissolved in CH$_2$Cl$_2$ (10 mM). The CH$_2$Cl$_2$ solution of Ag MPCs was mixed in equal volumes with 0.5 µM Au(I)[p-SCH$_2$(C$_6$H$_4$)C(CH$_3$)$_3$] also in CH$_2$Cl$_2$. The solution mixture was stirred and kept in the dark until the reaction was terminated by removal of the solvent.

2.2.4 Spectroscopic Measurements. For spectroscopic measurements, 3 mL of 1 µM solutions were prepared. Luminescence spectra were taken in a 90° geometry on a modified ISA Fluorolog FL321 spectrometer. The fluorometer was equipped with a 450 W xenon source, and Hamamastsu R928 PMT (visible wavelengths) and InGaAs (near-IR wavelengths) detectors. Near-IR luminescence spectra were taken using a long pass filter, placed in the sample compartment, with cutoff of 450 nm. UV-vis spectra were taken with a Shimadzu UV-1601 UV-visible spectrophotometer.

2.2.5 Transmission Electron Microscopy (TEM). TEM data were obtained on a Hitachi HF-2000 equipped with an Oxford Instruments energy dispersive spectroscopy (EDX) x-ray microanalysis system, operated at 200 kV. The TEM samples were prepared by drop casting onto holey carbon grids (Ted Pella, Redding, CA).

2.2.6 X-ray Photoelectron Spectroscopy (XPS). XPS data were obtained on a Kratos Analytical Axis Ultra with an Al-Kα X-ray source, a hybrid analyzer, charge neutralizer, and a delay-line detector (pass energy 120 eV). Peak positions were referenced to the C 1s peak at 284.9 eV. A survey scan and expanded scans were taken for C 1s, S 2p, Ag 3d and Au 4f.
2.2.7 Electrocchemistry. Voltammetry data were obtained with a Model 100B Bioanalytical Systems, Inc. (BAS) electrochemical analyzer, using 0.5 M KOH degassed solutions. The working electrode was a 3mm glassy carbon electrode, the counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl (aqueous) electrode.

2.3 RESULTS AND DISCUSSION

2.3.1 Spectra of Alloy AgAu Tiopronin MPCs. Visible luminescence and UV-vis spectroscopy of water soluble MPCs has been the topic of several reports.$^{10,19,20}$ Specifically of interest, Au Tiopronin MPCs$^{20}$ with an average core size of 1.8 nm have a broad emission peak centered at 890 nm when excited at 400 nm and exhibits featureless exponential decay absorbance. Also of interest, Ag Tiopronin MPCs$^{10}$ with an average core size of 1.6 nm have a broad emission peak centered at 520 nm when excited at 400 nm and a surface plasmon band at 480 nm. As reported previously$^{19}$ for water soluble MPCs, no luminescence is detected until sodium borohydride is added to the solution mixture to reduce the metal salts to nanoparticles. Solutions of all MPCs reported here were light brown in color.

Figure 2.2A shows the luminescence spectrum of AgAu Tiopronin MPCs when excited at 400 nm. Two broad emission peaks are centered at 520 nm and 890 nm. An expanded view of the visible region of the luminescence spectrum can be seen in the insert in Figure 2.2A. While luminescence centered at 520 nm is evident, it is slightly distorted by the water Raman peak as well as the onset of the peak at 890 nm. The positions of the peaks coincide nicely with the emission peak positions for Ag Tiopronin MPCs and Au Tiopronin MPCs, respectfully. It is believed that the band centered at 520 nm arose from Ag atoms in the core of the MPC and that the band centered at 890 nm is due to Au atoms in the core of the MPC. The presence of both bands suggests that there are both Ag and Au atoms on the core MPC surface, therefore the core is in a AgAu alloy formation. Figure 2.2B shows the absorbance
Figure 2.2  Luminescence spectrum (excited at 400 nm), with an expanded view of the visible region (a), and UV-vis spectrum (b) of 1 μM alloy AgAu Tiopronin MPCs in H$_2$O.
spectrum of AgAu Tiopronin MPCs. A surface plasmon band is observed at 500 nm, which lies between the Ag surface plasmon band at 480 nm\textsuperscript{10} and the Au surface plasmon band at 520 nm.\textsuperscript{17} The position of this surface plasmon band matches the literature value\textsuperscript{1} for AgAu alloy MPCs.

It has been previously reported that the quantum yield of Ag Tiopronin MPCs is 10-fold lower than the quantum yield for the corresponding Au Tiopronin MPCs.\textsuperscript{10} This same trend was observed for the alloy AgAu Tiopronin MPCs where the intensity of the Ag band was found to be sufficiently lower than that of the Au band.

Most recently it has been proposed that the emission is a result of localized electronic surface states.\textsuperscript{20} Additionally it has been shown the luminescence intensity is affected by different electronic polarization of the bonds between the core atoms and the thiolate ligands.\textsuperscript{22} It is from these findings that we can attribute changes in luminescence to changes in the different metals on the surface of the MPC core. For the MPCs studied here the protecting ligand was held constant, therefore, the changes in luminescence are a result of changes in the MPC core. It is clear that the luminescent mechanism is quite complicated, since it appears that both core metal and attached ligands will affect the emission intensity.

2.3.2 Solvent Dependence of Alloy AgAu Tiopronin MPC Emission. AgAu Tiopronin MPCs are soluble in various percentages of ethanol, methanol, and acetonitrile in water. It was found that as long as the MPCs are first dissolved in a small amount of water, up to 99% of the other solvent could be added and the MPCs would stay in solution for up to three days. The luminescence intensity of both emission peaks for the AgAu Tiopronin MPCs vary with solvent composition. As seen in Figure 2.3, as the percentage of ethanol is increased the intensity of the band centered at 520 nm decreases while the intensity of the band at 890 nm increases. The expanded visible region (insert of Figure 2.3) of the luminescence spectra
Figure 2.3  Luminescence spectra (excited at 400 nm), with an expanded view of the visible region, of 1 µM alloy AgAu Tiopronin MPCs in H₂O with 0, 40, and 70% ethanol.
more clearly shows that emission band centered at 520 nm is decreased upon addition of ethanol to the solution. This behavior suggests that the solvent composition has a direct effect on the behavior of the MPCs and possibly on the composition of the core itself. As the polarity of the solvent is decreased, an intensity increase in the band attributed to Au atoms on the surface of the core is observed. It is plausible that the solvent composition affects the relative number of Ag and Au atoms on the surface of the core of the MPC. The rearrangement of the atoms within the core serves as a possible example that the MPC core is not fixed to a certain arrangement; rather the atoms are continuously rearranging depending upon the environment in which the MPC exists. This theory is based upon the changes in intensity of the two emission bands which are believed to arise from surface sites on the MPC core, however it is also possible that the rates of radiation are changed by the solubility of the MPCs.

2.3.3 Core Metal Galvanic Exchange Reaction. As previously reported, bimetal tiopronin MPCs could be formed via the core metal galvanic exchange reaction.\textsuperscript{15} To obtain organic soluble Ag MPCs the H\textsuperscript{+} counterions of tiopronin are replaced with more bulky quaternary ammonium cations. Both triethylammonium MePEG-350 hydroxide and tetrabutlyammonium hydroxide could be used and gave comparable results. The quaternary ammonium salt used in the reaction was determined based upon the solvent conditions, where triethylammonium MePEG-350 hydroxide was used when the reaction was run in CH\textsubscript{2}Cl\textsubscript{2}. It should be noted that the emission and absorbance spectra of the organic soluble Ag MPCs match the spectra obtained in the aqueous phase.

The resulting organic soluble Ag MPCs reacted with Au(I)[SCH\textsubscript{2}(C\textsubscript{6}H\textsubscript{4})C(CH\textsubscript{3})\textsubscript{3}]. Au(I) thiolate complexes can be luminescent,\textsuperscript{23} however, the one used for this reaction is not luminescent and therefore did not interfere with the luminescence of the final product. Equal
solution volumes of the organic soluble Ag Tiopronin MPCs (10 mM) and Au(I) thiolate complex (0.5 µM) were mixed at a 1:1 mole ratio of Ag:Au. The mechanism of this reaction is not fully understood. It is believed that it is strictly a metal and not a ligand exchange since none of the Au(I) thiolate ligand is found on the resulting MPCs.

Figure 2.4A shows the luminescence of diluted aliquots of the core metal galvanic exchange reaction solution from its onset through 4 days of the reaction. Figure 2.4B shows the corresponding absorbance spectra. At the onset of the reaction it can be seen from Figure 2.4A that two luminescent bands centered at 520 nm and 890 nm exist. The spectrum is very similar to that of the alloy AgAu Tiopronin MPCs reported above, likewise since these bands match nicely with the bands for Ag Tiopronin MPCs and Au Tiopronin MPCs they are attributed to Ag (520 nm) and Au (890 nm) on the surface of the core of the MPCs. As seen previously, over time the band centered at 890 nm increases. The exchange of Ag atoms for Au atoms on the surface of the core of the MPC explains this behavior. As more Au is exchanged into the core of the MPC, the luminescence behaves more like that of Au Tiopronin MPCs and less like that of Ag Tiopronin MPCs.

As seen in Figure 2.4B the absorbance spectra support the claim that Au is exchanged into the core of the MPC. The absorbance spectra have a sharp increase at high energy that is due to the presence of Au(I) thiolate in the solution. This sharp increase distorts the Ag surface plasmon band, making it difficult to draw conclusions. At the onset of the reaction the Ag surface plasmon band is clearly present and after 4 days of the reaction it is debatable if the surface plasmon band is present at all or if it has decreased, broadened, slightly red shifted or some combination thereof. No matter how exactly the absorbance changes, all the suggestions are in agreement with the presence of Au in the core of the MPC.
Figure 2.4  Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 μM galvanic exchanged AgAu MPCs in CH$_2$Cl$_2$ as a function of time. Samples were prepared from diluted aliquots taken from the reaction mixture (concentrations were based off the known concentration of Ag Tiopronin MPCs initially present).
Like the alloy AgAu Tiopronin MPCs, galvanic exchanged AgAu MPCs luminescence behaves differently in different solvents. Figure 2.5 shows the luminescence in both toluene/ethanol (50:50) and ethanol. When the MPCs are in toluene/ethanol they behave as they did at the end of the 4 day reaction, with a spectrum similar to Au Tiopronin MPCs. The predominate Au Tiopronin MPC behavior leads one to believe that the core is in a core/shell formation with Au as its shell. Interestingly when the MPCs are dissolved in ethanol, the Ag luminescent band increases at first, but after 1 day in solution the band returns to its original intensity (seen in the insert of Figure 2.5). Also, as seen in Figure 2.5 if Au(I) thiolate complex is added to a fresh ethanol solution of galvanic exchanged AgAu MPCs the Ag band disappears. These results suggest that if the initial product is in a core/shell formation, the solvent environment may induce the rearrangement of the core surface into an alloy formation. The formation of the galvanic exchanged AgAu MPCs in a toluene/ethanol solution, presumably core/shell, appears to be the more stable form since the predominate Au like properties persist in an ethanol solution after time or upon the addition of the Au(I) thiolate complex. The proposed behavior of this core metal galvanic exchanged AgAu Tiopronin MPC is depicted in Figure 2.6. The possibility that the atoms rearrange in different environments is not surprising since there has been reports of such behavior.12

2.3.4 Transmission Electron Microscopy. Electron microscopy can be used to gain important information on the core size dispersity of MPCs. It has been shown that the thiol to gold ratio used in the synthetic procedure will lead to a certain average core size.17 This also holds true for the MPCs discussed here, where in all cases a 3:1 ratio of thiol to gold was used.

Figure 2.7 shows the TEM images for the alloy AgAu Tiopronin MPCs, which have an average core size of 2.1 ± 0.4 nm, and the galvanic exchanged AgAu MPCs which have an
Figure 2.5  Luminescence spectra (excited at 400 nm) of 1 µM galvanic exchanged AgAu MPCs in toluene/ethanol (50:50) and ethanol and upon the addition of Au (I) thiolate complex to the solution mixture (concentrations were based off the known concentration of Ag Tiopronin MPCs initially present). Insert shows an expanded view of the visible region.
In Toluene/Ethanol
In Ethanol
Au(I) added
Figure 2.6  Schematic representation of the possible core formations of the bimetal MPCs.
Core/Shell → Different Solvent → Alloy → Different Solvent → Core/Shell
Figure 2.7 Transmission electron micrographs and size histograms of alloy AgAu Tiopronin MPCs (a) and galvanic exchanged AgAu MPCs (b). HRTEM of single MPCs are shown in the inserts.
average core size of 1.5 ± 0.3 nm. The inserts in Figure 2.7 obtained from HRTEM view a single MPC core for each of the two MPCs where the lattice plane spacing can be clearly seen for both. For both MPCs the morphology of the MPC cores was found to be consistent (upon sampling 50 MPC cores) indicating that only one composition of MPC core is present. In Figure 2.8 the EDX of the AgAu Tiopronin MPCs can be seen where clearly both Ag and Au are present, therefore the sample consists of only bimetal MPCs with uniform composition. The degree of polydiserspity is high for both MPCs, where the various sizes for both can be seen in their respective histograms. Due to the high degree of polydispersity a size separation technique is desired. The size separation of these MPCs will be discussed in a later chapter.

It should be noted that the galvanic exchanged AgAu MPCs were stable for a limited amount of time. Figure 2.9 shows two HRTEM images obtained from the same grid of a one month old sample, which had been stored as a solid at room temperature in the dark, of presumed core/shell AgAu MPCs. By EDX analysis the large mass in Figure 2.9A was found to be primarily composed of Ag atoms and conversely the particles in Figure 2.9B were found to be primarily composed of Au atoms. These images suggest that after a certain time period the bimetal MPCs can decompose to form mono-metal Ag and Au MPCs. It was found by taking daily TEM images that the presumed core/shell bimetal MPCs were stable up to one week. The alloy AgAu Tiopronin MPCs were not found to have a stability problem. They could be dissolved, dried, and re-dissolved over the time period of months with no decomposition.

2.3.5 X-ray Photoelectron Spectroscopy. XPS provides information about the atomic composition of the bimetal MPCs. Figure 2.10 shows the Au4f and the Ag3d photoelectron spectra for the alloy AgAu Tiopronin MPCs and galvanic exchanged AgAu MPCs. These
Figure 2.8  Energy dispersive spectrum of the AgAu Tiopronin MPCs taken on the TEM grid from which the image in Figure 2.7a was obtained.
Figure 2.9 High resolution transmission electron micrographs of aged galvanic exchanged AgAu MPCs taken at two different sites on the TEM grid. Two compositions were observed, one with large Ag content (a), and one with large Au content (b).
Figure 2.10  X-ray photoelectron spectra of AgAu Tiopronin MPCs of Au4f (a) and Ag3d (b).

The Au 4f peaks are found at 84.2 and 88 eV and the Ag 3d peaks are found at 368 and 374 eV. From the peak intensities the metals were found to be at 1:1 ratio.
(a) Au 4f

(b) Ag 3d
spectra confirm the presence of the two metals in the MPC cores, where the binding energies matched those of pure Ag and Au. The atomic abundance of the metals was roughly found to be 50:50 Ag:Au for both MPCs, this was the expected ratio since in both cases a starting mole ratio of 1:1 Ag:Au was used in the sample preparation. The XPS for these bimetal samples proved to be more qualitative than quantitative. While the relative abundance of each element present could be approximated from peak intensity these abundances were found to vary slightly depending on which location on the sample the XPS was taken. For a given sample the abundance of Ag detected could range from 40-60%.

2.3.6 Electrochemistry. Electrochemistry is another tool that can be used to support the presence of bimetal MPCs. Figure 2.11 shows the cyclic voltammograms of 0.5 M KOH solutions of Ag Tiopronin MPCs and alloy AgAu Tiopronin MPCs. In alkaline solution the electrochemical reduction of the thiolate ligands from the metal core occurs at negative potentials. The potential at which this occurs is related to the metal-S covalent bond. It can be seen that the potential at which the reduction of the thiolate ligands occurs shifts to lower potentials for the alloy AgAu Tiopronin MPC. This change in the potential suggests a difference in the metal-S covalent bond, or Au on the surface of the metal core.

2.3.7 Conclusion. Two different synthetic routes to bimetal AgAu MPCs have been discussed. In one case a simple one phase synthesis resulted in alloy AgAu Tiopronin MPCs, and in another a core metal galvanic exchange reaction led to presumably core/shell AgAu MPCs. While the composition of the core may be different for the two MPCs they behave very similarly.
Figure 2.11  Cyclic voltammograms of 1 mM Ag Tiopronin MPCs and AgAu Tiopronin MPCs in 0.5 M KOH. The reduction of the thiolate ligands from the metal core occurs for Ag Tiopronin MPCs occurs at -1175 mV, and for AgAu Tiopronin MPCs at -1400 mV.
The graph shows the current (A) plotted against potential (mV) for two different MPCs: AgAu MPC (red line) and Ag MPC (blue line). The x-axis represents the potential in mV, ranging from -200 to -1400 mV, while the y-axis represents the current in A, ranging from -2 \times 10^{-5} to 6 \times 10^{-5}. The AgAu MPC curve starts at a lower current and shows a steeper increase compared to the Ag MPC curve, indicating a different electrochemical behavior.
2.4 REFERENCES


Chapter III

CHARACTERIZATION OF TIOPRONIN-COATED Pd and Pd-Au MONOLAYER PROTECTED CLUSTERS

3.1 INTRODUCTION

Bimetal nanoparticles containing the noble metals palladium and gold, and silver and gold, are of great interest because they have different properties than their mono-metal counterparts. Colloidal PdAu nanoparticles of a core size smaller than 3 nm give a unique broad range of properties to probe and therefore are of considerable interest. Monolayer protected clusters (MPCs) are a specific subset of nanoparticles that fall under this category of small colloidal nanoparticles.

Both Au and Pd have been used for catalytic applications and the combination of these metals opens up many more possibilities. PdAu bimetal nanoparticles have been used as catalysts in processes such as the direct synthesis of hydrogen peroxide, degradation of p-nitroaniline, and carbon monoxide oxidation. For such processes, these bimetal nanoparticles have been found to show different catalytic activity for such processes than the mono-metal nanoparticles alone.

The properties of bimetal clusters depend upon their composition which is highly dependent upon the synthetic procedure. There are a variety of synthetic procedures that have been used to yield PdAu nanoparticles, some of the most common being the simultaneous reduction of a mixture of metal salts with numerous different reducing
agents, seed mediated growth method, sonochemical method, and laser irradiation. These PdAu nanoparticles have core structures of \( \text{Pd}_{\text{core}}\text{Au}_{\text{shell}} \), \( \text{Au}_{\text{core}}\text{Pd}_{\text{shell}} \), or alloy, can have a variety of different stabilizing agents, and can be free solids or immobilized in a matrix depending upon the synthetic procedure used.

The different compositions of PdAu nanoparticles have properties that can be quite different given only minor differences in composition. While different synthetic procedures tend to produce particular compositions, it has been found that the same synthetic procedure can yield different compositions of the nanoparticles. This same phenomenon was observed for the AgAu bimetal MPCs discussed in Chapter 2. Looking specifically at MPCs they have shown great promise toward studying the properties of different compositions within a small size range. The PdAu MPCs studied here are shown to have unique properties dependent upon composition and size that are different then their mono-metal counterparts.

In this report, two synthetic routes to PdAu bimetal MPCs are investigated: the core metal galvanic exchange reaction and the simultaneous reduction of a mixture of metal salts. Like the AgAu bimetal MPCs, the PdAu bimetal MPCs reported here have tiopronin as their protecting ligand. As discussed previously, the use of this ligand gives the advantage of water soluble MPCs and makes biological applications conceivable. A mono-metal Pd tiopronin MPC will also be discussed. The properties and compositions of these MPCs were investigated with luminescence spectroscopy, UV-vis spectroscopy, transmission electron microscopy (TEM), x-ray photoelectron spectroscopy, energy dispersive spectroscopy (EDX), and electrochemistry.

3.2 EXPERIMENTAL

3.2.1 Chemicals. HAuCl\(_4\).xH\(_2\)O, Triethylammonium monomethyl polyethylene glycol (MePEG-350) hydroxide and Au(I)[p-SCH\(_2\)(C\(_6\)H\(_4\))C(CH\(_3\))\(_3\)] were synthesized according
to literature. Potassium tetrachloro-palladate (II) (K₂PdCl₄, 99%), N-(2-mercapto propionyl)glycine (tiopronin, 99%), sodium borohydride (NaBH₄, 99%), dodecanethiol (CH₃(CH₂)₁₁SH, 99%), tetra-octalammonium bromide (Oct₄NBr, 99%), tetra-buty lammonium perchlorate (Bu₄NClO₄, 99%), and tetra-buty lammonium hydroxide (Bu₄NOH, 99%) were purchased from Aldrich. Methylene chloride (HPLC grade), toluene (HPLC grade), and ethanol (HPLC grade) were purchased from Fisher and used as received. House-distilled water was purified on a Barnstead NANOpure system ($\geq 18M\Omega$).

3.2.2 Synthesis of MPCs. Pd Dodecanethiol MPCs were synthesized according to a published procedure.²¹ Briefly, Oct₄NBr (0.75, 1.4 mmol) was dissolved in 250 mL toluene, and K₂PdCl₄ (0.3g, 0.9 mmol) in 50 mL in H₂O was added. The water layer was then removed and discarded. To the organic layer, 0.2 mL of dodecanethiol (0.18g, 0.9 mmol) was added, immediately followed by NaBH₄ (0.35g, 9 mmol) in 20 mL of H₂O. The resulting black solution was stirred for 1 hour, and the water layer was removed and discarded. The toluene was removed under vacuum, and the final product was washed with ethanol and acetone.

For Pd Tiopronin MPCs, the same procedure used for Ag Tiopronin MPCs²⁰ was adapted. K₂PdCl₄ (0.49 g, 1.5 mmol) in 12.5 mL of H₂O, N-(2-mercapto propiony)glycine (0.96 g, 5.9 mmol) in 7 mL of H₂O, and NaBH₄ (0.15 g, 3.9 mmol) in 3.8 mL of H₂O were all cooled to 0 °C. Solutions were mixed simultaneously, resulting in a black solution, which was stirred for 30 min. The Pd MPCs were precipitated with 50 mL of methanol, then filtered and washed with methanol, ethanol and acetone. The black powder product was dissolved in 25mL of H₂O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.
A similar procedure was followed for PdAu Tiopronin MPCs, K$_2$PdCl$_4$ (0.1 g, 0.3 mmol) in 10 mL of H$_2$O and tetrachloroauric acid (0.12 g, 0.35 mmol) in 10 mL of H$_2$O were cooled to 0 °C, then mixed. To the salt solutions 5 mL of N-(2-mercaptobenzoyl)glycine (0.15 g, 0.92 mmol) in 10 mL of H$_2$O (cooled to 0 °C) was added. The solutions were combined and NaBH$_4$ (0.13 g, 3.4 mmol) in 5 mL of H$_2$O (cooled to 0 °C) was added. The resulting solution was stirred for 30 min. The PdAu MPCs were precipitated with 50 mL of methanol, then filtered and washed with methanol, ethanol and acetone. The black powder product was dissolved in 25 mL H$_2$O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.

### 2.2.3 Core Metal Galvanic Exchange Reaction

To phase transfer the Pd Tiopronin MPCs, triethylammonium (MePEG-350) hydroxide was added drop-wise to a 10 mM H$_2$O solution of Pd Tiopronin MPCs until a pH of 8. The water was removed under vacuum. The dodecanethiolate-coated or tiopronin-coated MPCs were dissolved in CH$_2$Cl$_2$ (10 mM). The CH$_2$Cl$_2$ solution of Pd MPCs was mixed in equal volumes with 0.2 µM Au(I)p-SCH$_2$(C$_6$H$_4$)C(CH$_3$)$_3$ also in CH$_2$Cl$_2$. The solution mixture was stirred and kept in the dark until the reaction was terminated by removal of the solvent.

### 3.2.4 Spectroscopic Measurements

For spectroscopic measurements, 3 mL of 1 µM solutions were prepared. Luminescence spectra were taken in a 90° geometry on a modified ISA Fluorolog FL321 spectrometer. The fluorometer was equipped with a 450 W xenon source, and Hamamatsu R928 PMT (visible wavelengths) and InGaAs (near-IR wavelengths) detectors. Near-IR luminescence spectra were taken using a long pass filter, placed in the sample compartment, with cutoff of 450 nm. UV-vis spectra were taken with a Shimadzu UV-1601 UV-visible spectrophotometer.
3.2.5 Transmission Electron Microscopy (TEM). TEM data were obtained on a Hitachi HF-2000 equipped with an Oxford Instruments energy dispersive spectroscopy (EDX) x-ray microanalysis system, operated at 200 kV. The TEM samples were prepared by drop casting onto holey carbon grids (Ted Pella, Redding, CA).

3.2.6 X-ray Photoelectron Spectroscopy (XPS). XPS data were obtained on a Kratos Analytical Axis Ultra with an Al-Kα X-ray source, a hybrid analyzer, charge neutralizer, and a delay-line detector (pass energy 120 eV). Peak positions were referenced to the C 1s peak at 284.9 eV. A survey scan and expanded scans were taken for C 1s, S 2p, Pd 3d, and Au 4f.

2.2.7 Electrochemistry. Voltammetry data were obtained with a model 100B Bioanalytical Systems, Inc. (BAS) electrochemical analyzer, using 0.5 M KOH degassed solutions. The working electrode was a 3mm glassy carbon electrode, the counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl (aqueous) electrode.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis of Tiopronin MPCs. Water soluble tiopronin MPCs have been reported for metal cores consisting of Au, Ag, and Pt, and in the previous chapter, a AgAu Tiopronin MPC was discussed. Alkanethiol-coated MPCs have been reported for a variety of noble metals including Au, Ag, Pt, and Pd, as well as various bimetal combinations of these metals. Since the synthesis of alkanethiol-coated Pd MPCs has been successful it is expected that Pd Tiopronin MPCs as well as PdAu Tiopronin MPCs can be synthesized via a similar synthetic procedure. A modified Brust synthesis is the most common procedure used to synthesize thiolated MPCs. Discussed here are two new additions to water soluble tiopronin MPCs using a modified Brust synthesis. These MPCs have been found to be stable for at least two months and can be dissolved, dried, and re-dissolved without decomposition.
Figure 3.1 shows the absorbance spectra of Pd and PdAu Tiopronin MPCs. It is known that Pd MPCs do not have a surface plasmon absorbance band in the visible region and that Au MPCs of a large enough core size will have a surface plasmon absorbance band in the visible region. The absorbance spectrum of the Pd Tiopronin MPCs is a featureless exponential decay as would be expected, while the absorbance spectrum of PdAu Tiopronin MPCs has a surface plasmon band at 540 nm. The presence of this band confirms the presence of Au in the core of the MPC and suggests that the average core diameter is larger than 2 nm.

As discussed in the previous chapter Ag, Au, and AgAu Tiopronin MPCs were all found to be luminescent. Unlike their Ag and Au counterparts the Pd and PdAu MPCs were found not to be luminescent. A variety of Pd complexes have been found to be luminescent, however to date no luminescence from Pd nanoparticles has been reported. The lack of luminescence for the Pd Tiopronin MPCs is therefore not surprising. Based on the proposed origin of MPCs luminescence, it is expected that the PdAu Tiopronin MPCs would pick up luminescent properties if there is Au on the surface of the core. The lack of luminescence could be the result of minimal presence of Au on the surface of the core, or the average core diameter could be too large. As the similarly synthesized AgAu Tiopronin MPCs were found to be in an alloy formation, it is expected that the PdAu Tiopronin MPCs likewise would also be in an alloy formation, and Au is expected on the core of the MPCs. It has been reported that the quantum efficiency of the luminescence of MPCs decreases as the core size increases, and there have not been any reports on luminescent MPCs with a core size greater than 2 nm. It is therefore likely that the lack of luminescence is most likely due to the size of the MPC.
Figure 3.1 UV-vis spectra of 1 μM Pd Tiopronin and PdAu Tiopronin MPCs in H₂O.
Based on the absorbance spectra it is expected that the average core size of the PdAu Tiopronin MPCs are larger than 2 nm. The TEM images of these clusters confirm this size range. Figure 3.2 shows the TEM images of Pd and PdAu Tiopronin MPCs, including histograms upon sampling of 50 MPC cores. The Pd Tiopronin MPCs have an average core size of 2.1 ± 0.4 nm. The PdAu Tiopronin MPCs have an average core size of 2.0 ± 0.3 nm. It has been shown that when a 1:3 mole ratio is used in a modified Brust synthesis, as was used here, the average core diameter is often less than 2 nm. It is evident that these Pd containing MPCs yield slightly larger core diameters than other noble metal counterparts under similar conditions. These MPCs also have a high degree of polydispersity as can be seen from the histograms. A size separation method for these clusters is desired and will be discussed in a later chapter.

The absorbance spectrum indicates the presence of Au in the core of the PdAu Tiopronin MPC and XPS confirms the presence of both metals. XPS spectra of the PdAu Tiopronin MPCs can be seen in Figure 3.3. The Au 4d and Pd 3d spectra clearly show the presence of both metals where the binding energies match those of the pure metals. The XPS gives an approximate ratio of 1:1 Pd:Au which is to be expected given the reaction conditions (1:1 mole feed ratio). As mentioned in the previous chapter, the relative abundance of each element present could be approximated from peak intensity, however the abundances were found to vary slightly depending on which location on the sample the XPS was taken. The abundance of Pd detected could range from 40-60% for a given sample.

Electrochemistry can be used to assess the catalytic nature of MPCs. For these water soluble MPCs in alkaline solution, proton reduction will dictate the potential window. One would expect that Pd would be more catalytic in nature than Ag, and Ag more so than Au. The cyclic voltammograms in Figure 3.4 are of Pd, Ag, and Au Tiopronin MPCs. It can be
Figure 3.2  Transmission electron micrographs and size histograms of Pd Tiopronin (a) and PdAu Tiopronin MPCs (b).
Figure 3.3 X-ray photoelectron spectrum of PdAu Tiopronin MPCs of Au 4d and Pd 3d.
The Au 4d peaks are found at 335 and 351 eV and the Ag 3d peaks are found at 335 and 341 eV. From the peak intensities the metals were found to be at 1:1 ratio.
Figure 3.4  Cyclic voltammograms of 1 mM Pd, Ag, and Au tiopronin MPCs in 5 mL of 0.5 M KOH  The working electrode was a 3mm glassy carbon electrode, the counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl (aqueous) electrode.
seen that proton reduction occurs at the most negative potential for Au Tiopronin MPCs and the least negative for Pd Tiopronin MPCs. It is expected that as the thiolate ligands are reduced from the metal core the resulting bare metal can be used to catalyze the proton reduction. The Pd Tiopronin MPCs are working as stronger catalysts for proton reduction than the respective Ag and Au Tiopronin MPCs.

3.3.2 Core Metal Galvanic Exchange Reaction. As reported and discussed in the previous chapter, bimetal MPCs can be formed via the core metal galvanic exchange reaction. In the reactions reported here, Pd Dodecanethiol or Pd Tiopronin MPCs (which have been titrated with triethylammonium MePEG-350 to yield organic soluble MPCs) are reacted with Au(I)[SCH₂(C₆H₄)C(CH₃)₃] in equal amounts.

The luminescence (excited at 400nm) and absorbance spectra after both 2 min. and 4 days of the galvanic exchange reaction starting with the Pd Dodecanethiol MPCs can be seen in Figure 3.5. There are clear changes in both the luminescence and absorbance spectra after the components had reacted for 4 days. While there are indeed changes in the spectra, a significant optical band that can be monitored over time is not present, making it hard to study this reaction optically. Even though the product was not optically interesting, it was found to be very stable over time unlike the AgAu galvanic exchanged product discussed in the previous chapter that was not stable for long periods of time.

Figure 3.6 shows the TEM image of the PdAu dodecanethiol galvanic exchanged product, drop cast from a one month old solution of the reaction mixture, giving an average core size of 1.6 ± 0.2 nm. The insert shows a HRTEM image of a single MPC core where the lattice plane spacing can be clearly seen. The lattice spacing matched that of Au(111). This supports the presumed core/shell structure of the core. The morphology of the MPC cores were found to be consistent (upon sampling 50 MPC cores) confirming that only one
Figure 3.5 Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 μM core metal galvanic exchanged PdAu dodecanethiol MPCs in CH$_2$Cl$_2$ after both 2 min and 4 days of reaction.
(a) Relative Intensity vs. Wavelength (nm)

(b) Normalized Abs vs. Wavelength (nm)

- Red line: 4 days
- Blue line: 2 min
Figure 3.6 Transmission electron micrograph (a) and size histogram (b) of core metal galvanic exchanged PdAu dodecanethiol MPCs. A HRTEM image of a single MPC is shown in the insert.
composition of MPC core is present. In Figure 3.7 the EDX of this sample can be seen where clearly both Pd and Au are present, therefore the sample consists of only bimetal MPCs with uniform composition. It is worth noting that the reaction between Ag and Au was found to be quite thermodynamically favorable whereas the reaction had reached completion after 1 day, while the reaction between Pd and Au was found to be quite slow not reaching completion until nearly 1 week. The standard redox potential for Ag$^+$ is 0.8 V where the standard redox potential for Pd$^{2+}$ is 0.9 V however, given these values, the reaction involving Pd should be less thermodynamically favorable. Even though the reaction was slow, it is encouraging that the reaction was a success therefore, it was expected that the reaction starting with Pd tiopronin MPCs would be a success as well.

The luminescence when excited at 400 nm and absorbance spectra after both 2 min. and 4 days of the core metal galvanic exchange reaction starting with the Pd Tiopronin MPCs can be seen in Figure 3.8. For this reaction, Pd Tiopronin MPCs (which have been titrated with triethylammonium MePEG-350 to yield organic soluble MPCs) were reacted with Au(I)[SCH$_2$(C$_6$H$_4$)C(CH$_3$)$_3$] (1:1 mole feed ratio). It is clear that after 4 days of reaction the product has an emission band centered at 900 nm. The position of this band is very similar to the emission band of Au Tiopronin MPCs (Figure 3.9),$^{31}$ this band is therefore attributed to Au on the surface of the MPC. The absorbance spectra show no change over time. The fact that there is no change in the absorbance spectra is not surprising since Pd does not have a surface plasmon band, and at a small enough average core size, neither does Au. A featureless exponential decay absorbance spectrum would therefore be expected for these MPCs.

Figure 3.10 shows the TEM image of a one month old solution of the PdAu tiopronin core metal galvanic exchanged product giving an average core size of 1.5 ± 0.3 nm. For this
Figure 3.7  Energy dispersive spectrum of the core metal galvanic exchanged PdAu dodecanethiol MPCs taken on the TEM grid from which the image in Figure 3.6 was obtained.
Figure 3.8 Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 µM core metal galvanic exchanged PdAu tiopronin MPCs in CH$_2$Cl$_2$ after both 2 min and 4 days of reaction.
Figure 3.9  Luminescence spectrum (excited at 400 nm) of 1µM Au Tiopronin MPCs.
Figure 3.10  Transmission electron micrograph (a) and size histogram (b) of core metal galvanic exchanged PdAu tiopronin MPCs.
core size, a Au surface plasmon band is not expected, which supports the absorbance findings. Figure 3.11 shows the XPS for the tiopronin galvanic exchanged PdAu MPC where the Au 4d and Pd 3d spectrum clearly shows the presence of both metals, and where the binding energies match that of the pure metals. The ratio of Pd:Au was found to be approximately 1:1. Again, the XPS for these bimetal samples proved to be more qualitative then quantitative, detecting anywhere from 40-60% Pd.

3.3.3 Conclusions. Two new additions to the water soluble tiopronin MPC family as well as two synthetic routes to PdAu bimetal MPCs have been discussed. Pd Tiopronin and PdAu Tiopronin MPCs synthesized via a modified brust synthesis with a core diameter of less than 2 nm were found to have featureless exponential decay absorbance, no fluorescence, and to be quite stable over time. Core metal galvanic exchange reactions on Pd dodecanethiol and Pd Tiopronin MPCs were thermodynamically slow but produced stable PdAu bimetal MPCs. The possible catalytic applications of Pd containing MPCs are of particular interest, and the potential catalytic nature of the MPCs is supported by the electrochemical results.
Figure 3.11  X-ray photoelectron spectrum of core metal galvanic exchanged PdAu tiopronin MPCs of Au 4d and Pd 3d. The Au 4d peaks are found at 335 and 351 eV and the Ag 3d peaks are found at 335 and 340 eV. From the peak intensities the metals were found to be at 1:1 ratio.
3.4 REFERENCES


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Chapter IV

CHARACTERIZATION OF Ir CONTAINING BIMETAL MONOLAYER PROTECTED CLUSTERS AND AN AGED SOLUTION OF Au(I)[p-SCH$_2$(C$_6$H$_4$)C(CH$_3$)$_3$]

4.1 INTRODUCTION

The synthetic procedures for iridium nanoparticles are currently not very well developed, however there has been some successful reports on the synthesis and characterization of iridium nanoparticles.$^{1-4}$ Most reported iridium nanoparticles are small colloids that are of interest primarily due to their catalytic properties.$^{3,4}$ These nanoparticles were characterized solely based on TEM and electron diffraction and no optical measurements were reported.

While there have been some reports on bimetal clusters of a few atoms that contain iridium,$^{5,6}$ the field of bimetal nanoparticles containing iridium has not been studied. The bimetal systems of AgAu and PdAu have been extensively studied and are discussed in the previous two chapters. The luminescence of AgAu and PdAu tiopronin-coated nanoparticles was investigated, and the luminescent properties were attributed to the presence of Au on the surface of the core of the MPC. The possible luminescence due to the presence of Au and the catalytic nature of Ir make bimetal nanoparticles containing Au and Ir an interesting prospect. The combination of Au and Ir into bimetal nanoparticles is not straightforward. As bulk metals, it is known that Au and Ir do not form alloys.$^7$ There has been a report however, where a Au film grown on Ir was found to yield advantageous catalytic results.$^8$ Also, a
bimetallic IrAu/γ-Al2O3 catalyst has been reported.9 Given these two examples, bimetal IrAu nanoparticles may be possible.

Two attempts to synthesize bimetal IrAu nanoparticles by the core metal galvanic exchange reaction are discussed here. Luminescence, UV-vis spectroscopy, and transmission electron microscopy were used to study the nanoparticles. While studying the IrAu nanoparticles, Au nanoparticles originating from a solution of the Au(I) thiolate complex used in the core metal galvanic exchange reaction were discovered. The formation of these Au nanoparticles and their role in the core metal galvanic exchange reaction are also discussed.

4.2 EXPERIMENTAL

4.2.1 Chemicals. HAuCl4.xH2O,10 triethylammonium monomethyl polyethylene glycol (MePEG-350) hydroxide,11 and Au(I)[p-SCH2(C6H4)C(CH3)3]11 were synthesized according to literature. Dihydrogen hexachloroiridate (IV) (H2IrCl6·H2O, 99%), N-(2-mercaptotropionyl) glycine (tiopronin, 99%), sodium borohydride (NaBH4, 99%), octadecanethiol (SC18H37, 99%), silver nitrate (AgNO3, 99%), and lithium triethylborohydride solution (super-hydride, 99%) were purchased from Aldrich. Methylene chloride (HPLC grade), ethanol (HPLC grade), methanol (HPLC grade), tetrahydrofuran (HPLC grade), and glacial acetic acid were purchased from Fisher and used as received. House-distilled water was purified on a Barnstead NANOpure system (≥ 18MΩ).

4.2.2 Synthesis of MPCs. Ir octadecanethiolate-coated MPCs were synthesized according to a published procedure.1 Briefly, octadecanethiol (0.4 g, 0.5 mmol) was added to 10 mL of distilled THF and then H2IrCl6·H2O (0.19 g, 0.5 mmol) was added to the solution which was stirred at all times. To the resulting reddish brown solution, 7 ml of super-hydride was added drop wise and then allowed to stir for 2 hours. The MPCs were crashed out and washed with
ethanol. Ir [SC\textsubscript{18}H\textsubscript{37}] thiolate was synthesized via the same method except in the absence of reducing agent.

For Au Tiopronin MPCs,\textsuperscript{12} tetrachloroauric acid (0.50 g, 1.5 mmol) and N-(2-mercaptopropionyl)glycine (0.63 g, 3.9 mmol) were co-dissolved in 63 mL 6:1 methanol/acetic acid producing a ruby red solution. NaBH\textsubscript{4} (0.95 g, 25 mmol) in 12.5 mL of H\textsubscript{2}O was added immediately, resulting in a black solution, that was stirred for 30 min. The solvent was removed under vacuum (\textless 35 °C). The black product was dissolved in 25 mL H\textsubscript{2}O; then concentrated HCl was added drop-wise to adjust to pH 1, and then dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. The water was removed under vacuum resulting in the final product.

4.2.3 Core Metal Galvanic Exchange Reaction. Triethylammonium (MePEG-350) hydroxide was added drop-wise to a 10 mM H\textsubscript{2}O solution of Au Tiopronin MPCs until a pH of 8. The water was removed under vacuum and the Au MPCs were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (10 mM). The CH\textsubscript{2}Cl\textsubscript{2} solution of Au MPCs was mixed in equal volumes with 0.5 µM Ir [SC\textsubscript{18}H\textsubscript{37}] thiolate also in CH\textsubscript{2}Cl\textsubscript{2}. The solution mixture was stirred and kept in the dark until the reaction was terminated by removal of the solvent. The reverse, mixing Ir MPCs with Au(I)[p-SCH\textsubscript{2}(C\textsubscript{6}H\textsubscript{4})C(CH\textsubscript{3})\textsubscript{3}] was done in the same way.

4.2.4 Spectroscopic Measurements. For spectroscopic measurements, 3 mL of 1 µM solutions were prepared. Luminescence spectra were taken in a 90° geometry on a modified ISA Fluorolog FL321 spectrometer. The fluorometer was equipped with a 450 W xenon source, and Hamamatsu R928 PMT (visible wavelengths) and InGaAs (near-IR wavelengths) detectors. Near-IR luminescence spectra were taken using a long pass filter, placed in the sample compartment, with cutoff of 450 nm. UV-vis spectra were taken with a Shimadzu UV-1601 UV-visible spectrophotometer.
4.2.5 Transmission Electron Microscopy (TEM). TEM data were obtained on a Hitachi HF-2000, operated at 200 kV. The TEM samples were prepared by drop casting onto holey carbon grids (Ted Pella, Redding, CA).

4.3 RESULTS AND DISCUSSION

4.3.1 Au(I) Thiolate. In the previous two chapters, the core metal galvanic exchange reaction\textsuperscript{13} was shown to successfully yield both AgAu and PdAu MPCs, where mono-metal MPCs were reacted with a salt of a more noble metal. Based on the results for the AgAu and PdAu MPCs, it was expected that the reaction between Ir MPCs and a Au(I) thiolate would yield IrAu MPCs.

Equal volumes of Ir octadecanethiolate-coated MPCs and Au(I) \([\text{SCH}_2(\text{C}_6\text{H}_4\text{C}(\text{CH}_3)_3])\] were mixed at a 1:1 mole ratio of Ir:Au. The solution mixture was continuously stirred and was not exposed to light over a time frame of at least one month. The luminescence (excited at 400 nm) and UV-vis spectra of the core metal galvanic exchange reaction solution, at its onset and after the solution mixture had stirred for one month, can be seen in Figure 4.1. While measurements were at first taken hourly and then daily, no significant changes were observed until at least three weeks of time had passed. The spectrum obtained from the one month old solution mixture seen in Figure 4.1A clearly shows an emission band centered at 890 nm. The luminescence appeared rather suddenly where it was not detected one day and was the next. The intensity of the luminescent band remained relatively stable once it was detected. The position of this band matches with that observed for Au MPCs. Figure 4.1B shows minimal changes in absorbance over time. The amount of time required to see any changes in the optical spectra lead to some questions regarding the origin of the luminescence.
Figure 4.1  Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 µM CH₂Cl₂ solutions from the core metal galvanic exchange reaction between Ir MPCs and Au(I) thiolate after 2 min and 1 month of reaction time.
Two CH$_2$Cl$_2$ solutions of the same concentration of Au(I) thiolate used in the core metal galvanic exchange reaction, one shielded from the light and one exposed to the light, were monitored over time. Figure 4.2 shows the typical luminescence and UV-vis observed from a one month old solution (not exposed to light) of Au(I) thiolate. The results are comparable to those obtained for the core metal galvanic exchange reaction discussed above, an emission band centered at 890 nm with minimal changes in the absorbance. When the solution of Au(I) thiolate was not exposed to light it took approximately one month before luminescence was observed, and when it was exposed to light it took approximately one week. The time frame of one month for luminescence to be observed, for the solution not exposed to light, is the same that was observed for the core metal galvanic exchange reaction (Figure 5.1). The light acted as a catalyst, reducing the time it took to generate luminescence. Due to the extreme similarities, it is believed that the luminescence observed for the core metal galvanic exchange reaction is the result of an aged solution of Au(I) thiolate.

The effects of an aged solution of Au(I) [SCH$_2$(C$_6$H$_4$)C(CH$_3$)$_3$] is also a concern in the core metal galvanic exchange reactions between Ag and Au, as well as Pd and Au. As was seen in Chapter 2, the core metal galvanic exchange reaction between Ag and Au did result in an emission band at 890 nm which is also observed for the aged solution of Au(I) thiolate. The reaction between Ag and Au was terminated before one week had passed which was not long enough to see the luminescence from an aged solution of Au(I) thiolate even if the reaction was exposed to light. It can be concluded, that within the time frame of one week which the reaction was conducted, that the luminescence from an aged solution of Au(I) thiolate is not playing a role in the core metal galvanic exchange reaction between Ag and Au. For the core metal galvanic exchange reactions between Pd and Au discussed in Chapter 3, the luminescent properties observed were not comparable to that of an aged solution of
Figure 4.2  Luminescence spectrum (excited at 400 nm) (a), and UV-vis spectrum (b) of a 1 month old 1 µM CH₂Cl₂ solution of Au(I) [SCH₂(C₆H₄)C(CH₃)₃] that was not exposed to light before measurements.
Au(I) thiolate, even though the solution mixture was monitored for over a month. A luminescent band centered at 890 nm was seen, however it differed in shape and intensity. In the case involving Pd and Au it appears as if the Pd MPCs are inhibiting the process that is occurring as the solution of Au(I) thiolate ages. It is clear that the luminescence seen for an aged solution of Au(I) thiolate is not interfering with the core metal galvanic exchange reactions involving Ag and Au or Pd and Au.

The question remains whether the luminescence in Figure 4.2A originates from Au nanoparticles or from some thiolate complex formed during the aging process. There have been several reports on the luminescence of Au(I) thiolates\(^\text{14-17}\) so it is conceivable that the luminescence could result from some thiolate complex. Also, the synthesis of nanoparticles from the reduction of Au(I) thiolates has been reported\(^\text{18}\). As long as there is a reducing agent present the production of nanoparticles is possible. Figure 4.3 shows the TEM image from an aged solution of Au(I) thiolate. Colloidal nanoparticles can be clearly seen with an average core size of 1.4 ± 0.3 nm. The insert shows a single particle core and its Au(111) lattice spacing. The clear lattice spacing confirms particles are indeed present and not some agglomeration of thiolate complexes. It should be noted that TEM images could not be obtained for samples of Au(I) thiolate that had yet to exhibit luminescent properties. This serves as evidence that upon the formation of Au nanoparticles luminescence is observed.

To explore the behavior of the Au(I) thiolate further, a 1µM CH\(_2\)Cl\(_2\) solution was mixed with excess of AgNO\(_3\). Figure 4.4 shows the luminescence spectrum (excited at 400 nm) after 1 hour of reaction time. An emission band centered 890 nm is observed that is similar in position and shape to the aged Au(I) thiolate samples. The Ag ion is therefore acting as a catalyst for generating luminescent properties from Au(I) thiolate in solution. The prolonged exposure to light or in the presence of Ag ion, Au(I) [SCH\(_2\)(C\(_6\)H\(_4\))C(CH\(_3\)_3] in solution
Figure 4.3 High resolution transmission electron micrograph of 1 month old solution of Au(I) \( \text{[SCH}_2\text{(C}_6\text{H}_4\text{C(CH}_3)_3\text{]} } \) in CH\(_2\)Cl\(_2\). An enlarged view of a single MPC is shown in the insert.
Figure 4.4 Luminescence spectrum (excited at 400 nm) of a 1 μM CH₂Cl₂ solution of Au(I) [SCH₂(C₆H₄)C(CH₃)₃] 1 hour after the addition of excess AgNO₃ to the solution mixture.
results in the same finding, luminescent Au nanoparticles are formed. The mechanism to this luminescence and the composition of the nanoparticles being formed at this point is unknown, and needs to be further investigated.

4.3.2 Core Metal Galvanic Exchange Reaction. The core metal galvanic exchange reaction between Ir MPCs and Au(I) thiolate was unsuccessful. It is possible that the reverse reaction, Au MPCs reacted with an Ir thiolate complex, could be more thermodynamically favorable. The standard redox potential for Au\(^{+}\) is 1.83 V compared to that of 1.2 V for Ir\(^{3+}\) however, based on these values, reactions between these two metals, in general are not favorable. Also, since Au is known to be the most noble metal,\(^{19}\) this goes against the concept that for the core metal galvanic exchange reaction to occur the mono-metal MPCs must be reacted with a salt of a more noble metal. On the other hand, the usual thermodynamic expectation might be changed by the relation stabilizations accorded by the different ligands.

Equal volumes of Au Tiopronin MPCs and Ir \([SC_{18}H_{37}]\) were mixed at a 1:1 mole ratio of Au:Ir. The solution mixture was continuously stirred, and not exposed to light. Figure 4.5 shows the luminescence (excited at 400 nm) and UV-vis of the core metal galvanic exchange reaction solution after 2 min., 1 hour, and 1 day of reaction time. The starting product of Au tiopronin MPCs is known to have an emission band centered at 890 nm. Over time, a decrease in the intensity of this band is observed. This could be the result of the incorporation of Ir onto the core of the MPC which therefore quenches the Au luminescence. It should also be noted that after 1 day of reaction time an emission band centered at 520 nm is observed, which can be seen in the enlarged view of the visible region in Figure 4.5 A. This luminescence could be originating from Ir on the MPC core however, this is just speculation at this time. Figure 4.5 B shows that no changes in absorbance were observed
Figure 4.5 Luminescence spectra (excited at 400 nm) (a), and UV-vis spectra (b) of 1 μM solution in CH$_2$Cl$_2$ of core metal galvanic exchanged AuIr tiopronin MPCs after 2 min, 1 hour, and 1 day of reaction time. A magnified view of the visible luminescence spectra is shown.
over time. Further characterization of the core metal galvanic exchanged IrAu tiopronin MPCs is needed however, at this time the luminescence results are encouraging and suggest the synthesis of AuIr bimetal MPCs.

4.3.3 Conclusions. Colloidal nanoparticles with an emission band centered around 890 nm can be generated simply from a solution of Au(I) \([\text{SCH}_2(\text{C}_6\text{H}_4)\text{C(CH}_3)_3]\). The formation of the nanoparticles can be catalyzed by the presence of light or Ag ion in solution. The generation of these particles does not play a role in the core metal galvanic exchange reaction involving Ag and Au discussed in Chapter 2 and is inhibited by the core metal galvanic exchange reaction involving Pd and Au discussed in Chapter 3. The synthesis of IrAu bimetal MPCs via the core metal galvanic exchange reaction between Ir octadecanethiolate-coated MPCs and Au(I) thiolate was found to be unsuccessful although the reaction between Au Tiopronin MPCs and Ir thiolate is promising.
4.4 REFERENCES


Chapter V

REVERSED PHASE ION-PAIR CHROMATOGRAPHY OF TIOPRONIN-COATED MONOLAYER PROTECTED CLUSTERS

5.1 INTRODUCTION

Monolayer protected clusters (MPCs) synthesized via the modified Brust synthesis are found to be quite polydisperse in nature. Depending upon the ligand to metal mole ratio used, the resulting MPCs will have core diameters with some extent of size dispersity.\(^1,2\) Even if core sizes only vary a few nanometers the properties of these MPCs are size dependent within this small size range. For example, simply looking at UV-vis absorbance properties, MPCs with a core size of about 1 nm exhibit molecular like features\(^3\) where MPCs of a core size greater then 2 nm have a surface plasmon band.\(^4\) Since the properties of the MPCs vary so drastically for minor changes in size, to study these properties further it is necessary to have separation methods to obtain samples of a single size.

A variety of different methods have been used to separate MPCs. These methods include: gel electrophoresis,\(^5,6\) capillary electrophoresis,\(^7-10\) continuous free-flow electrophoresis,\(^11\) size exclusion chromatography,\(^12-14\) reversed phase chromatography,\(^3,15,16\) ion exchange chromatography,\(^17\) and reversed phase ion-pair chromatography.\(^18\) Depending upon the MPC characteristics, different detection methods are used such as photodiode array (PDA),\(^3,12\) electrochemical,\(^16\) and fluorescence detection.\(^18\) These methods can be applied to
MPCs with differences in composition of their protecting ligands and metal cores, and span from organic soluble to water soluble MPCs.

Tiopronin MPCs are of interest due to their unique optical properties, and since they are water soluble they open up possibilities for biological applications. A number of different tiopronin MPCs with different metal cores have been discussed in previous chapters. As evident from the transmission electron micrographs of these tiopronin MPCs, the samples are quite polydisperse, and therefore further size separation is necessary.

Recently, a reversed phase ion-pair HPLC method has been used to separate Au Tiopronin MPCs, where the smaller MPCs eluted first. It was found that using tetrabutylammonium fluoride (Bu4N^+F^-) as the ion pair reagent, methanol as the organic component in the mobile phase, and buffering at a pH of 4.5 yielded the most efficient separation. Since this separation method utilizes the ion-pairing capabilities of the tiopronin ligand, the method should be applicable to other tiopronin MPCs. Reported here are the reversed phase ion-pair HPLC separation of Ag, AgAu, Pd and PdAu Tiopronin MPCs. Mulit-wavelength fluorescence (FL) and PDA detection were both used to determine the MPCs size and elution order.

5.2 EXPERIMENTAL

5.2.1 Chemicals. HAuCl4.xH2O was synthesized according to literature. Potassium tetrachloro-palladate (II) (K2PdCl4, 99%), silver nitrate (AgNO3, 99%), N-(2-mercaptopropionyl)glycine (tiopronin, 99%), sodium borohydride (NaBH4, 99%), and tetrabutylammonium fluoride (Bu4NF4, 99%) were purchased from Aldrich. Sodium hydrogen phosphate (Na2HPO4, 99%), methanol (HPLC grade), acetone (HPLC grade), and ethanol (HPLC grade) were purchased from Fisher and used as received. Sodium dihydrogen
phosphate monohydrate (NaH$_2$PO$_4$·H$_2$O, 99%) was purchased from Mallinckrodt Chemical. House-distilled water was purified on a Barnstead NANOpure system ($\geq$ 18MΩ).

**5.2.2 Synthesis of MPCs.** Ag Tiopronin MPCs were synthesized as reported previously.$^{23}$ Briefly, AgNO$_3$ (1.0 g, 5.89 mmol) in 50mL H$_2$O, N-(2-mercaptopropiony)glycine (2.8 g, 17.6 mmol) in 20 mL of H$_2$O, and NaBH$_4$ (0.6 g, 15.9 mmol) in 15 mL of H$_2$O were all cooled to 0 °C. Solutions were mixed simultaneously, resulting in a black solution, which was stirred for 30 min. The Ag MPCs were precipitated with 300 mL of methanol, then filtered and washed with methanol, ethanol and acetone. The black powder product was dissolved in 25 mL of H$_2$O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.

For AgAu Tiopronin MPCs a similar procedure was followed, AgNO$_3$ (0.06 g, 0.35 mmol) in 10 mL of H$_2$O and tetrachloroauric acid (0.12 g, 0.35 mmol) in 10 mL of H$_2$O were cooled to 0 ° C, then mixed. To the salt solutions, 5 mL of N-(2-mercaptopropiony)glycine (0.15 g, 0.92 mmol) in 10 mL of H$_2$O (cooled to 0 ° C) was added. The salt solutions were combined and NaBH$_4$ (0.13 g, 3.4 mmol) in 5 mL of H$_2$O (cooled to 0 ° C) was added. The resulting solution was stirred for 30 min. The AgAu MPCs were precipitated with 50 mL of methanol, then filtered and washed with methanol, ethanol and acetone. The black powder product was dissolved in 25 mL of H$_2$O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.

For Pd Tiopronin MPCs, the same procedure used for Ag Tiopronin MPCs$^{23}$ was adapted. K$_2$PdCl$_4$ (0.49 g, 1.5 mmol) in 12.5 mL of H$_2$O, N-(2-mercaptopropiony)glycine (0.96 g, 5.9 mmol) in 7 mL of H$_2$O, and NaBH$_4$ (0.15 g, 3.9 mmol) in 3.8 mL of H$_2$O were all cooled to 0 °C. Solutions were mixed simultaneously, resulting in a black solution, which was stirred for 30 min. The Pd MPCs were precipitated with 50 mL of methanol, then
filtered and washed with methanol, ethanol and acetone. The black powder product was dissolved in 25mL of H₂O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.

A similar procedure was followed for PdAu Tiopronin MPCs, K₂PdCl₄ (0.1 g, 0.3 mmol) in 10 mL of H₂O and tetrachloroauric acid (0.12 g, 0.35 mmol) in 10 mL of H₂O were cooled to 0 °C, then mixed. To the salt solutions 5 mL of N-(2-mercaptopropiony)glycine (0.15 g, 0.92 mmol) in 10 mL of H₂O (cooled to 0 °C) was added. The solutions were combined and NaBH₄ (0.13g, 3.4 mmol) in 5 mL of H₂O (cooled to 0 °C) was added. The resulting solution was stirred for 30 min. The PdAu MPCs were precipitated with 50 mL of methanol, then filtered and washed with methanol, ethanol and acetone. The black powder product was dissolved in 25 mL H₂O and dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. Water was removed under vacuum resulting in the final product.

5.2.3 Reversed Phase Ion-Pair HPLC. The chromatography was carried out with a Waters instrument equipped with a Model 600 controller pump capable of gradient elution, a Model 2996 PDA and Model 2475 multi-wavelength fluorescence detector. PDA spectra and fluorescence (excited at 400 nm) were taken for the respective peaks. The chromatographic column (150 X 4.6 mm i.d. stainless steel) was packed with 5 µM C₁₈ bonded-silica with 300 Å pore size (bioBasic-18, Thermo electron Corporation, Bellefonte, PA). Injections of 0.5 mg/mL solutions of MPC in H₂O (pre-filtered through at 0.2 µM HT Tuffryn® membrane Acrodisc® syringe filter, Pall Corporation, Ann Arbor, MI) were done on a Rheodyne 7725 injection valve with a 50 µL sample loop. Both gradient and isocratic elutions were carried out.

The mobile phase consisted of the appropriate concentration of Bu₄N⁺F⁻ as the ion-pair reagent, MeOH, and pH 4.5 phosphate buffer (prepared with NaH₂PO₄ and Na₂HPO₄). The
mobile phase was filtered through a 0.4 µM HTTP Isopore™ membrane filter (Millipore, Billerica, MA), and degassed. A flow rate of 0.7 mL/min was used and separations were conducted at room temperature.

5.3 RESULTS AND DISCUSSION

Reversed phase ion-pair HPLC has been shown to be an efficient separation method for water soluble Au Tiopronin and N-acetyl-L-cysteine MPCs. As reported, the efficiency of the separation is highly dependent upon numerous factors including: the concentration of the ion-pair reagent, the organic content in the mobile phase, and pH of the mobile phase. The exact conditions of the method, in order to optimize the separation, are different for only minor differences in MPCs. The method must therefore be optimized for each different MPC, however, the general concept of the method holds true. For each of the tiopronin MPCs discussed the methanol content of the mobile phase was varied, the concentration of Bu₄N⁺F⁻ was held constant at 0.05 M and pH 4.5 phosphate buffer was used.

5.3.1 Separation of Ag Tiopronin MPCs. Upon investigating the separation of Ag Tiopronin MPCs, elution of the MPCs from the column was only observed when the mobile phase was composed of at least 90% methanol. Figure 5.1A shows the chromatogram from PMT detection, obtained for isocratic elution with a mobile phase containing 90% methanol and 10% water, where a single peak is present. Figure 5.1B shows the absorbance spectrum obtained for the single peak, where the silver surface plasmon band at 480 nm is present.

Isocratic elution was sufficient for the separation of Au Tiopronin MPCs, however that is not the case for Ag Tiopronin MPCs. To obtain a size separation the use of gradient elution was explored. While the attempts at gradient elution never led to size separation some useful findings were made. A fluorescent side product is present in the Ag tiopronin samples and the Ag Tiopronin MPCs lead to ghosting on the HPLC column. With the use of
Figure 5.1  Isocratic elution of Ag Tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 90% MeOH and 10% water, pH 4.5 phosphate buffer: (a) chromatogram from PMT detector and (b) absorbance spectrum extracted from chromatographic peak at 9 min.
(a) Absorption vs. Time (min)

(b) Absorption vs. Wavelength (nm)
gradient elution two species in the sample mixture were identified, where the use of isocratic elution only gave an unresolved mixture (as seen in Figure 5.1A).

Figure 5.2A shows the chromatograms obtained for the PMT and FL detectors when a gradient from 100% water to 100% methanol is employed. From the chromatogram obtained with the PMT detector two distinctive peaks can be clearly seen. The chromatogram from the FL detector shows one predominant peak, however the presence of a second peak is visible. The respective absorbance and fluorescence spectra obtained for these peaks are shown in Figure 5.2B and Figure 5.2C respectively. The first peak to elute has an absorbance spectrum that is not typical for MPCs, however it is fluorescent. The second peak has minimal fluorescence and does have the characteristic absorbance for Ag Tiopronin MPCs. This second peak is the result of the Ag Tiopronin MPCs eluting off the column. The use of gradient elution made it possible to see the presence of a fluorescent species in the Ag Tiopronin MPC sample, which does not show the typical absorbance expected for MPCs. The origin of this species is under investigation. Oxide formation on arylthiolate-coated Ag MPCs has been reported. It is possible that oxide formation on Ag Tiopronin MPCs leads to the presence of this fluorescent species with sharp decay absorbance.

Upon conducting consecutive HPLC runs on the Ag tiopronin sample ghosting on the HPLC column was observed. Figure 5.3 shows the chromatogram from the PMT detector when the mobile phase gradient is from 100% water to 100% methanol and is then repeated during the same run. Upon repeating the gradient during the same run the peaks discussed from figure 5.2A are obtained again without making another injection. The ability to regenerate these peaks makes it clear that some of the sample is remaining on the column. After repeating the gradient for the fifth time all the sample was eventually removed from the
Figure 5.2  Gradient elution of Ag Tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 100% water to 100% MeOH, pH 4.5 phosphate buffer: (a) chromatograms from PMT (red) and FL (blue) detectors, (b) absorbance spectra, and (c) fluorescence spectra (excited at 400 nm) extracted from labeled chromatographic peaks at 17.5 and 22.5 min respectively.
(a) PMT detector vs FL detector

(b) Normalized Abs vs Wavelength (nm)

(c) Relative Intensity vs Wavelength (nm)
Figure 5.3  Chromatogram from PMT detector of gradient elution of Ag Tiopronin MPCs
using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 100% water to 100% MeOH, pH 4.5 phosphate buffer. Gradient was repeated; however no further injections were made.
column. When working with Ag Tiopronin MPCs, intensive washing of the column must be done between injections.

5.3.2 Separation of AgAu Tiopronin MPCs. The chromatograms obtained using gradient elution from 65% water to 65% methanol on the PMT and FL detectors for the AgAu Tiopronin MPCs can be seen in Figure 5.4A. The chromatograms show four distinctive peaks. The luminescence of AgAu Tiopronin MPCs was discussed in Chapter 2 and as would be expected, the FL detector shows that the MPCs are luminescent. The absorbance spectra for the four peaks are shown in Figure 5.4B. The absorbance spectra of the later eluting peaks 3 and 4 have a surface plasmon band at 500 nm which is indicative of AgAu Tiopronin MPCs with an average core diameter of 2.1 ± 0.4 nm. The absorbance spectra for peak 2 is a featureless exponential decay, however it has the typical shape expected for MPCs. It is known that poly-disperse Au MPCs of a small enough core size will have a featureless exponential decay absorbance spectrum. The absorbance spectrum obtained for peak 2 is likely from a smaller average core diameter than the later eluting peaks. The elution order was expected to be from the smaller core sizes to the larger core sizes\(^{18}\) and this is what is observed for the AgAu Tiopronin MPCs.

The absorbance spectrum for peak 1 (Figure 5.4B) is a sharp decay and not representative of typical MPCs. From the chromatogram obtained from the FL detector is Figure 5.4A it is clear that peak 1 is a highly fluorescent species. These findings for the AgAu Tiopronin MPCs are comparable to those of the Ag Tiopronin MPCs. It seems that for the samples where Ag is present in the MPC core, a fluorescent species, with absorbance not indicative of typical MPCs, is detected by HPLC. Peak 1 is Figure 5.2A shows similar absorbance (Figure 5.2B) and fluorescence (Figure 5.2C) as peak 1 in Figure 5.4A, the retention times are not comparable since different gradients were used. Like the Ag Tiopronin MPCs the AgAu
Figure 5.4 Gradient elution of AgAu tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 65% water to 65% MeOH, pH 4.5 phosphate buffer: (a) chromatograms from PMT (red) and FL (blue) detectors, (b) absorbance spectra extracted from labeled chromatographic peaks at 24, 29, 33, and 42 min respectively.
(a) Relative Intensity vs. Time (min)

- FL detector
- PMT detector

(b) Normalized Abs vs. Wavelength (nm)

- Peak 1
- Peak 2
- Peak 3
- Peak 4
Tiopronin MPCs were found to cause some ghosting (shown in Figure 5.3 for the Ag tiopronin MPCs), however to much less an extent.

5.3.3 Separation of Pd Tiopronin MPCs. The chromatogram using isocratic elution (65% methanol, 35 % water) on the PMT detector for Pd Tiopronin MPCs can be seen in Figure 5.5A. From the FL detector nothing but baseline was detected. This was expected since, as discussed in Chapter 3, the Pd Tiopronin MPCs are not luminescent. Using isocratic elution for the Pd Tiopronin MPCs gave a single peak with significant tailing. There is evidence of a few minor peaks present within the tail of the prevalent peak. It is clear that isocratic elution does not give sufficient separation for the Pd Tiopronin MPCs, however it is encouraging that there does appear to be some size separation. The use of an optimized gradient elution method would very likely yield an efficient separation of the Pd Tiopronin MPCs. The absorbance spectrum showing a featureless decay obtained for the main peak can be seen in Figure 5.5B. A featureless decay is what is expected for Pd Tiopronin MPCs.

It should be noted that unlike the Ag and AgAu Tiopronin MPCs, a fluorescent species, with a sharp decay absorbance spectrum not typical of MPCs, was not detected in the Pd Tiopronin MPC sample. This serves as further evidence that the presence of a luminescent species with sharp decay absorbance (detected in Ag and AgAu MPC samples) is likely connected to the presence of Ag in the MPC core. The previous separation of Au Tiopronin MPCs also did not show a fluorescent species with sharp decay absorbance, further supporting this claim. Ghosting on the HPLC column was observed for both the Ag and AgAu Tiopronin MPCs, however this was not the case for the Pd Tiopronin MPCs.

5.3.4 Separation of PdAu Tiopronin MPCs. The results obtained for the separation of PdAu Tiopronin MPCs are very similar to those obtained for Pd Tiopronin MPCs. No fluorescence was expected for PdAu Tiopronin MPCs and consequently only baseline was
Figure 5.5 Isocratic elution of Pd tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 65% MeOH and 35% water, pH 4.5 phosphate buffer: (a) chromatogram from PMT detector and (b) absorbance spectrum extracted from chromatographic peak at 6 min. The absorbance was not found to change at different locations throughout the peak.
(a) Absorption vs. Time (min)

(b) Absorption vs. Wavelength (nm)
detected on the FL detector. The chromatogram using isocratic elution (65% methanol, 35 % water) on the PMT detector for PdAu Tiopronin MPCs can be seen in Figure 5.6A. Like the Pd Tiopronin MPCs a single predominate peak is obtained, however no tailing of the peak is observed. The peak is preceded by a shoulder which could be the result of some size separation. The results for the isocratic elution are encouraging and an optimized gradient elution method should lead to size separation. Figure 5.6B shows the absorbance spectrum for the primary peak. The PdAu Tiopronin MPCs are expected to have a surface plasmon band at 520 nm and this is what is observed. Like the Pd Tiopronin MPCs, no fluorescent species was detected and there was no evidence of ghosting on the column.

5.3.5 Conclusions. Reversed phase ion-pair HPLC was carried out on a variety of different metal cores of tiopronin MPCs. Isocratic elution of Ag, Pd and PdAu Tiopronin MPCs gave encouraging results where it was confirmed that the MPCs were eluting from the column, however efficient size separation was not obtained. It is evident that for all the MPCs discussed that an optimized gradient elution method should lead to the most efficient separation. This is most clearly seen for the AgAu Tiopronin MPCs where a size separation, where small core sizes eluted first, was observed for gradient elution.
Figure 5.6  Isocratic elution of PdAu tiopronin MPCs using a mobile phase of 0.05 M Bu₄N⁺F⁻ in 65% MeOH and 35% water, pH 4.5 phosphate buffer: (a) chromatogram from PMT detector and (b) absorbance spectrum extracted from chromatographic peak at 17 min.
5.4 REFERENCES


Chapter VI

ACID/BASE PROPERTIES OF Au TIOPRONIN MONOLAYER PROTECTED CLUSTERS

6.1 INTRODUCTION

A significant amount of research has been dedicated toward studying monolayer protected clusters (MPCs) and the factors that will influence their properties. The physical, chemical, and optical properties of MPCs have been found to be dependent on the size of the core, metal composition of the core, and the attached protecting ligands. The interactions between the individual ligands on the core of the MPC are possible influencing factors that have not been extensively studied. Based on the structure of the MPCs the ligands are positioned such that interactions amongst the ligands are probable. Each given ligand is attached to the metal core and is constrained to a specific location where other ligands will be in close proximity.

The interactions between individual ligands can be studied by looking at MPCs with a protecting monolayer composed of a ligand with a terminal acid group, such as tiopronin. Using tiopronin as the protecting ligand coverage gives the advantage of studying the acid/base properties of the MPCs where the general theory of acid/base interactions is well known. The multiple tiopronin ligands attached to the metal core creates an overall system that can be viewed as a polyprotic acid. Classical linear polyprotic acids have the ability to elongate minimizing interaction between the various protonation sites. The structure of a
MPC does not allow for this and it is expected that closely positioned protonation sites will influence one another. Studying these effects will allow a greater understanding of how the individual ligands on the core are interacting.

A significant amount of information can be gained from acid/base titration curves of polyprotic acids, primarily in terms of protonation constants. For polyprotic acids there are three meaningful pK\textsubscript{a} values including macroscopic, microscopic, and quasisite.\textsuperscript{1} The macroscopic values describe how the protons bind to the molecule as a whole, the microscopic values describe the binding equilibria between different binding sites, and the quasisite values describe different binding sites assuming no interaction. While only pK\textsubscript{a} values defined thermodynamically are absolute, pK\textsubscript{a} values determined from titration curves give good approximations.

The acid/base properties of poly(propylene imine) and poly(amidoamine) dendrimers have been studied.\textsuperscript{2,3} The structure of a dendrimer is similar to that of an MPC and it is likely that the acid/base properties of the two would be comparable. Acid/base titration curves of the dendrimers indicated repulsive interactions between neighboring protonation sites. While the distinctive pattern of repulsive interactions for the dendrimers is unique to the structure, the same phenomenon of repulsive interactions holds true for MPCs. Acid/base titrations on tiopronin MPCs have shown that the MPCs behave differently than the tiopronin monomer,\textsuperscript{4} indicating that interactions between the tiopronin ligands on the MPC are occurring. In this chapter the further investigation of acid/base titrations of tiopronin MPCs is discussed. The pK\textsubscript{a} values obtained are compared for different core sizes of the MPCs, as well as the MPCs in the presence of different electrolyte concentrations.
6.2 EXPERIMENTAL

6.2.1 Chemicals. HAuCl₄·xH₂O⁵ was synthesized according to literature. N-(2-mercaptopropionyl)glycine (tiopronin, 99%), sodium borohydride (NaBH₄, 99%), sodium nitrate (NaNO₃, 99%), agarose, tris-borate-EDTA buffer, and sodium hydroxide were purchased from Aldrich. Ethanol (HPLC grade), methanol (HPLC grade), and glacial acetic acid were purchased from Fisher and used as received. House-distilled water was purified on a Barnstead NANOpure system (≥ 18MΩ).

6.2.2 Synthesis of MPCs. Briefly for Au Tiopronin MPCs,⁴ tetrachloroauric acid (0.50 g, 1.5 mmol) and N-(2-mercaptopropionyl)glycine (0.63 g, 3.9 mmol) were co-dissolved in 63mL 6:1 methanol/acetic acid producing a ruby red solution. NaBH₄ (0.95 g, 25 mmol) in 12.5 mL of H₂O was added immediately, resulting in a black solution, that was stirred for 30min. The solvent was removed under vacuum (≤ 35 °C). The black product was dissolved in 25 mL H₂O; then concentrated HCl was added drop-wise to adjust to pH 1, and then dialyzed (8 in. Spectra/Por CE, MWCO = 5000) for three days. The water was removed under vacuum resulting in the final product. Au tiopronin MPCs were separated by preparative gel electrophoresis (agarose gel, borate buffer). After 4-5 hours a smeared band that could be cut into 8 segments was obtained. The sample was removed from the gel material by placing cuts of the gel in water and applying a potential. The sample migrated out of the gel and into the water. Methanol washes removed any remaining gel material.

6.2.3 Spectroscopic Measurements. For spectroscopic measurements, 3 mL of 1 µM solutions were prepared. Luminescence spectra were taken in a 90° geometry on a modified ISA Fluorolog FL321 spectrometer. The fluorometer was equipped with a 450 W xenon source, and Hamamatsu R928 PMT (visible wavelengths) and InGaAs (near-IR wavelengths) detectors. Near-IR luminescence spectra were taken using a long pass filter,
placed in the sample compartment, with cutoff of 450 nm. UV-vis spectra were taken with a Shimadzu UV-1601 UV-visible spectrophotometer.

6.2.4 Acid/Base Titrations. Titrations were performed on a Mettler Toledo DL58 titrator of 1 µM Au tiopronin MPCs in 5 mL of H2O with 0.01 M NaOH. The pH measurements were taken on a Mettler Toledo DG 101-SC electrode. Various concentrations of NaNO3 were added to the titrated MPCs. The pKₐ values were determined by LabX light titration software.

6.3 RESULTS AND DISCUSSION

6.3.1 Electrolyte Concentration Relationship to pKₐ. It has been reported for titrations run on Au Tiopronin MPCs with an average core size of 1.8 nm that the average pKₐ decreases as the concentration of electrolyte is increased. For the MPCs with no electrolyte present, a pKₐ=5.6 was observed. In a 20mM electrolyte solution a pKₐ=4.8, and in a 1M electrolyte solution a pKₐ=4.0 were observed. In Figure 6.1, the auto-titrations of 1 µM solutions of tiopronin-coated Au MPCs, in varying electrolyte concentrations, with 0.01 M NaOH are shown. The general trend of decreased pKₐ with increased electrolyte concentrations previously determined is followed although to a much lesser extent. With no electrolyte, 0.01 M, 0.05 M, and 0.1 M electrolyte present, the MPCs were found to have pKₐ values of 6.1, 5.6, 5.4, and 5.3 respectively. These values were determined by labX software that extrapolated the values as typically done as the pH at half the equivalence point.

The thermodynamic cost of generating negative sites on the tiopronin ligand is lowered in the presence of electrolyte. The lower thermodynamic cost minimizes the charge repulsive interactions and allows the MPCs to behave more like that of the tiopronin monomer. The fact that the pKₐ of the MPCs never reaches that of the tiopronin monomer, even with a
Figure 6.1  Titration curves of 1 µM Au Tiopronin MPCs, at different electrolyte concentrations, with 0.01 M NaOH. The pK_a values were extrapolated from the curves and found to be 6.1, 5.6, 5.4 and 5.3 with no electrolyte, 0.01 M, 0.05 M, 0.1 M NaNO_3 respectively.
significant amount of electrolyte present, suggests that charge repulsive interactions are still prevalent. These results are expected given the structure of the MPC.

In general the pKₐ values are slightly higher than those previously observed.⁴ As will be discussed later, the observed pKₐ values for the MPCs are affected by both electrolyte concentration and size of the cluster. While the tiopronin-coated Au MPCs being studied show the characteristic optical properties (as seen in Figure 6.2) attributed to MPCs with an average core size of 1.8 nm,⁶,⁷ it is possible that the sample has a slightly larger average core size than the MPCs previously studied. Many factors such as the age of the sample, time the sample remained in solution, and the extent of purification will influence the average core size of the MPCs.⁸ It should be noted that the Au tiopronin MPCs used in these experiments were from a three month old batch and therefore the possibility of a size increase exists.

It should also be noted that periodically titration curves with a more sigmoidal shape than would be expected were observed. A typical curve representative of this can be seen in Figure 6.3A. This defect is attributed to the low concentrations used for the titrations which are necessary due to the limited availability of sample. Figure 6.3 shows the titration curves of tiopronin monomer at concentrations of 1 µM and 1 mM. It is clear that the increased concentration eliminated the problem. The determined pKₐ value for the tiopronin monomer was found to be 3.5 from both of the titration curves. The sigmoidal shape seen in Figure 6.3A did not affect the value obtained for the equivalence point used to determine the pKₐ value.

6.3.2 Core Size Relationship to pKₐ. Gel electrophoresis was used to separate Au tiopronin MPCs with an average core diameter of 1.8 nm where a smeared band of MPCs separated by size was obtained. The gel was cut into 8 segments (cuts labeled from 1-8, where cut 1 moved the least amount of distance) of various core sizes in which the smaller core sizes
Figure 6.2 Luminescence spectrum (excited at 400 nm) (a) and UV-vis spectrum (b) of 1µM Au Tiopronin MPCs.
Figure 6.3  Titration curves for 1 µM (a) and 1 mM (b) tiopronin with 0.01 M NaOH
(pK_a=3.5 was extrapolated from both curves).
moved the furthest. Figure 6.4 shows the UV-vis absorbance spectra of cuts 1 and 8. The absorbance spectrum obtained for cut 1 shows a clear surface plasmon band at 520nm indicative of larger core sizes. The absorbance spectrum obtained for cut 8 shows a featureless exponential decay indicating that the core size is smaller than the sample from cut 1. It is clear from the absorbance spectra that some size separation is achieved.

Figure 6.5 shows the auto-titrations of 1 µM solutions of tiopronin-coated Au MPCs from cuts 2, 4, and 6 with 0.01 M NaOH. In general the trend of decreasing pKₐ for decreasing average core size was observed. For cut 2 a pKₐ=5.8, cut 4 a pKₐ=5.4, and cut 6 a pKₐ=5.2 were observed. It is believed that for MPCs of smaller core sizes the monolayer is not as closely packed as it is in MPCs of larger core sizes. Presumably the less packed the ligands are, the less they will be affected by charge repulsive interactions, and therefore have a lower pKₐ. The observed trend supports this theory.

6.3.3 Conclusions. The pKₐ values of Au Tiopronin MPCs were found to decrease as the concentration of electrolyte was increased in solution. The core size of the Au Tiopronin MPCs also affected the observed pKₐ where smaller core size gave lower pKₐ values. Both these finding suggest charge repulsive interactions are occurring within the monolayer, however they are minimized by the presence of electrolyte and in smaller core sizes.
Figure 6.4  UV-vis spectra from 1 µM Au Tiopronin MPCs separated by gel electrophoresis, cuts 1 and 8.
Figure 6.5  Titration curves of 1 µM Au Tiopronin MPCs, separated by gel electrophoresis (cuts 2, 4, and 6), with 0.01 M NaOH. The pKₐ values were extrapolated from the curves and found to be 5.8, 5.4, and 5.2 for cuts 2, 4, and 6 respectively.
6.4 REFERENCES


