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UNIVERSITY OF CALIFORNIA, SAN DIEGO

Anisotropic Nanocrystals from Supramolecular Templates

A dissertation submitted in partial satisfaction of the

requirements for the degree of Doctor of Philosophy

in

Chemistry

by

Whitney M. Bryks

Committee in charge:

Professor Andrea Tao, Chair Professor Clifford Kubiak Professor Andrew Kummel Professor Shirley Meng Professor Michael Sailor Professor William Trogler

2017

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Chair

University of California, San Diego

2017

DEDICATION

This thesis is dedicated to my parents, Michael and Carolyn Bryks, who instilled in me such strong values that they didn't need to direct, guide or constrain my personal development in any way. While the path I have followed is entirely my own, any success I have met is attributed to the success of the tenets that they have taught.
Although the loving childhood amidst the most serene redwood forest coupled with the emergence of a box of science fiction books may have played some role in sparking my nascent curiosity.

EPIGRAPH

"Our belief is not a belief. Our principles are not a faith. We do not rely solely upon science and reason, because these are necessary rather than sufficient factors, but we distrust anything that contradicts science or outrages reason. We may differ on many things, but what we respect is free inquiry, openmindedness, and the pursuit of ideas for their own sake."

- Christopher Hitchens

| Signature Pag | ge | iii |
|----------------|--|-------|
| Dedication | | iv |
| Epigraph | | v |
| Table of Con | tents | vi |
| List of Abbre | eviations | ix |
| Lists of Figur | res and Tables | X |
| Acknowledge | ements | XV |
| Vita | | xvii |
| Abstract of th | ne Dissertation | xviii |
| Chapter 1 | Introduction to 2D Materials and Metallomesogens | 1 |
| 1.1. | Interest and applications for low dimensional nanomaterials. | 2 |
| 1.2. | Novel routes for expanding the library of 2D materials | 9 |
| 1.3. | 2D materials via Bottom-up Self-Assembly | 13 |
| 1.4. | Liquid Crystalline Phases of Metallomesogens | |
| 1.5. | References | 23 |
| Chapter 2 | Design and Self-Assembly of Metal Alkanethiolates | |
| 2.1. | General Synthetic scheme and considerations | |
| 2.2. | Metal Ion Selection | |
| 2.3. | Self-Assembly and Morphology of Copper Alkanethiolates | |
| 2.4. | Self-Assembly at the Air-Water Interface: | |
| | Copper Alkanethiolate Multilayers and Monolayers | |

TABLE OF CONTENTS

| Chapter 3 | Mesogenic Metal Alkanethiolates as Nanocrystal Precursors | 54 |
|-----------|---|-----|
| 3.1. | Background and Previous Studies with Cu, Ag, and Au | 55 |
| 3.2. | Ag Nanodisks from Supramolecular Ag Alkanethiolate | 60 |
| 3.3. | Supramolecular Precursors for the Synthesis | |
| | of Anisotropic Cu ₂ S Nanocrystals | 66 |
| | 3.3.1. Introduction | 66 |
| | 3.3.2. Results and Discussion | 68 |
| | 3.3.3. Nanodisk Growth mechanism | 76 |
| | 3.3.4. Supplemental Information | 79 |
| 3.4. | References | 86 |
| Chapter 4 | Chemical Modification of Copper Alkanethiolates | |
| | for Design of Thermal Properties | 89 |
| 4.1. | Effects of Alkyl Chain Modification | 90 |
| 4.2. | Effects of Intercalated Halide Ions | 95 |
| 4.3. | Digenite Nanosheets Synthesized by Thermolysis | |
| | of Layered Copper Alkanethiolate Frameworks | 102 |
| | 4.3.1. Introduction | 102 |
| | 4.3.2. Results and Discussion | 107 |
| | 4.3.3. Mechanism for SNC Growth | 120 |
| | 4.3.4. Optical Characterization and AFM of SNC Nanosheets | 122 |
| | 4.3.5. Conclusions | 124 |
| | 436 Materials and Methods | 125 |

| | 4.3.7. Supporting Information | 129 |
|-----------|--|-----|
| 4.4. | References | 133 |
| Chapter 5 | Metallomesogen Templates for Shape Control | |
| | of Metal Selenide Nanocrystals | 137 |
| 5.1. | Abstract | 138 |
| 5.2. | Introduction | 138 |
| 5.3. | Experimental Methods | 142 |
| 5.4. | Results and Discussion | 145 |
| 5.5. | Conclusions | 161 |
| 5.6. | Supporting Information | 163 |
| 5.7. | References | 167 |
| Chapter 6 | Structure and Thermal Properties of Supramolecular | |
| | Metal Alkanethiolates | 171 |
| 6.1. | Abstract | 172 |
| 6.2. | Introduction | 172 |
| 6.3. | Experimental Methods | 175 |
| 6.4. | Results and Discussion | 177 |
| 6.5. | Conclusions | 193 |
| 6.6. | References | 195 |

LIST OF ABBREVIATIONS

| AFM | Atomic force microscopy |
|--------|--|
| DSC | Differential scanning calorimetry |
| FTIR | Fourier-transform infrared spectroscopy |
| LC | Liquid crystal |
| LSPR | Localized surface plasmon resonance |
| NC | Nanocrystal |
| PL | Photoluminescence spectroscopy |
| SAM | Self-assembled monolayer |
| SEM | Scanning electron microscopy |
| TEM | Transmission electron microscopy |
| TGA | Thermogravimetric analysis |
| TMD | Transition metal dichalcogenide |
| UV-NIR | Ultraviolet-near-infrared wavelength absorption spectroscopy |
| UV-Vis | Ultraviolet-visible wavelength absorption spectroscopy |
| XRD | Powder X-ray diffraction |

LIST OF FIGURES AND TABLES

| Figure 1.1. | Schematic depiction of liquid crystalline phases | 21 |
|--------------|--|----|
| Figure 2.1. | Coordination complexes of Cu for water | |
| | and 4 other ligands tested | 37 |
| Figure 2.2. | A picture of Cu ²⁺ complexes formed in the presence | |
| | of various ligands | 38 |
| Figure 2.3. | Reaction kinetics of Cu-dodecanethiolate in the presence of various | |
| | coordinating ligands | 40 |
| Table 2.1. | Skew of water and ethanol composition during | |
| | precipitation of CuSC4H9 | 42 |
| Figure 2.4. | TEM and XRD of CuSC ₄ H ₉ | 43 |
| Figure 2.5. | TEM of Cu-butanethiolate precipitated in the presence | |
| | of various solvents and coordinating ligands | 44 |
| Figure 2.6. | TEM of CuSC ₄ H ₉ precipitated from oleylamine | |
| | as a function of time | 46 |
| Figure 2.7. | Assembly of Cu alkanethiolate at the air-water interface | |
| | via LB assembly | 48 |
| Figure 2.8. | SEM and TEM images of Cu-octadecanethiolate films | 50 |
| Figure 2.9. | AFM of Cu-octadecanethiolate film formed by LB assembly | 51 |
| Figure 2.10. | AFM of Cu-octadecanethiolate monolayer | |
| | formed by LB assembly | 53 |
| Figure 3.1. | Structure and thermal properties of Ag alkanethiolates | 60 |

| Table 3.1. | Interlayer spacing parameters for Ag alkanethiolates | 61 |
|--------------|--|----|
| Figure 3.2. | Time-dependent TEM imaging of AgSC ₁₂ H ₂₅ | 62 |
| Figure 3.3. | Structure and morphology of Ag NCs | 63 |
| Figure 3.4. | Structure and morphology of Ag ₂ S NCs | 64 |
| Figure 3.5. | Thermal properties of Cu alkanethiolates | 70 |
| Figure 3.6. | Characterization of Cu ₂ S nanodisks | 72 |
| Figure 3.7. | Characterization of Cu ₂ S nanosheets | 74 |
| Figure 3.8. | Time-dependent TEM analysis | 76 |
| Figure 3.9. | Decomposition of non-mesogenic Cu-thiolates | 78 |
| Figure 3.10. | XRD patterns of Cu alkanethiolates and spacing parameters | 80 |
| Figure 3.11. | TEM image of string-structures | 81 |
| Figure 3.12. | CuSC ₄ H ₉ DSC and TGA curves | 82 |
| Figure 3.13. | Nanodisk FTIR spectrum | 83 |
| Figure 3.14. | Nanosheet AFM | 84 |
| Figure 3.15. | Time-dependent nanosheet TEM | 85 |
| Figure 4.1. | XRD patterns and photograph of CuSC ₄ H ₉ precursors | |
| | arranged by sample aging | 92 |
| Figure 4.2. | Cu alkanethiolates modified with -OH and -COOH groups | 94 |
| Figure 4.3. | XRD, FTIR, and TGA of CuSC ₄ H ₉ synthesized | |
| | in the presence of NaCl | 96 |
| Figure 4.4. | TEM images of CuSC ₄ H ₉ precipitated in the presence of various | |
| | concentrations of NaCl. | 97 |

| Figure 4.5. | Optical extinction spectra and color differences in CuSC ₄ H ₉ |
|--------------|--|
| | samples prepared in increasingly saline solutions |
| Figure 4.6. | XRD and DSC of $CuSC_{10}H_{20}COOH$ synthesized |
| | with various halides |
| Figure 4.7. | TGA of CuSC ₁₀ H ₂₀ COOH synthesized |
| | with various halides |
| Figure 4.8. | Reaction scheme for digenite sheets and chalcocite particles |
| Figure 4.9. | Comparison of thermal properties of CuSC ₁₂ H ₂₅ |
| | and CuSC ₁₀ H ₂₀ COOH |
| Table 4.1. | FTIR assignments of CuSC ₁₀ H ₂₀ COOH precursor |
| | synthesized with and without Cl ⁻ 111 |
| Figure 4.10. | FTIR spectra of CuSC ₁₀ H ₂₀ COOH precursor111 |
| Figure 4.11. | Thermal properties of pristine and Cl-intercalated $CuSC_{10}H_{20}COOH$ |
| | precursors as measured by DSC and TGA |
| Table 4.2. | Lamellar bilayer d-spacing shown as a function of Cl ⁻ content 113 |
| Figure 4.12. | XRD of $CuSC_{10}H_{20}COOH$ precursors prepared with |
| | varying [Cl ⁻]115 |
| Figure 4.13. | Effect of varying Cl ⁻ incorporation |
| Table 4.3. | EDX results comparing [Cl ⁻] of the precursor vs. that of the product |
| | after thermolysis for 6 h at 200 °C118 |
| Figure 4.14. | Time-dependent electron microscopy of chalcocite |
| | particle formation and digenite sheet formation |

| Figure 4.15. | AFM and optical characterization of digenite nanosheets. | 123 |
|--------------|---|-----|
| Figure 4.16. | EDX of Cu _{2-x} S products generated from precursor | |
| | in which [Cl ⁻] increases for the series | 129 |
| Figure 4.17. | TEM images of Cu _{2-x} S nanoparticles after varying | |
| | thermolysis conditions | 130 |
| Figure 4.18. | Supplemental AFM profiles of the nanosheet products. | 131 |
| Figure 4.19. | Comparison of $CuSC_{10}H_{20}COOH$ precursor with and without | |
| | Cl ⁻ , shown at RT and at 125 °C | 132 |
| Figure 5.1. | Reaction scheme depicting metal-selenolate synthesis | 145 |
| Figure 5.2. | Precursor characterization for CuSeC ₁₂ H ₂₅ | |
| | and AgSeC ₁₂ H ₂₅ | 149 |
| Figure 5.3. | Thermolysis of CuSeC ₁₂ H ₂₅ | 151 |
| Figure 5.4. | Time-dependent thermolysis of CuSeC ₁₂ H ₂₅ at 160 °C | 152 |
| Figure 5.5. | Thermolysis of AgSeC ₁₂ H ₂₅ | 154 |
| Figure 5.6. | Time-dependent thermolysis of AgSeC ₁₂ H ₂₅ at 150 °C | 156 |
| Figure 5.7. | Characterization of Ag _{0.5} Cu _{0.5} SeC ₁₂ H ₂₅ | 157 |
| Figure 5.8. | Thermolysis of Ag _{0.5} Cu _{0.5} SeC ₁₂ H ₂₅ | 159 |
| Figure 5.9. | In-situ XRD spectra | 167 |
| Figure 5.10. | FTIR spectra taken of solid AgSeC12H25 and | |
| | CuSeC ₁₂ H ₂₅ precursor compounds | 163 |
| Figure 5.11. | Additional TEM images taken from side-on | |
| | vantage of Cu _{1.8} Se nanoribbon structures | 164 |

| Figure 5.12. | Ag ₂ Se spherical particles from AgSeC ₁₂ H ₂₅ at 185 °C164 |
|--------------|--|
| Figure 5.13. | Ag ₂ Se nanorods synthesized from AgSeC ₁₂ H ₂₅ at 150 °C165 |
| Figure 5.14. | Polarized optical microscope images of Ag _{0.5} Cu _{0.5} SeC ₁₂ H ₂₅ 166 |
| Figure 6.1. | XRD of metal n-dodecanethiolate complexes by oxidation |
| | state of metal ion used |
| Table 6.1. | Interlayer <i>d</i> -spacings of metal dodecanethiolate complexes |
| Table 6.2. | Tabulated temperatures of phase transition |
| Figure 6.2. | DSC thermograms of selected metal dodecanethiolate complexes181 |
| Figure 6.3. | TGA thermograms of metal dodecanethiolate complexes |
| | separated by oxidation state of ion used183 |
| Table 6.3. | Tabulated data for mass retention and maximum thermolysis |
| | rate, <i>T_{max}</i> , of metal dodecanethiolate complexes |
| Figure 6.4. | Decomposition temperature T_{max} of Zn(II) thiolates |
| Table 6.4. | Phase transition temperatures for various metal alkanethiolates187 |
| Figure 6.5. | POM of In-dodecanethiolate at various temperatures |
| Figure 6.6. | Mesophase modification with functional groups190 |
| Table 6.5. | Phase transitions for functionalized Ag and Pb alkanethiolates190 |
| Figure 6.7. | Solventless thermolysis reactions of several metal alkanethiolates 193 |

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PUBLICATIONS

Whitney Bryks, and Andrea R. Tao. "Structure and Thermal Properties of Supramolecular Metal Alkanethiolates." *(in preparation)*.

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FIELDS OF STUDY

Major Field: Chemistry

Studies in NanoEngineering and Inorganic Chemistry Professor Andrea Tao

ABSTRACT OF THE DISSERTATION

Anisotropic Nanocrystals from Supramolecular Templates

by

Whitney M. Bryks Doctor of Philosophy in Chemistry University of California, San Diego, 2017

Professor Andrea Tao, Chair

The study of nanocrystals has proven to be a rapidly developing field in the last couple of decades. Advances in synthetic control, characterization techniques, and an expanding pool of applications has spurned continual interest in the development of these highly specialized optoelectronic materials at ever-decreasing dimensions. The phenomena encountered at the nanoscale, such as quantum confinement and localized surface plasmon resonances, represent incredibly powerful tools to be utilized in nextgeneration optoelectronic devices. Accordingly, there has been a significant push towards understanding fundamental processes at the nanoscale, such as self-assembly, crystalline nucleation and growth, and surface chemical interactions. Moreover, synthetic work continues to expand the existing libraries of nanomaterials to include more compounds and shapes that are challenging to synthesize, such as highly confined 1D or 2D structures.

This dissertation discusses a method of producing supramolecular assemblies for the purposes of obtaining highly anisotropic and shaped nanocrystals from confined nucleation and growth. This method is noteworthy in that it differs significantly from conventional nanocrystal syntheses. Traditional nanocrystal growth is accomplished via solvothermal reaction of anions and cations, or reduction of cations in the case of a metal, in the presence of coordinating ligands or polymer in methods broadly termed colloidal synthesis. In such reactions, the resulting shape of the nanocrystal generated is dictated by the chemisorption or physisorption of coordinating chemical groups to specific crystalline facets, according to their surface energy. In the present work, we initially synthesize metal alkanethiolate complexes, which function as precursor molecules to metal sulfide crystals upon pyrolytic decomposition. The precursor molecules are designed to form supramolecular structures which can behave as thermotropic liquid crystals, where pseudo-liquid crystalline "mesophases" can be adopted with heating. Thus, these precursors can be heated in a solventless thermolysis reaction to afford metal sulfide crystallization occurring within the soft template afforded by an ordered mesophase.

The scope of this work has several components. First, to understand the

xix

synthesis and self-assembly of metal alkanethiolate complexes, we probe selfassembly in various media and conditions. Next, we seek to understand the chemical interactions which give rise to phase transitions. By understanding the chemical interactions which determine thermal properties, we seek to attain chemical control over thermal properties such that there is some tunability of the decomposition temperature or structural phase during thermolysis. In doing so, we can design precursors with the proper thermal properties to exhibit nanocrystal nucleation and growth within a desired structural phase in order to control nanocrystal shape. We show that these supramolecular templates can facilitate nucleation and growth of nanocrystals within ordered, pseudo-liquid crystalline melts which have the capacity to impart extreme anisotropy to the nanocrystal morphology. Herein, we report the synthesis and characterization of a host of metal alkanethiolates and some metal alkaneselenolates, detail their thermal properties, and utilize them as platforms to synthesize an array of shaped metal, metal sulfide, and metal selenide nanocrystals. Chapter 1

Introduction to 2D Materials and

Metallomesogens

1.1 Interest and Applications for Low Dimensional

Nanomaterials

Synthesis of nanomaterials has garnered increasing interest in recent years due to the optical, electronic, and physical properties enabled at the nanoscale. One of the hallmark attributes of "low dimensional" nanomaterials is that, by virtue of being "confined" in one or more dimensions, they possess extremely high surface area to volume ratios. Beyond this, there is the property of quantum confinement which exists in semiconductor crystals in the nanoscale regime. Quantum confinement dictates that as a semiconductor is scaled in dimension below its exciton Bohr radius, the bandgap increases. In theory, this enables bandgap to be tuned from nominal "bulk" levels to that of an insulator (and everywhere in between) if one could establish precise control over the size of a semiconducting nanocrystal (NC). The principle is illustrated most beautifully by quantum dots such as CdSe, where precise size control (diameter between 1.5 and 5 nm) enables a narrow photoluminescence response tunable throughout the visible spectrum.¹ Such quantum dots are the penultimate "0D" nanomaterial; being confined in all 3 dimensions; nanorods, tubes and wires are representative of 1D nanomaterials, and disks, films, and nanosheets are representative of 2D nanomaterials. Although this dissertation covers a bottom-up approach for the synthesis of these "low dimensional" nanomaterials, there is a focus on 2D materials from which much of the inspiration for the work was derived.

The guintessential 2D material of our time is the atomically thick allotrope of carbon, graphene, discovered by Novosolov and Geim in 2004.² Previous to these findings, it was predicted that such ultrathin 2D materials would be thermodynamically unstable; that even the thermal energy at room temperature would disrupt their bonding scheme and lead to their collapse. Quite contrarily, graphene exhibits remarkable mechanical strength due to its incredibly strong in-plane sp^2 bonding system. More interestingly however, that sp^2 bonding system gives rise to remarkable electronic properties; despite its carbonaceous composition, graphene behaves as a semi-metal, and exhibits extraordinary conductivity (15,000 cm²V⁻¹s⁻¹). These findings spurred great excitement in the scientific community, which propelled research on graphene to an unprecedented level. They also instigated greater investigations into similar materials; most notably, a class of compound materials which possessed similar structure, where 2D layers some number of atoms thick are held together solely by van der Waals interactions. This class of materials is the 2D transition metal dichalcogenides (TMDs), which take on the formula MX_2 (M = metal, X = O, S, Se, Te). Unlike graphene however, many TMDs are inherent semiconductors, which makes them more readily suitable for many applications including nanoelectronics, a role which the community was desperately trying to fill with graphene.

The synthesis of TMDs has met with much progress in recent years. For the most part, synthetic routes have been developed following two separate pathways: first, a top-down approach, where a bulk layered crystal is separated into many-

layered or few-layered subcomponents; and a bottom-up approach, where monolayers of material are chemically synthesized in solution, or grown on a substrate. While mechanical exfoliation used to be the most prominent method for separating single and few-layered crystals from bulk, recent work has extensively developed chemical exfoliation methods. Now, one of the more common methods for obtaining single and few-layered TMDs is through simple ultrasonication in a strongly coordinating solvent. Coleman and co-workers reported obtaining single or few-layered crystals of MoS₂, WS₂, MoSe₂, NbSe₂, TaSe₂, NiTe₂, and MoTe₂ by simply sonicating the crystals in *N*-methyl-pyrrolidone (NMP), or dimethylformamide (DMF).^{3,4} The key to this chemical exfoliation method is the matching of the surface energy between the solvent and the layered crystal. Another chemical exfoliation method involves intercalating Li⁺ between TMD layers, and then sonicating in water to disperse the sheets.⁵ In this method, exposure of a TMD to alkyl lithium forms a Li-intercalated TMD which will reduce water to form H₂ gas between TMD layers, which helps to drive them apart and facilitate exfoliation. This "intercalation and exfoliation" method has been greatly developed, such that an electrochemically driven Li-intercalation is now able to reach 90% yield of single layer MoS₂ and TaS₂ sheets.⁶

Synthesis of 2D TMDs from the bottom up is quite distinct from the top-down exfoliation methods. Here, extreme care must be taken to control the crystal growth process in order to facilitate growth of single or few-layered crystals. The most common method being employed to grow 2D TMD crystals is chemical vapor phase deposition (CVD), where precursor gases are exposed to a growth substrate with

controllable temperature and flow rate. In this scheme, the deposition of TMD is very sensitive to the substrate; features such as step edges can substantially reduce the nucleation energy barrier of TMDs, such that substrate patterning can help to control nucleation points of TMDs.⁷ However, CVD can use a variety of metal and chalcogen sources to achieve the growth of metal chalcogenide on the surface, including exposing a metal or metal oxide film to sulfur/selenium gas, or using a vapor phase metal source (MOCVD).^{8,9} Alternatively, another bottom-up approach is to directly synthesize TMDs by colloidal synthesis in a solvent-based reaction. In this strategy, the inherent 2D nature of the TMD crystal structure is amenable to the growth of single and few-layered crystals so long as the capping ligand used and chalcogen reaction rate are carefully controlled. These colloidal growth methods were pioneered by Cheon and co-workers, who used oleylamine as a ligand and either CS₂ or Se as the chalcogen source to prepare TiS₂, ZrS₂, HfS₂, VS₂, NbS₂, TaS₂, TiSe₂, VSe₂, NbSe₂, and TaSe₂ colloidal crystals with few-layers.¹⁰ This method was further refined in time, such that single-layer TMDs could be obtained by controlling the flow rate of H_2S gas used as S source, or by proper ligand selection.^{11,12}

Graphene and TMDs are interesting materials which undoubtedly injected a fresh bout of interest into such low-dimensional nanostructures. However, graphene and TMDs are but a limited class of select materials possessing an inherently layered crystal structure. For years, chemical synthetic methods have been able to yield NCs which are "ultrathin" (typically, < 5 nm) with 0, 1, and 2D confinement. The applications which drive the investigations of all of the aforementioned nanomaterials

are myriad. Beginning with the field of electronics, we note that the semiconductor industry has, for decades, been in search of materials as potential replacements for Si in next-generation electronic devices. Thus, low-dimensional semiconductor nanomaterials are being studied extensively for work as field effect transistors (FETs).¹³ For example, researchers demonstrated that MoS₂ with HfO₂ (as dielectric) was capable of a current ON/OFF ratio of 108 at room temperature, two orders of magnitude beyond the requirements for electronic circuits.¹⁴ MoS₂ transistors have subsequently demonstrated operation in the Ghz range.¹⁵ Thus, these low-dimensional nanomaterials could in theory power next-generation FETs, thereby enabling nanoscale dimensions that are still difficult to obtain with current standards of atomic layer deposition and photolithography. Moreover, such ultrathin NCs offer the added benefits of transparency and flexibility, promising potential use for flexible or transparent electronic devices.^{16,17} Accordingly, several reports have been able to demonstrate flexible FETs based on MoS₂, using several other flexible materials (such as liquid gels or boron nitride) as the dielectric component.^{18,19} However, incorporation of standalone NCs (depositing or inserting with proper orientation and alignment) into electronics produced at scale remains a challenge that will likely persist for some time.

2D materials are also being extensively investigated for uses in energy generation and storage. Another particularly useful aspect of layered 2D materials is the ability to reversibly intercalate ions between adjacent layers. This has led to much research into the potential use of layered 2D materials as energy storage devices and

even supercapacitors. A class of 2D materials known as MXenes (a reduced layered carbide or nitride of an early transition metal) has shown large volumentric capacitance (900 F·cm⁻³), due to the ability for exfoliated sheets to restack.²⁰ Such expansion and contraction allows ions to flow in and out reversibly. Accordingly, TMDs have been applied similarly, where they have proven to be a good storage medium for Na⁺ ions, functioning as a Na battery with high cycling life.²¹ Along the lines of energy production, an umnet need exists in finding an energy-efficient way to generate H₂ to power H₂ fuel cells, and 2D materials including TMDs are being studied for activity in the hydrogen evolution reaction (HER). The edges of MoS_2 were found to be active sites in catalyzing H_2 evolution,²² prompting further research into TMDs as HER catalysts. Many layered metal sulfides, including the pyrite series (NiS₂, FeS₂, CoS₂), have shown strong catalytic activity.²³ Interestingly, work on amorphous MoS_3 and MoS_x showed greater HER catalytic activity than nominal crystalline MoS₂, which has been attributed to unsaturated S atoms being able to form S-H bonds.^{24,25} This implies that such catalytic activity is not unique to these layered sulfides, but may be universal to metal sulfides with unsaturated surface S atoms. Since TMDs show little edge surface area, other undiscovered metal sulfide nanomaterials may hold the key to unlocking the HER.

Solar cells represent another research area which has grown with alacrity, and many improvements in solar cell efficiency have been realized from incorporation of nanomaterials. For instance, semiconductor NCs can aid in the charge transfer role, and varying the size of a semiconductor further allows band gap modulation to

optimize solar absorption and increase absorption cross section.²⁶ In a different method, NCs supporting localized surface plasmon resonances (LSPRs) can drastically increase solar cell efficiency through a "light trapping" effect.²⁷ In a LSPR, charge carriers (holes or electrons) within a NC interact with incident electromagnetic radiation, causing them to oscillate. This oscillation of charge carriers produces strong electric field effects in the immediate vicinity of the particles, making them optical scatterers with large cross section. In solar cells, this serves to effectively trap light by creating light absorption and scattering that may be controlled to optimize photocurrent generation by the cell. As one might guess, the strong scattering capability of plasmonic NCs also enables their use as nanoantenna for sensing platforms. For example, Ag NCs exhibit a highly sensitive LSPR that responds to changes in the local dielectric environment with a shift in the absorption spectrum. This was used as a nanoscale biosensor by conjugating Ag NCs with biotin, such that addition of streptavidin could be detected because the biotin-streptavidin bond induces a 27 nm red-shift in the absorption spectra.²⁸ Although in these examples, semiconductor and plasmonic NCs used are not necessarily "ultrathin" materials, however their applications are highly relevant to the most prevalent material to be discussed in this dissertation, copper sulfide.

Copper sulfide of the β -chalcocite crystal structure is a self-doped semiconductor with the Cu_{2-x}S, where x represents the number of Cu vacancies, or holes, which are highly mobile charge carriers in the Cu_{2-x}S crystal structure. When the value of x becomes significant, the number of charge carriers becomes great

enough to support an LSPR, which is excitable in the near infrared (NIR) regime. While a great deal of previous work has established robust synthetic methods for Cu_{2-x}S NCs and demonstrated impressive tunability of their optical properties,^{29,30,31} it should be noted that some of the most desirable morphologies for plasmonic structures are low-dimensional structures with high anisotropy. The reason for this is that plasmonic crystals with well-defined facets, edges and corners exhibit some of the most strong electromagnetic field effects.³² Cu_{2-x}S has seen applications ranging from photovoltaics,³³ electrochemical sensors,³⁴ and photothermal therapy.³⁵ A great driving force for this work has been to take the Cu_{2-x}S system and investigate synthetic routes for new ultrathin semiconductor NCs which might be comparable to TMDs, but are designed from bottom-up assembly and possessing of structure supporting optical properties inaccessible to the TMDs.

1.2 Novel Routes for Expanding the Library of 2D Materials

The successful isolation of either single or few-layered crystals of materials such as graphene and layered TMDs stems invariably from their innate crystal structure. Top-down exfoliation is enabled by the van der Waals interactions between stacked layers, which can be overcome by intercalation and exfoliation techniques, and the success of bottom-up growth strategies is predicated on the in-plane growth facilitated by the 2D crystal structure (where the high-energy edges grow far faster than the faces). However, only select materials are capable of forming unbonded stacked layers, which means ultimately, the pool of optical, electronic, and physical properties accessible which benefit from these uniquely confined structures is limited. A great deal of computational modeling has been employed to analyze the greater pool of TMDs. Modelling has been able to show which TMDs are stable as monolayers (and with which structures), as well as predict physical and electronic properties. One such example is the work of Ataca et al, which used first-principles structure optimization and phonon calculations based on DFT to show that a variety of TMDs out of the 88 compositions analyzed are actually stable as free-standing monolayers.³⁶ Since this work, many of these TMDs have been successfully synthesized, however the contribution was demonstrating that while the diversity of electronic properties attainable with TMDs is high, they are not without inherent limitations.

Although graphene and TMDs provided the initial spark of interest, researchers soon looked to alternative materials. It was in essence a paradigm shift; graphene was predicted to be thermodynamically unstable and "impossible," which was taken by the scientific community as fact until disproven in 2004. In the wake of this paradigm shift, new materials that had before also been categorized as "impossible" seemed intriguing, and work was revived on "archaic" 2D structures which had been identified long ago. This shifting perspective is captured well in a 2013 publication by Koski et al titled "The New Skinny in Two-Dimensional Nanomaterials."³⁷ The narrative here conveys the lack of bounds for new 2D materials, and several prominent systems of 2D van der Waals materials including nitrides, thiophosphates, oxychlorides, and metal halides are shown to revitalize interest in these areas. Another great driver for this new perspective on 2D materials was the advent of hydrogenated monolayer materials and silicene.

The issue with creating truly 2D materials is the high surface energy involved; the "faces" of a 2D sheet are high area, and in most crystal structures, contain dangling bonds where the surface atoms are in electronically unsatisfied environments. TMDs, graphene, and select other 2D materials are unique in that their faces are terminated by atoms without dangling bonds; they have crystal structures which are uniquely suitable to this 2D configuration. However, it is possible to stabilize these surface atoms by giving them a bond to hydrogen, as is the case for graphene and germanane. In 2009, the same researchers who initially reported graphene reported on its hydrogenated analog, graphane.³⁸ Graphane is a crystalline insulator and retains the hexagonal lattice of graphene, they reported. Further, they showed the reaction with hydrogen is reversible, and so graphene and graphene can interconvert freely, with corresponding change from insulator to semimetal. The consequences of this discovery were profound; what other materials might be hydrogenated, and can this satisfy the electronic requirements of non-2D materials? The answer came several years later with the report of germanane. While germanium itself is a bulk material, germanane obtained by topochemical deintercalation of CaGe₂ shows GeH structure completely analogous to graphene.³⁹ Moreover (as with many of the TMDs) the confined 2D structure of germanane grants it a direct band gap, and electron mobility 5 times greater than bulk Ge, which lends itself to certain niche electronic applications.

Perhaps less expected than the discovery of stable monolayer graphane and germanane was the discovery of a monolayer analog of Si called silicene. Whereas graphane and germanane relied on terminal hydrogen to satisfy dangling bonds, silicene shows an entirely different electronic structure than its bulk form. Bulk Si is sp³ hybridized, where each atom has 4 bonds; silicene is sp² hybridized, and so each atom only needs 3 bonds.⁴⁰ The sacrifice of the 4th bond means that the dangling bond issue at a 2D surface is eliminated, and the 2D surface is thermodynamically stable. The synthesis of silicene met with initial complications, but Ag(111) emerged as the ideal substrate for growing silicene monolayers.⁴¹ Silicene sports some strong appeal because of its compatibility with Si based electronics, and so applications have included FETs, spin filters and spin FETs, band engineering, thermoelectrics, etc.⁴²

In the previous examples of graphane, germanane, and silicene, 2D materials were achieved either hydrogenating the surface atoms or realizing a bonding scheme which foregoes the dangling bonds at the surface. Another approach to synthesizing novel 2D materials is to use ligands to passivate a surface in lieu of the terminal –H groups. Specifically, amine ligands are useful here for stabilizing terminal metal cations with the lone pair of electrons. Such inorganic "hybrid" materials were synthesized extensively in the work of Jing Li and co-workers.^{43,44,45} In the general synthetic scheme, 2D hybrid materials are formed consisting of the general formula [$M_x C_x(A)$], where M = Zn/Cd, C = S/Se, $A = \text{primary alkyl amine, and x increases as the layers become thicker, but can attain a value of <math>x=1$. Essentially, the synthetic strongly with primary amine ligands so as to confine growth to 2D, creating ultrathin inorganic slabs capped with amine ligands which then stack into a layered hybrid material. As the Zn/Cd/S/Se materials are highly photoluminescent, they show

interesting photoemission tailored by their exact composition. However, ideally the materials could be obtained as individual sheets and not just as stacks, but the strong van der Waals interactions of the stacks was challenging to overcome. After several failed attempts, a publication by Sun et al reported a method where ZnSe was obtained as single layers and fee of capping amines.⁴⁶ They formed hybrid ZnSe-propylamine hybrids, which they exfoliated from stacks into freestanding sheets, and then annealed off the amine. The unique 2D morphology thusly produced showed enhanced water splitting efficiency, photostability, and photocurrent density than the bulk material. The approach witnessed by this layered hybrid material is interesting, as we see 2D morphology realized by a synergistic interplay of the organic crystal structure and the strong interactions of the amine ligands. In the next section, we will look at a similar system of bottom-up synthesis of 2D materials which relies entirely on self-assembly.

1.3 2D Materials via Bottom-up Self-Assembly

Whereas section 1.2 provided an overview of alternative methods to obtain confined 2D nanomaterials, the topic which is most germane to this dissertation is specifically self-assembly. A great deal of research has been undertaken to generate entirely novel 2D material compositions from a bottom-up synthetic approach relying on molecular self-assembly. Whereas graphene and TMDs have been pulled from a limited group of naturally 2D materials, such self-assembled materials can break out of the mold to deliver programmable compositions and materials properties. Such selfassembled materials rely on strong in-plane coordination to enable assembly of 2D layers, and van der Waals forces of organic components to hold the layers together. If such 2D materials could be designed using inorganic compounds, routes such as pyrolysis might lead to the isolation of 2D materials comparable to TMDs. We would thus like to present 2D materials including TMDs as the inspiration and driving force for the design of new 2D materials, and now move on to self-assembled 2D materials which have received comparatively little attention, yet may hold the key to the synthesis and isolation of 2D crystals with programmable composition.

In-plane bonding schemes showing strong integrity have been achieved using metals and strongly chelating ligands. Such strong M-L bonds result in an extremely polar moiety which can be likened to the headgroup of an amiphiphile. By drawing some inspiration from 2D structures in biology, such as lipid bilayers, an all-trans alkyl chain can be attached to the ligand to provide a tail group. Self-assembly of such amphiphilic metal complexes is achieved by metal-ligand coordination and hydrophobic assembly of the alkyl chains, which in tandem command a large thermodynamic incentive to direct the formation of lamellar bilayer structures. A great incentive driving the synthesis and study of such lamellar materials is to use them as templates for the crystallization of 2D inorganic materials. Such metal-organic lamellar bilayer templates have been shown to form with *n*-alkylamines and alkanoates, which will be reviewed in this section as a prelude to the metal alkanethiolate complexes which the remainder of the dissertation focuses on.

Amines are strong, L-type ligands which can use their lone pair electrons to passivate surface bound metal atoms. Amines are therefore traditionally found as metal coordinating ligands for colloidal synthesis, and as capping ligands for metallic or semiconducting nanoparticles. For example, *n*-alkylamines were recently used as part of an intercalation/exfoliation strategy for isolating single layer TMDs.⁴⁷ *N*-alkylamines indeed have a history of being used for intercalation compounds within various inorganic systems, and are particularly developed for the metal hydrophosphate system. Here, amines are excellent intercalation agents because they can accept a proton to form strong O₃P⁻⁺H₃NR complexes, such that the alkylamines impart lamellar ordering to successive metal hydrophosphate layers.^{48,49} These materials were exciting because the supramolecular templates offered a liquid crystal (LC) like mesostructure, and attempts were made to calcine these lamellar structures, using the amines as a sacrificial template. However, compounds were found to be thermally unstable to under calcination conditions, and the alkylamines could not be removed.⁵⁰ So while there was success in generating lamellar templates, the isolation of 2D inorganic materials from the template remained a challenge.

Beyond intercalation however, *n*-alkylamines such as *n* -octylamine were shown to spontaneously form lamellar bilayer structures with upon addition of Cd halides.⁵¹ Follow-up work demonstrated that this was general for R = n -propyl, *n*-pentyl, and oleyl groups.⁵² In both cases, the lamellar-bilayer structures were selenated to form magic-size CdSe clusters. The so-called "magic size" particles are stable CdSe sheet-like clusters with quantized size. This instance represents a successful implementation of the 2D templating by self-assembly, and the isolation of specific cluster sizes leads to extremely narrow photoluminescence and excitonic absorption properties. Subsequent publications further developed the synthesis and optoelectronic
properties of what were dubbed "quantum platelets" made from the Cd *n*-alkylamine lamellar templates.^{53,54,55}

Carboxylic acids themselves are relatively weak chelating ligands, but are made strong upon deprotonation due to the electrostatic charge interaction with metal cations. Similarly to the case of *n*-alkylamines, carboxylate ligands containing long alkyl chains may chelate metal ions and subsequently self-assemble into a lamellar bilayer structure. This system began to generate considerably more interest when copper (II) laurate was reported to possess a LC discotic mesophase when heated above 107 °C (for more detailed background on LC phases, see section 1.3).⁵⁶ Within a couple years, the system was fleshed out with analysis of a host of copper alkanoates with the number of carbons *n* ranging from 12-22.⁵⁷ The system of copper alkanoates that so developed was similar to the metal alkanethiolates that will be discussed next in greater detail. Copper alkanoates adopt a lamellar bilayer structure, where the interlayer thickness is linearly proportional to the number of carbons in the alkyl chains. Copper atoms and carboxylate groups thus lie in a pseudo-2D coordination network. Sample "melting" occurs between 110 and 121 °C for the various copper alkanoates reported. Polarized microscopy and X-ray diffraction of the melts reveal them to be LC phases with discotic columnar configuration. This work thus established metal alkanoates as nominal 2D nanomaterials and also as potential metallomesogens.

Later work expanded the 2D metal alkanoates to include other metals, including Zn and Pb, although mesomorphism was not reported.⁵⁸ A few years later

however, Ag alkanoates were synthesized across a great range of alkyl chains, and reported to exhibit LC-like mesomorphism.⁵⁹ This work characterized the lamellar crystalline to mesophase transition, and the mesophase to isotropic transition, which enabled the construction of a phase diagram as a function of alkyl chain length. The results are pertinent to metal alkanethiolates as there are some commonalities; the shortest alkyl chains examined (n=2,4) do not exhibit a mesophase at all, and decompose directly from the lamellar structure. Unfortunately, this work provided no structural characterization on Ag alkanoates, so it is unknown how the coordination compares to Cu alkanoates.

Interestingly, a new line of research was initiated which sought to use the nominal 2D metal alkanoates as molecular templates for CdS and PbS nanocrystals. The premise here was to generate a 2D lamellar bilayer precursor template using Cd or Pb with alkanoates, and then expose the precursor to sulfide to generate CdS or PbS.^{60,61} This was accomplished by using H₂S in a gas-solid reaction at room temperature to provide S²⁻. In a contemporary work, 2D metal thioalkanoates were used as templates for site directing nucleation of CdS NCs achieved via H₂S sulfidation.⁶² However, in each of these cases the NCs reported were often embedded within organic residue and the morphology was quasi spherical; evidently the effect of the 2D template was only to constrain the nucleation and growth of spherical NCs to quasi-2D regimes between bilayers. The small crystallites produced and continued presence of the alkanoate lattice however both point to an incomplete growth process, and the need to devise a method to remove the organic template.

The research on lamellar constructs made from a metal with either alkylamine or alkanoates ligand flows naturally into layered metal alkanethiolates. The layered metal alkanethiolates form via the same principles of self-assembly, and show structures comparable to said amine and alkanoates. However, the key difference with thiolates is that the S moiety is especially suited to thermolysis. Metal alkanoates need high temperatures to decompose into metal oxides, and metal nitrides from amine precursors require even greater temperatures. Metal thiolates however undergo a metal-catalyzed C-S bond cleavage at relatively low temperature. This allows the metal alkanethiolate's organometallic framework to be intact at the decomposition temperature, and allows for the generation of a metal sulfide within this template. Moreover, as we saw with the amines and alkanoates, metal alkanethiolates are suited to forming liquid-crystalline polymorphs. Thus, metal alkanethiolates can form metal sulfides through lamellar or liquid crystalline phases, which act as structural templates. The concept of liquid crystalline templating of anisotropic nanocrystals is the theme of this dissertation, and will reappear in Chapters 3, 4, and 5. Next however, a short primer is available so that the later discussions of liquid crystalline properties are clear.

1.4 Liquid Crystalline Phases of Metallomesogens

The liquid crystalline (LC) phase is a phase intermediate to the solid and liquid phases; being *between* phases, this phase has come to be known as a *meso*phase. A LC may flow like a liquid, but contain ordered molecular arrangements reminiscent of a crystal. LCs may be classed as lyotropic or thermotropic; thermotropic LCs show

phase behavior that is temperature dependent, while lyotropic LCs show phase behavior that is dependent on concentration within a solvent. A compound may be termed a mesogen if it displays an identifiable mesophase, and a metal-containing mesogen is thusly called a metallomesogen. Metallomesogens have been studied for decades, and a review has delineated several interesting subsets which include lanthanides, metallocenes, macrocyclic metallomesogens, ionics and polymers.⁶³ But while metallomesogens were investigated extensively for applications which included electron paramagnetic resonance (for paramagnetic metallomesogens), and physical and magnetic properties, few applications have been realized outside of solid-state chemistry, where some lyotropic metallomesogens have been used as templates for mesoporous materials.

In the present context, we will be investigating metallomesogens as templates for the growth of low-dimensional NCs. The metallomesogens studied herein selfassemble within solution to form a lamellar bilayer solid as a precipitate. These precipitates are isolated, dried, and because they are thermotropic LCs, all melting discussed is done by heating the powder in a solventless state. These powders are technically classed as coordination polymers since only dative bonds and van der Waals forces maintain the integrity of the supramolecular structure. However, the high degree of ordering present within these materials imparts crystalline-like regularity such that their structures can be accurately represented by repeating unit cells and they are efficient Bragg X-ray scatterers. Therefore, the nominal lamellar bilayer structure is termed a *lamellar crystalline* phase. Heating may induce one or more phase transitions as the energy level varies, and the various phase transitions result as the interplay between entropy and enthalpy. Generally speaking, as the system is heated, the enthalpy of molecular interactions is overcome in order to facilitate the greater entropy as defects and disorder manifest. Since the alkyl bilayer structure is largely comprised of *n*-alkanes, disorder manifests prominently in the conformational change from all-trans to some gauche conformations. As the linear alkyl chains are nominally close-packed, the steric strain is another factor that impacts this system.

While metallomesogens are capable of adoping many LC phases, the phases pertinent to this dissertation are the *lamellar smectic* phase and the *columnar* phase. In the nominal lamellar crystalline phase, the structure is rigid and highly ordered (Schematic 1, left). Phase transitions from the lamellar crystalline phase usually occur at temperatures over 100 °C, depending upon the metallomesogen. One of the possible phases that can be assumed is a *smectic* phase. In the smectic phase, such as the smectic A and C shown (Schematic 1, middle), molecules from the lamellar phase begin to lose coordination. While layered ordering is loosely maintained, molecules are now able to rotate, and successive layers are able to slide. Although the smectic phases still show lamellar ordering, the crystallinity is gone and as such, visually the sample loses the texture of a powder: its color darkens, and it appears as a melted

phase.



Figure 1.1. Schematic depiction of liquid crystalline phases. Left: crystalline lamellar bilayer phase. Middle: lamellar smectic phase. Right: hexagonally packed columnar phase.

In the *columnar* phase (Figure 1.1, right), the alkyl chain interactions which hold the lamellar structure together have been largely overcome. This is primarily caused by the gauche conformers which arise at higher temperature, which cause the alkyl chains to bend and "kink," (increasing their steric term) and essentially causing neighboring chains to "push" each other apart. Such molecules rearrange themselves into discotic micelles, where the headgroups containing metal achieve ring-like coordination near the core and the tails project radially from this central ring. A simplified depiction of a discotic micelle for Cu alkanethiolate is shown in Figure 1.1, right. These discotic micelles stack into columns, and the columns pack hexagonally. Discotic micelles show severe disorder in the alkyl chains beyond what is depicted in Figure 1.1, such that the length is significantly contracted compared to the all-trans conformation. When stacked, van der Waals interactions from alkyl units persist albeit weakly, and successive stacked micelles facilitate interactions between the polar headgroups at the micelle cores. Because the interactions governing the columnar phase are significantly weaker than that in a smectic phase, it is accordingly far less

viscous. Throughout this dissertation, any reference to the columnar phase refers more precisely to a hexagonally packed columnar mesophase comprised of discotic micelles as explained here.

An identifying property of LCs is birefringence; an optical property where the refractive index of a material changes with its orientation. Because of this, birefringent materials have the capability of rotating polarized light, which enables their characterization via polarized optical microscopy (POM). Since POM is used extensively in Chapter 6, it is first reviewed here. In POM, light from a confocal objective passes through a polarizer before reaching the sample. The polarizer filters the light, aligning it to a single orientation. Passage through a birefringent specimen will change the velocities of the ordinary and the extraordinary wave fronts, essentially causing some of the light to be rotated, depending on the thickness and birefringence of the specimen. This light then passes through an analyzer, which is crossed with regard to the polarizer, and thus does not allow any white light through. The analyzer will recombine the rotated light with constructive and destructive interference, visually producing vivid colors. Beyond simply showing color for a birefringent sample and no color for non-birefringent samples however, POM will also show textures which appear because different domains of the LC may possess Because different phases represent different hierarchical different orientations. arrangements of molecules, the textures produced are different enough to be useful in identifying LC phases.

1.5 References

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Chapter 2

Design and Self-Assembly of Metal

Alkanethiolates

2.1 General Synthetic Scheme and Considerations

The synthesis of metal alkanethiolates is a facile reaction which has been reported extensively for various metals and within various media. Generally, one prepares a thiol solution and a metal solution separately, and combines them under high stir rate through dropwise addition. Here, the thiol tends to be of hydrophobic character (for example, 1-hexadecanethiol) and the usual solvent of choice is ethanol. Ethanol will dissolve the long-chained alkanethiols, as well as the short-chained varieties with polar moieties (for example, 3-mercaptopropionic acid and 4-mercapto-1-butanol). The concentration has not been found to be of great importance when forming metal alkanethiolates, although sufficient volumes are needed to prevent the precipitation from becoming so viscous as to cease stirring capability. Therefore, the thiol solution should be prepared at a maximum of 1.0 M and less is often preferred. The media for the metal solution depends on the choice of metal salt; typically, watersoluble salts such as metal nitrates and chlorides are chosen. The water-soluble salts are occasionally soluble in ethanol, and ethanol is preferable to water here because the precipitate is very hydrophobic (which makes isolation and washing more difficult). For these reasons, the metal salt is typically dissolved in water, ethanol, or acetonitrile. As with the thiol, the concentration of metal should not exceed 1.0 M. The ratio of thiol to metal used can be either stoichiometric or include a moderate excess of thiol.

Upon dropwise addition of either solution to the other, metal alkanethiolate tends to form and precipitate spontaneously, being immediately evidenced by a change in solution color. Metal alkanethiolates tend to be white, yellow or beige in color, although that is not necessarily always true (for example, Co^{2+} thiolates tend to form dark purple complexes). After completion of dropwise addition, the solutions are left stirring for at least 15 m to ensure completion of the precipitation reaction. If the concentration is anywhere close to the upper limit of 1.0 M, the solution will now be very viscous. The precipitates are next washed and isolated by centrifugation. We prepare them in 20 mL scintillation vials, which may be directly centrifuged, and 3000 RPMs for 5 minutes is a time-tested parameter to pack down the metal alkanethiolate precipitate. Higher speeds are not recommended, as they can pack the metal alkanethiolate too much and make more difficult to disperse. After centrifugation, the supernatant (ostensibly carrying the unreacted metal ions and thiol molecules) is discarded. Next the solvents previously used to dissolve metal and thiol (e.g., ethanol & acetonitrile) are added back to the precipitate in equal-volume ratios and the precipitate is gently dispersed before centrifuging back down. This process represents one wash, and is repeated twice more to fully purify the precipitated metal alkanethiolate of reactants. Finally, the washed precipitate is stored under vacuum, where it may dry within about 24 hours depending on its volume and surface area as it is stored.

Sometimes it is necessary to use great excesses of thiol relative to the amount of metal ion. This is because of the *redox chemistry* inherent to thiols. Thiols are readily oxidized, with two thiol groups forming a disulfide bond, as shown in Equation (1):

$$2 RSH \rightleftharpoons RS - SR + 2 H^+ + 2 e^- \tag{1}$$

The redox potential E° varies, and hasn't been reported for all of the alkanethiols used here. However, additions of alkanethiols to Au^{3+} , Fe^{3+} and Cu^{2+} solutions are all known to cause disulfide formation. For the exemplary case of Cu, the redox reaction proceeds according to Equation (2):

$$RSH + Cu^{2+} \rightleftharpoons \frac{1}{2}RS - SR + H^+ + Cu^+ \tag{2}$$

Thus when Cu²⁺ is used, every Cu atom requires an additional thiol molecule which is expended to reduce the *cupric* ions to the *cuprous* form while forming disulfide. Because the molecular weight of the disulfide is doubled relative to the thiol, their solubility in moderately polar solvents such as ethanol is poor. Disulfides tend to precipitate out alongside the metal alkanethiolate, and so can prove problematic if a pure product is desired. The formation of disulfide may be noticed by its mass loss with thermogravimetric analysis (TGA), or by a S-S stretching vibrational mode that shows up on fourier transform infrared spectroscopy (FTIR) near 465 cm⁻¹. Disulfide formation has been noted in the synthesis of Cu alkanethiolates by using Cu(NO₃)₂ and alkanethiols including 1-octanethiol, 1-dodecanethiol, and 1-hexadecanethiol. Interestingly, precipitates from 1-butanethiol were not found to possess the disulfide. This is almost certainly due to the fact that dibutyl disulfide is still solvated by ethanol and hence easily removed during the washing steps. However, unwanted disulfide can be removed by refluxing the metal alkanethiolate in toluene. Upon cooling, the disulfide will remain within the toluene and is easily separated.

The majority of metal ions are not reduced by thiols, as is the case for Ag^+ . Therefore, the following reaction shown in Equation (3) for Ag^+ is typical for how monovalent metals bond with alkanethiols in solution:

$$RSH + Ag^+ \rightleftharpoons AgSR + H^+ \tag{3}$$

Of course, the formation constant of AgSR is >>1, favoring the formation of AgSR in a high yield, however the acidification of the solution due to H⁺ generation can inhibit the formation of some metal alkanethiolate complexes. This can be overcome by employing one of the following strategies. First, a metal salt may be selected where the counter ion functions as a weak base. For example, acetate ions suffice to conjugate excess H⁺ and generate acetic acid in solution. Second, a weak base may be added, usually in a 1:1 molar ratio with the thiol, to conjugate H⁺ and form the conjugate acid. Towards this purpose, we and others have employed triethylamine as the weak base of choice. As an example of this mechanism in action, Ni(NO₃)₂ combined with 1-dodecanethiol in ethanolic media fails to produce a precipitate. However, upon addition of triethylamine, the Nickel thiolate immediately forms. The overall metal thiolate generation in the presence of triethylamine is shown in Equation (4):

$$2RSH + Ni^{2+} + 2Et_3N \rightleftharpoons Ni(SR)_2 + 2Et_3NH^+$$
(4)

Because FTIR has shown that triethylamine does not incorporate into the precipitated metal alkanethiolate, triethylamine is a suitable base.

Metal alkanethiolates are typically stored under the same light vacuum conditions that they are dried in. It is considered ideal not to allow metal alkanethiolates to persist under atmosphere due to the exposure to O_2 and moisture. Nevertheless, our studies have shown that metal alkanethiolates are generally resilient to atmospheric conditions and do not readily uptake water. The notable exception is CuSC₄H₉, which changes color with storage duration, even under vacuum. These color changes were linked to a degradation in the lamellar bilayer structure, and so may be derived from poor overall thermodynamic stability of the bilayer using a short alkyl chain. This degradation is covered in more detail in Chapter 4.1. The majority of metal alkanethiolates however have been found to maintain their color, structural integrity, and thermal properties for months to years.

2.2 Metal Ion Selection

The metal ions which form metal alkanethiolate complexes are found to be *soft* metal ions. The word *soft* comes from hard soft acid base theory (HSAB), which is widely used for explaining the reactivity of compounds, particularly ionic compounds. In HSAB, hard applies to species that are typically small, highly charged, or both. Thus in describing their electronic environment, hard species have tight, weakly polarizable electron clouds. For instance, Ti⁴⁺ is a hard ion. On the other hand, soft species are large, have lower charge states, and are more polarizable. An example of a soft ion is Au⁺. The RSH thiol ligands used here are deprotonated and react with metal as alkyl sulfide, (RS⁻) which is a soft base. Therefore, it is unsurprising that only soft metal ions are compatible with metal alkanethiolate forming reactions.

The late transition metals and several others enjoy some of the "softest" electronic structures. Thiolate complexes using such soft metals as Au, Hg, and Tl can be found going back through decades of inorganic synthesis. We have found Cu⁺ to be an especially amicable ion, forming complexes with each of several dozen thiol molecules attempted. We and others have prepared metal thiolate complexes with metals including Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn, Au, Hg, Tl, Pb, and Bi.

When considering the choice of metal salt from which to form metal alkanethiolate, the oxidation of the metal ion as well as the counter ion used are both primary concerns. As was mentioned in Section 2.1, some metals at higher oxidation states are susceptible to reduction at the cost of oxidative disulfide formation. As this is usually undesirable, lower oxidation states are preferable. As expected, higher oxidation states complex a greater number of thiol molecules. For instance, M⁺, M²⁺, and M³⁺ will form MSR, M(SR)₂, and M(SR)₃ compounds, respectively. Regarding the counterion, the water-soluble salts including metal nitrates, sulfates, and halides are ideal. However, we do note that halide ions have the capability to incorporate into Cu alkanethiolates (covered in greater detail in chapter 4.2). Another suitable counterion is an acetate salt, which provides acceptable solubility, and further acts to sponge excess protons during thiolate generation. Sometimes, it is desirable to precipitate a metal alkanethiolate directly into an organic phase, or open up compatibility to a more hydrophobic system. In this scenario, the acetylacetonate (AcAc) counter ion excels.

A final consideration which must be given when designing a metal alkanethiolate is how the metal will react under thermolysis conditions, if thermal properties are to be studied. The bond formed between a sulfur and a metal is a strong covalent linkage, and as such, it can be thought of as effectively withdrawing electron density from the adjacent sulfur-carbon bond. In essence, the thiolate linkage enables *metal catalyzed* C-S bond thermolysis, where the C-S bond can be thermally cleaved at unusually low temperatures. This will be discussed in greater detail in the next section. However, the metal ion chosen here does have some effect on overall bond thermolysis. In some metals (e.g. Au), C-S bond cleavage is outcompeted by M-S homolytic bond cleavage to form reduced M⁰ at elevated temperature, rather than metal sulfide. We have observed this several times, and found the correlation to lie within the reduction potential of the metal. The evidence suggests that higher reduction potentials tend to favor M-S homolytic bond cleavage over C-S bond cleavage. While this can lead to the formation of pure metals, high enough thermolysis temperatures always tend to produce metal sulfides.

Mechanisms for the two competing pathways of homolytic M-S bond cleavage and heterolytic C-S bond cleavage are shown in Equations (5a-c) and (6a-d):

$$2M - SR \to 2M^0 + 2 \bullet SR \tag{5a}$$

$$2 \bullet SR \to RSSR \tag{5b}$$

$$2M - SR \to 2M^0 + RSSR \tag{5c}$$

In Equation (5a), homolytic M-S bond cleavage reduced M from M⁺ to M⁰, and creates residual thiyl radicals, which subsequently recombine to form disulfide (5b). The overall reaction thus generates metal product and disulfide byproduct (5c).

$$M - SR \to MS^- + R^+ \tag{6a}$$

$$M - S^- + M - S - R \to M_2 S + RS^- \tag{6b}$$

$$R^+ + RS^- \to RSR \tag{6c}$$

$$2M - S - R \to M_2 S + RSR \tag{6d}$$

In Equation (6a), heterolytic cleavage of the S-R bond places the electron density on the more electronegative group, the S, generating a charged metal sulfide and a carbocation. In the next thermolysis event, an MSR unit undergoes heterolytic cleavage of the M-S bond while metal coordinates to adjacent M-S⁻, forming the metal sulfide MS₂ and the cleaved alkyl sulfide RS⁻ (6b). Lastly, the residual R⁺ and RS⁻ can recombine to form the dialkyl sulfide, RSR (6c). The overall reaction thus generates metal sulfide product and dialkyl sulfide byproduct (6d).

2.3. Self-Assembly and Morphology of Copper Alkanethiolates

Reaction between alkyl thiols and compatible metal ions (as outlined in Chapter 2.2) is typically rapid, and the precipitation of the corresponding metal alkanethiolate is perceived instantly. As we demonstrated in Chapter 2.2, some design rules such as metal ion compatibility or solution pH can play roles in modulating the formation of metal alkanethiolate molecules and thus subsequent precipitation of supramolecular metal alkanethiolates. In our preliminary work on metal alkanethiolates, we sought to gain better understanding of reaction kinetics, and also of the self-assembly process. In particular, we sought to influence the morphology of supramolecular copper alkanethiolate assemblies by introducing interactions between chelating ligands and Cu ions, and also by modulating the interactions between solvent and ligand. This work was also motivated by the desire to obtain high-area 2D assemblies of Cu alkanethiolate through which ultrathin Cu_{2-x}S nanosheets might be derived by thermolysis process. The results of thermolysis reactions of Cu alkanethiolates will be covered in Chapters 3 and 4. In section 2.4, we will explore some of the key findings regarding precipitation and assembly of Cu alkanethiolates.

Firstly, in order to alter the kinetics of Cu alkanethiolate generation, we sought to introduce ligands which strongly chelate Cu^{2+} ions. The hypothesis here was that strongly bound metal ions would be less susceptible to nucleophilic attack by thiols, and thus less to slower metal alkanethiolate rate of formation. The complex chemistry of Cu^{2+} in aqueous solutions is fairly well-studied territory, and we were able to come up with a series of suitable ligands which would form coordination complexes of Cu, and with formation constants on the order of 10^{10} . Figure 2.1 shows the series of Cu coordination complexes that were tested, arranged roughly in order of ascending chelating strength as based off of the formation constant for the complex.



Figure 2.1. Coordination complexes of Cu for water and 4 other ligands tested.

Coordination compounds of Cu follow *d*-orbital splitting as outlined by ligand field theory. The lack of degeneracy so induced causes d-d orbital transitions with excitation energy in the visible range, thus leading to complexes which exhibit vibrant colors, as shown in Figure 2.8. The vivid colors created by these complexes allows one to track the concentration of Cu^{2+} ions by the magnitude of the absorption as measured by UV-vis absorption spectroscopy. The absorption of a species is linearly related to its concentration, as per Equation (7):

$$A = \varepsilon bc \tag{7}$$

which is known as the Beer-Lambert law, where A = measured absorbance, ε is the molar absorptivity coefficient, b is the pathlength, and c is the analyte concentration. Thus the concentration of Cu²⁺ ions may be directly correlated to the absorption intensity as measured by UV-vis spectroscopy.



Figure 2.2. A picture taken of Cu^{2+} complexes formed in the presence of various ligands. The colors demonstrate the effect of the ligand on the optical absorption of the complex, which enables monitoring of concentration.

We examined reaction kinetics by producing a biphasic solution, whereby an aqueous solution of Cu^{2+} ions in the presence of one of five ligands (water, H₂O, Cl⁻, EN, DETA, or EDTA) is exposed to a top organic phase of 1-dodecanethiol. The biphasic solution retards Cu alkanethiolate generation by limiting the reaction coordinate to the 2D interface between organic and aqueous phases such that at various points in time, the aqueous phase can be pipetted out and its concentration analyzed with UV-Vis spectroscopy. The aqueous subphase was analyzed over time to measure the depletion of Cu^{2+} species across the set of ligands, and the results are displayed in Figure 2.9.



Figure 2.3. Reaction kinetics of Cu-dodecanethiolate in the presence of various coordinating ligands.

Figure 2.9 shows the results of our kinetic studies of Cu alkanethiolate formation as measured by the depletion of Cu^{2+} from the aqueous subphase. With just water present as a ligand (e.g. the control), depletion of Cu^{2+} occurred after 90 minutes. In contrast, Cu^{2+} in the presence of Cl⁻, EN, and DETA reached depletion within 10, 15, and 12 minutes respectively. However, the anticipated strongest ligand EDTA produced no precipitate at any time duration, and so it is not included in Figure 2.4.3. For the most part, these results contradicted the hypothesis; rather than slowing Cu alkanethiolate formation, coordinating ligands may actually play a constructive role in the reaction alkyl thiols with Cu^{2+} ions. The hypothesis only held for the strongest ligand, EDTA, which apparently bound Cu^{2+} so strong as to disable thiolate formation. An uncontrolled variable is pH, which is increased substantially by the amine-rich ligands DETA and EN, and can be expected to increase the formation rate by removing H⁺ from the product side of the reaction (see Equation 2.2.1). However, Cl⁻ is nonparticipative in pH processes, and shows comparable effects to EN and DETA on the formation kinetics of Cu alkanethiolate. These results thus spurred a different approach to looking at supramolecular Cu alkanethiolate formation: if coordinating ligands have a constructive effect on formation rate, how might they affect the morphology of Cu alkanethiolate assemblies?

We began the study of molecular interactions with Cu alkanethiolate formation by studying relatively "weak" ligands, represented by the intermolecular forces of various solvents. In one such study, CuSC₄H₉ was precipitated from various solutions where the solvent system was a mixed composition of water and ethanol. This investigation was prompted after we ran into difficulties producing highly ordered supramolecular CuSC₄H₉ when dissolving the Cu in water. We varied the water/ethanol composition with 20% intervals, as shown in Table 2.1. We postulated that more hydrophobic solvents would show superior interactions with the alkyl chains terminating the top and bottom faces of 2D CuSC₄H₉ supramolecular assemblies; therefore, the more ethanol in the composition, the higher the aspect ratio of the 2D assemblies.

| Sample ID | H ₂ O | Ethanol |
|-----------|------------------|---------|
| Α | 0% | 100% |
| В | 20% | 80% |
| С | 40% | 60% |
| D | 60% | 40% |
| Ε | 80% | 20% |
| F | 100% | 0% |

Table 2.1. Skew of water and ethanol composition during precipitation of CuSC₄H₉.

The results of this study shown in Figure 2.4 are partially corroborative of this hypothesis. Transmission electron microscopy (TEM) was used to image the $CuSC_4H_9$ assemblies. When ethanol content was highest (samples A and B), clearly layered 2D assemblies were obtained. However, when water content exceeded 20% (samples C-F), 2D assemblies were no longer observed and instead the morphology became more irregular and reminiscent of a polymer. In previous work on precipitation and organization of Au alkanethiolate assemblies researchers claimed that first 1D stringlike structures formed, which would eventually align and assemble into sheet-like structures. Our results show that similar 1D coordination may be forming, but the structure itself may differ in the presence of water. Figure 2.4, right panel, shows the XRD patterns for the sample IDs A-F. Where 2D sheet structures are observed, the lamellar bilayer structure is present. However, the less ordered samples produced in the presence of increasing water content show the lack of lamellar bilayer structure; indeed, a new spacing parameter of appears near $2\theta = 8^{\circ}$ corresponding to the calculated *d*-spacing ca. 1.2 nm, which is substantially less than the expected ~ 1.6 nm for a butanethiolate bilayer. This spacing parameter may apply to a highly interdigitated lamellar bilayer, or some intermediate 1D chain-like structure. Several

conclusions can be drawn from these results. Firstly, that solvent influences the assembly of CuSC₄H₉ sufficiently to account for structural and morphological changes. Second, that water molecules may play an antagonistic role in disrupting CuSC₄H₉ assemblies, leading to alternative assemblies schemes. This data led us to postulate that increasing hydrophobicity may be linked to stronger in-plane growth of Cu alkanethiolates and thus longer-ranged 2D domains.



Figure 2.4. TEM and XRD of CuSC₄H₉. Left panels show TEM images of CuSC₄H₉ precipitated from a mixed water/ethanol solution with the composition outlined for samples A-F in Table 2.4.1. The right panel shows stacked XRD spectra corresponding again to samples A-F.

To further test the aforementioned hypothesis that CuSC₄H₉ assembly may show stronger 2D character in the presence of hydrophobic solvents, we skewed the solution composition to create a range of increasing hydrophobicity with the following solutions: ethanol, 1:1 ethanol:acetone, and 1:1 ethanol:chloroform. Additionally, we included oleylamine as a ligand with hydrophobic character, and DETA as a ligand with hydrophilic character. As per the hypothesis, we expected the largest 2D assemblies should be found using chloroform as the solvent, and using no ligand or the more hydrophobic oleylamine ligand. The results are shown in Figure 2.5. Although the sizes and morphologies are not highly regular and thus not conducive to quantitative analysis of particle size, the qualitative evidence presented here shows that larger assemblies do tend to form for the ethanol/chloroform system in the absence of a coordinating ligand. Coordinating ligands tend to enhance the 2D area of supramolecular assemblies, in comparison to no coordinating ligand. Coordinating ligands might affect the addition of Cu alkanethiolate monomers to the supramolecular assembly, as the assemblies precipitated in the presence of coordinating ligands tend to exhibit straighter edges and sharper corners.



Figure 2.5. TEM of CuSC₄H₉ precipitated in the presence of various solvents and coordinating ligands.

In a final study on the self-assembly of CuSC₄H₉, we determined that precipitation of CuSC₄H₉ does not immediately occur when oleylamine is used as both solvent *and* ligand. However, precipitation occurs slowly over time. We used this kinetically retarded system to study the precipitation of assembly of supramolecular CuSC₄H₉ over time with TEM to image the morphology. A 10:1 solution of oleylamine:thiol was prepared and pipetted into a Cu²⁺ solution in oleylamine. The results are shown in Figure 2.6, where panels A-D correspond to 30, 150, 270, and 390 minutes, respectively. The results show that many string-like assemblies present early in the reaction attain alignment and form greater 2D assemblies. Interestingly, as can be seen in panels C,D, the 2D assemblies contain striated domains which likely trace back to the original string-like assemblies. As a similar time-dependent growth mechanism was demonstrated for Au alkanethiolates, the evolution from 1D string-like structures to aligned 2D structures may be general for metal alkanethiolates.



Figure 2.6. TEM of CuSC₄H₉ precipitated from oleylamine as a function of time; A) 30, B) 150, C) 270, and D) 390 minutes post-addition.

2.4 Self-Assembly at the Air-Water Interface: Copper Alkanethiolate Multilayers and Monolayers

In section 2.3, we used various solvents, ligands, and time-dependent studies to assess the assembly of Cu alkanethiolates, as evidenced by the resulting supramolecular morphologies. The results showed that relatively large-area (> 1 μ m) assemblies could be obtained by using more hydrophobic solvents and/or coordinating ligands. We estimated that these assemblies might be several hundred nanometers

thick, corresponding to dozens or even hundreds of stacked bilayers. However, we envisioned an alternative method which might enable the assembly of even higherarea Cu alkanethiolate assemblies at thicknesses as low as a single bilayer. Working with single or few-layered Cu alkanethiolates is appealing for several reasons: a monolayer on a substrate is a pseudo alkanethiol SAM and as such, imparts physical properties to the substrate such as extraordinary hydrophobicity. Unlike a SAM however, the metal thiolate might also be used as a single-source precursor to deposit a thin layer or residue of Cu_{2-x}S to the substrate. All of these ideas however hinged on successfully assembling just a few layers of Cu alkanethiolate, a process that from our precipitation reactions in section 2.3 is apparently difficult to control. The novel idea here was to use Langmuir Blodgett (LB) techniques to form an alkanethiol monolayer on water, and then metallate the aqueous subphase with Cu ions, theoretically producing a Cu alkanethiolate monolayer at the air-water interface.

In LB films, a molecular species is dissolved in a volatile and hydrophobic solvent such as CHCl₃ and dropcast onto an aqueous surface. Solvents like CHCl₃ are immiscible with water and so they spread on the surface and then rapidly evaporate. This serves to deposit a monolayer of the molecular species, so long as the concentration and rate of dropcasting is properly controlled. Initially this monolayer is poorly ordered and oriented. It is useful to have surfactant-like molecules, and in this scenario, the –SH headgroups of the thiol molecules used are the more hydrophilic component and thus ostensibly orient down to interaction with the aqueous subphase, forming a pseudo-SAM. Careful compression of the film will compress the molecules

together until a continuous molecular monolayer is produced. Monitoring of the surface pressure allows one to achieve molecular monolayers with good reliability, as this is a well-studied phenomenon. Next, an aqueous solution of Cu^+ ions is pipetted into the aqueous subphase, where it can diffuse to the surface and react with thiols and form Cu alkanethiolate at the interface. After generation of Cu alkanethiolate assemblies at the air-water interface, a substrate may be dipped through the film to produce a film-like coating on the substrate. This general scheme is depicted in Figure 2.7.



Figure 2.7. Assembly of Cu alkanethiolate at the air-water interface via LB assembly. In the first step, alkyl thiols dispersed in CHCl₃ are dropcasted onto an air-water interface. In the second step, movable teflon barriers are compressed to push the molecules into contact while the surface pressure is monitored. In the final step, a Cu^+ solution is introduced into the aqueous subphase, which may subsequently react with thiols to form Cu alkanethiolate at the air water interface. The grey line at the right represents a substrate to be coated by withdrawing after film formation.

We devised the approach shown in Figure 2.14 after testing with a variety of alkyl thiols. Formation of a molecular monolayer via LB assembly is tracked by measuring the surface pressure as the barriers of the LB trough are compressed. Surface pressure is expected to increase as monolayer domains contact each other and merge into larger domains, and this trend continues until a monolayer is produced. Once all molecules are more or less in contact, the as-formed monolayer has near

crystalline coordination, and so attempts to compress any further will show a rapid increase in surface pressure. The relationship between LB barrier compression and surface pressure is called an isotherm, and we observed isotherms indicative of slow dissolution for shorter chained alkyl thiols. This means that equilibrium can exist pulling a small fraction of the molecules into the aqueous phase and disrupting the integrity of the monolayer. Alkyl thiols with shorter alkyl tails are also not preferable because of the strong thiol smells involved. However, we achieved close to ideal isotherms by using 1-octadecanethiol, a relatively long-chained alkyl thiol. For the metalation step, we chose to use a Cu(I) acetate salt. An issue with Cu(I) salts is that they are poorly solvated, and undergo slow redox to Cu(II) species. However, in this case using Cu(I) was deemed critical, as Cu(II) ions would result in our Cu alkanethiolate assemblies being contaminated with disulfide. Therefore, after equilibration of a 1-octadecanethiol monolayer, we pipetted excess Cu(I) acetate dissolved in water into the aqueous subphase. Formation of Cu-octadecanethiolate at the air-water interface could be visibly observed by the creation of a sheen at the surface.

As-formed Cu alkanethiolates on the air-water interface may then be transferred to a substrate by dip coating said substrate. More typically however, LB troughs (including ours) are equipped with a mechanical dipping arm which holds the substrate. Rather than dipping the substrate into the formed LB film, the substrate is dipped before the film is formed, held in the aqueous subphase during film formation, and then retracted at a controlled rate after film formation. This may be accompanied by continuous, slow compression of the LB barriers to ensure that the film stays "pushed" into contact with the substrate as it is being retracted. We employed this technique to dip-coat several 1 cm² Si substrate, which are polished to a flat surface. We also dip-coated several TEM grids, in order to better image the films. SEM and TEM images of the Cu-octadecanethiolate films are shown in Figure 2.8. Under SEM, the films are difficult to perceive except where large discontinuities occur. However, under TEM the sheet assemblies are observed. There are obvious wrinkles and folds in the films, and often large gap between continuous film segments. The gaps are to be expected, as one would expect a 50% decrease in surface area upon metalation of the alkanethiol monolayer into a metal alkanethiolate bilayer. Subsequent compression of the LB barriers can fill some of the voids created, but much of the voids remain.



Figure 2.8. SEM and TEM images of Cu-octadecanethiolate films. Left and middle show SEM images of the films on a Si substrate. Right shows TEM image of a section of film under higher magnification, showing some wrinkles and folds. film formation.

Although imaging with SEM and TEM showed that the Cu-octadecanethiolate obtained was clearly thinner than previous Cu alkanethiolates imaged, the actual thickness was unknown. To quantify this parameter, we used atomic force microscopy (AFM). Films of Cu-octadecanethiolate coated onto Si substrates were examined with an AFM probe engaged in tapping mode. Figure 2.9 shows one of these AFM images. The height of the film is clearly observed to occur in multiples of 5 nm. 5 nm is the expected value for Cu-octadecanethiolate, representing two all-trans octadecanethiol molecules (~ 2.3 nm each) with the linking Cu atoms adding ~ 0.5 nm thickness. Several cross-sections are drawn (in black and red) to highlight the clearly quantized film thickness. In the first section (black), the majority of the sections are 2 layers, but a third stacked layer is clearly observed at the far left. In the second cross section (red), 3 layers are observed at the far left and right, while two layers comprise the middle segment.



Figure 2.9. AFM of Cu-octadecanethiolate film formed by LB assembly. Cross sections show the thickness in most spots corresponds to 2-3 stacked bilayers.

As shown in Figure 2.9, the majority of the Cu alkanethiolate film produced by LB technique is a minimum of 2-3 layers. Many spots show 4 or more layers, indicating that the alkanethiolate layers have a strong thermodynamic incentive to assemble. One downside of generating the Cu alkanethiolate at the air-water interface is that the interaction between hydrophobic alkyl chains and water is so poor that the
resulting high surface energy interaction causes the vast majority of the Cualkanethiolate lamella to stack after metalation. That said, we did observe domains that were entirely of monolayer thickness. Figure 2.10 shows a domain of Cuoctadecanethiolate with the cross section (blue) showing height which corresponds to ca. 4.5 nm. Thus, we have demonstrated that LB assembly is a method capable of making films of Cu alkanethiolate with monolayer thickness. Although the films are 5 nm thick, the significance of this monolayer is that the Cu-S network formed is close to atomic thickness. Theoretically, this precursor film could serve as a scaffold or template for depositing Cu_{2-x}S or Cu₂O through pyrolytic methods, or a compound Cu-containing semiconductor with introduction of a complementary species. The significance of this work is that unlike dip pen nanolithography (DPN) (introduced in Chapter 1.3), LB films are scalable to many cm^2 of surface area compared to nm^2 or μ m². Where DPN can print microarchitectures using metal alkanethiolate mono and multilayers, LB assembly might form larger µm-sized domains, which may then be patterned down by lithography processes. The possibilities here are intriguing, especially given that the LB process presented here may be greatly optimized to produce monolavers by changing the physical properties of the aqueous subphase to decrease surface tension and polarity.



Figure 2.10. AFM of Cu-octadecanethiolate monolayer formed by LB assembly.

Chapter 3

Mesogenic Metal Alkanethiolates as

Nanocrystal Precursors

3.1 Background and Previous Studies with Cu, Ag, and Au

The discovery and subsequent study of 2D metal alkanethiolates in the early 1990's may be viewed as a consequence of two major events: the previous work on mesogenic 2D metal alkanoates, and the recent impact of a number of reports of spontaneously generated self-assembled monolayers (SAMs) of thiols on metal surfaces.^{1,2,3} As SAMs have since promised a host of applications including etch resists, insulating layers, substrates for bioconjugation and superhydrophobic surfaces,⁴ interest in the molecular analog of a SAM was not lacking. In 1991, Dance et. al. synthesized and reported on a group of AgSR compounds, proclaiming them to possess layers structurally analogous to monolayers of thiols on gold surfaces.⁵ They reported a lamellar bilayer structure that is akin to metal-alkylamine complexes and metal alkanoates, but went further in proposing a more detailed 2D Ag-S bonding scheme in a staggered hexagonal lattice reminiscent of graphene. This structure was supported by diffraction data and consistent across a set of Ag alkanethiolates synthesized. The Ag alkanethiolates would become the best characterized model for the greater system of metal alkanethiolates.

In a follow up work in 1992, Baena et. al. characterized the phase transition of Ag alkanethiolates to a hexagonally packed, columnar mesophase.⁶ Thus these metal alkanethiolates were also metallomesogens acting as thermotropic LCs, and the lamellar to columnar transition was ca. 130 °C. The mesophase exhibited by Ag alkanethiolates was similar to that found in Cu alkanoates, and again, the mesophase was only produced by longer alkyl chains (n > 6). In the following years, a bevy of

reports further examined the lamellar bilayer structure, alkyl chain ordering, and the thermodynamics of the phase transition. Fijolek et. al. investigated disorder in Ag butanethiolates by examining *cis* and *trans* conformations within the alkyl chain.⁷ The work lent credence to the staggered hexagonal Ag-S bonding model proposed by Dance, and showed that order can be tracked by FTIR and NMR by looking at gauche conformers. Later reports continued to probe the 2D structural and mesogenic transition in Ag alkanethiolates by employing X-ray diffraction, differential scanning calorimetry, and infrared spectroscopy, which have become staple characterization methods for this system.^{8,9}

More recently in 2005, Levchenko et al examined the mesophase transition of silver alkanethiolates in greater detail.¹⁰ In particular, they established the energetics of the phase transition from a thermodynamics perspective. In studying the alkyl chain lengths conducive to mesogenic transition, they found that the lamellar to mesophase transition is largely independent of chain length because the chain-length dependent enthalpy change is compensated by the entropic change as alkyl chains are disordered. The researchers also sought to produce the most ordered lamellar structures possible by recrystallizing Ag alkanethiolate, which albeit remarkably insoluble, will eventually dissolve in refluxing toluene. The most useful contribution of this publication however is that it contains one of the first reports on thermolysis of a metal alkanethiolate to form NCs. High temperature thermal decomposition experiments ended up producing Ag NCs amidst the organic slurry. However, the NC morphology

was not characterized, which begged the question of how the ordering within a mesogenic state might affect NC nucleation and growth.

Years after the Ag alkanethiolate system had been fully established, reports emerged showing that analogous behavior had been found in Cu alkanethiolates.^{11,12} This might have been anticipated earlier, as Ag alkanethiolates were a structural offshoot of thiol self-assembled-monolayers, which form on both Ag and Cu. These works purported that Cu alkanethiolates possess a mesogenic phase transition near 130 °C to a hexagonally packed columnar phase. This phase was thought to be nearly identical to that present in Ag alkanethiolates, save for the arrangement of the discotic micelles, which were thought to be composed of fewer molecules. The impact of this work was to demonstrate that the 2D structure and mesomorphic behavior of Ag alkanethiolate was not unique, but was part of a greater system of metallomesogens.

Au alkanethiolates were unsurprisingly found to form similar lamellar bilayer complexes with alkanethiols. In their pioneering work on the subject, Kim et al reported the synthesis of Au alkanethiolates with supramolecular structure, which would form Au NCs through electron beam irradiation by TEM.¹³ The authors found that supramolecular AuSC₁₈H₃₇ formed lamellar bilayer structure which melted by DSC at 157 °C into an isotropic phase. Interestingly, cooling the sample below the phase transition would produce birefringent texture. Also of note was the fact that longer alkyl produced more ordered layered structures and thus more uniform Au NCs when reduced by the TEM beam than shorter alkyl chains. In a follow-up work from the same group, a series of AuSC_nH_{2n+1} with 2 < n < 18 were studied in greater

detail.¹⁴ XRD studies again purported an increased in lamellar ordering for the longer alkyl chains, which coincided with an increase in photoluminescence intensity of these complexes when taken as dispersions in THF. The study concluded that the photoemission was likely caused by aurophilic interactions which depend on alkyl chain length, and so these properties are unique to Au alkanethiolates. Within a year, the same aforementioned group released a third publication on Au alkanethiolates which focused on their thermolysis into Au NCs.¹⁵ Temperature dependent XRD and FTIR showed that in contrast to Ag and Cu alkanethiolates, the melting transition for Au alkanethiolates occurs at higher temperature, results in rapid formation of Au NCs, and is thus irreversible. Thus, the rapid reduction of Au(I) thiolate complexes to metallic Au⁰ NCs when at or above the melting temperature prevents carrying out thermolysis within a mesogenic phase. However, it is interesting that birefringent textures had been noted in this group's second report when cooling the samples from the irreversible isotropic transition, as this implies that some molecules are sufficiently intact to form ordered mesogenic domains.

A more recent work investigated the dynamic self-assembly of Au alkanethiolates by using a pH-sensitive thiol (3-mercaptopropionic acid, or MPA).¹⁶ The AuMPA complex would nominally form a lamellar bilayer structure, but upon basisification, the –COOH groups would deprotonate to –COO⁻, which would repel and cause dissolution of the bilayer structure. For the first time here, researchers were able to conduct time resolved studies of the assembly and disassembly process of a layered metal alkanethiolate. In-situ UV-Vis spectroscopy enabled researchers to

assess the assembly process as controlled by pH, and then TEM and AFM were used to characterize morphological evolutions. The data showed the assembly of loosely organized string structures, which would then align into coils and assemble into large sheet structures as the assembly process progressed. This work provided the first insight on the assembly and morphology of metal alkanethiolates into the sheet-like supramolecular assemblies.

Although very few thermolysis reactions have been carried out on metal alkanethiolates, several reports detail the state of understanding in the field prior to the work presented in this dissertation. In the first of these reports, solventless thermolysis of $CuSC_{12}H_{25}$ (in the presence of surfactant molecules, however) produced $Cu_{2-x}S$ nanodisks, attributed to the anisotropic growth and diffusion afforded by the higher energy <110> facets of the disk edges.¹⁷ In the second of such reports, AgSC₁₂H₂₅ precursor was carried out at 180 °C for 2 hours, producing Ag nanodisks.¹⁸ The growth mechanism was concluded to be nucleation and growth confined to 2 dimensions by the parent lamellar structure. This mechanism is irreconcilable with the data which was readily available at the time showing that Ag alkanethiolates adopt a columnar mesophase at 180 °C. The exact same case exists for the Cu alkanethiolates, which curiously also produce nanodisks. Such was the state of the field before my work began. In the next sections, the Ag and Cu alkanethiolate systems will be examined to posit a more likely growth mechanism for the nanodisk morphologies observed here.

3.2 Ag Nanodisks from Supramolecular Ag Alkanethiolate

The system of Ag alkanethiolates seemed to be relatively well-understood from the standpoint of structure and mesomorphism. However, much of this work as we discussed earlier was carried out in the 1990's and early 2000's, when the synthesis of anisotropic NCs was really an emerging field. Thus, the potential of metal alkanethiolates as NC precursors was overlooked. To revisit the system, with a goal of discerning the true mechanism of nanodisk formation, we synthesized a variety of Ag alkanethiolates (AgSR, R = butane, octane, dodecane, hexadecane). As per the outstanding literature, we obtained white-yellow powders with clear lamellar bilayer structure as indicated by XRD, shown in Figure 3.1. The interlayer *d*-spacings are in good agreement with expectations from literature. If we take the Ag-S network to lie in the (101) plane then the reflections observed here are the interplanar (0*k*0) reflections. These reflections are indexed in Table 3.1.



Figure 3.1 Structure and thermal properties of Ag alkanethiolates. a) shows XRD spectra taken of Ag alkanethiolates for varying alkyl chain lengths as indicated. b) shows overlaid TGA (black) and DSC (red) thermograms for AgSC₁₂H₂₅.

| | Interlay | er spacin | g <i>d</i> , for ol | bserved <i>k</i> | d reflecti | ons of (0/ | k0), in nm |
|------------------------------------|--------------|--------------|---------------------|------------------|--------------|--------------|------------|
| Compound | <i>k</i> = 1 | <i>k</i> = 2 | <i>k</i> = 3 | <i>k</i> = 4 | <i>k</i> = 5 | <i>k</i> = 6 | k = 7 |
| AgSC₄H ₉ | 1.53 | 1.55 | 1.54 | 1.54 | - | - | - |
| AgSC ₈ H ₁₇ | - | 2.45 | 2.47 | 2.47 | 2.47 | 2.48 | 2.47 |
| $AgSC_{12}H_{25}$ | - | 3.28 | 3.37 | 3.40 | 3.41 | 3.43 | 3.43 |
| AgSC ₁₆ H ₃₃ | - | - | 4.34 | 4.37 | 4.42 | 4.37 | 4.41 |

Table 3.1 Interlayer spacing parameters for Ag alkanethiolates.

The major difference between the Cu and Ag thiolates is that the reducing potential of Ag favors homolytic bond cleavage of the Ag-S bond, reducing Ag(I) to Ag⁰. This should also result in the formation of sulfide radicals, which recombine to form disulfide byproducts. As a result, we expect to form metallic Ag nanodisks rather than Ag₂S. TGA was used to characterize the decomposition of Ag dodecanethiolate (Figure 3.1b black). The thermolysis of silver dodecanethiolate is expected to yield pure Ag, with a mass retention of 34.9% corresponding to the loss of dodecyl disulfide. We observed a mass retention of 39%, which is significantly higher than expected. This has been previously observed in the decomposition of Ag thiolates¹⁰ and likely corresponds to the production of Ag₂S at temperatures beyond 200°C. Ag alkanethiolates melt when heated to 200°C, which can be observed visually. DSC analysis in Figure 3.1b (red) shows a strong endothermic peak at 131°C for Ag dodecanethiolate, corresponding to melting of the crystalline solid into the hexagonal mesophase¹⁰.



Figure 3.2 Time-dependent TEM imaging of $AgSC_{12}H_{25}$. Reactions carried out at 200 °C for a) 30 minutes b) 60 minutes and c) 180 minutes.

To synthesize Ag NCs, we carried out thermolysis reactions of AgSC₁₂H₂₅ at 200 °C. Time-dependent TEM imaging was carried out to observe Ag NC formation over time. The decomposed residues were washed with CHCl₃ prior to imaging to remove all soluble byproducts. After 30 minutes of thermolysis (Figure 3.2a), we observe aligned columns of particles, taken to be vestiges of the hexagonal mesophase present at higher temperatures. Small particles are observed in these columns, with some larger particles showing a circular shape corresponding to nascent nanodisks. After 1 hour, Ag nanodisks are clearly observed, although many small silver particles and undecomposed thiolate material are still present (not shown). After 3 hours of solventless thermolysis, nanodisks are the major product and exhibit an average diameter of 31.4 ± 6.9 nm and average thickness of 15.1 ± 1.5 nm. Many particles appear to have a rod-like morphology, but these are disks which have assembled faceto-face. It should be noted that the only other colloidal methods reported to generate uniform dispersions of Ag nanodisks involve the reduction of $\mathrm{Ag}^{\!\!+}$ in aqueous solutions of surfactants such as sodium di(2-ethyl-hexyl)sulfosuccinate, also known as Na(AOT), and cetyltrimethylammonium bromide (CTAB). In these solution-based

approaches, nanodisk formation is attributed to soft-templating by reverse micelle structures.

XRD (Figure 3.3a) demonstrated that the NCs were indeed pure Ag, and had a mean crystallite size of $\tau = 18.3$ nm using the Scherrer equation which is roughly consistent with TEM images. To better examine the particle morphology, atomic force microscopy (AFM) was performed, shown in Figure 3.3b. AFM shows a height profile of around 10 nm, for a particle around 30 nm long, correlating loosely with our measured aspect ratio of about 2:1. The rounding of the edges belies a saucer shape which is inconsistent with our TEM imaging, where the radius of curvature is substantially less and disk faces appear flat. This implies that the resolution of our AFM probe is lacking, or that most NPs which exhibit face-to-face stacking in the TEM images do so because of their flat faces, while disks with convex faces fail to assemble in this way but are present in the sample.



Figure 3.3 Structure and morphology of Ag NCs. a) shows the XRD pattern, purporting a FCC Ag structure as expected. b) shows the nanodisk morphology, with height around 9 nm and diameter around 30 nm. The rounded edges are likely accentuated by the contact mode AFM which was employed.

The evidence demonstrates that Ag alkanethiolates, and particularly the AgSC₁₂H₂₅ that we studied in detail here, melt into a columnar phase and then form Ag NCs from within this columnar template. The strongest indicator of this are the columnar striations observed in Figure 3.2a. Since the columnar rearrangement is a feature of all *n*-alkanethiolates of Ag however, we can test this hypothesis by studying the thermolysis of Ag alkanethiolates which do *not* adopt the columnar phase. In order to test this, we synthesized Ag alkanethiolates with sterically bulky ligands which can't possibly adopt the lamellar bilayer structure, specifically by using phenylamethanethiol and *tert*-dodecanethiol as ligands. The Ag phenylmethanethiolate is obtained as a clear fluid (because the side methyl groups prevent self-assembly).



Figure 3.4 Structure and morphology of Ag₂S NCs. Precursors are Agphenylmethanethiolate and Ag*-tert*-dodecanethiolate. a) XRD patterns of the NCs obtained from 200 °C by 90 minute thermolysis corresponding to Acanthite phase Ag₂S; b) TEM image of the NCs from Ag *tert*-dodecanethiolate. The NCs obtained from Ag phenylmethanethiol are not pictured because a non-dispersible bulk material was obtained.

Thermolysis reactions were carried out with both Ag phenylmethanethiolate and Ag tert-dodecanethiolate using 200 °C for 90 minutes as the decomposition parameter. The XRD patterns for the resulting thermolysis residues are shown in Figure 3.4a. In both cases, Ag₂S resulted rather than Ag. There are a couple different mechanisms by which thermolysis of Ag phenylmethanethiolate and tertdodecanethiolate may differ from the *n*-dodecanethiolate. Firstly, the local electronic environment of the Ag/S atoms is different in each case; Ag phenylmethanethiolate is a nonlamellar crystal, tert-dodecanethiolate is an isotropic fluid, and ndodecanethiolate is a columnar liquid crystal. The bonding interactions surrounding Ag and S atoms have some small impact on the energetics of bond thermolysis. However, the more likely mechanism here is the carbocation stability of tertdodecanethiolate and phenylmethanethiolate being greater than the ndodecanethiolate. The effect of carbocation stability is probed in Chapter 6.4. Whereas Ag n-alkanethiolates tend to undergo Ag-S homolytic bond cleavage, the greater carbocation stability of tert-dodecanethiol and phenylmethanethiol ligands lowers the energetic barrier for C-S bond cleavage and thus promotes C-S bond cleavage in lieu of Ag-S bond cleavage. As observed in Figure 3.4b, the morphology of the resulting Ag₂S NCs is fairly irregular, with misshapen spherical shapes observed. This is consistent with the lack of templating mechanism, and consistent with our hypothesis that the columnar phase is the cause of nanodisk formation.

3.3 Supramolecular Precursors for the Synthesis of Anisotropic Cu₂S Nanocrystals

3.3.1. Introduction

Copper alkanethiolates are organometallic precursors that have been used to form Cu₂S nanodisks upon thermal decomposition. Here, we demonstrate that molecular assembly of Cu alkanethiolates into an ordered liquid crystalline mesophase plays an essential role in templating the disk morphology of the solid-state product. To examine this templating effect, we synthesize Cu alkanethiolate precursors with alkane tails of varying chain length and sterics. We demonstrate that short chain precursors produce two-dimensional (2D) nanosheets of Cu₂S, while longer-chained variants produce Cu₂S nanodisks exclusively. This work provides new insights into the use of liquid crystalline phases as templates for nanocrystal synthesis and as a potential route for achieving highly anisotropic inorganic nanostructures.

Copper sulfide nanomaterials are p-type semiconductors that are being explored for applications in photovoltaics,¹⁹ electrochemical sensors,²⁰ and battery electrodes.²¹ More recently, colloidal chalcocite (Cu₂S) nanocrystals have gained interest as a plasmonic material that is capable of supporting the excitation of localized surface plasmon resonances.^{22,23,24,25} Cu₂S nanocrystals exhibit tunable optical resonances in the near- to mid-infrared range²⁵ and have the potential to enable strong near-field localization (i.e., light focusing) at these frequencies. Because anisotropic nanostructures are known to support the strongest field localizations,^{26,27} fabricating

highly anisotropic Cu₂S nanostructures will be a major challenge for plasmonic applications. Toward this end, we and others have investigated the optical resonances of colloidal Cu₂S nanocrystals such as shells,²⁸ rods,²⁹ wires,³⁰ and disks.²⁴ It would be highly advantageous to be able to synthesize colloidal Cu₂S nanocrystals with these anisotropic morphologies in a controlled, rational manner.

One common method for synthesizing colloidal Cu₂S nanocrystals is via thermolysis of Cu thiolates, which behave as a single-source molecular precursor. This method of solventless thermolysis was first reported by Sigman et al.,¹⁷ who synthesized Cu₂S nanodisks from the thermal treatment of Cu dodecanethiolate (CuSC $_{12}H_{25}$). In these studies, nanodisk formation was attributed to faster deposition at the high surface energy facets that comprise the disk edges, facilitating radial growth. However, nanodisk size and aspect ratio were limited to a narrow range, which is not accounted for by this growth mechanism. In a later work, Chen et al. also carried out solventless thermolysis at 200–220 °C with CuSC₁₂H₂₅.³¹ Their precursor was shown to have a lamellar structure at room temperature, and the formation of nanodisks was attributed to the aggregation of small Cu₂S nucleates constrained within this lamellar structure. The decomposition of CuSC₁₂H₂₅ was also investigated by Wang et al. using the hot injection method, where copper sulfide is obtained using a solvent-based synthesis at temperatures between 160 and 220 °C.³² In their study, lamellar CuSC₁₂H₂₅ was identified as the precursor to copper sulfide formation. However, both of the above studies did not account for melting of the lamellar

 $CuSC_{12}H_{25}$ structure (~140 °C),¹¹ which occurs well below the thermolysis temperatures used in their experiments.

Herein we report an alternative mechanism for the synthesis of anisotropic Cu₂S nanodisks and nanosheets via solventless thermolysis, where shape control is enabled by the formation of a liquid crystal-like molecular template. Metal alkanethiolates are known to form mesogenic phases due to hydrophobic interactions between neighboring alkane chains and strong metal–sulfur coordination.¹⁰ We investigate the thermolysis of various Cu thiolates that adopt lamellar, micellar, and isotropic (disordered) phases at the thermolysis reaction temperature and examine how these phases template the nucleation and growth of solid-state Cu₂S nanocrystals. We observe that Cu₂S nanodisks form only from Cu alkanethiolate precursors that adopt a lamellar phase at the thermolysis temperature. We also observe that isotropic phases give rise to nanocrystals that exhibit little-to-no shape control. These results provide new insights into the shape control mechanism for Cu₂S nanodisks and provide a rational route for producing highly anisotropic Cu₂S nanostructures.

3.3.2. Results and Discussion

Cu thiolate precursors are prepared by precipitating an aqueous solution of $Cu(NO_3)_2$ with the desired alkylthiol. A detailed procedure may be found in section 3.4.4. Cu alkanethiolates were synthesized with alkyl backbone chain lengths of n = 4, 8, 12, or 16 carbons. Figure 3.10 (found in section 3.3.4) shows the XRD spectra (Rigaku RU200B) of these precursors. The periodically spaced low-angle peaks from

 $2\theta = 5^{\circ}-19^{\circ}$ are attributed to multiple reflections (*kd*, where *k* is an index and *d* is spacing) characteristic of a lamellar solid (Figure 3.5a, left). These peaks are fully indexed in Figure 3.10 (found in section 3.3.4) and show an increase in *d*-spacing from 1.59 to 4.55 nm as the alkyl chain increases from 4 to 16 methylene units. Our thermogravimetric analysis (PerkinElmer TGA 7) measurements for CuSC₁₂H₂₅ show the loss of alkyl sulfides and disulfides to yield the solid-state Cu₂S product, which is obtained as a black powder (Figure 3.5b). Mass retention is ~4% lower than expected, likely indicating a nonstoichiometric yield of Cu₂S. Based on our thermal characterization, we carried out thermolysis of Cu alkanethiolates at or near 200 °C.



Figure 3.5. Thermal Properties of Cu alkanethiolates. Schematic diagrams of the lamellar to mesophase transformation upon melting (a), and overlaid TGA and DSC curves for $CuSC_{12}H_{25}$ (b).

We visually observed melting of the supramolecular CuSC₁₂H₂₅, which was corroborated by a strong endothermic peak measured by differential scanning calorimetry (PerkinElmer PYRIS Diamond) at 132 °C (Figure 3.5b). Previously, Sigman and Chen attributed this endothermic peak to C–S bond thermolysis.^{17,31} However, TGA shows that thermolysis occurs at much higher temperatures. Thus, we attribute the peak to a melting phase transition. Previous reports for Cu alkanethiolates indicate that these mesogens undergo a lamellar-tomicellar phase transition at approximately 140 °C.^{11,12} These micellar columns are composed of stacked discotic micelles, where alkyl chains trail radially from the micelle edges (Figure 3.5a, right).¹¹ Cu alkanethiolates likely adopt this columnar mesophase during thermolysis, which is carried out well above 140 °C. As confirmation, we isolated one-dimensional "strings" or columns of mesogenic CuSC₁₂H₂₅ upon thermal annealing above the melting transition (Figure 3.11 found in section 3.3.4).

For the short-chained Cu alkanethiolate (CuSC₄H₉), no melting transition is observed prior to thermolysis at 200 °C. However, we observe that the precursor changes color from dark yellow to orange before gradual blackening of the powder. This color change is attributed to a transition from the crystalline lamellar phase to a smectic-like lamellar phase, which is known to occur for short-chain Ag alkanethiolates (n = 4-10).⁶ This color change is accompanied by an endothermic peak on the DSC curve at around 160 °C (Figure 3.12 found in section 3.3.4). Thus, we expect the thermolysis product of supramolecular CuSC₄H₉ to be templated by a lamellar structure. The resulting thermolysis product showed significant signs of oxidation, likely due to poor surface passivation of the resulting Cu₂S nanocrystals by the short butyl chains. To address this issue, we carried out CuSC₄H₉ decomposition under N₂ flow for 24 h at 200 °C. These significantly longer reaction times are necessary for oxygen-free conditions, which have been demonstrated to decrease the thermolysis reaction rate.³³



Figure 3.6. Characterization of Cu_2S nanodisks. TEM images of the products obtained from the solventless thermolysis of copper alkanethiolates: $CuSC_8H_{17}$ (a), $CuSC_{12}H_{25}$ (b), and $CuSC_{16}H_{33}$ (c), and the corresponding XRD patterns (d).

To characterize all of the solid-state products obtained by thermolysis, we carried out transmission electron microscopy (TEM, FEI Tecnai G2 Sphera) on samples prepared by dispersing the Cu₂S product in ethanol and drop-casting the dispersion directly onto a carbon-coated support grid. Figure 3.6 shows TEM images of the resulting nanocrystals obtained by solventless thermolysis of the Cu alkanethiolates. For n = 8-16, disk-like particles were obtained. Nanodisks obtained from the thermolysis of $CuSC_8H_{17}$ display the greatest polydispersity, with an average diameter of 21.48 ± 15.95 nm and average thickness of 3.66 ± 0.87 nm. These disks were found among many smaller, mostly ovoid particles ranging from 2 to 12 nm in size. Nanodisks obtained from CuSC₁₂H₂₅ possess an average diameter of 25.76 ± 5.83 nm and an average thickness of 5.47 ± 0.68 nm. Nanodisks obtained from $CuSC_{16}H_{33}$ were 23.50 ± 5.25 nm in diameter and 7.80 ± 1.09 nm thick. FTIR spectra indicate that all disks are terminated with alkyl groups (Figure 3.13 found in section 3.3.4). This surface passivation renders the disk surface hydrophobic, causing them to preferentially assemble into face-to-face stacks.

Figure 3.6d shows XRD spectra obtained for the resulting Cu₂S nanodisks. The nanodisks are composed mainly of high-temperature β -chalcocite, with some Cu-deficient Cu_{1.96}S present. Several peaks from $2\theta = 31^{\circ}-34^{\circ}$ that are unidentifiable with chalcocite are also present. These peaks likely stem from the significant amount of Cu deficiencies that are symptomatic of solventless thermolysis carried out under ambient atmosphere (due to Cu oxidation).

Nanocrystals obtained from the thermolysis of CuSC₈H₁₇ are notably heterogeneous in comparison to products from the longer-chained Cu alkanethiolates. Alkyl chain length is likely to affect the stability of the resulting columnar mesophase. We observe that shorter alkyl chains fail to induce the columnar mesophase transition; at least an 8-carbon chain is required to observe sample melting, and a 12-carbon chain is required to produce monodisperse nanodisks. It is likely that an 8-carbon chain is long enough to induce melting to form a columnar mesophase, but results in only partial phase ordering. This dependence of phase stability on chain length is similar to the observation made for self-assembled monolayers (SAMs), where 10-carbon chains have been shown as the minimum chain length required to produce a well-ordered, solidly packed SAM on Cu.³⁴

Nanocrystals obtained from the thermolysis of supramolecular CuSC₄H₉ do not possess a disk-like shape and instead adopt a sheet structure (Figure 3.7a). The nanosheets vary in length from 50 nm platelets to ribbons over 1 μ m long. Atomic force microscopy (AFM, Bruker Scanning Probe Microscope) measurements reveal that the nanosheets are 5.4 ± 1.7 nm thick and that this thickness is fairly consistent across a nanosheet (Figure 3.7b,c and Figure 3.14 found in section 3.3.4). This 2D morphology is consistent with thermolysis of the lamellar CuSC₄H₉ precursor, which we believe is responsible for templating these planar structures. XRD spectra indicate that the nanosheets are composed of the low temperature α -chalcocite phase (Figure 3.7d).



Figure 3.7. Characterization of Cu₂S nanosheets. TEM image of the Cu₂S nanosheets from thermally decomposed CuSC₄H₉ (a), AFM topology image of nanosheets (b), AFM height profile of a nanosheet displaying a thickness of 7.5 nm corresponding to the dashed line in the topology image (c), XRD profile of the Cu₂S nanosheets showing α -chalcocite (d, RRUF ID: R120113.9)

To further elucidate the growth mechanism of nanodisks and the effects of supramolecular templating, we monitored nanodisk growth by stopping the thermolysis reaction of $CuSC_{12}H_{25}$ at various time intervals and analyzing the products by TEM (Figure 3.8). After 5 min of thermolysis, $CuSC_{12}H_{25}$ has only undergone a

minor degree of decomposition. We observe small particles in aligned columns (Figure 3.8a). Based on XRD measurements and imaging contrast, most of the product observed by TEM corresponds to undecomposed $CuSC_{12}H_{25}$. After thermolysis has proceeded for 15 min, we observe the appearance of disk-like nanostructures. The nanodisks appear highly oriented within the dense organic matrix, suggesting that they precipitate within the aligned columns. After 30 min of thermolysis, we obtain the final nanodisk product. The nanodisks form aligned columns that appear to be embedded in a low density matrix, which we believe is undecomposed $CuSC_{12}H_{25}$. We have observed tracts of these aligned nanodisks over 1 µm long (corresponding to several thousand nanodisks). At thermolysis times longer than 30 min, the $CuSC_{12}H_{25}$ precursor is almost completely decomposed. We observe that the final nanodisks are free-standing (Figure 3.6b).



Figure 3.8. Time-dependent TEM analysis. TEM images of $CuSC_{12}H_{25}$ precursor decomposed for various times: 5 min (a), 15 min (b), and 30 min (c).

3.3.3. Nanodisk Growth mechanism

These observations indicate that the discotic micelles serve as nucleation points for Cu₂S particles, which are templated into disks within the mesophase columns. Gradual thermal decomposition of the discotic micelles facilitates the transport of Cu alkanethiolate units to the outer surfaces of the stacked particles, enhancing radial growth. This is consistent with other reports where columnar mesophases have been shown to template nanowires³⁵ and nanoplates.³⁶

To further demonstrate this mechanism of liquid crystalline templating, we carried out thermolysis reactions for nonmesogenic Cu thiolates. We chose ligands with steric groups that would preclude the formation of either the ordered lamellar or micellar phases. *tert*-Dodecanethiol (CuSC(CH₃)₂C₉H₁₉) possesses side-methyl groups

that provide a large steric hindrance to close-packing; consequently, CuSC(CH₃)₂C₉H₁₉ is an isotropic liquid. Benzylmercaptan (CuSCH₂Ph) contains aromatic phenyl groups that produce radically different packing structures than alkanes due to π -stacking interactions. While CuSCH₂Ph was isolated as a crystalline powder, the XRD spectrum revealed no evidence of lamellar order in the solid.

We carried out solventless thermolysis with both of these Cu thiolates at 200 °C for various reaction times. For CuSC(CH₃)₂C₉H₁₉, we also explored a range of thermolysis temperatures from 140 to 200 °C. Both Cu thiolates routinely yielded nano- and microparticles that were not uniform in size or shape. These products were characterized by scanning electron microscopy (SEM) and XRD (Figure 3.9). Interestingly, the thermolysis products obtained from these thiolates are not composed of chalcocite, as with the nanodisk and nanosheet products. Instead, thermolysis of the nonlamellar Cu thiolates produced particles composed of digenite (Cu₉S₅) and covellite (CuS) phases, with traces of an intermediate Cu_{1.8}S phase observed for decomposed CuSCH₂Ph. The higher sulfur content of these phases may be explained by the ability of both ligands to stabilize a carbocation on the primary carbon more favorably than a linear alkane. This would promote C–S bond cleavage over Cu–S bond cleavage, resulting in a higher retention of sulfur in the final solid-state product.



Figure 3.9. Decomposition of non-mesogenic Cu-thiolates. SEM image (a) and XRD pattern (b) for the particles obtained from the thermolysis of CuSCH₂Ph for 60 min at 200 °C, and SEM image (c) and XRD pattern (d) for the particles obtained from the thermolysis of CuSC(CH₃)₂C₉H₁₉ for 45 min at 200 °C.

In conclusion, we show that supramolecular Cu alkanethiolates with varying chain lengths are able to template the formation of Cu₂S nanodisks and Cu₂S nanosheets. Melting of lamellar Cu alkanethiolates to the columnar mesophase is essential for generating the nanodisk shape. Nonmesogenic Cu thiolates produce irregularly shaped copper sulfide particles. Thus, supramolecular order of the Cu thiolate precursor dictates the resulting morphology of the nanocrystals obtained by thermolysis. This synthetic route has the potential to generate nanocrystal

morphologies with highly anisotropic dimensions. These ultrathin semiconducting nanostructures may serve as key building blocks for nanoelectronic and optoelectric devices.

3.3.4. Supplemental Information

Detailed synthetic procedure:

In a general synthesis of $CuSC_{12}H_{25}$, 0.465g $Cu(NO_3)_2$ is added to 2mL of DI water in a flask and stirred to make a 1M solution. Separately, 1.92mL dodecanethiol is added to 4mL of ethanol to form a 2M solution – this is stirred until thoroughly mixed. This latter solution is added rapidly to the former under vigorous stirring, which results in instantaneous precipitation of the copper thiolate and dodecyl disulfide. Dodecyl disulfide results from the reduction of Cu^{2+} to Cu^+ and the corresponding oxidation of dodecanethiol to the disulfide. The solution is stirred for about 10 minutes, or until an even white-yellow color is achieved. This is then washed copiously with water and ethanol. Copper dodecanethiolate is obtained as a waxy, white-yellow powder consisting partly of co-crystallized dodecyl disulfide, and allowed to dry in a vacuum desiccator before use. The disulfide plays a noncritical role in nanodisk synthesis.



Interlayer spacing, d, for observed kd reflections of (0k0), in nm

| | <i>k</i> = 1 | k= 2 | <i>k</i> = 3 | <i>k</i> = 4 | k= 5 | <i>k</i> = 6 | k= 7 |
|------------------------------------|--------------|------|--------------|--------------|------|--------------|------|
| CuSC₄H൭ | 1.57 | 1.59 | 1.59 | - | - | - | - |
| CuSC ₈ H ₁₇ | - | 2.52 | 2.54 | 2.55 | 2.55 | - | - |
| $CuSC_{12}H_{25}$ | - | 3.40 | 3.46 | 3.35 | 3.49 | 3.51 | 3.53 |
| CuSC ₁₆ H ₃₃ | - | - | 4.52 | 4.38 | 4.55 | 4.58 | 4.60 |

Figure 3.10. XRD Patterns of Cu alkanethiolates and spacing parameters. The XRD spectra (top) show the regularly-spaced peaks characteristic of a lamellar structure, in correspondence with previous reports. The large peak at $2\theta = 20^{\circ}$ is assigned to alkyl-alkyl spacing, representing a d-spacing of about 4.4Å, which is characteristic of close packed alkanes. The table (bottom) shows the interlayer spacing parameter for each Cu alkanethiolate.



Figure 3.11. TEM image of string-structures. $CuSC_{12}H_{25}$ heated beyond the mesophase transition and then slowly cooled to room temperature loses in-plane coordination of the lamellar structure, which is not reformed during cooling. Strings correspond to 1D chains of $CuSC_{12}H_{25}$. These tend to pack together with a spacing parameter of ~4nm, while the spacing parameter found between layers of the lamellar $CuSC_{12}H_{25}$ structures is ~3.5nm.



Figure 3.12. CuSC₄H₉ DSC and TGA curves. The DSC curve shows a large endothermic peak at around 160°C, which we assign to the crystalline lamellar to lamellar mesophase transition. Peaks beyond 200°C likely correspond to volatilized byproducts rather than phase transitions. The TGA curve shows steady massloss which proceeds rapidly beyond about 260°C. The mass retention of ~49% is in good agreement with the theoretical mass retention of ~52% for the generation of Cu₂S, the difference possibly stemming from the sample not being completely dry.



Figure 3.13. Nanodisk FTIR Spectrum. Nanodisks were obtained from thermolysis of $CuSC_{12}H_{25}$ for 45m at 200 °C. The peaks at 2851, 2871, 2920 and 2954 cm⁻¹ correspond to various C-H modes of the capping alkane chains.



Figure 3.14. Nanosheet AFM. Nanosheets were obtained from solventless decomposition of CuSC₄H₉ for 24h at 200 °C. AFM samples were prepared as follows: the nanosheet particles were dispersed in CHCl₃ and dropcast onto an air/water interface to form a film, and then dip-coated onto a Si substrate that had been hydroxylated with piranha solution and then treated with hexamethyldisilazane. NP height is generally 5.4 ± 1.7 nm nm thick. The above AFM image shows particle that appear to be significantly taller than this average. However, the particles are hydrophobic and tend to stack. The corresponding image obtained from the AFM deflection signal shows that these taller particles consist of multiple nanosheets that are stacked on top of each other, as indicated by discrete steps in nanosheet height.



Figure 3.15. Time-dependent nanosheet TEM. TEM analysis was carried out for the Cu-butanethiolate precursor at different time intervals during thermolysis from 0-24 h at 200 °C under N₂ flow, where XRD indicated full decomposition of the precursor to the solid-state copper sulfide nanocrystals after 24 h of thermal treatment.

Chapter 3, in part, is a reprint of the materials that appears in *The Journal of the American Chemical Society* (Whitney Bryks, Melissa Wette, Nathan Velez, Su-Wen Hsu, and Andrea R. Tao. "Supramolecular Precursors for the Synthesis of Anisotropic Cu₂S Nanocrystals." *J. Am. Chem. Soc.*, **2014**, *136*, 6175-6178). The dissertation author was the primary investigator and author of this material.

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Chapter 4

Chemical Modification of Copper Alkanethiolates for Design of Thermal

Properties

4.1 Effects of Alkyl Chain Modification

In Chapter 3, the thermal properties and subsequent thermolysis of Cu alkanethiolates were shown. We observed that alkanethiols between 8-16 carbons in length supported the columnar phase during thermolysis, and that the "short-chained" butanethiolate instead supported a lamellar phase during thermolysis. This lamellar phase, which we postulated to be a lamellar smectic phase, was of key interest; the 2D configuration provides an exemplary template for the synthesis of metal chalcogenides with ultrathin sheet structures akin to TMDs. However, if realizing large-area, ultrathin metal chalcogenide nanosheets is the goal, then the CuSC₄H₉ precursor shown in Section 3.3 had several significant drawbacks. These drawbacks should be elucidated in more detail before discussing how we might rationally design a Cu alkanethiolate which overcomes them.

First and foremost, we found the structure of CuSC₄H₉ precursor to be unstable; it would undergo structural decay over time. This was evidenced visually by an obvious change in color, which coincided with the loss of lamellar bilayer structure as observed by XRD. This data is provided below, in Figure 4.1. Four samples of CuSC₄H₉ precursor were arranged by age, from freshly synthesized (Sample A) to several months aged (Sample D). Samples were aged under vacuum in a benchtop desiccator, so the result of aging should not be caused by oxidation. The obvious difference in sample color as a function of time (Figure 4.1B) was a point of concern; absorption in Cu alkanethiolates derives from the electronic environment of the metal center, such as a metal-ligand charge transfer (MLCT). Accordingly, change in optical absorption indicates a change in the metal-thiolate bonding. CuSC₄H₉ precursors are nominally synthesized in yellow-green color, and with aging take on more orange and then brown coloration. As shown in Figure 4.1A, the evolution of color correlates with a loss of lamellar bilayer structure, which is shown for Sample A which has regularlyspaced peaks near 2θ =5.5, 11, 16.5°. After aging, the loss of lamellar bilayer peaks is accompanied by the emergence of a single broad peak near 2θ =7.5° corresponding to a greatly diminished *d*-spacing as compared to the bilayer. We interpreted this as most likely belonging to a collapsed and interdigitated bilayer, where some level of disordered interdigitation explains the contracted *d*-spacing and the peak broadness. However, it is also possible that the singular XRD peak 2θ =7.5° corresponds to an unidentified structural regime such as a 1D molecular chain configuration.¹



Figure 4.1. XRD patterns (A) and photograph (B) of CuSC₄H₉ precursor arranged by sample aging. Samples aged under vacuum, from newest (Sample A) to oldest (Sample D).

The structural instability of CuSC₄H₉ precursor was deemed to originate from its short alkyl component, which provides relatively little in the way of in-place van der Waals attractions compared to the longer alkyl chains. We believe the poor structural integrity of the CuSC₄H₉ precursor is responsible for the small nanosheet particle sizes observed in Chapter 3.3. The logic is that the structural contiguity is related to small domains which restricts the potential crystallize sizes. Therefore, in order to better exploit the lamellar smectic phase witnessed for CuSC₄H₉, we sought to synthesize a Cu alkanethiolate with a sufficiently long alkyl chain to produce stable and large-area precursor domains, and yet also increase in-plane attractive forces to increase stability of the lamellar structure and suppress the columnar transition temperature. We hypothesized that the most simple and effective way to increase the in-plane attractive forces of the supramolecular Cu alkanethiolate would be to add hydrogen bonding to the attractive terms. This could be easily accomplished by using commercially available alkanethiolates which are terminated by either –OH or – COOH functionalities. Therefore, we chose –OH and –COOH terminated alkanethiols with overall length comparable to 1-dodecanethiol: 11-mercaptoundecanol (referred to as MUO) and 11-mercaptoundecanoic acid (referred to as MUA) and prepared the corresponding Cu alkanethiolates. The results are shown in Figure 4.2.



Figure 4.2. Cu alkanethiolates modified with –OH and –COOH groups. A) shows the ligands chosen with comparable length, with 11-mercaptoundecanoic acid represented in blue, 11-mercaptoundecanol represented in red, and 1-dodecanethiol respresented in black. B) shows XRD patterns, supporting that all three thiols form lamellar bilayer structures; C) and D) show DSC and TGA thermograms respectively.

Figure 4.2 compares and contrasts Cu alkanethiolates synthesized with MUO and MUA ligands compared to 1-dodecanethiol previously shown in Chapter 3.3. Both the MUO and MUA ligands form Cu alkanethiolates with lamellar bilayer structure (Figure 4.2B). However, we observe marked differences in the thermal properties owing to the installed functional groups. Figure 4.2C shows the corresponding DSC thermograms, where the endothermic transition near 135 °C (black curve) is the lamellar to columnar transition. Interestingly, we observe phase transitions at lower temperatures with the –OH and –COOH functionalities installed (red and blue curves)

respectively). However, this phase behavior is complex because the phases are not readily identifiable; Cu alkanethiolates synthesized with MUO and MUA show initial phase transition near 85 °C, however this appears to be a crystal to crystal phase transition and no "melting" is visibly observed. Furthermore, there are additional phase transitions which occur starting near 164 °C (MUA) and 180 °C (MUO), both of which lead to "melting" and substantial loss of viscosity and are tentatively assigned to a lamellar smectic to columnar transition.

Because mesophase transitions appear to occur circa 160-180 °C, the stability of the lamellar smectic phase somewhat lacking. For Cu alkanethiolates, C-S bond thermolysis occurs as a negligibly slow rate near 160 °C, so thermolysis within the limited window as shown in Figure 4.2C is not an option. Ideally, we would like to stabilize a lamellar phase in excess of 200 °C. We found that we had to go a single step further in order to stabilize the lamellar smectic phase. In Chapter 4.2, we will detail how halide ions can coordinate to the Cu centers in Cu alkanethiolates and consequently modify their thermal properties.

4.2 Effects of Intercalated Halide Ions

Early on in the synthesis of Cu alkanethiolates, we became cognizant of variations in the supramolecular precursor that traced back to the counter ion present within the Cu salt. Among other things, we noticed that when CuCl or CuCl₂ were used as the Cu source, the XRD pattern of the lamellar bilayer structure indicated greater order. We took this as an indication that, as the ligands shown in Chapter 2.4, Cl⁻ ions may coordinate to Cu and have some effect on the self-assembly process. We

tested this hypothesis by synthesizing $CuSC_4H_9$ precursor from $Cu(NO_3)_2$ salt dissolved in saline solution, with the NaCl concentration of 0 (A), 1:100 with Cu (B), 1:10 with Cu (C), and 1:1 with Cu (D). We analyzed the 4 precursors thus produced with XRD, FTIR, and TGA, and the results are shown in Figure 4.3 below.



Figure 4.3. XRD (a), FTIR (b), and TGA (c) of $CuSC_4H_9$ synthesized in the presence of NaCl. The TGA thermogram shows only sample D which used NaCl 1:1 with Cu, and the expected mass retention demonstrates that no Cl is intercalated into the precursor structure.

Figure 4.2 a) shows XRD spectra for samples A-D; we observed negligible differences in full width half max of the supramolecular assemblies. Figure 4.3b) shows the FTIR spectra, which again show negligible differences between samples prepared in the presence of varying NaCl content. These results were unanticipated, as we expected more apparent discrepancies in structural order to correlate with NaCl content. Disorder is known to demonstrate in significant C-H peak shifts in the FTIR spectra which were not observed. Moreover, we expected that some Cl may become intercalated within the supramolecular structure and so we performed TGA on Sample D. However, the mass retention of 52.1% corresponds perfectly with the expected mass retention, so no significant amounts of Cl⁻ were incorporated.

However, when analyzed with TEM, obvious discrepancies in the morphology of supramolecular assemblies in the samples A-D were apparent. Figure 4.4 show TEM images of samples A-D, labeled accordingly. While sample A shows stringlike morphology, B shows both stringlike structures and large-area, sheet structures, while C and D are only sheets. This is actually very similar to what was observed in the time-dependent assembly of Au alkanethiolates, as was discussed in Chapter 3.1. It would seem that Cl⁻ plays some role in promoting the assembly of smaller lamellar domains with stringlike coordination into larger 2D arrays. The results are interesting in light of the TGA data shown in Figure 4.3C however, that indicates no Cl⁻ intercalation. So Cl⁻ is likely coordinating to Cu during Cu alkanethiolate selfassembly, but not so strongly as to incorporate into the supramolecular structure.



Figure 4.4. TEM images of $CuSC_4H_9$ precipitated in the presence of NaCl. The concentration of NaCl was 0 (a), 1:100 with Cu (b), 1:10 with Cu (c), and 1;1 with Cu (d).

During our many syntheses of Cu alkanethiolates, we had observed that the sample coloration can exhibit some variation. Often, the color is white-yellow, but some samples can appear more white, and others more yellow. Interestingly, when we precipitated CuSC₄H₉ samples A-D from increasingly saline solutions, we noticed a trend with the sample color. The greater the NaCl concentration, the more white the

sample appearance. As this is a very qualitative observation, we quantified this trend by using UV-Vis spectroscopy. The results of this analysis are shown in Figure 4.5. In Figure 4.3a, UV-Vis absorption spectra show that there is a visible absorption in the blue region. The samples each have a singular peak which occurs at $\lambda_{max} = 360, 361,$ 364, and 367 nm for samples A-D respectively. The absorption almost certainly results from the Cu-S interaction, and is likely a metal-ligand charge transfer (MLCT) or similar interaction. Based on the TEM images shown in Figure 4.4, we suspect that there are structural discrepancies which do not manifest in the XRD patterns. These structural discrepancies could include different trans to gauche ratios within the alkyl groups, or slight deviations in the Cu-S bonding network. Whichever the case, the energy and intensity of the MLCTs are likely caused by these structural differences.



Figure 4.5. Optical extinction spectra and color differences in CuSC₄H₉ samples prepared in increasingly saline solutions. a) shows optical extinction spectra, showing that supramolecular assemblies precipitated in the presence of greater Cl⁻ concentration show redshifted λ_{max} with decreased intensity. b) shows a photograph taken of the samples, highlighting the plainly observed color differences.

As shown in section 4.2, we can synthesize Cu alkanethiolates using various terminal functional groups, including –OH and –COOH. These functional groups produce some interesting data when combined with halide ions. In Figures 4.3-4.5, we presented data which purports that CuSC₄H₉ self-assembles in saline solutions and is affected morphologically by Cl⁻, but does not intercalate Cl⁻. However, Cu alkanethiolates which bear hydrophilic functional groups, particular –COOH, show a greatly enhanced proclivity for the intercalation of halides. After examining the data presented in Chapter 4.1, we focused our studies on a –COOH functionalized alkanethiolate, CuSC₁₀H₂₀COOH. To further our studies on modified Cu alkanethiolates, we synthesized CuSC₁₀H₂₀COOH in the presence of different halide salts including KI, NaBr, and NaCl. For these precipitation reactions, Copper(I) acetate was the Cu source. However, we also synthesized CuSC₁₀H₂₀COOH using Cu(I) chloride as the Cu source. In Figure 4.6, we contrast the CuSC₁₀H₂₀COOH thusly synthesized.



Figure 4.6. XRD and DSC of $CuSC_{10}H_{20}COOH$ synthesized with various halides. Halide sources include CuCl, NaCl, NaBr, and KI. a) shows XRD spectra, b) shows stacked DSC thermograms for the corresponding Cu alkanethiolates.

Figure 4.6 shows the XRD patterns of $CuSC_{10}H_{20}COOH$ synthesized from Cu(I) acetate (CuAc) with halide salts NaCl, NaBr, and KI, and also $CuSC_{10}H_{20}COOH$ synthesized form Cu(I) chloride (CuCl). For the most part, the spectra are comparable. It should be noted that there is residual crystalline NaCl peaks (boxed in), indicating that the salt precipitated out during the self-assembly process. Figure 4.6b) shows DSC thermograms for the aforementioned samples, as well as $CuSC_{10}H_{20}COOH$ prepared using just CuAc. There is a significant dip that occurs in the green spectra (KI) which likely corresponds to instrumentational noise and should be ignored. What the spectra do have in common is one or more endothermic peaks occurring in excess of 200 °C, and a singular peak which we attribute to melting which occurs near 95 °C. Curiously, the CuSC₁₀H₂₀COOH prepared from CuCl does not show this melting event at 95 °C.

We next analyzed the CuSC₁₀H₂₀COOH precursors with TGA to determine halide intercalation. Some intercalation was expected for NaCl, which showed crystalline NaCl domains within the precursor as evidenced by its XRD pattern. However, we did not expect halide intercalation in the other samples, because halide intercalation did not occur in the previous example shown for CuSC₄H₉ in Figure 4.3. Figure 4.7 shows the TGA thermograms for the corresponding CuSC₁₀H₂₀COOH samples. Halide intercalation is up to about 5 wt. % for the NaCl, NaBr, and KI samples. However, it is an unprecedented ~20% for the sample produced from CuCl. The data shown here and in Figure 4.6 demonstrate that precipitation of CuSC₁₀H₂₀COOH from CuCl results in some significant variations in the thermal properties of the precursor, which can be attributed to the presence of large amounts of Cl- in the precursor.



Figure 4.7. TGA of $CuSC_{10}H_{20}COOH$ synthesized with various halides. Compared to the absence of halide ion, halide salts NaCl, NaBr, and KI exhibited significant halide incorporation, however Cl incorporation for $CuSC_{10}H_{20}COOH$ precipited from CuCl was extraordinarily high in comparison.

The results represented by Figures 4.6 and 4.7 are very intriguing; if all the supramolecular assemblies are lamellar bilayer structures, they should all lose the crystalline lamellar configuration at elevated temperature. If the melting peak from the nominal lamellar phase is suppressed, perhaps this indicates that the lamellar phase can be preserved during thermolysis. Since large amounts of Cl⁻ are apparently incorporated, it's very likely that intercalated Cl⁻ might actually serve to stabilize the lamellar bilayer phase. Since obtaining highly anisotropic 2D sheets of Cu_{2-x}S has

been a goal, this prompted the work in the next section, Chapter 4.3. Chapter 4.3 goes into great detail examining $CuSC_{10}H_{20}COOH$ precursor synthesized from CuCl, which we show does indeed maintain a lamellar bilayer phase during thermolysis in order to facilitate nucleation and growth of large area Cu_9S_5 nanosheets.

4.3 Digenite Nanosheets Synthesized by Thermolysis of

Layered Copper-Alkanethiolate Frameworks

Copper sulfide nanocrystals support localized surface plasmon resonances in the near-infrared wavelengths and have significant potential as active plasmonic nanomaterials due to the tunability of this optical response. While numerous strategies exist for synthesizing copper sulfide nanocrystals, few methods result in nanocrystals with both controlled morphological shapes and crystallinity. Here, we synthesize and characterize ultrathin (<5 nm) Cu₉S₅ nanosheets that are formed by solventless thermolysis, utilizing Cu alkanethiolates as single-source precursors. Layered Cu alkanethiolate precursors adopt a highly ordered structure which can be further stabilized in the presence of Cl⁻ and also serve to template the formation of nanosheets. We show that, in the absence of Cl⁻, only isotropic and disk-like Cu_{2-x}S nanocrystals form. These findings offer further insight into the use of layered metal– organic single-source precursors as templates for anisotropic nanocrystal growth.

4.3.1. Introduction

Low-dimensional metal and semiconducting nanostructures that support localized surface plasmon resonances (LSPRs) are highly desired materials due to

their ability to propagate, manipulate, and confine light. In particular, anisotropic nanostructures that possess well-defined edges and facets exhibit strong electromagnetic confinement effects that give rise to diverse optical phenomena. ^{2,3,4} Such plasmonic nanomaterials have impacted research in a broad range of applications where light localization or focusing is key, including platforms for optical spectroscopy, photovoltaics, and near-field microscopy.^{5,6,7,8} LSPRs in the near-IR can be excited by fabricating highly anisotropic Ag or Au nanoparticles or by arranging metal nanoparticles into clusters.^{9,10,11} For example, Au nanorods possess elongated shapes that enable LSPR excitation from 500 to over 1300 nm¹² and have been demonstrated as a viable contrast agent for photothermal therapy and photoacoustic imaging.^{13, 14,15} However, field localization in the near- to mid-IR range is limited by the intrinsic electromagnetic permittivity of Ag and Au.¹⁶ Few metals are capable of supporting LSPRs in the IR range because they are highly absorbing and possess interband transitions at these wavelengths.¹⁶ In addition, conventional metals used in plasmonic applications possess large free carrier densities ($>10^{22}$ cm⁻³) that are not readily modulated by chemical or electrical means, impeding the ability to actively tune the dielectric response of the corresponding nanomaterials.

More recent focus has been extended to nanocrystals composed of highly doped semiconductor nanocrystals (SNCs) that exhibit LSPRs in the near- to mid-IR range, such as $Cu_{2-x}S$,^{17,18, 19} $Cu_{2-x}Se$,^{20,21} highly doped ZnO,²² and Sb-doped SnO₂.²³ These SNCs exhibit appropriate electromagnetic permittivities and sufficiently large free carrier concentrations to support LSPR excitations in the IR at frequency ranges far

beyond what can be achieved by metallic nanostructures.^{24,25} In addition, SNCs have demonstrated a high degree of LSPR tunability achieved through carrier density modulation, either by material doping (e.g., with In, Sn, Al) or by self-doping (e.g., introduction of holes via oxidative processes).^{26,27,28,21} Because of their tunable IR response, SNCs could provide unprecedented opportunities for plasmonics in a new range of fields where manipulation or focusing of IR light is critical, including wireless telecommunication,²⁹ chemical sensing,^{30, 31} bioimaging,³²⁻³⁵ and IR spectroscopy.³⁶⁻³⁸

For applications that depend on IR light focusing, a major challenge is the fabrication of highly anisotropic SNCs that support strong electromagnetic field localization. Of particular interest are two-dimensional (2D) nanomaterials, which display unique optoelectronic and mechanical properties resulting from in-plane confinement.^{39,40,41} Such low-dimensional materials are often prepared by solvothermal routes. For instance, coordinating surfactant molecules can act in tandem with halide ions to promote planar growth and shape-focusing effects in CuS nanocrystals.⁴² Another successful strategy for achieving shaped SNCs is by employing a molecular template, where low-dimensional nanocrystal morphologies are achieved using organic coordinating ligands to confine crystal growth. Such templates typically rely on the self-assembly of surfactant molecules into supramolecular structures such as micelles and bilayers that limit growth to just one or two dimensions. For example, CuS nanorods with sub-nanometer thickness were grown by sulfidation of $Cu[CH_3(CH_2)_{18}COO]_2$ precursors, where

Cu[CH₃(CH₂)₁₈COO]₂ forms a bilayer structure on a solid support. This bilayer serves as a template by confining Cu²⁺, yielding arrays of ultrathin CuS nanorods upon sulfidation.⁴³ In a similar fashion, PbS quantum platelets were prepared using an alkylamine lamellar bilayer as a template. In this approach, *n*-octylamine formed lamellar mesophases *in situ*, leading to 2D nucleation and growth of PbS nanosheets from lead(II) acetate [Pb(OAc)₂] and S^{2–} provided by thiourea.⁴⁴ In each of these examples, strong ligands (typically containing amine and carboxylate moieties) coordinate to metal ions while close-packed alkyl components provide confinement of SNC nucleation and growth processes.

Ag and Cu alkanethiolates are self-assembled supramolecular compounds that also form supramolecular structures, but are particularly notable because they take the form of liquid crystals with lamellar and micellar phases.^{45,46,47,48,49,50} Previously, we and others demonstrated that Cu_{2-x}S nanocrystals with disk-like shapes could be synthesized using Cu alkanethiolate precursors, which serve as both a shapecontrolling template and a single-source precursor for SNC formation.^{51,52} We were able to isolate intact supramolecular Cu alkanethiolates in both the layered and micellar forms, which we then used as templates for the formation of anisotropic SNC shapes such as nanosheets and nanodisks, respectively. One promising strategy to form higher aspect-ratio 2D SNCs utilized CuSC₄H₉ precursors, which maintain lamellar structures at thermolysis temperatures of ~200 °C to form ultrathin (~5 nm) Cu_{2-x}S nanosheets.⁵² However, we observed that the supramolecular structure of CuSC₄H₉ was significantly less stable than longer-chained Cu alkanethiolates, which we attributed to weaker in-plane van der Waals forces stabilizing the lamellar form. As a result, $CuSC_4H_9$ is more susceptible to disorder and the lamellar structure tends to degrade over time. This instability limited the size of resulting $Cu_{2-x}S$ nanosheets to widths of approximately 25 nm.

To obtain higher aspect-ratio 2D SNCs, it would be advantageous to develop single-source precursors that possess both a high degree of lamellar order and greater supramolecular stabilities at working thermolysis temperatures. Toward this end, we have explored the synthesis of single-source precursors that possess increased in-plane interactions to template the formation of $Cu_{2-x}S$ nanosheets. In this work, we report the synthesis and characterization of single-source Cu alkanethiolate precursors generated from bifunctional alkanethiols that are terminated with carboxylic acid groups. Increased in-plane interactions due to hydrogen bonding or attractive electrostatic interactions enable the preservation of lamellar supramolecular structures during thermolysis reactions. We also observe that bifunctional precursors enable the intercalation of halide ions, which further stabilizes the lamellar structure. Figure 4.8 shows the schematic for precursor formation with and without intercalated Cl⁻ and then subsequent precursor thermolysis to form copper sulfide. The stabilization of the lamellar bilayer structure with intercalated Cl-leads to 2D nucleation and growth of Cu₉S₅ sheets rather than Cu_{2-x}S particles. The data obtained allow us to posit a mechanism, and last, the resulting nanosheets are characterized by photoluminescence and absorption spectroscopy to determine their optical properties.



Figure 4.8. Reaction scheme for digenite sheets and chalcocite particles. Decomposition of $CuSC_{10}H_{20}COOH$ leads to oval or discotic chalcocite nanoparticles. Cl⁻ incorporation during supramolecular assembly leads to an alternative decomposition mechanism and nanosheet product.

4.3.2. Results and Discussion

CuSC₁₀H₂₀COOH precursors were synthesized by precipitating Cu(OAc) with HSC₁₀H₂₀COOH in solution (see experimental for more details). The isolated powder was analyzed with X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) to characterize molecular structure and thermal properties. Figure 4.9a shows the XRD spectrum for CuSC₁₀H₂₀COOH and contrasts the results with Cu dodecanethiolate (CuSC₁₂H₂₅), which is made by similar precipitation methods.⁵² The XRD spectra for both precursors possess sharp peaks that correspond to equally spaced lamellar bilayers, where the *d*-spacing between bilayers is calculated to be 3.25 nm for CuSC₁₀H₂₀COOH and 3.45 nm for CuSC₁₂H₂₅. However, both thiol ligands in all-trans conformation are expected to be ~1.5 nm in length, while the presence of the terminal –COOH group in CuSC₁₀H₂₀COOH results in a decrease in the interlayer *d*-spacing parameter by approximately 0.2 nm. We attribute this to strong hydrogen-bonding interactions between terminal –COOH groups, where some overlap of the carboxyl groups

establishes a highly coordinated hydrogen-bonding network and slightly contracts the bilayer thickness.



Figure 4.9. Comparison of thermal properties of $CuSC_{12}H_{25}$ and $CuSC_{10}H_{20}COOH$. (a) XRD patterns for each precursor, demonstrating both have lamellar bilayer structures, while the DSC curves (b) and TGA curves (c) show show the change in thermal properties.

Figure 4.9b shows DSC thermograms for CuSC₁₀H₂₀COOH and CuSC₁₂H₂₅. Sharp endothermic peaks are indicative of structural transformations for CuSC₁₀H₂₀COOH and CuSC₁₂H₂₅ at 94 and 132 °C, respectively. We previously identified that the peak for CuSC₁₂H₂₅ near 132 °C corresponds to a molecular rearrangement from a crystalline lamellar to a columnar mesophase, which is observed visually as a melting event from a tan-white powder to a viscous yellow fluid. For CuSC₁₀H₂₀COOH, the endothermic peak at 94 °C is more difficult to assign. When heated beyond 94 °C, the precursor powder loses granular texture and changes color, but remains solid. When heated between 150 and 175 °C, for which we observe a minor endothermic event on the DSC thermogram, the CuSC₁₀H₂₀COOH precursor is observed to melt into a lower viscosity fluid. We believe the first transition at 94 °C corresponds to a smectic mesophase, while the higher-temperature phase transition corresponds to rearrangement into the columnar mesophase. Figure 4.9c shows the TGA curves for CuSC₁₀H₂₀COOH and CuSC₁₂H₂₅. The thermolysis byproducts (primarily dialkyl sulfides) show that the mass loss onset is \sim 70 °C greater for CuSC₁₀H₂₀COOH than for CuSC₁₂H₂₅. The higher evaporation temperature observed for CuSC₁₀H₂₀COOH is attributed to intermolecular interactions between the polar –COOH groups. The TGA curve for CuSC₁₂H₂₅ shows a mass retention of approximately 30.0%, which correlates well with the formation of Cu₂S stoichiometry. In contrast, the curve for CuSC₁₀H₂₀COOH shows continued mass loss up to 500 °C, dipping below the expected 28% mass retention for Cu₂S. This indicates that the CuSC₁₀H₂₀COOH precursor is more stable and undergoes slower C–S thermolysis to the point where decomposition occurs in lieu of stoichiometric Cu₂S generation.

To understand how the intermolecular forces between these single-source precursors can be exploited for tuning thermal stability, we further explored how deprotonation of the –COOH group affects the mesophase transitions of the supramolecular CuSC₁₀H₂₀COOH thermolysis precursor. In general, conversion of –COOH to –COO[–] is expected to create electrostatic repulsive forces that might serve to increase the separation distance between the individual lamella. To do so, we incorporated halide ions into the precursor by using Cu(I) halides as the Cu source. While halides incorporated poorly into CuSC₁₂H₂₅, they were readily incorporated into CuSC₁₀H₂₀COOH, and this was found to drastically alter the precursor's thermal characteristics. According to energy dispersive spectroscopy (EDS) analysis, the Cl[–] intercalated is 48% as great as the Cu content by atomic weight, for the approximate

formula [CuSC₁₀H₂₀COOH]·1/2Cl. To examine how Cl⁻ intercalation affects precursor thermolysis, we performed Fourier transform IR spectroscopy (FTIR) on both Cl⁻-intercalated and pristine samples of CuSC₁₀H₂₀COOH upon thermal treatment. Figure 4.10 shows FTIR spectra obtained for each sample before and after thermal annealing of the precursors at 200 °C for 10 min. Figure 4.10a shows the asmade precursors, which both possess a strong v(C=O) stretch near 1698 cm⁻¹ and a weaker $v(COO^{-})$ asym mode at 1592 cm⁻¹. This indicates that prior to heating, both the pristine and Cl⁻-intercalated CuSC₁₀H₂₀COOH are present as the carboxylic acid and not the deprotonated carboxylate. After thermal annealing, the precursors were cooled to room temperature. The FTIR spectra in Figure 4.10b shows that conversion from carboxylic acid to carboxylate takes place for both the pristine and Cl⁻-intercalated CuSC₁₀H₂₀COOH. For the pristine precursor, annealing increases the v(COO⁻) asym to v(C=O) intensity ratio from 0.32 to 0.70, which is a 120% increase. For the Cl⁻intercalated precursor, this conversion is significantly higher and the intensity ratio increases from 0.17 to 1.19, corresponding to a 590% increase. These FTIR assignments are provided in Table 4.1.

| | sans Cl [–] | | with Cl [–] | |
|------------------|----------------------|------------|----------------------|------------|
| assignment | preanneal | postanneal | preanneal | postanneal |
| v(C=O) | 1694 | 1694 | 1694 | 1696 |
| v(COO–)asym | 1590 | 1587 | 1591 | 1584 |
| δ(CH2) | 1471 | 1470 | 1471 | 1464 |
| δ(CH2) | 1434 | 1427 | 1434 | 1429 |
| v(COO–)sym | 1409 | 1410 | 1408 | 1412 |
| δ(CCH) | 1200-1300 | 1200-1300 | 1200-1300 | 1200-1300 |
| а <u>г</u> 1 · 1 | 1 | . 1. | | |

Table 4.1. FTIR Assignments of CuSC₁₀H₂₀COOH Precursor Synthesized with and without Cl^{-a}

^{*a}</sup>Each is shown pre- and post-annealing*.</sup>



modified precursor (Cl = 20% Cu composition). (a) As-made precursors and (b) both precursors after thermal annealing at 200 °C for 10 min.

Figure 4.11 compares thermal properties of the pristine and Cl⁻-intercalated CuSC₁₀H₂₀COOH precursors. DSC thermograms are shown in Figure 4.11a. The presence of Cl⁻ is not found to affect the endothermic transition at 94 °C, and both powders were observed to lose their granular textures and take on a viscous gel-like appearance. However, the presence of Cl⁻ suppresses the broad endothermic peak centered near 164 °C, and instead the Cl⁻-intercalated CuSC₁₀H₂₀COOH shows an endothermic peak centered near 210 °C. Side-by-side visual observation during the

heating of both compounds shows that, near the temperature of 175 °C, the pristine $CuSC_{10}H_{20}COOH$ exhibits a greater loss of viscosity. These data suggest that $CuSC_{10}H_{20}COOH$ undergoes a phase transition near 164 °C that is suppressed by the intercalation of Cl⁻. Figure 4.11b shows TGA curves for the pristine and Cl⁻-intercalated CuSC₁₀H₂₀COOH precursors heated at a rate of 5 °C min⁻¹. Intercalated Cl⁻ is observed to slow the rate of mass loss. This could be due to Cl⁻ coordination to Cu, which could weaken the Cu–S bond and by extension increase the energetic barrier for C–S bond thermolysis. TGA curves also show that Cl⁻-intercalated CuSC₁₀H₂₀COOH retains a significantly greater mass at the final temperature of 500 °C. This is likely due to the incorporation of Cl⁻ in the decomposed product. EDX data shown in Table 4.2 present a positive correlation between precursor [Cl⁻] and product [Cl⁻], which is likely to occur if Cl⁻ is coordinating to Cu within the precursor.



Figure 4.11. Thermal properties of pristine and Cl-intercalated CuSC₁₀H₂₀COOH precursors as measured by (a) DSC and (b) TGA. (c,d) Characterization of the pristine and intercalated precursors by *in situ* high-temperature XRD, with spectra taken at 125, 150, and 175 °C for CuSC₁₀H₂₀COOH prepared without and with Cl⁻ respectively.

Table 4.2. Lamellar Bilayer d-Spacing Shown As a Function of Cl⁻ Content Cl(% of Cu) 48% 41% 27% 23%

| CI(70 OI CU) | 4870 | 4170 | 2170 | 2370 |
|----------------|-------|-------|-------|-------|
| d-spacing (nm) | 3.342 | 3.337 | 3.300 | 3.274 |

To confirm whether the lamellar structure is retained at thermolysis temperatures, we carried out *in situ* XRD measurements of the pristine and Cl⁻-intercalated CuSC₁₀H₂₀COOH precursors near the mesophase transitions observed by DSC. Figure 4.11c–d shows the XRD data for pristine and intercalated Cl⁻ samples heated at T = 125, 150, and 175 °C. At temperatures up to 125 °C, no significant

features distinguish the two compounds, and the peaks representing a lamellar bilayer spacing of $d = \sim 3.3$ nm are prominent near $2\theta = 5.5^{\circ}$, 8°, and 10.5°. Between 150 and 175 °C, the pristine precursor shows a greater decrease in lamellar order, which can be seen as a decrease in the intensity and a broadening of the peaks at $2\theta = 5.5^{\circ}$ and 10.5°, with the latter disappearing altogether. This decrease in lamellar character is accompanied by the emergence of a new peak at $2\theta = 4^{\circ}$, correlating to a spacing parameter of 2.24 nm. This is consistent with the *d*-spacing observed for columnar mesophases.^{49,50} These thermal data strongly suggest that Cl⁻ serves to stabilize the lamellar phase.

In order to better understand the role that Cl⁻ plays in SNC nucleation and growth, we tuned [Cl⁻] across a range of Cl:Cu ratios. We achieved an indirect means of modulating Cl⁻ intercalation in the CuSC₁₀H₂₀COOH precursor by varying the concentration of the solution it is precipitated from. Cl:Cu ratios were computed from energy dispersive spectroscopy (EDS) of the precursors (see experimental section for more details). The EDS results of this series are shown in Table 4.2. Expressed as a percentage of the Cu atomic weight %, the [Cl⁻] of this series was found to be approximately 23%, 27%, 41%, and 48%. We then carried out XRD analysis to determine where the intercalated Cl⁻ resides. Two different sites for Cl⁻ are possible: (i) coordinated to Cu near the Cu–S network, or (ii) near the highly polar carboxyl groups in the center of the bilayer. The presence of Cl⁻ in position (i) should show no change in XRD data; however Cl⁻ in position (ii) should expand the lamellar bilayer spacing. Figure 4.12 shows the XRD patterns for samples prepared with varying [Cl⁻].

Whereas CuSC₁₀H₂₀COOH synthesized from Cu(OAc) has a lamellar bilayer spacing parameter of 3.25 nm, CuSC₁₀H₂₀COOH synthesized from CuCl with [Cl⁻]/[Cu] = 48% showed a lamellar bilayer spacing of 3.34 nm, or a 0.9 Å increase. The lamellar bilayer expansion suggests that intercalated Cl⁻ ions reside between carboxyl groups. This placement makes sense in terms of sterics; the alkyl groups in self-assembled metal alkanethiolates are thought to be similar to an alkanethiol self-assembled monolayer, where densely packed alkanes should not be sterically accommodating for Cl⁻. It should be noted that an additional set of XRD peaks is present at $2\theta = 6^{\circ}$ and 12° . These peaks are often present in the precursor at room temperature, which we attribute to a bilayer stacking defect. Interestingly, the peaks are no longer present when the precursor is heated to temperatures exceeding 125 °C (Figure 4.11c,d), which suggests that the stacking defect is annealed when the precursor undergoes the lower-temperature phase transition at 94 °C.



Figure 4.12. XRD of CuSC₁₀H₂₀COOH precursors prepared with varying [Cl⁻]. The interlayer *d*-spacing is found to increase with [Cl⁻].

Figure 4.13 shows the SNCs obtained as products for $CuSC_{10}H_{20}COOH$ precursors with varying [Cl⁻] contents after carrying out thermolysis at 200 °C for 6 h. XRD and transmission electron microscopy (TEM) imaging of the products show that higher [Cl⁻] favors the formation of digenite (Cu₉S₅) SNCs with a 2D nanosheet morphology, while lower [Cl⁻] favors β -chalcocite (Cu₂S) SNCs with disk-like morphology. Figure 4.13a shows the XRD patterns from lowest (top) to highest [Cl⁻] contents (bottom). The sample with the lowest [Cl⁻] content produced β -chalcocite SNCs, similar to products obtained for thermolysis of pristine CuSC₁₀H₂₀COOH. However, when [Cl⁻] increases beyond 25%, the crystal phase of the SNC product is observed to be predominantly digenite (Cu₉S₅). Figure 4.13b-e shows the corresponding TEM images with increasing Cl⁻intercalation. For the precursor with [Cl⁻] = 23% (Figure 4.13b), disk-like SNCs are the majority product and sheets are rarely observed. With [Cl⁻] = 27% of Cu content in the precursor (Figure 4.13c), disklike particles are no longer observed and more distinct 2D morphologies are present. However, much of the material is observed to exist within large, nondispersible aggregates. With $[Cl^-] = 41\%-48\%$ of Cu content in the precursor (Figure 4.13d,e), 2D SNCs are observed as the majority product.



Figure 4.13. Effect of varying Cl⁻ incorporation. (a) XRD patterns of nanoparticles obtained from thermolysis of precursor containing various [Cl⁻], showing that chalcocite phase preferred sans chloride gives rise to digenite when chloride content increases. (b–e) TEM images for the respective XRD patterns, from least to most [Cl⁻].

Table 4.3 shows EDS of the SNC products shown in Figure 4.13b-e. The data demonstrated an obvious trend between [Cl⁻] in the precursor and [Cl⁻] in the thermolysis product. The amount of Cl⁻ intercalated within the product structure is

substantial, reaching a ratio 2:5 with Cu. Because the increasing Cl⁻ content coincides with decreasing S content (Figure 4.16 found in section 4.3.7), this indicates that Cl⁻ is indeed intercalated and not simply present as surface species. The results suggest Cl⁻ is responsible for both the digenite phase and the nanosheet morphology of the SNCs obtained via thermolysis.

Table 4.3. EDX results comparing [CI⁻] of the precursor vs. that of the product after thermolysis for 6 h at 200 °C

| | Cl ⁻ (% of Cu) | | | |
|-----------|---------------------------|-----|-----|-----|
| Precursor | 23% | 27% | 41% | 48% |
| Product | 8% | 11% | 16% | 43% |

We further characterized the SNC products obtained after thermolysis at 200 °C for times of 30, 180, and 360 min. Figure 4.14a-c shows TEM images of the formation of β -chalcocite Cu₂S nanocrystals obtained with pristine CuSC₁₀H₂₀COOH. Small seed particles around 2 nm large are seen to precipitate within aligned columns of precursor material in the early stages of the reaction (Figure 4.14a). We previously observed aligned nanoparticle columns embedded in organic matrix during partial thermolysis of CuSC₁₂H₂₅. We attributed this alignment to the presence of the columnar mesophase during thermolysis of CuSC₁₂H₂₅. Mesogenic rearrangement to a columnar phase would explain the striated texture observed when CuSC₁₀H₂₀COOH sans Cl⁻ is incompletely decomposed (Figure 4.14a). Image analysis of the striations in Figure 4.14a reveals a center-to-center spacing of ~2.3 nm. This spacing parameter correlates to the XRD peak at $2\theta = 4^{\circ}$ observed at elevated temperature (Figure 4.11c). Figure 4.14b,c show that, with increased thermolysis time, larger particles are obtained with roughly discotic or ovoid morphology (diameter: 14.5 ± 3.8 nm;

thickness: 9.6 ± 1.7 nm). The XRD pattern in Figure 4.14d matches β -chalcocite Cu₂S. This is consistent with our previous thermolyses of long-chained Cu alkanethiolates, for which we obtained β -chalcocite nanodisks.



Figure 4.14. Time-dependent electron microscopy of chalcocite particle formation and digenite sheet formation. Top: compound (I) sans chloride after decomposition for (a) 30 min, (b) 180 min, (c) 360 min, and (d) the XRD pattern of the 360 min product corresponding to Cu₂S. Bottom: compound (I) with chloride after decomposition for (e) 30 min, (f) 180 min, (g) 360 min, and (h) the XRD pattern of the 360 min product corresponding to Cu₂S₅.

Figure 4.14e–g show time-dependent TEM imaging of CuSC₁₀H₂₀COOH precursor generated from CuCl. In the presence of Cl⁻ an alternate SNC growth pathway is observed where nucleation and growth occurs in distinct 2D planes. In Figure 4.14e which shows TEM images of the SNC products after 30 min of thermolysis, aligned arrays of electron-dense material (which we attribute to the solid-state SNC product) appear embedded within low-contrast material. We attribute the low-contrast material to partially decomposed precursor. Figure 4.14f shows that, after 180 min, 2D sheets are obtained and many of these are unencapsulated. However, multiple sheets are observed to form large aggregates due to incomplete

decomposition of the organic phase. Figure 4.14g shows that, after 6 h of thermolysis, free-standing nanosheets are obtained. The XRD pattern in Figure 4.14h best matches the metastable, rhombohedral form of digenite Cu₉S₅.

4.3.3. Mechanism for SNC Growth

To explain nanosheet formation we propose a mechanism where intercalated Cl⁻ stabilizes the lamellar phase during thermolysis. The thermal data demonstrates that Cl⁻ affects structure and C–S thermolysis of CuSC₁₀H₂₀COOH precursor. DSC data does show a commonality between Cl⁻-bearing and Cl⁻-deficient precursor in the presence of an endothermic peak near 94 °C. The most feasible explanation here is that this peak corresponds to a crystalline lamellar to lamellar smectic transition, where minor alkyl chain disorder is present and adjacent lamella are capable of slipping. The transition to a lamellar smectic mesophase could enable reordering of lamellar domains and therefore explain why peaks observed at $2\theta = 6$ and 12° attributed to a stacking defect (Figure 4.12) are no longer present beyond 125 °C (Figure 4.19 and Figure 4.11c,d). This phase would further explain why the precursor is visually observed to change color and texture beyond 94 °C even as the high temperature XRD patterns show the structure is still lamellar. The DSC peak at 164 °C is likely the columnar mesophase transition and correlates with loss of lamellar character and emergence of a peak characteristic of the columnar phase as shown by XRD (Figure 4.11a,c). Conversely in the presence of Cl⁻, the 164 °C DSC peak is suppressed, and heated precursor shows stronger retention of lamellar character (Figure 4.11b,d).

The exact role played by Cl⁻ is more difficult to decipher; although it should be present within the alkyl bilayer, the impact of Cl⁻ on thermolysis as shown by mass loss (Figure 4b) and retention of Cl^- within the crystallized product (Table 4.3) support that Cl⁻ coordinates to Cu during thermolysis and is subsequently incorporated into the crystal structure. A possible explanation is that conversion of -COOH to $-COO^{-}$ (Figure 4.10) creates negative charges which help drive Cl⁻ from the alkyl bilayer toward Cu sites in the Cu-S plane. For Cl⁻ to stabilize the lamellar phase, it must either decrease the thermal disorder occurring among alkyl components or reinforce in-plane attractive forces. We find the latter explanation more compelling: Cl⁻ coordination to Cu within the Cu–S planes represents another interaction which must be overcome prior to mesogenic rearrangement. During thermolysis, this lamellar template serves to encourage anisotropic nucleation and growth along the Cu–S planes, resulting in nanosheet formation. The formation of digenite phase Cu_{1.8}S has previously been shown to result when CuCl is used as the copper source and can also be explained by intercalated Cl^{-.53,54}

Work conducted by van der Stam et al. previously demonstrated a similar system where Cu_{2-x}S nanosheets were obtained from a solvothermal reaction in 1-octadecene/TOPO which generated a halide-stabilized Cu alkanethiolate intermediate.⁵⁵ The authors suggested that the nanosheet template is offered by the columnar mesophase of the Cu alkanethiolate existing in solution at elevated temperature. Our data support the conclusion by van der Stam et al. that halides coordinate directly to Cu to influence thermolysis, which manifests as substantial Cl⁻

content in the crystallized product (Figure 4.16). However, our results suggest that halide interactions stabilize the lamellar phase during thermolysis leading to nanosheet formation and that columnar rearrangement leads to the formation of small nanoparticles (Figure 4.17). The XRD patterns of Cl⁻ stabilized precursor at 175 °C in Figure 4.11c indicate a layered structure with no evidence of columnar rearrangement. Furthermore, decomposition of this precursor at 175 and 180 °C produces nanosheets, although at these temperatures they are often still adjoined by precursor material (Figure 4.17). The data, taken together, support conclusions from our previous work that mesogenic rearrangement of Cu alkanethiolates during thermolysis causes the formation of disk-like nanocrystals, while nanosheets are realized from thermolysis in the lamellar phase.⁵²

4.3.4. Optical Characterization and AFM of SNC Nanosheets

Figure 4.15 shows photoluminescence (PL) spectroscopy and visible to nearinfrared (vis/NIR) absorption spectroscopy, as well as atomic force microscopy (AFM), of the nanosheets obtained from decomposition of the Cl⁻ intercalated precursor. The PL emission spectra shown in Figure 4.15a ($\lambda_{\text{excitation}} = 325$ nm) were obtained in an ethanol dispersion and shows the PL emission band centered around 450 nm. This is in contrast to previously reported Cu₉S₅ nanoparticles where emission was centered between 387 and 440 nm depending on the excitation wavelength.⁵⁶ Curiously, in this report CuS particles showed identical PL emission to the Cu₉S₅ particles. Emission of Cu₉S₅ nanocrystals with irregular octahedral shape centered at 360 nm using $\lambda_{\text{excitation}} = 300$ nm has also been reported.⁵⁷ Interestingly, this report again showed invariance between the crystal phase and PL emission; particle compositions which included CuS, Cu₉S₅, and a CuS-Cu₇S₄ mixture all produced PL emission at 360 nm. While we might expect the ultrathin nature of our Cu₉S₅ sheets to increase photoemission energy due quantum confinement, this was not observed, and so we note that photoemission in the Cu_{2-x}S system is still not well-understood.



Figure 4.15. AFM and optical characterization of digenite nanosheets. (a) Photoluminescence spectrum of the digenite sheets dispersed in ethanol (inset: image of dispersion) using excitation of 325 nm. (b) Extinction spectrum of a film of digenite sheets made on a transparent quarts substrate, with an LSPR peak near 2400 nm attributed to the out of plane mode. (c) AFM topology image showing where height profiles were taken along 3 of the digenite nanosheets. (d) Height profiles are plotted which demonstrate a high degree of planarity and a thickness of 4.0–4.5 nm.
UV–vis–NIR absorption spectra were taken with a dried dispersion of nanosheets on a quartz substrate. Copper sulfides are known to support LSPR bands in the NIR due to the high mobility and density of holes as free charge carriers. The LSPR of the Cu₉S₅ nanosheets in Figure 4.15b is centered around 2400 nm and observed to be quite broad. Based on our previous characterization of Cu_{2–x}S nanodisks,¹⁹ we assign this LSPR band to the resonant out-of-plane mode. The in-plane mode expected for a 2D structure is predicted to appear at lower energy and due to a large degree of noise on our spectrophotometer, our measurement was limited to 2500 nm. The breadth of the out-of-plane mode may arise from stacked nanosheets resulting in plasmonic coupling, which would serve to red-shift and broaden the mode.

Figure 4.15c shows the AFM topology of several large sheets, with height profiles consistently between 4.0 and 4.5 nm (Figure 4.15d). Although several faceted edges are observed, the nanosheet sizes and edge morphologies are not uniform, consistent with TEM images. AFM analysis of multiple SNC samples indicates that nanosheets possess a uniform thickness of 4–4.5 nm (Figure 4.18). Many rounded spots observed in the AFM scans are attributed to incompletely decomposed precursor material, which is difficult to separate via centrifugation because the precursor is insoluble in solvents at room temperature. The largest nanosheet (blue section) in Figure 4.15c-d displays an edge length of 2.25 μ m and a thickness of ~4.5 nm for a total aspect-ratio of ~500. To the best of our knowledge, this is the highest reported aspect ratio for a single freestanding copper sulfide nanosheet (of any phase) as verified by AFM.

4.3.5. Conclusions

The 2D metal-chalcogen networks formed via assembly of metal alkanethiolates provide a viable platform for 2D nanocrystal synthesis. In our previous work, we showed that the length of the alkyl thiol chain used dictates the precursor's structural phase during thermolysis. Here, we showed that the lamellar phase is stabilized at the thermolysis temperature by using a combination of in-plane Hbonding provided by terminal carboxyl groups and the addition of intercalated Cl⁻ ions. Thermolysis of [CuSC₁₀H₂₀COOH]·1/2Cl led to formation of ultrathin Cu_9S_5 nanosheets. This method presents the chemical design of a single source precursor which doubles as a morphological template. This mechanism may not be unique to Cu-based alkanethiolates, but may well carry over to other metals, and even other alkyl chalcogenols. This could potentially allow one to program metal chalcogenide composition and morphology all through rational design of the single source precursor. We are currently investigating the use of this templating motif as a general platform for the realization of metal chalcogenides with ultrathin 2D morphologies.

4.3.6. Materials and Methods

Chemicals

All reagents were used as-purchased. 1-Dodecanethiol (98%), 11mercaptoundecanol (97%), 11-mercaptoundecanoic acid (95%), and copper(I) acetate (97%) were purchased from Sigma-Aldrich. Copper(I) chloride was purchased from Fisher Scientific. Ethanol was purchased from Gold Shield Chemical Company. Chloroform was purchased from Avantor Performance Materials. Water was obtained via a Millipore Milli-Q Advantage A10 water filtration system. All reagents were used as purchased.

Preparation of CuSC₁₀COOH

The following synthesis for $CuSC_{10}COOH$ is representative of a standard reaction for producing $CuSC_{10}COOH$ without chloride. 11-Mercaptoundecanoic acid is (1.37 mmol) is dissolved in 1.37 mL of ethanol to make a 1 M solution. In a separate flask equipped with a stir bar, copper(I) acetate (0.687 mmol) is dispersed in 2.748 mL of water to make a 0.25 M dispersion which is stirred rapidly.

Copper(I) salts are generally insoluble; however, copper(II) is readily reduced to copper(I) by alkanethiols generating disulfide in the process, which was deemed undesirable here.

The ethanolic thiol solution is added dropwise to the copper solution while stirring, and a white slurry indicating the precipitation of $CuSC_{10}COOH$ is immediately observable. This is allowed to stir for 15 additional minutes. A milky white precipitate is obtained and isolated via centrifugation at 3000 rpms for 5 min. After the supernatant was decanted, the precipitate is washed with a 1:1 mixture of water and ethanol and centrifuged again under the same conditions. This process is repeated twice more; however, the last wash is performed with only ethanol and no water. The precipitate is then stored in a vacuum desiccator until dry of ethanol. In order to prepare CuSC₁₀COOH with chloride, copper(I) chloride is substituted in

place of copper(I) acetate.

Synthesis of Chalcocite-Phase Nanoparticles

A 25 mg amount of the CuSC₁₀COOH precursor generated from copper(I) acetate is measured into a scintillation vial under ambient conditions, capped tightly, and immersed in a hot oil bath at 200 °C for 6 h. The whitish powder melts into a viscous yellow fluid before gradually darkening to black with further decomposition. After the reaction is complete, the vial is cooled to room temperature. The black residue is dispersed in 12 mL of pure ethanol, through ample ultrasonication before being centrifuged down at 7,500 rpms for 7.5 min. After the supernatant was decanted, the particles are redispersed in ethanol, and this process is repeated 3 times. The final product is allowed to dry in a vacuum desiccator overnight to obtain a black powder.

Synthesis of Digenite Phase Nanosheets

To prepare digenite phase nanosheets, the preceding synthesis is used. However, 25 mg of $CuSC_{10}COOH$ precursor generated from Cu(I) chloride is used. Similarly, this powder is observed to change colors, from off-white to yellow-green and then black, and is accompanied by a change of texture indicative of melting albeit not into a fluid that can flow.

Sample Characterization

Powder X-ray diffraction (XRD) was performed using a Rigaku RU200B diffractometer running MDI Datascan5 software. The operating voltage was set to 100 kV with a step size of 0.02° and a dwell time of 1.0 s. Transmission electron microscopy (TEM) was performed on an FEI Tecnai G2 Sphera running a LaB₆ filament at 200 kV. A Gatan Ultrascan 1000 UHS CCD camera running Gatan

Digital Micrograph was used for imaging. TEM samples were typically prepared by dispersing particles in ethanol and dropcasting directly onto a 200 mesh carbon-film Cu grid. Atomic force microscopy (AFM) was obtained using tapping mode on an Innova AFM, a Bruker controller, and the Nanodrive software. AFM samples were dropcast directly onto Piranha-washed Si chips. Thermogravimetric analysis (TGA) was performed using a PerkinElmer TGA 7 Thermogravimetric Analyzer attached to a PerkinElmer TAC 7/DX Thermal Analysis Controller. Optical absorption measurements were taken using a PerkinElmer Lambda-1050 spectrophotometer. Nanosheet samples were dropcast onto a quartz substrate for optical extinction spectra. Differential Scanning Calorimetry (DSC) was performed using a PerkinElmer PYRIS Diamond DSC. Fourier-Transform Infrared Spectroscopy (FTIR) was performed using a PerkinElmer UATR Two FT-IR Spectrometer running PerkinElmer Spectrum software. Energy dispersive spectroscopy (EDX) was obtained using a Philips XL30 ESEM with an Oxford EDX attachment. Cu foil was used for calibration prior to taking spectra, which were averaged over 3 spots per sample at 90 s acquisition per spot. Reported percentages of Cl represent Cl as a fraction of the Cu content.





Figure 4.16. EDX of Cu_{2-X}S products generated from precursor in which [Cl⁻] increases for the series. Samples 1-4 correspond to samples shown in Figure 4b-e respectively. Cl⁻ content increases at the expense of S, and consequently may be intercalating into S positions. Charge neutrality might be maintained due to the preponderance of S existing as $S_2^{2^-}$ dimers rather than S^{2^-} .



Figure 4.17. TEM images of $Cu_{2-x}S$ nanoparticles after varying thermolysis conditions. Top row demonstrates the propensity for small nanoparticle formation in the range of 175 to 220 °C. Bottom row: TEM images of Cu_9S_5 nanosheets after varying thermolysis conditions, demonstrating the propensity for the Cl⁻ bearing precursor to form the nanosheet structure in the range of 175 to 220 °C.



Figure 4.18. Supplemental AFM profiles of the nanosheet products. These further support the uniform flatness of the sheets and the consistency of the ~ 4.5 nm height profile.



Figure 4.19. Comparison of CuSC₁₀H₂₀COOH precursor with and without Cl⁻, shown at room temperature (RT) and at 125 °C. This data shows the $2\theta = 6$, 12° peaks attributed to a stacking defect present in both samples decreased as the samples were brought to 125 °C.

Chapter 4, in part, is a reprint of the material that appears in *The Journal of the American Chemical Society* (Whitney Bryks, Eduardo Lupi, Charles Ngo, and Andrea R. Tao. "Digenite Nanosheets Synthesized by Thermolysis of Layered Copper-Alkanethiolate Frameworks." *J. Am. Chem. Soc.*, **2016**, *138* (41) 13717-13725). The dissertation author was the primary investigator and author of this material.

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Chapter 5

Metallomesogen Templates for Shape Control of Metal Selenide Nanocrystals

5.1 Abstract

Metal alkanethiolates are organometallic single-source precursors that have been used to synthesize metal sulfide nanocrystals (NCs) from thermal decomposition reactions. Ag and Cu alkanethiolates are remarkable because they adopt lamellar bilayer nanostructures that give rise to mesogenic behavior akin to thermotropic liquid crystals. Such metallomesogen precursors have been demonstrated to template the nucleation and growth of highly anisotropic NC morphologies. In the present work, we synthesize novel metallomesogen compounds, namely CuSeC₁₂H₂₅ and $AgSeC_{12}H_{25}$, in order to target shaped metal selenide NCs. We show that these compounds adopt lamellar bilayer structures and undergo mesogenic transitions at elevated temperatures. We find that structural disparities between the CuSeC₁₂H₂₅ and $AgSeC_{12}H_{25}$ mesophases lead to the formation of distinct 2D and 1D NC morphologies, respectively. Moreover, both compounds exhibit an isotropic phase which produces either nanospheres or irregularly shaped particles. By exploiting the morphology-directing capability of the mesogenic regime, we detail the synthesis of ultrathin Cu₂Se nanoribbons, Ag₂Se nanorods, and AgCuSe nanospheres. This work demonstrates that metallomesogens can serve as a novel class of NC precursors with the ability to access highly anisotropic morphologies and tailored compositions.

5.2 Introduction

Metal chalcogenide NCs are a remarkable class of nanomaterials encompassing an extensive array of chemical compositions and crystal structures. The combinatorial variation of metal and chalcogen atoms has led to ternary and

quaternary metal chalcogenides, as well as highly doped NC systems, which have opened up an incredibly diverse set of optoelectronic properties. Accordingly, metal chalcogenide NCs have been pursued for a myriad of applications including lightemitting devices,¹ photodetectors,² solar cells,³ electrochemical water-splitting,^{4,5} thermoelectric materials,⁶ nonlinear optics,⁷ and more. Such NCs are typically produced through solvothermal and hot injection syntheses to produce highly uniform colloidal dispersions.⁸ Yet, significant challenges remain in the synthesis of shaped metal chalcogenide NCs, particularly in obtaining highly anisotropic morphologies. To overcome challenges in synthesizing shaped NCs, we have pursued a strategy that uses supramolecular metallomesogens as both single-source precursor and as molecular template for shaped metal chalcogenide NC formation. Cu and Ag alkanethiolates form molecular MSR units (R = n-alkane) that self-assemble in situ into lamellar bilayer supramolecular structures isolated as powders. Earlier works extensively characterized this lamellar bilayer structure, its transition to a hexagonally packed columnar mesophase, and the rheology of this phase transition.^{9,10,11,12,13} While many syntheses have been devised using similar metal alkanethiolates as single-source precursors for metal sulfide NCs in solvothermal reactions, such reactions dissolve the precursor, causing it to lose its supramolecular structure and consequently produce only spherical NCs.^{14,15,16,17} In contrast, *solventless* thermolysis of CuSC₁₂H₂₅ and AgSC12H25 precursors were found to yield shaped particles, including Cu2-xS nanodisks and Ag nanodisks.^{18,19} In the former case, disk formation was attributed to high surface energy of <110> facets, while in the latter case disk formation was

attributed to anisotropic nucleation and growth imparted by the lamellar precursor structure (which does not exist at high reaction temperatures). The existence and possible effects of the mesophase on NC nucleation and growth were not well understood.

Using Cu alkanethiolates as a model system, our previous work gained a better understanding of how these mesogenic single-source precursors result in shaped NCs. We determined the relationship between alkyl chain length and the mesogenic transition, which we exploited to obtain either β -chalcocite Cu_{2-x}S nanodisks or α chalcocite Cu_{2-x}S nanosheets via solventless thermolysis.²⁰ This work established that the columnar mesophase is directly responsible for the nanodisk morphology, as nanodisks precipitate within the columnar arrays formed by the mesongenic precursor, while non-mesogenic precursors synthesized with sterically bulky ligands produce irregular Cu_{1.8}S and CuS NCs. Additionally, we established that by tuning chemical interactions within the lamellar bilayer precursor, the columnar phase transition can be suppressed sufficiently to carry out thermolysis within a lamellar smectic-like phase to obtain ultrathin Cu₉S₅ nanosheets with high surface area and aspect-ratio up to 500.²¹ These works indicate that metallomesogens have the potential to serve as templating agents that dictate both morphology and crystal phase of the resulting NCs.

We seek to demonstrate that mesogenic templating can be used as a general strategy for synthetic control over NC nucleation and growth. To do so, we extend the metallomesogen library to alkylselenolates in order to target the synthesis of shaped Cu_{2-x}Se and Ag₂Se NCs. Cu_{2-x}Se nanospheres, nanodisks, and other nanoparticles have

already been demonstrated by other synthetic strategies due to large interest in tunable optoelectronic properties, such as surface plasmon excitation in the near-infrared.²²⁻²⁵ Ag₂Se quantum dots that exhibit NIR fluorescence have been actively pursued as *in vivo* imaging probes.^{26,27,28} While large-area Cu_{2-x}Se nanosheets as thin as 12 nm have been reported, the authors report that typical cubic Cu_{2-x}Se structure is not conducive to the growth of 2D NCs.²⁹ Although ultrathin Cu_{2-x}Se NCs have been fabricated via cation exchange from CdSe nanosheets,³⁰ the direct synthesis of ultrathin Cu_{2-x}Se NCs has not yet been demonstrated. Regarding the Ag₂Se system, many shaped NC heterostructures have been reported such as Ag₂Se-MSe nanorods (M = Cd, Zn)³¹ and Ag₂Se-ZnS nanorods,³² however the direct synthesis of shaped Ag₂Se NCs has also proved challenging. Zhang et al reported Ag₂Se nanotubes synthesized from Se nanotube templates,³³ and Qian et al reported Ag₂Se nanorods embedded within CNTs,³⁴ but to the extent of our knowledge, no freestanding Ag₂Se nanorods have been reported. Additionally, it should be noted that Ag₂Se is nominally synthesized in orthorhombic phase (β -Ag₂Se) and undergoes reversible phase transformation to cubic phase (α -Ag₂Se) at ca. 133 °C.^{35,36} Cubic α -Ag₂Se is a desirable material due to its behavior as a superionic conductor; however, α-Ag₂Se is not thermodynamically stable at room temperature and is rarely obtained.³⁷ However, it has been shown that thermal annealing of β -Ag₂Se nanowires can achieve majority conversion to α -Ag₂Se which is stable at room temperature.³⁸ More generally, it has been demonstrated that ion exchange reactions from a cubic ZnSe template with Ag^+ ions can afford α - Ag_2Se stable at ambient conditions.^{39,40}

Here, we report the synthesis and characterization of the supramolecular metal alkaneselenolates, AgSeC₁₂H₂₅ and CuSeC₁₂H₂₅. We demonstrate that these compounds serve as single-source precursors to metal selenide NCs upon thermal decomposition. We use polarized optical microscopy (POM) in conjunction with differential scanning calorimetry (DSC) to demonstrate that both AgSeC₁₂H₂₅ and CuSeC₁₂H₂₅ behave as metallomesogens that undergo a structural transition from a lamellar crystalline to mesophase, and then a mesophase to isotropic phase transition at elevated temperatures. We show that for each compound, thermolysis reactions carried out within the isotropic regime lead to shaped NCs while thermolysis reactions carried out within the isotropic regime lead to spherical or highly irregular NC morphologies. Evidence of this templating effect is observed by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) throughout the reaction duration, supporting the role of these compounds as molecular templates for highly anisotropic and alloy NCs.

5.3 Experimental Methods

Chemicals

All reagents were used as-purchased. AgNO₃ (99.0% and 1dodecylmagnesium bromide (1.0 M in diethyl ether) were purchased from Sigma Aldrich. Elemental selenium powder (200 mesh, 99.999%) was purchased from Alfa Aesar. Cu(NO₃)₂·2.5 H₂O (98+%) was purchased from Acros Organics. Acetonitrile was purchased from Fisher Chemical. Ethanol was purchased from Gold Shield Chemical Company. Chloroform was purchased from Avantor Performance Materials. Water was obtained via a Millipore Milli-Q Advantage A10 water filtration system.

Preparation of 1-dodecaneselenol

Our synthesis was adapted from previously reported methods.⁴¹

Preparation of CuSeC12H25

2.0 mmol Cu(NO₃)₂ (~465 mg) is weighed into a 50 mL round bottom flask with a stir bar and then dissolved in 25 mL ethanol. This is degassed via N₂ bubbling while stirring for approx. 10 minutes. Next, 1-dodecaneselenol (4.0 mmol; ~ 2.4 mL) is drawn under N₂ and injected into the Cu solution dropwise. A green precipitate immediately forms from the blue Cu(NO₃)₂ solution. This is allowed to stir overnight. With stir time, the precipitate is observed to become yellow-tan and the solution is often a light green color. The precipitate is then washed 3x with EtOH via centrifugation (3,000 RPM for 5 minutes), and then dried and stored under vacuum prior to use.

Preparation of AgSeC12H25

 5.0 mmol AgNO_3 (~850 mg) is weighed into a 50 mL round bottom flask with a stir bar and then dissolved in 30 mL acetonitrile. This is degassed via N₂ bubbling while stirring for approx. 10 minutes. Next, 1-dodecaneselenol (6 mmol; ~ 3.5 mL) is drawn under N₂ and injected into the Ag solution dropwise. A yellow precipitate forms immediately agglomerates over the next few minutes of stirring. Stirring is continued about 10 minutes; at this point, the solution is totally clear and a thick yellow precipitate is obtained. This is isolated via centrifugation, dispersed in ethanol (~36 mL) and washed 3x with EtOH via centrifugation (3,000 RPM for 5 minutes), and then dried and stored under vacuum prior to use.

Preparation

of

Ag0.5Cu0.5SeC12H25

1.0 mmol Cu(NO₃)₂ and 1.0 mmol Ag(NO₃) are weighed into a 50 mL round bottom flask with a stir bar and then dissolved in 12 mL acetonitrile. This is degassed with N₂ bubbling while stirring for approx. 10 minutes. 1-dodecaneselenol (3.0 mmol; ~ 1.8 mL) is drawn under N₂ and injected into the Cu/Ag solution dropwise. The formation of yellowish precipitate is immediate and the residual solution color is clear green. The precipitate tends to agglomerate while it stirs for ~ 10 minutes. The offyellow precipitate is isolated via centrifugation, and then washed 3x by dispersing in EtOH (~ 8 mL), precipitating with addition of acetonitrile (~ 8 mL) and centrifuging (3,000 RPM for 5 minutes). The isolated powder is dried and stored under vacuum prior to use.

Preparation of Cu₂Se, Ag₂Se, and AgCuSe NCs

Thermolysis reactions for Cu₂Se, Ag₂Se, and AgCuSe utilizing their precursors CuSeC₁₂H₂₅, AgSeC₁₂H₂₅ and Ag_{0.5}Cu_{0.5}SeC₁₂H₂₅ respectively follow a standard method. 50 mg of precursor is measured into a 25 mL round bottom flask, which is then equipped w/ septum and purged with N₂. The flask containing precursor is then immersed in a silicone oil bath for the specified reaction parameters. After the specified reaction duration, the flask containing thermolysis residue is removed and cooled to room temp under exterior H₂O flow. Next, 8 mL CHCl₃ is pipetted into the flask and the thermolysis residue is dispersed via ultrasonication for several minutes.

The resulting colloidal solution is then washed 3x with CHCl₃ by centrifugation (~7,500 RPM for 10 m). Finally, the particles are re-dispersed in CHCl₃ and stored for use.

5.4 Results and Discussion

We adapted a previously reported method to obtain 1-dodecaneselenol as a viscous yellow fluid.⁴¹ The as-made 1-dodecaneselenol was then combined with solutions of Cu or Ag nitrate salts under N₂ environment to precipitate the corresponding Cu- or Ag- dodecaneselenolates as tan-yellow powders. For both precursor powders, Fourier transform infrared spectroscopy (FTIR) shows a clear M-Se-C stretching mode at *ca*. 638 cm⁻¹ (Figure 5.10). This precipitate results from the self-assembly and coordination of individual metal-dodecaneselenolate molecules into an ordered, supramolecular structure. For a detailed description of the experimental procedure, see the experimental section. After drying the precipitates, CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅ were employed as single-source precursors for the synthesis of Cu_{2-x}Se and Ag₂Se NCs via solventless thermolysis. The full synthetic scheme is depicted in Figure 5.1.



Figure 5.1. Reaction scheme depicting metal-selenolate synthesis. Steps include the synthesis of 1-dodecaneselenol, metalation to form the metal alkaneselenolate, and thermolysis to form the inorganic metal selenide NCs

Figure 5.2 shows the structural and thermal characterization of CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅. Figure 5.2a shows the XRD patterns for CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅ taken at low angles, where the regularly spaced peaks indicate the formation of a lamellar bilayer structure. If we assign the 2D metal-chalcogen lattice to preside in the (110) plane, then observed reflections of the lamellar bilayer are reflections of (00 ℓ), with ℓ = 2-7 labeled accordingly. This indicates that the coordination solids obtained via precipitation of the alkylselenol possess a nanostructured morphology analogous to the corresponding metal alkanethiolates synthesized in our previous work.^{20,21} The *d*-spacings are indexed as 3.54 and 3.44 nm for CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅ respectively. The slightly narrower lamellar bilayer spacing observed for Ag may result from stronger Ag-Se coordination interactions which could contract the thickness of the metal-chalcogen network.

Figure 5.2b shows the corresponding thermal gravimetric analysis (TGA) thermograms for $CuSeC_{12}H_{25}$ and $AgSeC_{12}H_{25}$. Mass loss begins at temperatures above 200 °C and concludes at 275-325 °C. Mass losses correlate precisely with those expected for the generation of Cu_2Se and Ag_2Se from their corresponding precursors:

for CuSeC₁₂H₂₅, 34.5% mass retention with a 33.0% mass retention expected; AgSeC₁₂H₂₅, 41.8% mass retention with a 41.4% mass retention expected. Due to the monovalent nature of the metal salts used to precipitate the dodecaneselenol, a 1:1 ratio of M:Se is not retained in the final crystalline products (M₂Se). Dodecyl selenides are the likely byproduct, which evaporate at temperatures above 200 °C, consistent with the TGA thermograms. However, it is important to note that thermolytic C-Se bond cleavage responsible for M₂Se NC formation and the generation of alkyl selenide byproducts occurs at temperatures below 200 °C.

Figure 5.2c shows the corresponding DSC thermograms for CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅. Here, DSC shows a peak for endothermic heat flow at T=132.8 °C for CuSeC₁₂H₂₅ and T=146.2 °C for AgSeC₁₂H₂₅, which is comparable to temperatures previously observed for metal alkanethiolates. We then screened these precursors for liquid crystalline activity by using POM. We used an optical microscope equipped with a controlled heating stage to image the selenolate precursors through crossed polarizers at a range of temperatures. Specifically, we observed changes in the optical activity of precursors at temperatures above the phase transition temperatures measured by DSC. Samples were observed to melt near the onset of the heat flow event, at approximately T=130 °C for CuSeC₁₂H₂₅ and T=145 °C for AgSeC₁₂H₂₅. Visually, CuSeC₁₂H₂₅ adopted a highly viscous phase with a yellow-brown color while AgSeC₁₂H₂₅ exhibited a less viscous phase with a dark red color. Under crossed polarizers, birefringence indicative of supramolecular ordering was observed for both samples: CuSeC₁₂H₂₅ is shown at T=130 °C (Figure 5.2d) and AgSeC₁₂H₂₅ is shown at

T=150 °C (Figure 5.2e). The difference in optical textures observed for the mesophases is an important distinction. For $CuSeC_{12}H_{25}$, the textures are indecipherable, whereas for $AgSeC_{12}H_{25}$, conical and fan-shaped textures are clearly observed and consistent with a columnar mesophase.⁴²

POM further allowed us to detect a mesogenic to isotropic clearing point, where the sample loses birefringence and appears dark when observed through crossed polarizers. This occurs at approximately T=180 °C for both CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅. This transition is not clearly manifested in the DSC thermogram. Above T=180 °C, rapid precursor thermolysis leads to the precipitation of a solid phase that also coincides with the isotropic transition. This results in the sample blackening under crossed polarizers, while uncrossed polarizers show the presence of dark precipitates within clear fluid. This presents difficulties in producing textures useful for phase identification. Ideally, the liquid crystal precursor should be heated beyond the mesogenic phase to facilitate growth of large ordered domains. However, our sample precursors undergo sufficient thermolysis above T=180 °C such that the reversibility of this phase transition is impaired and well-defined textures cannot be observed.



Figure 5.2. Precursor characterization for $CuSeC_{12}H_{25}$ and $AgSeC_{12}H_{25}$. Figure 5.2a-c show the corresponding XRD patterns, TGA thermograms, and DSC thermograms. Figure 5.2d,e show polarized optical images for $CuSeC_{12}H_{25}$ and $AgSeC_{12}H_{25}$ at 130 °C and 150 °C respectively.

Synthesis of Cu2-xSe NCs from CuSeC12H25

Figure 5.3 shows the results of CuSeC₁₂H₂₅ precursor thermolysis at various temperatures. Figure 5.3a-c show POM images taken at T=150, 160, and 185 °C respectively. As previously noted, at temperatures above 180 °C, CuSeC₁₂H₂₅ undergoes a mesophase to isotropic phase transition that is observed by the POM image fading to black as birefringence is lost. We hypothesized that at temperatures below the isotropic transition at T=180 °C, the mesophase would template highly anisotropic NC morphologies. Conversely, thermolysis reactions carried out above the isotropic transition should result in spherical NCs. To test this hypothesis, we carried out solventless thermolysis of CuSeC₁₂H₂₅ in N₂-purged flasks at various temperatures

and reaction times. Figure 5.3d-f show TEM images of NCs obtained using thermolysis conditions of 150 °C for 12 hours, 160 °C for 6 hours, and 185 °C for 1 hour respectively. The time parameter was not kept constant but varied to compensate for the thermolysis rate. Low temperatures result in slow thermolysis and show insoluble precursor mixed with Cu₂Se at lower durations. Higher thermolysis temperatures used for longer reaction times lead to extended thermal annealing after the molecular template has decomposed, which can cause changes in crystallinity and capping ligand coverage.

TEM images in Figure 5.3d-e show the ribbon-like NC morphology present when thermolysis is carried out within the mesogenic regime. In contrast, Figure 5.3f shows that thermolysis carried out within the isotropic regime produces $Cu_{2-x}Se$ NCs with no clear nor uniform morphology. Figure 5.3g shows the XRD patterns for the product NCs shown in Figure 5.3d-f. At *T*=150 and 160 °C, the NCs are best represented by a cubic, copper-deficient phase of $Cu_{2-x}Se$. However, at *T*=185 °C, the peaks of cubic $Cu_{2-x}Se$ are shifted slightly to higher 2 θ and better indexed by $Cu_{1.8}Se$. Additionally for the sample reacted at *T*=185 °C, a bevy of new peaks arise which are indexed to Cu_3Se_2 . It is likely that a higher reaction temperature accelerates C-Se bond thermolysis over Cu-Se thermolysis, promoting a more Se-rich phase. However, these results unambiguously show that the precursor mesophase is directly responsible for templating the resulting nanoribbon morphology.



Figure 5.3. Thermolysis of $CuSeC_{12}H_{25}$. a-c) show POM images taken at 150, 160, and 185 °C respectively. d-f) show TEM images from thermolysis reactions conducted at 150 °C for 12 hours, 160 °C for 6 hours, and 185 °C for 1 hour respectively. g) shows XRD patterns for the corresponding 3 thermolysis conditions.

To better understand the mechanism of $Cu_{2-x}Se$ nanoribbon formation, we carried out time-dependent thermolysis reactions with the temperature held constant at T=160 °C. TEM images of the obtained solid-state products in Figure 5.4a-d show the presence of ribbon-like structures observed after thermolysis for 1, 2, 4, and 6 h respectively. These ribbons have a tendency to stack and, when viewed edge-on appear, as strings; however, additional TEM imaging indicates the nanoribbon morphology (Figure 5.11). Figure 5.4e shows the corresponding time-dependent XRD patterns. While the low-angle precursor peaks corresponding to the lamellar precursor are apparent at 1 and 2 hours, they are greatly diminished at 4 hours and by 6 hours, the products are dominated by crystalline $Cu_{2-x}Se$. More detailed TEM analysis of the nanoribbons obtained after 6 hours of thermolysis demonstrates that they have a thickness of 2.30 ± 0.25 nm (Figure 5.11). As the $Cu_{1.8}Se$ cubic structure has a lattice

constant of a= 0.5767 nm, this thickness corresponds to exactly 4 unit cells (expected 2.3068 nm). These results purport that lamellar bilayer precursor crystallizes into ultrathin 2D ribbons of Cu_{2-x}Se upon sustained thermolysis at *T*=160 °C.



Figure 5.4. Time-dependent thermolysis of $CuSeC_{12}H_{25}$ at 160 °C. a-d) show TEM images taken after 1, 2, 4, and 6 hours of thermolysis respectively. e) shows the corresponding XRD patterns, which are indexed as $Cu_{2-x}Se$.

Synthesis of Ag₂Se NCs from AgSeC₁₂H₂₅

Figure 5.5 shows the results of $AgSeC_{12}H_{25}$ precursor thermolysis under various reaction conditions, including at reaction temperature above and below the mesogenic to isotropic phase transition. Figure 5.5a-c show POM images taken at T=150, 160, and 185 °C respectively. Birefringence is observed at T=150 and 160 °C and diminishes rapidly at temperatures above 180 °C. Figure 5.5d-f show TEM images of the NCs obtained from thermolysis conditions of T=150 °C for 12 hours, T=160 °C for 6 hours, and T=185 °C for 90 minutes respectively. Here, the mesogenic phase appears to template nanorod morphology (Figure 5.5d-e). These rods are fairly uniform in their width (~ 7 nm) yet irregular in their length. In Figure 5.5c, quasispherical NCs result from thermolysis of isotropic precursor at T=185 °C. The spherical NCs shown in Figure 5.5c are of size 9.7 ± 0.9 nm although larger particles that appear to be aggregates of the smaller particles can also be observed in the images, suggesting the possibility of Ag₂Se NCs undergoing oriented attachment (Figure 5.12).

Figure 5.5g shows the corresponding XRD spectra for the three samples shown in Figure 5.5d-f. After reacting the precursor at T=150 °C for 12 h, it is notable that the crystal structure is primarily the cubic phase of Ag₂Se, which displays peaks at 2θ = 36, 45, and 52°. Increasing the decomposition temperature to T=160 °C for 6 hours leads to the orthorhombic phase becoming dominant. Under the highest temperature conditions tested at T=185 °C, the orthorhombic phase remains favored. These results contradict what may be expected of Ag₂Se, where the cubic phase is preferred at *higher* temperatures.³⁶ We suspect that the mesophase is responsible for directing the crystallization of the thermodynamically unfavorable cubic phase, and that higher temperatures may weaken this effect by producing a mesophase which is less ordered or shorter lived. It is notable that across the various thermolysis temperatures tested here, the (111) peak from face-centered cubic Ag is present near $2\theta = 38^{\circ}$, representing a minor Ag impurity amidst the Ag₂Se. The Ag product is not surprising since the higher reduction potential of Ag^+ versus Cu^+ ($E^\circ = 0.799$ V vs 0.518 V respectively) could lead to enhanced rates of Ag-Se homolytic bond cleavage to form Ag^{0} . This is consistent with the thermolysis products observed for the thiolate analog $AgSC_{12}H_{25}$. Therefore, conversion of precursor to Ag_2Se product is not stoichiometric

and small amounts of pure Ag are generated. Overall, the results shown in Figure 5.5 support our hypothesis that the mesophase serves as a molecular template, here forming nanorods, whereas the isotropic phase can form only spherical NCs.



Figure 5.5. Thermolysis of $AgSeC_{12}H_{25}$. a-c) show polarized optical images taken at 150, 160, and 185 °C respectively. d-f) show TEM images from thermolysis reactions conducted at 150 °C for 12 hours, 160 °C for 6 hours, and 185 °C for 1.5 hour respectively. d) shows XRD patterns for the corresponding 3 thermolysis conditions, showing $Ag_{2-x}Se$ NCs are the consistent product, however the cubic phase is dominant at lower thermolysis temperature and the orthorhombic phase is dominant at higher thermolysis temperature.

To observe the evolution of the nanorod morphology, we carried out timedependent thermolysis reactions of AgSeC₁₂H₂₅ at 150 °C (Figure 5.6). We observed the best NC shape uniformity at thermolysis temperatures of T=150 °C, which may be caused by superior ordering or persistence of the mesophase. Figure 5.6a shows the presence of mostly small particles, as well as some string-like particles (after only 1 h of thermolysis, very little insoluble precipitate was collected). However, after 3 h of thermolysis, bundles containing material in aligned columns were observed (Figure 5.6b). After 6 h of thermolysis we observed individual rod-like particles which still may exhibit some connectivity (Figure 5.6c). Finally, after 12 h of thermolysis, nanorods of varying lengths were observed (Figure 5.6d). We believe these rods have a square cross-section; this is not discernable from side-on TEM images, but some nanorods assembled along their long axes perpendicular to the TEM grid (Figure 5.13). The rod thicknesses tend to be relatively uniform, measuring 5.0 ± 0.6 , 7.0 ± 0.9 and 6.9 ± 1.5 nm for 3, 6, and 12 h thermolysis reactions, respectively.

The corresponding XRD patterns shown in Figure 5.6e indicate that a mixture of orthorhombic and cubic Ag₂Se is produced. At 1 h of thermolysis at T=150 °C, little-to-no crystalline material is present, but at 3 h the characteristic peaks for the cubic Ag₂Se become apparent. Because of the broadness of the peaks, however, we believe the crystalline domains within these bundles are small and metal-organic precursor is still present. After 6 h of thermolysis, the orthorhombic phase is also present, and the changes from 6 to 12 h thermolysis are minimal. It is not clear if the cubic and orthorhombic phases correlate to separate NCs or the presence of many grain boundaries. However, the data clearly shows that more of the cubic phase is produced at 150 °C than at higher temperatures. Thus, it is reasonable to assume that the prevalent cubic phase we observe here is a result of the templating effect imparted by the mesophase of the AgSeC₁₂H₂₅ precursor. These results demonstrate the capacity for the mesophase to enable nucleation and growth of thermodynamically unfavorable phases.



Figure 5.6. Time-dependent thermolysis of $AgSeC_{12}H_{25}$ at 150 °C. a-d) show TEM images taken after 1, 2, 4, and 6 hours of thermolysis respectively. e) shows the corresponding XRD patterns, which are indexed as a mixture of cubic and orthorhombic Ag_2Se with minor FCC Ag impurity.

Synthesis of AgCuSe NCs from Ag0.5Cu0.5SeC12H25

In addition to CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅, we hypothesized that a mixed solution of Cu and Ag salts might allow co-precipitation of molecular CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅ into a homogeneous, co-assembled Ag_{0.5}Cu_{0.5}SeC₁₂H₂₅ framework upon selenol addition. We report the characterization for this "mixed-metal" precursor in Figure 5.7. The XRD characterization for the resulting mixed Cu-Ag-Se compound shows one set of low-angle XRD peaks (Figure 5.7a) and not a superposition of peaks observed for the unique Cu and Ag selenolates. This is indicative that molecular CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅ co-assemble into the supramolecular precursor rather than forming separate domains. The *d*-spacing parameter derived from the indexed XRD peaks for the lamellar bilayer is d = 3.52 nm, which is between the values measured for CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅. Figure 5.7b shows the TGA thermogram for the Cu-Ag-Se compound, where the mass residue is within 1% of the expectation

for AgCuSe generation (38.3% mass retention measured vs. 37.5% expected). Thus, we confirm that the compound is Ag_{0.5}Cu_{0.5}SeC₁₂H₂₅. The DSC thermogram shown in Figure 5.7c also demonstrates that Ag_{0.5}Cu_{0.5}SeC₁₂H₂₅ behaves as a homogeneous coordinated material and not a mixture because a single peak is observed at T=136.3 °C, intermediate to the two separate DSC peaks observed at T=132.8 and 146.2 °C for CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅, respectively. By optical microscopy, the mixed precursor was observed to melt around T=135 °C into a highly birefringent phase (Figure 5.7d). This phase was particularly low-viscosity compared to both CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅, and the mesophase lost birefringence rapidly when heated above 160 °C.



Figure 5.7. Characterization of $Ag_{0.5}Cu_{0.5}SeC_{12}H_{25}$. a-c) show XRD, TGA, and DSC respectively while d) shows polarized optical microscope image of $Ag_{0.5}Cu_{0.5}SeC_{12}H_{25}$ taken at 145 °C.

As a result of this low mesogenic clearing point, we carried out thermolysis reactions with Ag_{0.5}Cu_{0.5}SeC₁₂H₂₅ at T=150 °C. Figure 5.8a-c show TEM images of the NCs resulting from thermolysis reactions carried out for 6, 12, and 24 h respectively. For T=150 °C and a 6 h reaction time, semi-spherical NCs are observed with diameter ca. 13.3 ± 4.3 nm. After 12 h, the NC morphology is observed to be highly irregular and the average NC size increases to 28.7 ± 10.7 nm. After 24 h of

thermal decomposition, drastically larger and significantly more polydisperse NCs are observed with a bimodal distribution of NC sizes: 86.3 ± 29.2 nm and smaller NCs of 16.5 ± 2.5 nm. Figure 5.8d shows the corresponding XRD patterns, showing good agreement for AgCuSe. Several peaks near $2\theta = 44-45^{\circ}$ are not well-indexed by a single phase of AgCuSe and might be explained by another indexed phase of AgCuSe (PDF#00-010-0451). The peaks in this region are consistent with experimental results for the β -phase of AgCuSe measured at room temperature.⁴³ AgCuSe is clearly the dominant phase for all three reaction conditions; we show the cubic peaks for Cu_{2-x}Se to demonstrate its absence from these spectra. However, under the 24 h thermolysis condition, minor peaks for Ag₂Se (PDF#04-001-9362) are present; this may account for the much smaller NCs which are observed between larger NCs in Figure 5.8c.

While the formation of AgCuSe solid-state products (rather than a mixture of Ag₂Se and Cu_{2-x}Se NCs or heterostructures) indicate the formation of a homogeneously mixed mesophase, the spherical morphologies observed here were unexpected and inconsistent with our previous thermolysis reactions carried out for the neat mesogenic compounds for which anisotropic NC morphologies were obtained. In further examining the Ag_{0.5}Cu_{0.5}SeC₁₂H₂₅ precursor, we found that the mesophase underwent an isotropic transition at temperatures well below T=160 °C after sufficient dwell time. Specifically, the mesophase clears to isotropic within 25 minutes at T=150 °C and 35 minutes at T=145 °C (Figure 5.14). We believe that the morphologies observed for AgCuSe NCs are consistent with the presence of an isotropic phase and the lack of an ordered supramolecular template. We hypothesize that the short-lived

birefringent phase is a columnar phase. Our observations indicate that the M-Se covalent and dative bonds present within the discotic micelles is sufficiently different for Cu- and Ag-selenolate molecules such that the micellar structure is a thermodynamically unfavorable intermediate. In validation of this hypothesis, we ramped $Ag_{0.5}Cu_{0.5}SeC_{12}H_{25}$ to the isotropic phase at 160 °C and subsequently cooled it to its solid form. We did not observe the presence of a birefringent phase on the second heating cycle, but instead, observed a direct transition into an isotropic phase.



Figure 5.8. Thermolysis of $Ag_{0.5}Cu_{0.5}SeC_{12}H_{25}$. a-c) correspond to thermolysis conditions 150 °C for 6, 12, and 24 h respectively. d) shows corresponding XRD patterns indexed to AgCuSe. A slight Ag₂Se impurity is noted for the 24 h thermolysis condition.

in situ XRD

To better understand why CuSeC₁₂H₂₅ templates nanoribbons while AgSeC₁₂H₂₅ templates nanorods, we performed high-temperature, *in-situ* XRD on CuSeC₁₂H₂₅ and AgSeC₁₂H₂₅ samples, shown in Figure 5.9. Samples were heated to T=150 °C and equilibrated for 6 minutes prior to initiating a XRD scan. For the Ag selenolate precursor (Figure 5.9a), heating to T=150 °C results in a new phase with three prominent peaks present at 20 = 3.32, 5.70, and 6.65°, corresponding to calculated *d*-spacings of 2.66, 1.55, and 1.33 nm. These *d*-spacings are indicative of a 2D hexagonal lattice and correspond to (100), (110) and (200) planes, respectively.
Here, the (100) plane refers to the spacing between successive columnar rows (Figure 5.9a, inset). Thus, the columnar spacing parameter is 2.66 nm, where the 0.8 nm contraction from the nominal lamellar bilayer is partly caused by disordering of alkyl chains. This columnar spacing parameter is in agreement with a Ag alkanethiolate columnar mesophase, for which a 2.5-2.6 nm spacing is expected for a 12-carbon chain.⁴⁴ The verification of the hexagonally packed columnar mesophase strongly supports that the Ag₂Se nanorods are the result of anisotropic nucleation and growth along the column axis.

In contrast, CuSeC₁₂H₂₅ brought to T=150 °C does not show a clear mesophase (Figure 5.9a, top). In the very-low angle regime, superimposed peaks cover the *d*-spacing range 3.6 to 2.33 nm, which encompasses both the expected lamellar bilayer and micellar spacing parameters. Two broad peaks at $2\theta = 4.65$ and 6.8° peaks may correspond to (002 and (003) reflections of a weakly ordered lamellar bilayer with and expanded *d*-spacing parameter (approx. 3.8 nm), with the (001) shoulder showing at the far left of the spectrum. However, the high intensity of overlapped peaks between $2\theta = 2.5$ and 4.0° indicate the likely coexistence of an intermediate or frustrated phase. Several factors point to CuSeC₁₂H₂₅ exhibiting a lamellar smectic rather than a columnar mesophase: the higher melt viscosity, lack of recognizable birefringent texture, and time-dependent thermolysis results all support the existence of a lamellar mesophase.

In a previous work, we reported similar results when carrying out thermolysis reactions of CuSC₄H₉.²⁰ A 2D sheet-like morphology results from anisotropic growth

rates, where the lamellar bilayer structure facilitates fast intraplane diffusion while interplane diffusion is retarded by the alky chain bilayer. It is interesting that the Cu_{2-x}Se nanoribbon thicknesses observed here are just 2.3 nm while the Cu_{2-x}S nanosheets from CuSC₄H₉ were 5.4 nm thick, a discrepancy which may be due to the greater interplane diffusion pathlength of CuSeC₁₂H₂₅ (~ 3.5 nm) vs. CuSC₄H₉ (~ 1.6 nm). However, this comparison suggests that CuSeC₁₂H₂₅ forms a weakly-ordered lamellar smectic phase that gives rise to ribbon-like Cu_{2-x}Se products upon thermolysis.



Figure 5.9. In-situ XRD spectra. Measurements at 150 °C (red color) are shown in comparison to room temperature spectra (black color) for $AgSeC_{12}H_{25}$ (a) and $CuSeC_{12}H_{25}$ (b). For $AgSeC_{12}H_{25}$, peaks are indexed to a hexagonal lattice with several peaks labeled accordingly and (100) plane depicted (inset).

5.5 Conclusions

This work provides insight into the use of metallomesogens as molecular templates for NC synthesis, in addition to the synthesis of previously unreported NC morphologies such as Ag₂Se nanorods and AgCuSe nanospheres. Here we establish that when thermolytic bond cleavage occurs in a temperature regime overlapping with the mesophase, metallomesogens can serve as general molecular templates for shaped NC synthesis. This anisotropic templating effect has not been universally observed. For example, some metallomesogens, like Au alkynylisocyanides, display brilliant mesogenic phases yet only template the growth of Au nanospheres.⁴⁵ However, the supramolecular precursor initially decomposes into alkynyl stabilized Au⁰ dimers, which then undergo isotropic agglomeration. Our work establishes the critical requirement that the supramolecular structure of the metallomesogen is stable at thermolysis temperatures. The selenolate compounds reported here (as well as previously reported thiolate compounds) maintain their structural coordination long enough to serve as effective molecular templates anisotropic NC growth. This synthesis strategy has the potential for targeting highly anisotropic metal chalcogenide NC morphologies, including the growth of 2D transition metal chalcogenides, from lamellar phase precursors.

5.6 Supporting Information



Figure 5.10. FTIR spectra taken of solid $AgSeC_{12}H_{25}$ and $CuSeC_{12}H_{25}$ precursor compounds. The *n*-alkane backbone follows expectations, which are well established in literature. The C-Se-M stretching vibration is shown at 639 cm⁻¹ for the Cu analog, and 637 cm⁻¹ for the Ag analog.



Figure 5.11. Additional TEM images taken from side-on vantage of $Cu_{1.8}Se$ nanoribbon structures. The calculated average thickness from 30 measurements is 2.30 +/- 0.25 nm. As the $Cu_{1.8}Se$ cubic structure has a=b=c=0.5767 nm, this thickness might correlate with exactly 4 unit cells (expected 2.3068 nm). Far right shows a zoomed-out image of the nanoribbon sample for added perspective, with a twisted ribbon shown (inset).



Figure 5.12. Ag₂Se spherical particles from AgSeC₁₂H₂₅ at 185 °C. Particles show vaguely hexagonal faceting and align along these facets to produce dimers, trimers, etc. with some examples highlighted here in red.



Figure 5.13. Ag₂Se nanorods synthesized from AgSeC₁₂H₂₅ at 150 °C. A propensity to self-assemble into closed packed arrays is observed. We believe the TEM imaging indicates that these nanorods are aligned along their long axis. Interestingly, these rods show cubic cross section. However, it is not clear if these rod arrays are indicative of the entire sample. Possibly, these nanorods with cubic cross section simply account for one crystallographic phase, e.g. the population of NCs with a cubic phase. However, the measured edge length of these NCs is 6.8 ± 0.6 nm which is in close agreement with measurements for the rod populations lying on their sides.



Figure 5.14. Polarized optical microscope images of $Ag_{0.5}Cu_{0.5}SeC_{12}H_{25}$. Top row images at 150 °C after 3, 10, 20, and 25 minutes on the heating stage (a-d); bottom row images at 145 °C after 3, 20, 30, and 35 minutes (e-h). These images demonstrate the decreased stability of the mixed-metal dodecaneselenolate, which undergoes slow isotropic transition at a lower temperature than is observed for either AgSeC₁₂H₂₅ or CuSeC₁₂H₂₅ individually.

Chapter 5, in part, is a reprint of the material that appears *Chemistry of Materials* (Whitney Bryks, Stephanie Smith, and Andrea R. Tao. "Metallomesogen Templates for Shape Control of Metal Selenide Nanocrystals." Manuscript Just Accepted). The dissertation author was the primary investigator and author of this paper.

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Chapter 6

Structure and Thermal Properties of

Supramolecular Metal Alkanethiolates

6.1 Abstract

Metal alkanethiolates have attracted increasing use as precursors to metal and metal sulfide nanocrystals (NCs) via thermal decomposition methods. A wide variety of metal alkanethiolates have been reported in literature, serving as single-source precursors to be used in solventless, solvothermal, or polymer-mediated thermolysis processes. However, understanding of the structure and thermal properties of metal alkanethiolate complexes remains relatively high-level in scope. Fundamental questions regarding the structure of supramolecular complexes, mesomorphic behavior, metal-catalyzed bond thermolysis, and effects of the alkyl substituents on thermolysis have been relatively unexplored. In this article, we codify the system of metal alkanethiolates to better understand its capabilities and limitations with respect to NC synthesis. We generate an array of metal alkanethiolates from which we report structure, phase transition, and decomposition temperature of each metal complex. We explore the chemical factors which influence the formation of a mesogenic phase, showing several unreported metallomesogens. Lastly, we use select examples to showcase the synthesis by solventless thermolysis of various dispersed NCs.

6.2 Introduction

For decades, metal thiolates have been synthesized and utilized as singlesource precursors for metal sulfides by means of thermal decomposition. Metal thiolate complexes are uniquely suited as single source precursors because of the thiol chemistry; strong M-S bonds catalyze the thermolysis of the C-S bond to enable metal sulfide formation at relatively low temperatures (\sim 140 – 200 °C). Obtaining metals sulfides from processing of metal-thiolate complexes has appealed where a costsavings motivation can be found in the simplicity of the technique and the lowtemperature conditions. For example, another popular method for forming compound metal sulfide materials is through a "hot injection" reaction involving separate metal and sulfur sources; however, these rely on reactive or toxic precursors, require temperatures in excess of 300 °C, and are highly sensitive to oxidation.^{1,2} On the other hand, decomposition of metal thiolates spurred research aimed at obtaining low-cost compound-semiconductor thin films.³ Towards this route and more generally obtaining inorganic nanomaterials, bis(diethyldithiocarbamato) complexes gained wide use both through solvothermal processing and spray pyrolysis methods.^{4,5}

Herein, we limit our scope from speaking generally of metal thiolate complexes to more specifically of metal *alkane*thiolate complexes, which are differentiated by a linear *n*-alkyl moiety. Long alkyl chains such as 1-dodecanethiol are miscible with hydrophobic solvent and so generally, metal alkanethiolates were formed in-situ in high b.p. solvents and heated to afford the corresponding metal sulfide. In this regard, alkyl thiol molecules have been used simultaneously as capping ligands and as sulfur sources. Similar methods have been employed in the more recent years, to synthesize nanocrystals (NCs) of ZnS, Cu_{2-x}S, CdS, Ni₃S₄, PbS, and Ag₂S.^{6,7,8,9} These works demonstrated a key advantage of using long *n*-alkyl chain rather than a smaller yet sterically bulkier molecule is the improved capping on the nanocrystal surface afforded by the *n*-alkane. Strong capping of nanocrystal surfaces is important for uniform growth processes leading to monodispersed nanocrystal

populations, superior dispersibility in solvent, and protection from oxidative processes. The use of such hydrophobic groups also makes such precursors amenable for embedding metal or metal sulfide NCs within polymer matrices for optoelectronic nanocomposites.^{10,11}

Another consequence of the use of *n*-alkanethiols is the resulting metal complexes, with few exceptions, form into supramolecular assemblies with lamellar bilayer structure. Earlier work on Ag alkanethiolates delved considerably into the details of the self-assembly process, structure, and the thermodynamics of a phase transition into a hexagonally packed columnar phase.^{12,13,14} However, broader applications of the lamellar bilayer structure and the potential for mesogenic activity at elevated temperature have received only limited attention. For instance, metal alkanethiolates are terminated in close-packed alkyl chains, and so can be added to coat a surface with hydrophobicity characteristic of a self-assembled-monolayer of thiol on metal.¹⁵ Another consequence of the lamellar bilayer structure is the highly confined, 2D planes of coordinated metal and sulfur atoms, which give rise to unique magnetic and luminescent properties.^{16,17} More recently, Pd alkanethiolates were shown to be assembled via layer-by-layer assembly for potential application of catalytic Pd(0) surfaces, which led to attempts to generate ultrathin Pd(0) sheets from the lamellar structure.^{18,19}

The use of the lamellar alkanethiolates as "templates" for metal sulfide NCs is an area of research that we have some experience with, having demonstrated that the structural coordination of the supramolecular Cu alkanethiolate assemblies affects both the shape and the crystal structure of the NCs.^{20,21} Specifically, non-linear alkyl groups produced non-lamellar structure, and the length of the alkyl group or the presence of a terminal polar group affected the phase transition of lamellar structures. However, the effects of the alkyl group used, the structural phase transition, and the decomposition temperature is not explored for most metals. Herein, we detail the synthesis of a variety of metal alkanethiolates and report their structure and thermal properties. We leverage knowledge from previous works to modify Pb- and Ag-alkanethiolate for enhanced mesogenic stability, and report several previously unreported metallomesogens.

6.3 Experimental Methods

Detailed synthetic procedure of metal alkanethiolates. In a general synthesis of $M(SC_{12}H_{25})_n$, from some metal, M^{n+} (n = 1, 2, 3), 1 mmol of metal salt is dissolved in 2 mL of DI water in a flask and stirred to form a $\frac{1}{2}$ M solution. Separately, 2n mmol of dodecanethiol is added to 2n mL of ethanol to form a 1M solution. This solution is stirred separately until thoroughly mixed. This latter solution is then added, dropwise, to the former (metal) solution under vigorous stirring. The precipitations of metal alkanethiolate complexes tend to occur spontaneously upon addition of the thiol. Notably however, for M = Ni & Co, precipitation of the metal dodecanethiolate requires the addition of n equivalents of base such as triethylamine. It should be noted that solubility of the metal salt can present challenges; metal salts with high solubility in aqueous media are preferred, and dilution of the metal solution is stirred for about 15 minutes.

This is then washed copiously with water and ethanol 2-3x, and then finally again with only ethanol. Precipitated metal alkanethiolates range in color from white to tan/brown to bright yellow. These are then dried under vacuum until all solvent has been removed prior to characterization.

Solventless thermolysis reactions. Solventless thermolysis reactions for metal sulfide nanocrystal formation from the respective precursor follows a standard method. 50 mg of precursor is measured into a 25 mL round bottom flask, which is then equipped w/ septum and purged with N₂. The flask containing precursor is then immersed in a silicone oil bath for the specified reaction parameters, which varies by metal: (1) Ag nanodisks 200 °C x 3 h; (2) PbS nano-octahedra 200 °C x 24 h; (3) Bi nanodisks 200 °C x 1 h; (4) Tl₂S particles 200 °C x 3 h. After the specified reaction duration, the flask containing thermolysis residue is removed and cooled to room temp under exterior H₂O flow. Next, 8 mL CHCl₃ is pipetted into the flask and the thermolysis residue is dispersed via ultrasonication for several minutes. The resulting colloidal solution is then washed 3x with CHCl₃ by centrifugation (~7,500 RPM for 10 m). Finally, the particles are re-dispersed in CHCl₃ and stored for use.

Characterization. Powder X-ray diffraction (XRD) was performed using a Rigaku RU200B diffractometer running MDI Datascan5 software. Transmission electron microscopy (TEM) was performed on an FEI Tecnai G2 Sphera running a LaB₆ filament at 200 kV. A Gatan Ultrascan 1000 UHS CCD camera running Gatan Digital Micrograph was used for imaging. TEM samples were typically prepared by drop casting NC colloidal dispersions in CHCl₃ onto an air-water interface to form a film

and subsequently dip-coating the TEM grid. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA 7 Thermogravimetric Analyzer attached to a Perkin Elmer TAC 7/DX Thermal Analysis Controller. Differential Scanning Calorimetry (DSC) was performed using a Perkin Elmer PYRIS Diamond DSC. Polarized optical microscope images were taken with a PixelLink Capture TWAIN device CCD running μ Scope Essentials Software on a Nikon Eclipse LV100 microscope. Samples were heated using an Instec HCS302 heating stage by placing several mg of powder between a glass slide and cover slip. Samples were given several minutes to equilibrate at each temperature before an image capture was taken.

6.4 Results and Discussion

The selection of metal alkanethiolates studied in this work merits some initial discussion. Not all transition metals will spontaneously form complexes; an observation we trace primarily to the tenets of hard-soft acid base theory. Sulfide ions are particularly large (184 pm for S²-) and therefore "soft," so compatibility appears to correlate with larger metal ions found amongst some of the heavier metals. Indeed, we found the tetravalent species such as Ti⁴⁺ and Zr⁴⁺ totally unreactive, as was Fe²⁺. Ga³⁺ apparently formed a dodecanethiolate complex, but appeared as a denser liquid phase, indicating very weak Ga-S bonds incapable of maintaining a solid coordinated assembly at room temperature. Co and Ni, also amongst the smallest metal species used, did not form metal dodecanethiolate precipitates initially but were coaxed into precipitation with the complementary use of Et₃N as described in the experimental section.

Synthesized metal *n*-dodecanethiolates were isolated as powders and initially characterized with X-ray diffraction (XRD) to examine the structure. We found that a variety of metals, including monovalent, divalent, and trivalent metal cations all show a proclivity towards forming a lamellar bilayer structure. Figure 1 shows XRD patterns for select metal dodecanethiolate complexes including Cu, Ag, Ni, Pb, In, Tl, and Bi. The peaks of high intensity near low 2θ correspond to multiple reflections of the interlayer spacing parameter, *d*. The order of these supramolecular assemblies is variable as some metal lend themselves to more highly-ordered structures with greater numbers of stacked layers than others, which manifests in the diffraction patterns as decreased full-width-half-maximum of the low-angle peaks. Zn and Co dodecanethiolate assemblies were also isolated as powders, but showed such poor ordering of the lamellar structure that *d*-spacing values could not be computed.



Figure 6.1. XRD of metal *n*-dodecanethiolate complexes by oxidation state of metal ion used. a) monovalent Ag, Cu; b) divalent Ni, Cd, Pb; c) trivalent In, Tl, Bi.

Figure 1a shows XRD patterns of the monovalent Ag^+ and Cu^+ complexes, which are in accord with previous reports. Evidence of the in-plane structure is observed at higher angles ($2\theta > 20^\circ$) and forms the basis for the proposed metal

coordination here, which is assumed to be trigonal planar.¹² Figure 1b shows XRD patterns of divalent metals Ni^{2+} , Pb^{2+} , and Cd^{2+} . The in-plane structure here is weak or absent, though broad peaks are observed near $2\theta = 22^{\circ}$. Indeed, this peak often appears remiss of the lamellar bilayer structure and corresponds to $4.0 \le d \le 4.5$ Å, which is close to the C-C distances between packed alkanes and likely correlates to diffraction between parallel alkyl chains. Interlayer *d*-spacing varies from 3.262 nm (Ni) to 3.681 nm (Pb), likely originating from differences in the tilting of alkyl chains. In general, it has been difficult to positively identify metal alkanethiolate M-S coordination because large crystalline domains have not been attained during synthesis or recrystallization. However, we believe it is intuitive that with increasing number of alkylthiols per metal core, M-S coordination interactions between individual molecules becomes limited by sterics, which should impose higher order geometries and greater bond lengths. Some precedents in the literature however allow us to consider structure further. Hückel calculations support the formation of [Ni(SR₂)]_n toroids, with the Ni in square planar configuration, and Pb^{2+} forming various complexes with S tends to coordinate to 3-4S atoms.^{22,23} Coordination of Pb to 4 total S atoms is most likely here to facilitate the 2D M-S network, which would suggest a distorted trigonal bipyramidal structure taking into account the electron lone pair. Figure 3c shows XRD patterns of trivalent In, Bi, and Tl, which have escaped classification in terms of coordination but are most likely a distorted trigonal bipyramidal coordination of the metal centers to allow for 2 M-S dative bonds for assembly. Invoking a coordination number of 6 would place a $\sim 90^{\circ}$ bond angle between alkyl groups, which is at odds with lamellar assembly.

| Ion | Cu ⁺ | Ag^+ | Ni ²⁺ | Cd^{2+} | Pb ²⁺ | In ³⁺ | T1 ³⁺ | Bi ³⁺ |
|---|-----------------|--------|------------------|-----------|------------------|------------------|------------------|------------------|
| Interlayer <i>d</i> -spacing (nm) | 3.576 | 3.387 | 3.262 | 3.387 | 3.681 | 3.591 | 2.846 | 3.291 |

 Table 6.1. Interlayer d-spacings of metal dodecanethiolate complexes

Figure 2 presents DSC data for the host of metal ions described. Each metal dodecanethiolate complex was visually observed to melt near the onset of the exothermic peaks observed in Figure 2, with the exception of Cd²⁺. The Cd dodecanethiolate complex stayed apparently solid with a mild change in its optical texture marked by a complex DSC thermogram, and we have eliminated it from further study because its unusual behavior is still not fully understood. We observe a peak near 55 °C for Ni²⁺, which is attributed to a pre-melting event; usually the onset of alkyl chain disordering as the phase transition temperature is approached. A similar event is observed for Pb²⁺ near 100 °C. For the rest of the metal complexes characterized, the temperature at the maximum endothermic heat flow was tabulated (Table 2). Table 2 shows an apparent trend between metal ion valency and the melting transition of the metal thiolate complex; monovalent Cu and Ag melt near 130 °C, divalent Ni and Pb melt closer to 100 °C, and trivalent In, Tl, and Bi melt closer to 70 °C. The decrease in phase transition as the number of alkylthiols per metal core increases can be rationalized in terms of both enthalpy and entropy. Heating increases entropy of the alkyl chains, which take on gauche conformers with greater degrees of conformational freedom, implying a faster increase in entropy with heating as the

number of alkyl chains increases with respect to a single metal center. Meanwhile, as sterically active alkyl chains are added to a metal center, increasingly complex geometries with greater bond lengths are necessitated which entail lower enthalpies of formation. For perspective, in the absence of the extended M-S network, the melting point (e.g. of neat 1-dodecanethiol) is ⁻8 °C.

Table 6.2. Tabulated temperatures of phase transition. Measurement taken at the maximum heat flow.

| Ion | Cu ⁺ | Ag^+ | Ni ²⁺ | Pb^{2+} | In ³⁺ | T1 ³⁺ | Bi ³⁺ |
|-------------|-----------------|--------|------------------|-----------|------------------|------------------|------------------|
| Transition | 132.8 | 129.1 | 94.3 | 106.2 | 62.0 | 73.3 | 63.3 |
| Temperature | | | | | | | |
| (°C) | | | | | | | |



Figure 6.2. DSC thermograms of selected metal dodecanethiolate complexes. Heat flow is plotted such that "up" signals an endothermic process.

Figure 3 shows TGA data separated for monovalent, divalent, and trivalent metals. The final mass retention correlates with the formation of metal sulfides and evaporation of all residual organics. Due to the different metal oxidation states shown

here, different metal sulfides are produced; M_2S for monovalent metals, MS for divalent metals, and M_2S_3 for trivalent metals. The TGA thermograms support the formation of these stoichiometries within 1-2 percentage points, so at the temperatures employed here we are not seeing the formation of metals, nor do we observe oxidation of the existing metal cations due to the use of N_2 flow. An exception however is Tl^{3+} , which shows greater mass retention than expected by ca. 17%. This is in better correlation with a reduced Tl^+ forming Tl_2S upon thermolysis, which is addressed later in the discussion.

In order to obtain a better understanding of the thermal stability of the metal dodecanethiolate complexes, we calculated the temperature at which the rate of mass loss reached its maximum and termed it T_{max} . T_{max} is taken to correlate inversely with the strength of the M-S bond and positively with the strength of the C-S bond, because stronger M-S bonds weaken the C-S bond and catalyze its cleavage. This process is generally thought to occur through heterolytic C-S bond cleavage, ostensibly placing the electron density on S to form an intermediate charged complex and a carbocation. Accordingly, we have sought to corroborate this with quantifiable electronic properties, and point out that a trend exists where metals with higher reduction potentials show lower T_{max} : 0.799 (Ag), 0.521 (Cu), -0.126 (Pb), -0.25 (Ni), and -0.403 (Cd). However, any trend here is lost for trivalent metals: 0.72 (Tl), -0.3382 (In), and .3172 (Bi). A couple factors are likely at play here which convolute interpretation of the data. First, Bi and Ag complexes have generated metallic Ag and Bi NCs, and so two-step thermolysis would result in metals capped with alkyl sulfides prior to metal

byproducts (for perspective, b.p. of 1-dodecanethiol is 266 °C) is occurring well beyond the onset of thermolysis.



Figure 6.3. TGA thermograms of metal dodecanethiolate complexes separated by oxidation state of ion used. a) monovalent Cu, Ag; b) divalent Ni, Cd, Pb; c) trivalent In, Tl, Bi.

| Ion | Cu^+ | Ag^+ | Ni ²⁺ | Cd^{2+} | Pb^{2+} | In ³⁺ | T1 ³⁺ | Bi ³⁺ |
|------------------|--------|--------|------------------|-----------|-----------|------------------|------------------|------------------|
| % Mass | 28.9 | 38.5 | 18.5 | 29.3 | 41.4 | 22.2 | 47.8 | 31 |
| Retention | | | | | | | | |
| (experimental) | | | | | | | | |
| % Mass | 30.0 | 40.0 | 19.7 | 28.0 | 39.2 | 22.7 | 31.2 | 31.6 |
| Retention | | | | | | | | |
| (calculated) | | | | | | | | |
| % Mass | 1.1 | 1.5 | 1.2 | 1.3 | 2.2 | 0.5 | 16.6 | 0.6 |
| Retention | | | | | | | | |
| (delta) | | | | | | | | |
| T _{max} | 259.8 | 260.0 | 294.9 | 311.3 | 289.4 | 261.3 | 290.9 | 277.5 |

Table 6.3. Tabulated data for mass retention and maximum thermolysis rate, T_{max} , of metal dodecanethiolate complexes.

To address the aforementioned issue of metal alkanethiolate thermolysis occurring before it may be detected by mass loss via TGA, we chose a metal which exhibited the greatest decomposition temperature for 1-dodecanethiol to study in further detail. Zn^{2+} was not included in the diffraction data onward because the structure is too poorly ordered to identify as lamellar bilayer; however, its dodecanethiol complex possessed the highest T_{max} measured (322.7 °C) and thus it serves to clearly separate thermolysis temperature from alkyl byproduct evaporation. We have theorized that C-S thermolysis places electron density on S and forms an intermediate carbocation; accordingly, we hypothesize that alkyl groups which stabilize a carbocation will facilitate C-S bond cleavage and decrease T_{max} , and conversely, alkyl groups which destabilize a carbocation will increase T_{max} . Choosing the appropriate alkyl thiols for this experiment invokes recollection of basic organic chemistry: increasing alkyl substitution and contributions from resonance structures are two ways to stabilize a carbocation. And a carbocation will be particularly unstable

if it is placed such that it disrupts resonance. Using these design rules, we selected the following series of alkyl thiols (in ascending carbocation stability): benzenethiol, 1-butanethiol, 1-octanethol, 1-dodecanethiol, *tert*-dodecyl mercaptan, benzyl mercaptan, and triphenylmethanethiol. Benzenethiol is aromatic, and the loss of electron density of an aromatic carbon causes loss of aromaticity, and so can be expected to increase T_{max} . Longer alkyl chains do little to contribute more electron density, but the inductive effect has been demonstrated beyond 4 carbons, and so was worth probing for any modest changes in T_{max} . Benzyl mercaptan has a resonance form which can stabilize a carbocation at the benzylic position and finally, triphenylmethanethiol exhibits both tertiary substitution and resonance stabilization and should decrease T_{max} .

Figure 4 shows the results of probing decomposition temperature (T_{max}) with ligands that vary in their ability to stabilize a carbocation for Zn²⁺. The least carbocation stability is expected for thiophenol, which appropriately shows the highest T_{max} (332 °C). The *n*-alkanes show no trend, and their T_{max} values vary from 308-324 °C. The resonance stabilized structure benzyl mercaptan shows a significantly decreased temp T_{max} of 255 °C. The tertiary alkanethiol, *tert*-dodecyl mercaptan, shows a further decreased of T_{max} of 240 °C. The structure we would expect to best support a carbocation, triphenylmethanethiol, similarly scores a T_{max} of 240 °C. We believe this trend is sufficient evidence to conclude that the nature of the alkyl substituent with respect to thermolysis of the Zn²⁺ complex is clear: increasing ability to support a carbocation intermediate lowers the energetic barrier to C-S bond cleavage. It is likely that Zn is not unique in this regard, but reflective of C-S bond thermolysis in other metal thiolate complexes. This trend is not disrupted by the cleaved evaporation points of the alkanes, as the largest molecule (triphenylmethanethiol, M.W. = 276.4) shows the lowest T_{max} , and the second-lightest molecule (thiophenol, M.W. = 110.2) shows the highest T_{max} . Individual comparisons are also quite telling, such as the resonance stabilized benzyl mercaptan compared to thiophenol, where the difference of the benzylic carbon causes to decrease ~ 80 °C, and the tertiary *tert*-dodecyl mercaptan which shows T_{max} decreased again by ~ 80 °C compared to *n*-dodecanethiol.



Figure 6.4. Decomposition temperature T_{max} of select Zn(II) thiolates. Y-axis is the expected carbocation stability of the respective thiol molecule.

Having established a firmer grasp on the decomposition pathway of metal alkanethiolates to metal sulfides, we wanted to further probe the structural transition. This investigation was motivated by reports that Ag and Cu alkanethiolates adopt a hexagonally packed columnar mesophase (Col_H) at their melting transition. However, phase transition to pseudo-liquid crystalline phases of other metal alkanethiolate complexes has not been well-studied and we asked if the monovalent ions Cu and Ag were unique in their behavior. We used polarized optical microscopy (POM) on a heating stage to view metal alkanethiolates through crossed polarizers during their phase transition. The results of this analysis are tabulated in Table 4. Strong birefringent textures supported previous observations that Cu and Ag adopt a columnar mesophase at their melting transition and slowly convert to isotropic in a window between approx. 200 and 210 °C. Ni, Pb, Tl, and Bi however failed to show birefringence, and melted directly into fluids with no significant birefringence

| | Cu | Ag | Ni | Pb | In | TI | Bi |
|------------------------------------|------|------|----|-----|-----|----|----|
| Lamellar Crystalline \rightarrow | | | | | | | |
| Col _H | 132 | 129 | - | - | - | - | - |
| Lamellar Crystalline \rightarrow | | | | | | | |
| Iso | - | - | 94 | 106 | - | 73 | 63 |
| $Col_H \rightarrow Iso$ | ~206 | ~208 | - | - | - | - | - |
| Lamellar crystalline \rightarrow | | | | | | | |
| mesophase | | | | | | | |
| (unidentified) | - | - | - | - | 62 | - | - |
| Mesophase | | | | | | | |
| (unidentified) \rightarrow | | | | | | | |
| mesophase (uidentified) | - | - | - | - | 187 | - | - |

Table 6.4. Phase transition temperatures for various metal alkanethiolates.

The In complex shows markedly unique behavior, which is captured by POM in Figure 5. The initial melting transition (near 60 °C) is from the lamellar crystal to a strongly birefringent, as of yet unidentified mesophase (Figure 5a). This phase is stable until ~ 187 °C (Figure 5b), where it rapidly undergoes changes in color and texture (Figure 5c). These mesophases are likely to be subtypes of a smectic class, where directional order of stacked lamella is maintained. In light of our results, it seems unlikely that any of the metal complexes save Cu and Ag adopt the Col_H phase. We believe this is a consequence of the steric requirements of di- and trialkanethiolates, which prevents the packing arrangements of the discotic micelles described for Cu and Ag.^{13,24} However, further characterization is necessary to positively identify the nature of the In thiolate metallomesogen reported here.



Figure 6.5. POM of In-dodecanethiolate at various temperatures. Top panels (a,c,e) are uncrossed polarizers; bottom panels (b,d,f) use crossed polarizers. a,b) are taken at 100 °C; c,d) taken at 180 °C; e,f) taken at 200 °C.

In a previous work, we studied phase transition of several Cu alkanethiolates and determined that the lamellar structure can be stabilized by installation of in-plane attractive forces, namely H-bonding. Here, we observed primarily lamellar to isotropic phase transition, and hypothesized that one might induce thermodynamic favorability of mesophase by bolstering the enthalpy of the lamellar phase with H-bonding, as from terminal –COOH or –OH groups. To illustrate this effect, Figure 6 shows several examples using Ag and Pb complexes. The relevant phase transitions for this data are tabulated in Table 5. In Figure 6a bottom, DSC thermograms compare melting transitions of Ag complexed with 11-mercaptoundecanoic acid compared to dodecanethiol (AgSC₁₀H₂₀COOH vs. AgSC₁₂H₂₅ respectively). Whereas AgSC₁₂H₂₅ undergoes Col_H \rightarrow Iso transition below 210 °C, the –COOH derivative forms a mesophase stable at 210 °C and persists beyond 220 °C before darkening with decomposition (Figure 6d,e). In this case, it is likely the columnar phase which is being stabilized by H-bonding interactions at the periphery of discotic micelles, because textures observed in Figure 6e have fanlike and conical qualities indicative of Col_H.

For the Pb center, we have shown that nominal Pb dodecanethiolate is isotropic beyond its melting transition. Figure 6a shows a short chain hydroxyl functionalized thiolate $[Pb(SC_4H_8OH)_2]$ and a long chain carboxyl functionalized thiolate $[Pb(SC_{10}H_{20}COOH)_2]$ compared to the dodecanethiolate $[Pb(SC_{12}H_{25})_2]$. The melting transition of the –COOH derivative is ca. 165.5 °C, or substantially increased by imparted H-bonding. Melting at this point results in a very weakly birefringent phase (Figure 6b) which we have tracked up to 230 °C. Interestingly, the combination of a short alkyl chain and hydroxyl group from 4-mercapto-1-butanol $[Pb(SC_4H_8OH)_2]$ led to a lamellar crystalline \rightarrow mesophase transition near 120 °C. This is a brightly birefringent phase with striated textures (Figure 6c). However, this phase undergoes mesophase \rightarrow Isotropic transition near 150 °C. Our results demonstrate that with chemical programming through functional groups and chain length, the interplay of enthalpy and entropy can be shifted to favor certain structural arrangements, or induce arrangements previously inaccessible.



Figure 6.6. Mesophase modification with functional groups. a) shows DSC thermograms for metal complexes with functional groups compared to dodecanethiolate standard. b,c) show polarized optical image of $Pb(SC_{10}H_{20}COOH)_2$ at 200 °C and $Pb(SC_4H_8OH)_2$ taken at 125 °C respectively. d,e) respectively compare $AgSC_{12}H_{25}$ at 210 °C to $AgSC_{10}H_{20}COOH$ at 210 °C.

| Table 6.5 | . Phase | transitions | for | function | alized | Ag | and Pb alkanethiolates. |
|-----------|---------|-------------|-----|----------|--------|----------|-------------------------|
| | | | | | | <u> </u> | |

| | Ag- | Ag- | Pb- | Pb- | Pb- |
|---------------------------|-----------------|-------------|---------------------|-----------------|-------------------------|
| | $SC_{12}H_{25}$ | SC10H20COOH | $(SC_{12}H_{25})_2$ | $(SC_4H_8OH)_2$ | $(SC_{10}H_{20}COOH)_2$ |
| Lamellar | | | | | |
| Crystalline | | | | | |
| →Col _H | 129 | ~190 | - | - | - |
| Lamellar | | | | | |
| Crystalline | | | | | |
| → Iso | - | - | 106 | - | - |
| $Col_H \rightarrow Iso$ | ~208 | - | - | - | - |
| Lamellar | | | | | |
| crystalline \rightarrow | | | | | |
| mesophase | | | | | |
| (unidentified) | - | - | - | 120 | ~166 |

Having thus established the structure, phase transition, and thermolysis of metal alkanethiolate complexes, we next examined the NCs obtained by solventless thermolysis processes of select metal alkanethiolate complexes. One of the parameters which interested us was shape control of nanocrystal morphology, having established that the columnar mesophase of Cu alkanethiolate dictates Cu_{2-x}S nanodisk formation.²⁰ However, NCs synthesized by solventless thermolysis of other metal alkanethiolate complexes remains poorly characterized. Figure 7 shows the XRD patterns (top panels) and TEM images (bottom panels) of metal and metal sulfide NCs synthesized by solventless thermolysis of metal alkanethiolates made from Ag (Figure 7a,e), Pb (Figure 7b,f), Bi (Figure 7c,g), and Tl (Figure 7d,h). An earlier report has also isolated Ag nanodisks from the thermolysis of Ag dodecanethiolate, a result we have corroborated in Figure 7a,e.²⁵ However, we would like to point out that in the prior publication, nanodisk morphology was attributed to anisotropic nucleation and growth imposed by the lamellar phase. As we demonstrated in Figure 4, Ag precursor is actually within a columnar mesophase at thermolysis temperatures, and the anisotropic nucleation and growth forming Ag nanodisks is imparted by the columnar phase. The next materials, Pb, Bi, and Tl complexes all form isotropic phases and therefore the octahedra, hexagonal disks, and hexagon particles respectively shown are the result of the strong capping afforded by the thiolate molecules.

PbS octahedral have been previously synthesized in solvothermal reactions involving surfactants such as oleic acid and oleylamine or CTAB.²⁶,²⁷ However, here we demonstrate that the octahedral morphology can be synthesized with good size

control (46.6 \pm 5.0 wide, 66.1 \pm 3.7 nm end-to-end) by a more facile & scalable solventless thermolysis of Pb alkanethiolate precursor. Bi nanodisks have been reported previously from solventless thermolysis of Bi alkanethiolate, so our result corroborates the previous result.²⁸ It is noteworthy however in that we optimized the thermolysis process to produce a significant decrease in polydispersity (75.5 ± 11.6) nm diameter and 24.4 ± 3.0 nm thickness compared to 35-80 nm or 100-260 nm sizes). Lastly, the results from Tl alkanethiolate decomposition are notable in that an unexpected Tl_2S structure results, with a 1+ oxidation state differing from initial 3+ oxidation state. This result can be rationalized if Tl³⁺ undergoes redox with 1dodecanethiol to form Tl+ and disulfide. The mass retention of the isolated precipitate (Figure 3c) show mass retention of 47.8%, which is closer to a Tl monoalkanethiolate forming without disulfide (expected 54.3%). However, mass loss continues at a slow rate as the TGA temperature approaches 500 °C; likely what is happening is polymerization via polysulfide formation is occurring with thermolysis. This material might account for the irregular smaller particles observed in Figure 7h and some organic residue is noted (bottom right corner) although it is not clear why only the Tl is apparently unique in this regard. This finding is notable because few syntheses have targeted thallium sulfide NCs, and individual faceted crystals have not been observed.²⁹



Figure 6.7. Solventless thermolysis reactions of several metal alkanethiolates. a-d) show respective XRD patterns of NCs synthesized from Ag, Pb, Bi, and Tl alkanethiolates; e-h) show TEM images of the respective NCs.

6.5 Conclusions

We have delved into the structure and thermal properties of metal alkanethiolate complexes in order to better elucidate the system and understand the potential of these materials as nanocrystal precursors. As demonstrated here and previously, the fact that metal alkanethiolates are single-source precursors that can also behave as metallomesogens is intriguing because of their potential to serve as "liquid crystalline" like templates for controlling nanocrystal morphology. While here we find that the majority of metal alkanethiolates simply melt into isotropic phases, we do demonstrate that functional groups can be used to impart mesogenic stability. To appreciate this potential however, it would be ideal to design metal alkanethiolates which can undergo C-S bond thermolysis within the appropriate mesogenic regime, and so understanding how alkyl groups can affect C-S bond thermolysis bolsters control in this respect. There are clear limitations however, as solventless thermolysis reactions of Cd and In alkanethiolates for instance routinely produced non-dispersible nanocrystal aggregates. The system possesses great potential for shape control from solventless processes when a mesogenic phase is supported. The majority of metal alkanethiolates only appear to support isotropic melts however, which provide a facile and scalable option for the synthesis of equilibrium NCs as shown here, such as PbS octahedral and Bi nanodisks.

Chapter 6, in part, is currently being prepared for submission for publication of the material. **Whitney Bryks**, and Andrea R. Tao. The dissertation author was the primary investigator and author of this material.

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