2- & 3-D Assembly of Cluster and Coordination Materials

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

By

Natasha M. Khatri, B.S.

Washington, DC
September 9, 2016
2- & 3-D ASSEMBLY OF CLUSTER AND COORDINATION MATERIALS

Natasha M. Khatri, B.S.

Thesis Advisor: Sarah L. Stoll, Ph.D.

ABSTRACT

The assembly of materials with diverse properties has come to the forefront of attention recently due to the potential wide-ranging applications. Two systems are studied here: first, molecular clusters for their unique magnetism, and second, coordination polymers with a range of luminescent behavior.

Single molecule magnets (SMMs) have long been of great interest because of the potential ability to store information on the nanometer and sub-nanometer length scale. Organization of surface attached clusters, as well as magnetic characterization, has been investigated with the hope of potentially utilizing these molecules in nanodevices. The prototype and most well-known example of an SMM is the molecule studied here, Mn$_{12}$O$_{12}$(O$_2$CCH$_3$)$_{16}$, or Mn$_{12}$. The goal is to design ligands to confer self-organization, and study the effects of varying alkyl chain lengths on the 2- and 3-D self-assembly. Mn$_{12}$ readily undergoes ligand exchange, which is utilized to exchange the acetates with other carboxylic acids. We first studied the long-chained decanoic acid ligand as the prototype for surface assembly and then branched out to different chain lengths in order to determine the ligand effects on the packing of the molecules. The challenges were to maintain an intact core and to ensure full substitution upon ligand exchange before studying thin and thick film assemblies for controlled organization.

Luminescent materials have also come to attention in the pursuit for enhanced optical displays, LEDs, and sensors. Copper(I) halides are particularly attractive due to their ability to
assemble coordination polymers and similar networks that are highly emissive. The structure of these copper-organic frameworks largely depends on the nature of the organic ligand and the halide. Despite the rich structural diversity, there are some commonly observed structures of copper(I) halides in combination with mono- and bidentate ligands, including tetramers, single stranded polymer chains, and double stranded ‘stair’ polymers. We have synthesized a series of copper (I) iodide coordination polymers and select bromide analogs to investigate their photophysical properties. The focus was on polymers with the double stranded ladder or stair backbone. The luminescence at both room temperature and low temperature as well as the lifetime measurements were determined for all compounds.
The research and writing of this thesis is dedicated to my loving parents, Arun and Miriam, who have always encouraged and supported me throughout all of my endeavors, keeping me grounded through the most frustrating and stressful times.
ACKNOWLEDGEMENTS

First, I would like to thank my mentor, Dr. Sarah L. Stoll for her guidance and support throughout my time at Georgetown. She pushed me to do the best work possible with the kindness and patience that drove me to do my best and not let her down. Joining her group was my best decision and made these graduate years successful and enjoyable.

I would also like to thank my committee members, Dr. Jennifer Swift, Dr. YuYe Tong, and Dr. Edward Van Keuren. Their probing questions were appreciated and allowed me to better polish this thesis.

Much of this work would not be possible without many collaborations. Within our department, Dr. Kaveh Jorabchi was quite accommodating in allowing me to collect ESI-MS data and Dr. Jeffrey Bertke and Dr. Karah Knope spent much time helping me solve crystal structures. Dr. Julie Borchers at NIST Center for Neutron Research was instrumental in obtaining beamtime, running experiments, and analyzing neutron data. I learned a great deal from her knowledge and passion. Her colleagues Dr. Paul Butler and Dr. Brian Kirby also provided a great deal of help in scheduling beamtime and running the experiments. STM experiments were performed at Franklin & Marshall College with Dr. Kate Plass. Her willingness to train me and answer all of my questions was much appreciated. I also thank Dr. David Keavney for helping me obtain time and run my experiments on the synchrotron at the Advanced Photon Source. I appreciate Dr. Sam Lofland at Rowan University for sending me all the magnetic data I could ask for. Finally, Dr. Ana de Bettencourt Dias and Dr. Jorge Monteiro at University of Nevada at Reno for answering all of my emails and getting the luminescence data.

I would like to thank the Knope group for being so understanding and helpful in collecting crystal structures and solving the structures. Additionally, I thank Kelly Tran (Itchiye group) and Meg Dailey (Kertesz group), both who have been supportive colleagues, teaching me how to use computational programs, and great friends.

I cannot thank my lab-mates enough, both former and current members, all of whom were a constant source of entertainment, support, and knowledge throughout the years. They helped make my graduate experience memorable. I also thank the hard-working undergraduate students who have contributed to these projects.

I appreciate all of the wonderful friendships I have formed with other graduate students at Georgetown University. They helped the time pass quickly and provided great company as we went through grad school together.

Finally, I thank my parents, Arun and Miriam, and siblings, Anjoli and Jeremy, for all of their support, love, and patience. I owe them a lot for providing me with the best upbringing imaginable, full of laughter and love.

Natasha M. Khatri
# Table of Contents

Chapter 1. Introduction ................................................................................................. 1
  1.1 Introduction ........................................................................................................... 1
  1.2 Nanoscale Magnetic Materials ............................................................................ 2
  1.3 Design of Cluster Assembly ............................................................................... 6
  1.4 Probing the Assembly and Magnetic Behavior .................................................. 9
    1.4.1 Imaging and Organization ............................................................................. 10
    1.4.2 Magnetism ..................................................................................................... 12
    1.4.3 Bridging Assembly and Magnetism ............................................................... 14
  1.5 Assembly of Luminescent Materials ................................................................... 15
  1.6 Applications ......................................................................................................... 17

Chapter 2. Molecular Self-Assembly of Manganese Oxo Clusters ............................. 18
  2.1 Introduction ......................................................................................................... 18
  2.2 Experimental Section ......................................................................................... 20
    2.2.1 General Information ...................................................................................... 20
    2.2.2 SANS & Neutron Reflectometry .................................................................. 21
    2.2.3 STM ............................................................................................................... 22
  2.3 Results and Discussion ....................................................................................... 22
    2.3.1 Synthesis and Characterization of Mn_{12}(C_{10})_{16} .................................. 22
      2.3.1.1 Full Substitution ..................................................................................... 23
    2.3.2 Surface Organization ..................................................................................... 26
      2.3.2.1 X-Ray Diffraction .................................................................................. 26
      2.3.2.2 Neutron Diffraction .............................................................................. 28
      2.3.2.3 Surface Imaging ...................................................................................... 30
  2.4 Conclusion ........................................................................................................... 34

Chapter 3. Controlled Organization of Mn_{12} through Alkyl Chain Modification .... 35
  3.1 Introduction ......................................................................................................... 35
  3.2 Experimental Section ......................................................................................... 38
    3.2.1 General Information ...................................................................................... 38
    3.2.2 SANS ............................................................................................................ 42
  3.3 Results and Discussion ....................................................................................... 42
    3.3.1 Synthesis of Mn_{12} Substituted Clusters .................................................... 42
    3.3.2 Characterization of Substitution ................................................................... 43
    3.3.3 Thermal Properties ...................................................................................... 44
    3.3.4 Magnetic Properties ..................................................................................... 46
    3.3.5 X-Ray Diffraction ......................................................................................... 50
    3.3.6 Film Organization .......................................................................................... 63
  3.4 Conclusion ........................................................................................................... 54

Chapter 4. Magnetic Investigation of Mn_{12} Ordered Films ...................................... 56
  4.1 Introduction ......................................................................................................... 56
  4.2 Experimental Section .......................................................................................... 59
4.2.1 General Information .......................................................... 59
4.2.2 SQUID .............................................................................. 59
4.2.3 XAS/XMCD ................................................................. 60
4.2.4 SANS .............................................................................. 60
4.3 Results and Discussion ......................................................... 60
  4.3.1 Magnetism of Bulk Powders ........................................... 61
  4.3.2 X-Ray Magnetism ............................................................ 64
  4.3.3 Neutron Magnetism .......................................................... 68
4.4 Conclusion ......................................................................... 74

Chapter 5. Luminescence in Copper(I) Halide Extended Networks ....... 76
5.1 Introduction ...................................................................... 76
5.2 Experimental Section ......................................................... 79
  5.2.1 General Information ....................................................... 79
  5.2.2 Photophysical Characterization ....................................... 82
  5.2.3 Non-linear Optical Properties ......................................... 82
  5.2.4 Single Crystal X-ray Crystallography ............................... 83
  5.2.5 Computational Methods ................................................ 83
5.3 Results and Discussion ....................................................... 84
  5.3.1 Synthesis of CuI Coordination Polymers ......................... 84
  5.3.2 Structure Determination ................................................. 86
  5.3.3 Luminescence Studies ..................................................... 89
    5.3.3.1 Bromide-vs-Iodide ................................................. 90
    5.3.3.2 Chain-vs-Stair Structure ......................................... 91
    5.3.3.3 Ligand Binding Mode ............................................. 92
    5.3.3.4 Ligand Electronic Structure ................................... 92
  5.3.4 Luminescence Lifetime Measurements .......................... 95
  5.3.5 Non-linear Optical Properties ........................................ 96
5.4 Conclusion ...................................................................... 98

Chapter 6. Conclusion ............................................................ 99

References ............................................................................ 101
LIST OF FIGURES

Figure 1.1. Mn$_{12}$ structure................................................................. 4
Figure 1.2. Assembly of SMMs on surfaces............................................. 5
Figure 1.3. Mn$_{12}$ self-assembly on a gold surface ................................. 6
Figure 1.4. Langmuir Blodgett film of Mn$_{12}$ ........................................... 8
Figure 1.5. Mn$_{12}$ aggregates on gold.................................................... 9
Figure 1.6. Optimized orientation of Mn$_{12}$ on surfaces............................. 11
Figure 1.7. XMCD instrument schematic .................................................. 13
Figure 1.8. Structure types of coordination polymers.................................... 16

Figure 2.1. AC susceptibility of Mn$_{12}$(C$_{10}$)$_{16}$................................ 23
Figure 2.2. ESI-MS of less substituted cluster .......................................... 24
Figure 2.3. ESI-MS of more fully substituted cluster .................................. 25
Figure 2.4. ESI-MS of cluster after 1 week in solution ................................ 26
Figure 2.5. PXRD comparison of solvent effects ....................................... 27
Figure 2.6. Neutron reflectometry of Mn$_{12}$(C$_{10}$)$_{16}$.............................. 29
Figure 2.7. SANS of Mn$_{12}$(C$_{10}$)$_{16}$.................................................... 30
Figure 2.8. STM image of Mn$_{12}$(C$_{10}$)$_{16}$.......................................... 31
Figure 2.9. Geometry optimized model of localized group of clusters ............ 32
Figure 2.10. Fast Fourier Transform of STM image ................................. 33
Figure 2.11. STM image of less substituted Mn$_{12}$(C$_{10}$)$_{16}$.................... 34

Figure 3.1. Structure of modified Mn$_{12}$ cluster .................................... 36
Figure 3.2. FTIR spectra of substituted Mn$_{12}$ clusters .............................. 44
Figure 3.3. TGA of Mn$_{12}$(C$_{10}$)$_{16}$.................................................... 44
Figure 3.4. PXRD of cluster decomposed to Mn$_3$O$_4$ ............................... 45
Figure 3.5. Out-of-phase ac susceptibility of Mn$_{12}$(C$_9$)$_{16}$ ...................... 46
Figure 3.6. Arrhenius plot of Mn$_{12}$(C$_9$)$_{16}$ ........................................ 47
Figure 3.7. In-phase susceptibility of Mn$_{12}$(C$_9$)$_{16}$ ............................ 48
Figure 3.8. Bulk PXRD of Mn$_{12}$(C$_{10}$)$_{16}$ ................................. 50
Figure 3.9. (001) peak of substituted clusters ...................................... 51
Figure 3.10. Correlation between ligand chain length and d-spacing .......... 52
Figure 3.11. GI-PXRD of Mn$_{12}$(C$_{10}$)$_{16}$ .......................................... 53
Figure 3.12. GI-PXRD of Mn$_{12}$(C$_9$)$_{16}$ ........................................... 54
Figure 3.13. SANS of clusters with varied chain lengths ............................ 55

Figure 4.1. Hysteresis curves at 2K ..................................................... 61
Figure 4.2. Remnant magnetization curves .......................................... 62
Figure 4.3. Field-cooled and zero-field-cooled measurement ...................... 63
Figure 4.4. Isothermal magnetization of Mn$_{12}$(C$_{12}$)$_{16}$ .................... 64
Figure 4.5. Calculated XMCD spectra for $^{4}$Mn .................................. 65
Figure 4.6. XMCD spectrum of Mn$_{12}$ ................................................. 66
Figure 4.7. XMCD spectra of Mn$_{12}$ on gold and silicon ......................... 67
Figure 4.8. XMCD spectra of Mn$_{12}$(C$_{10}$)$_{16}$ .................................. 68
LIST OF TABLES

Table 3.1. Elemental analysis ................................................................................................. 43
Table 3.2. TGA weight loss ...................................................................................................... 45
Table 3.3. Energy barrier and relaxation times ........................................................................ 48
Table 3.4. Curie constant & Weiss temperature ...................................................................... 49
Table 3.5. Calculated ground spin states ................................................................................ 50

Table 5.1. Structural information for copper compounds ....................................................... 87
Table 5.2. Crystallographic information ................................................................................ 88
Table 5.3. Luminescence data ............................................................................................... 89
# ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Molecule Magnet</td>
<td>SMM</td>
</tr>
<tr>
<td>X-Ray Absorption Spectroscopy</td>
<td>XAS</td>
</tr>
<tr>
<td>X-Ray Magnetic Circular Dichroism</td>
<td>XMCD</td>
</tr>
<tr>
<td>Scanning Tunneling Microscopy</td>
<td>STM</td>
</tr>
<tr>
<td>Highly Ordered Pyrolytic Graphite</td>
<td>HOPG</td>
</tr>
<tr>
<td>Powder X-Ray Diffraction</td>
<td>PXRD</td>
</tr>
<tr>
<td>Grazing Incidence Powder X-Ray Diffraction</td>
<td>GI-PXRD</td>
</tr>
<tr>
<td>Small Angle Neutron Scattering</td>
<td>SANS</td>
</tr>
<tr>
<td>Fourier Transform Infrared Spectroscopy</td>
<td>FTIR</td>
</tr>
<tr>
<td>Elemental Analysis</td>
<td>EA</td>
</tr>
<tr>
<td>Electrospray Ionization Mass Spectroscopy</td>
<td>ESI-MS</td>
</tr>
<tr>
<td>Thermogravimetric Analysis</td>
<td>TGA</td>
</tr>
<tr>
<td>Superconducting Quantum Interface Device</td>
<td>SQUID</td>
</tr>
<tr>
<td>Second Harmonics Generating</td>
<td>SHG</td>
</tr>
<tr>
<td>Non-Linear Optics</td>
<td>NLO</td>
</tr>
<tr>
<td>Thermally Activated Delayed Fluorescence</td>
<td>TADF</td>
</tr>
<tr>
<td>Curie Constant</td>
<td>C</td>
</tr>
<tr>
<td>Weiss Temperature</td>
<td>θ</td>
</tr>
<tr>
<td>Pyrazine</td>
<td>Pyz</td>
</tr>
<tr>
<td>Quinazoline</td>
<td>Quinz</td>
</tr>
<tr>
<td>3-Benzoylpyridine</td>
<td>3-Bzpy</td>
</tr>
<tr>
<td>4-Benzoylpyridine</td>
<td>4-Bzpy</td>
</tr>
</tbody>
</table>
CHAPTER 1. INTRODUCTION

1.1 Introduction

Investigation of novel materials with a range of unique magnetic, optical, and electronic properties has come to the forefront of attention in recent years due to the evolution of technology. One of the biggest challenges in nanomaterial control is in assembling and positioning them in the desired locations within a composite material.\(^1\) The ability to control the ordering requires knowledge of the intra- and intermolecular interactions occurring throughout the materials. Furthermore, their attractive properties must be maintained. Our main focus is on the assembly of Single Molecule Magnet (SMM) clusters, probing both the organization and magnetism of films.

SMMs display unusually high paramagnetism due to the coupling of spins that causes a barrier for spin reversal.\(^2\) This results in both a hysteresis loop (with steps due to quantum tunneling between the spin-up and spin-down states) as well as an out-of-phase component to the magnetic susceptibility (due to the slow relaxation of spins).\(^3\) These properties have brought forward possibilities for the use of SMMs as magnetic memory in quantum computing devices. However, the exact placement of the clusters must be precisely controlled before any applications can be developed. Most research has focused on the first discovered and most highly studied SMM, Mn\(_{12}\)O\(_{12}\)(C\(_2\)H\(_3\)O\(_2\))\(_{16}\), due to the easy modification of the shell of organic ligands (C\(_2\)H\(_3\)O\(_2\)).\(^4\) Clusters of other transition metals and rare-earth elements have also been synthesized though in the quest to obtain as large a magnetic moment at as high of a temperature as possible.\(^5\)–\(^9\) Attempts to prepare addressable films of these materials have had mixed results, with aggregation or loss of magnetism observed, so further effort must be made to reliably apply these materials.
In parallel, as we describe in Chapter 5, luminescent copper halides have been shown to organize into polymeric frameworks, which sparked interest in these materials as well. Chains, ladders, square grids, and porous structures can be assembled with a variety of ligands, which allows for the tuning of their optical properties. Copper halide materials are of interest due to the metal earth abundance and low cost, while displaying effective electroluminescent behavior. Both three- and four-coordinated Cu(I) complexes have been developed in the hopes of obtaining a range of luminescence with lifetimes that indicate thermally activated delayed fluorescence, or TADF. This process allows for fast and efficient luminescence.

This thesis focuses on the assembly of materials to address the key concern of preparing a variety of ordered materials with addressable properties. The first part of this introduction will discuss magnetic molecular materials and the distinctive SMM behavior. Then, methods for attempted organization and investigation of the properties of the films will be discussed in the second and third sections. The fourth section will detail the assembly of luminescent materials, followed by applications in the final section.

1.2 Nanoscale Magnetic Materials

With the evolution of technology comes a pressing need to develop new materials, so much multi-disciplinary research is being devoted to this endeavor. This work focuses on the discovery and design of materials with a variety of suitable properties applicable for device development, which requires an extensive understanding of their structure and processes. This requires study from the atomic all the way up to the macro scale. Types of materials also range between metals, clusters, semiconductors, and polymers.
Immense interest has been garnered in nanoscale materials due to their range of attractive properties present as an intermediate between the molecular level and bulk material. The small size of these materials allows for remarkable magnetic, optical, electronic, and chemical properties not present in the bulk, thought to be due to the increased surface area. The potential of nano-sized particles has in fact been recognized for thousands of years even though the understanding of them has only been investigated in the past couple of decades with the development of new characterization tools. Despite incomplete understanding, ancient cultures observed different optical properties based on size and thus utilized colloidal dispersions as pigments in stained glass windows and pottery. As methods of characterization developed, an interest in the fundamentals of nanomaterials grew. The advantages of these materials became apparent, as size-dependent magnetic and electronic properties were also observed. There exist distinctions in terminology based on size, composition, and morphology of these materials. First known as “ultrafine particles,” the mainstream term “nanoparticle” is defined as a particle with a diameter less than 100 nm, though the most interesting properties have been observed at dimensions smaller than 50 nm. Crystalline nanoparticles are often named based on their shape seen through imaging techniques, including but not limited to nanosphere, nanorod, and nanoflowers. Smaller materials composed of less than $10^4$ particles and a diameter on the order of less than 10 nm are referred to as clusters, with the added distinction of being atomically precise species.

One class of cluster materials are SMMs, which exhibit superparamagnetic-like behavior below their blocking temperature. The first discovered and most highly studied SMM was $\text{Mn}_{12}\text{O}_{12}(\text{C}_2\text{H}_3\text{O}_2)_{16}$, or simply $\text{Mn}_{12}$. The cluster is composed of an heterometallic inner core of
Mn$^{3+}$ and Mn$^{4+}$ and an outer shell of organic ligands (Figure 1.1). Interest developed in these clusters due to their high spin of S=10 and large anisotropy barrier, raising hope that it could be used as magnetic memory since each molecule holds a magnetic moment.$^{2,23}$

**Figure 1.1. Mn12 structure.** The purple spheres represent the four Mn$^{4+}$ atoms and the green spheres are the eight Mn$^{3+}$. Reproduced with permission from John Wiley and Sons.$^{2}$

The advantage these clusters have over other nanoparticles is that they are molecular, atomically precise and perfectly monodisperse. The challenge, however, is organizing these materials in such a way that the surface placement can be controlled.$^{24}$ Efforts to organize SMMs on surfaces has been undertaken with other transition metal complexes, such as Fe$_4$$^{2,25}$, and lanthanide clusters, like bis(phthalocyaninato) terbium(III), or TbPc$_2$.$^{7,26-29}$ The most promising advance has been to utilize the butterfly shape of TbPc$_2$ to organize them on gold, graphite, and carbon nanotubes. The flat rings of the ligand allowed for non-covalent interaction with these substrates (Figure 1.2).
Figure 1.2. Assembly of SMMs on surfaces. Attempts to assemble SMMs on surfaces take advantage of the shape of TbPc$_2$ to interact on different surfaces, including (a) gold, (b) graphite, and (c) carbon nanotubes. Reproduced with permission from the Royal Society of Chemistry.

The Fe$_4$ SMMs on the other hand have been modified with thiol groups, such that the gold-thiol interactions could anchor them to gold surfaces. This latter approach has been applied to Mn$_{12}$, taking advantage of its ability to undergo ligand exchange with other carboxylic acids according to scheme 1.1:

$$\text{Mn}_{12}O_{12}(CH_3\text{COO})_{16} + C_nH_{2n}OOH \rightarrow \text{Mn}_{12}O_{12}(C_nH_{2n-1}O_2)_{16} + CH_3\text{COOH} \quad \text{(Scheme 1.1)}$$

It is possible to control not only the terminal ends, but also the size and shape of Mn$_{12}$ clusters through alteration of its ligand shell. Thiol terminated carboxylic acids could exchange with the acetates, seemingly providing a means to organize the clusters on surfaces, as was previously demonstrated by our group with Mn12, followed by the work of Bucher with Mn12 derivatives (Figure 1.3).
The ability for modification has brought much attention to these materials since the possibilities for ligand substitution is seemingly endless. Thus, there is much ground to cover for investigation into the fabrication of enhanced nanostructures. The interest in discovering novel structures, as well as their controlled assembly is what drives much of the work on materials synthesis. Understanding the interactions between the molecules is paramount for making advances in the fundamentals of device development.

1.3 Design of Cluster Assembly

Though much work has been invested in the discovery of new materials, a key factor is the ability to control their placement and organization on surfaces while maintaining their attractive properties. There are two approaches taken for assembly: top-down and bottom-up.
The former relies on micromachining materials to the desired sizes and patterns, therefore being subtractive in nature. This includes photolithography, mechanical machining, laser and electron beam processing, and electrochemical removal. In contrast, bottom-up methods takes already developed molecules or clusters and assembles them in a pre-tailored architecture, relying on the energetics of the assembly process as a guide. Since this approach allows for the preparation of large quantities of material, it is more attractive for application.

Great interest has been taken in the design and syntheses of inorganic-organic hybrid frameworks by using metal clusters as fundamental building blocks and organic ligands as spacers. Changing the reaction conditions and ligands of inorganic-organic hybrid materials attains a range of properties. The organization of these materials is very important, so attempts have been made to arrange them into superlattice architectures through self-assembly in order to create porous materials with tunable pore sizes, as Zheng proposed with linked $[\text{Cd}_8(\text{SPh})_{12}]^{4+}$ clusters with dye molecules. The controlled assembly of clusters is greatly important in the enhancement of materials design by creation of composite materials. Many other studies to organize clusters includes synthesis of metal-organic frameworks (MOFs) to form 3-D networks. Forming the networks and varying the pore sizes could allow for other materials to be contained within the frameworks, enabling unique properties for device fabrication. The organization of 2-D films of magnetic clusters have been attempted through a number of techniques, including templated film growth, spinoidal dewetting, directed-assembly, and self-assembly.

Langmuir Blodgett films have been used to form multilayer films of clusters by placing them in a media of lipids and altering the lipid:cluster concentrations (Figure 1.4). The clusters
trapped within the films displayed hysteresis with weak coercivity, consistent with other substituted Mn\textsubscript{12}. Interestingly, the field was unable to orient the molecules, contrary to what has been observed with crystalline powder and frozen glass\textsuperscript{45,46}. The same phenomenon was seen with polyoxometalates and ferratin molecules, which were successfully organized in monolayers while preserving the paramagnetic behavior of the bulk material\textsuperscript{45}.

![Diagram](image)

**Figure 1.4. Langmuir Blodgett film of Mn\textsubscript{12}.** Adjusting the lipid:cluster ratio showed potential to control the assembly of Mn\textsubscript{12}. Reproduced with permission from John Wiley and Sons\textsuperscript{44}.

Chemical approaches for assembly have taken advantage of self-assembly with both direct and indirect attachment of the clusters. The indirect method relies self-assembled monolayers, where functionalized surfaces are carboxylate terminated, which can undergo ligand exchange with Mn\textsubscript{12} clusters, organizing the SMMs into layered structures. This method has produced mixed results, with some forming ordered films, and others disordered aggregates (Figure 1.5). Either way, thick films exhibited hysteresis, behaving like the bulk, whereas the monolayers seemingly lost this magnetization\textsuperscript{35,47}. The direct method first relies on ligand exchange of the acetates surrounding the Mn\textsubscript{12} core with thiol terminated carboxylates, allowing the clusters to covalently bond to gold surfaces. Unfortunately, this resulted in disordered films as the clusters tend to aggregate.
A promising technique seems to be the nanopatterning, where lithography is employed to first template substrates to direct the assembly of clusters. Spinoidal dewetting patterning, is one such method, which develops through either nucleation and growth of holes, or fluctuations of the film surface with the emergence of a characteristic wavelength that is controlled by the thickness. The structured surfaces direct the deposition and growth of the films, where the pattern has the potential to control the placement. Early investigations reported consistent magnetic behavior and a promising outlook for achieving addressable films. However, there is still a great need for advanced control of the materials and investigations into both intra- and inter-cluster interactions. Addressing the behaviors will allow for greater control, and thus, more effective means of preparing addressable films.

1.4 Probing the Assembly and Magnetic Behavior

Being able to attach clusters to surface is only one part of the challenge. The structural and magnetic behavior must be explored in order to determine the extent of ordering and whether the properties are maintained. Since no one method exists to fully investigate these materials, a
combination of individual techniques are employed to provide a complete understanding of the entire system.

1.4.1 Imaging and Organization

Both structural and morphological characterization are important for obtaining full understanding of materials. Methods such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are excellent tools for morphology determination. They utilize electron beams to project a magnified image of the specimen by striking individual atoms and detecting electrons, thereby extracting surface detail and inner structure. A suspension can be dropped on a grid to determine the packing of particles. With this technique, the close-packing of nanoparticles on surfaces has been discovered. Cluster materials, however, can be too small to be well imaged by these techniques and the risk of degradation by the electron beam is high. Therefore, Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM), which can image surfaces down to the atomic scale has become a powerful characterization tool. STM is limited to metals and semiconductors since a tunneling current is employed, while AFM enables detection of insulating surfaces.

STM records images through electron transfer between an atomically precise tip—usually composed of a metal such as tungsten or Pt/Ir—and the sample surface, an exchange which involves very few atoms. The image results from spatial variation of the tunneling current or of the tip height, since the tunneling current decreases exponentially with increased distance between the sample and tip. The driving motion of the instrument is controlled by a piezoelectric scanner, which changes the dimensions according to applied voltage. This allows for images to be obtained in two different modes: constant height and constant current. With a constant height,
the tip is restricted to a fixed vertical position to detect changes in tunneling current to probe interaction, while the latter allows for its movement with a fixed current. Regardless of the mode, one of the most important parameters that affects the surface imaging is the bias voltage, which is varied during imaging to obtain the best image. This determines which levels of the excited state participate in the tip-sample electron transfer. A positive voltage indicates a flow of electrons from the tip to the surface while a negative value represents an electron flow from surface to tip. Altering the bias also allows affects what components of the film are measured, i.e. substrate or different layers.

As such, STM has been heavily utilized to characterize different clusters on surfaces to determine cluster sizes and packing on the surface, as well as substrate effects. Highly ordered pyrolytic graphite (HOPG) is commonly used, though Ge(100), Si(100), and Au(111) have also been used in previous cluster studies. One such study of Mn$_{12}$ on Au(111) found disordered aggregation of the clusters, sparking interest in molecular modeling to investigate interactions with the substrate and between molecules. It was found that the molecules preferentially adopt a tilted configuration on the surfaces, forming complex aggregates as calculations indicate this canted behavior to have the greatest molecule-molecule and molecule-substrate binding energy (Figure 1.6).

**Figure 1.6. Optimized orientation of Mn$_{12}$ on surfaces.** Calculations depict stronger interactions between two clusters (left) and cluster-substrate (right) when canted on a surface. Reproduced with permission from Nature Publishing Group.
In order to obtain highly-ordered arrays of SMMs, gold-thiol interactions have been taken advantage of by substituting the acetates with thiol groups. One such study pre-patterned a Si(100) surface with Au dots, then deposited thiol substituted clusters on top.\textsuperscript{55} Ordered arrays were formed, with each 100 x 100nm\textsuperscript{2} nanodot containing approximately 300 Mn\textsubscript{12} clusters. However, the magnetization of clusters on the gold is unknown. Since direct deposition of Mn\textsubscript{12} on Hall microprobe magnetometer revealed that the magnetic properties of the core remained intact through the process of liquid phase deposition, it is assumed that these arrays also maintain their magnetic behavior. In order to confirm, X-Ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) studies are required (as will be discussed in the next section).

1.4.2 Magnetism

The defining characteristic of an SMM is a frequency dependent out-of-phase component of the AC susceptibility. This technique monitors the response of the magnetic moment to an externally applied oscillating magnetic field.\textsuperscript{56} A peak occurs for materials that have a slow relaxation of spin and appears when the magnetization of the sample cannot stay in phase with the alternating field.\textsuperscript{31} An Arrhenius plot can be constructed from the observed peak to determine the effective energy barrier and relaxation time. SMMs have exhibited long relaxation times to the order of months and years, due to high energy barriers.\textsuperscript{57} For Mn\textsubscript{12}, this observed barrier is 65K since it experiences quantum tunneling of molecular spins over the barrier.

While all SMMs display this out-of-phase component, it has been suggested that false signals can be observed due to intermolecular interactions and phonon bottlenecks.\textsuperscript{58,59} As such, a full hysteresis curve can confirm the SMM behavior. Below the blocking temperature, SMMs
behave similarly to superparamagnets, displaying increased coercivity. The hysteresis for Mn$_{12}$ exhibits steps due to the quantum tunneling of magnetization.

**Figure 1.7. XMCD instrument schematic.** XMCD takes advantage of circularly polarized x-rays in a magnetic field in order to provide information about the spin states of the compounds. Reproduced with permission from Elsevier.$^{60}$

Since the overall goal is organization on surfaces, it is important to investigate the magnetism of films. In this regard, synchrotron radiation and neutron experiments are extremely useful and have been recently applied to SMM studies. X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) at synchrotron light sources have the advantage of providing oxidation state information, which is particularly important for materials like SMMs that contain redox-active ions.$^{61}$ By measuring the L$_{2,3}$ edge, which measures the absorption of the 2p $\rightarrow$ 3d transitions, the composition of Mn can be determined. Since Mn$_{12}$ is composed of both Mn$^{\text{III}}$ and Mn$^{\text{IV}}$, this technique can provide a measure of whether the oxidation state of Mn has occurred. The first XAS studies on bulk samples found the expected amounts of Mn$^{\text{III}}$ and Mn$^{\text{IV}}$ in Mn$_{12}$ complexes with different thiolate ligands. However, upon measurement of thin film monolayers, there was an unexpected reduction to Mn$^{\text{II}}$ observed for most cases.$^{62,63}$ It was postulated that the solvent, ligand, and deposition methods play a role in the reduction.
1.4.3 Bridging Assembly and Magnetism

Though a single method of characterization cannot provide all the necessary information on a system, neutron scattering can provide a means of investigating both structure and magnetism, supplementing the information gleaned through the other methods. Previous neutron studies on other SMMs investigated the kinetics of relaxation of spins, spin dynamics, and excited state transitions. Neutron diffraction is a valuable tool for these types of characterization since neutrons are sensitive to spin and elemental isotopes. It is especially useful for probing thin and thick films. Similar to x-ray diffraction, neutrons scatter according to Bragg’s Law. However, the scattering occurs due to interaction with the nucleus rather than the electron cloud. Two different types of neutron diffraction experiments that are used in this thesis are Neutron Reflectometry and Small Angle Neutron Scattering (SANS). Neutron reflectometry provides depth information, probing the organization of the layers perpendicular to the surface of the film \((z)\). On the other hand, SANS provides information on how the particles are organized across a surface \((x-y)\). Thus, these two methods can provide complementary data on the assembly of different materials.

Both techniques identify the Bragg peak of a superlattice. For reflectometry this indicates the distance between layers; for SANS it’s the intercluster spacing across the layer. Obtaining a well-defined peak at the expected Bragg peak is indicative of well-ordered systems. Magnetic ordering can also be investigated by determining the position of this peak upon application of an external magnetic field. Applying a spin-polarized beam through the use of spin flippers in front of the sample allows only neutrons with spins pointed in the same direction—either spin-up or
spin-down—to pass through to the sample. The subsequent scattering provides details about how the clusters are magnetized on the surface.

1.5 Assembly of Luminescent Materials

Additional interest in material fabrication provoked research into materials with attractive optical properties. Gold nanoparticles were among the first studied in this regard, dating back to the 1800s with Faraday’s investigations. Further studies by Mie quantified the extinction, scattering, and absorption cross-sections of gold, finding a dependence on the size of the particles. Many of the synthetic methods in preparing optical nanoparticles have been adapted for use in the present day, with advances in the techniques and characterization methods. As this research evolved, other transition metals, such as Cu(I), Ir(III), and Pt(II), and lanthanides have become the focus for their phosphorescent behavior. Three- and four-coordinate Cu(I) has been investigated in this regard, with an interest in tuning the luminescence based on ligand and coordination sphere. As such, a range of luminescence has been observed, with interest being renewed due to the thermally activated delayed fluorescence (TADF) which has been shown to give fast and efficient luminescence.

Optical properties are of great interest for the development of new materials. Nanoparticles have been shown to display tunable optical properties, but interest has also been turned to coordination polymers that exhibit a wide range of photoluminescence. The formation of 1- and 2-D composites have been developed, for their own unique photoluminescent abilities. Lanthanide networks were found to have directed assembly due to the hydrogen bonding between ligands. Transition metals are more commonly used due to the flexibility of their coordination environments. These polymers have been shown to adopt a
variety of motifs, depending on the coordination sites, such as chains, ladders, helices in the 1D, grids and t-shapes in the 2D, and porous 3D materials (Figure 1.8).\textsuperscript{10}

![Diagram of coordination polymers]

**Figure 1.8. Structure types of coordination polymers.** Coordination polymers can take on a variety of structure types, a few of which are depicted here. Reproduced with permission from Elsevier.\textsuperscript{10}

These different structure types have been taken advantage of to obtain ranges of photoluminescence and organize the frameworks for use in structured devices. Assembly of materials still remains a challenge, however, as many possibilities exist for obtaining the most efficient design of heterostructures.

Copper is known to form both complexes and coordination polymers that are highly emissive even at room temperature.\textsuperscript{76–78} Halide complexes have been shown to produce efficient electroluminescence, which is attractive for thin film devices.\textsuperscript{77} Bridging the two, copper halide coordinated networks can be synthesized to establish efficient luminescent materials. Furthermore, investigating these materials further for possession non-centrosymmetric space groups allows for the potential to emit second harmonic generating (SHG) light upon laser irradiation.\textsuperscript{79,80} In addition to structural constraints, the presence of a charge transfer transition has also been identified as an important electronic feature that leads to second-order non-linear
optical (NLO) response.\textsuperscript{81} Alignment along a specific direction of related chromophores has been observed to increase SHG efficiencies in organic salts.\textsuperscript{82}

1.6 Applications

The unique properties detailed here allow for a wide range of application in numerous industries. Traditional applications include use in stained glass windows and as catalysts, but in recent years this has evolved to include magnetic drug delivery, hypothermic cancer therapy, contrast agents in magnetic resonance imaging, magnetic and fluorescent tags, solar photovoltaics, nano-barcodes, and emission control in diesel vehicles.

SMMs in particular were initially brought to attention due to their high spin, providing hope that they could be utilized as magnetic memory. This idea that each individual molecule would hold a bit of information in electronic devices was exciting and promoted much interest in these materials. Unfortunately, in order for them to be applied, the properties must be upheld at room temperature or higher, but the highest known blocking temperature is about 20K.\textsuperscript{83} Nonetheless, increased work is being performed to apply SMMs in devices, as quibits for supercomputers or in spintronics. Modification of SMMs has also been applied as use as contrasting agents for MRI purposes or for drug delivery. As knowledge increases with greater investigations into the behaviors of clusters, the applications of clusters greatly increase. Luminescent materials with a range of emissions are of interest for OLED devices, biological sensors, catalysis, and fluorescent dyes.\textsuperscript{70,84} As technology evolves, so does the need to develop more efficient materials for devices. The development of these luminescent polymer fills the need and enhances functionality of a variety of materials.
CHAPTER 2. MOLECULAR SELF-ASSEMBLY OF MANGANESE OXO CLUSTERS

2.1 Introduction

Materials with diameters of 1-2 nm, either atomically precise clusters or monodispersed nanoparticles, have been investigated with the goal of controlling the ensemble structure.\textsuperscript{85,86} Ordered structures from discrete building blocks have been synthesized that exhibit novel optical,\textsuperscript{87} electronic,\textsuperscript{88} or magnetic\textsuperscript{89} properties. The properties are the result both of the individual components (composition, size, shape) and the organization of the resulting solid. The rules that determine assembly are actively being developed, but already the collective properties appear to be sensitive to the symmetry,\textsuperscript{90} inter-particle distance,\textsuperscript{91,92} and the number of layers\textsuperscript{93} of nanoclusters in the final material. The collective properties of the superlattice can be distinct from both the bulk material and the individual nanocrystals.\textsuperscript{94}

Molecular clusters have been used as a building block to form 2 and 3D arrays. For example, polyoxometalates (POMs), can be used to form covalent hybrid materials,\textsuperscript{95} as well as POM monolayered arrays.\textsuperscript{96} Several strategies have been identified for controlled assembly, that generally utilize shape and size, as well as surface chemistry to control inter-particle or inter-cluster interactions. For nanoparticles a highly versatile approach has been developed by Mirkin, which takes advantage of recognition of biomolecules such as nucleic acids.\textsuperscript{97} Design rules have been developed for these novel systems, producing a large number of structure types, built with interchangeable nanoparticle cores.\textsuperscript{98}

There is significant interest in monolayers of 2D organized molecules, which are considered to be critical for nanoscale magnetic device development.\textsuperscript{99} Like their counterpart for organic monolayers where molecular electronics are part of the long term goal. Among the
recent studies of SMMs on surfaces, the evidence has been growing to suggest that Mn$_{12}$ is too ‘fragile’ to maintain the novel magnetic properties while organized on a surface.$^{100}$ Quantum tunneling of magnetization has been observed for monolayers of SMM clusters such as Fe$_4$$^{100}$ and [(Pc’)$_2$Tb(III)] (Pc’=octa(butoxy)-substituted phthalocyaninato).$^{101}$ There remain many unanswered questions as to the role of the substrate, the nature of the coordinating ligands when surface bound, as well as the relative orientation of molecules to each other and to the surface.

Surface patterning of Mn$_{12}$ has been achieved through some version of Self-Assembled Monolayers (SAMs), utilizing gold-thiol chemistry. Our group has grafted the cluster onto carboxylate terminated SAMs to form a monolayer of cluster,$^{34}$ whereas others have used Mn$_{12}$ substituted with thiol terminated ligands, to form a surface one layer thick.$^{102}$ It is also possible to prepare analogous films starting with a functionalized surface and cluster ligands with complementary groups for coupling.$^{103}$ Each of these self-limiting surface reactions result in clusters bound to gold surfaces through a thiol ligand. However, direct deposition of Mn$_{12}$ onto gold surfaces has demonstrated a lack of long range ordering,$^{63}$ forming disordered aggregates and filaments.$^{48}$ Mn$_{12}$ with ligands with peripheral phenyl groups (e.g. Mn$_{12}$O$_{12}$ (O$_2$CC$_6$H$_4$C$_6$H$_5$)$_{16}$(H$_2$O)$_4$), can physio-sorb on gold, where the aggregation into wires along the surface is even more pronounced.$^{63}$ Efforts to control 2D ordering almost all involve gold-thiol interactions. However, it has become clear that gold is a poor choice of substrate because it results in electron transfer to the cluster,$^{62}$ with deleterious effects on the magnetic properties.$^{104}$ It remains unclear whether the loss of magnetic properties is the result of chemical reduction, which could be avoided with an alternate substrate, or if the anisotropy of the cluster is disturbed
as a result of the change in symmetry when some ligands are covalently attached to the surface and some not.

Our approach avoids symmetry changes and surface grafting, but does not address the relative orientation of the cluster moment to the substrate, which would also need to be controlled. Our primary interest is understanding the mechanism of assembly, in comparison to organic molecules and nanoparticles. Here we demonstrate that substituting the acetates in $(\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CCH}_3)_{16})$ or $\text{Mn}_{12}$, the prototypical single molecule magnet, with a long alkyl chain carboxylate we have imposed lamellar ordering. This new cluster, $\text{Mn}_{12}(\text{C}_{10})_{16}$ where C$_{10}$ = decanoic acid, exhibits a peak in the $\chi''$-vs-$T$, the distinguishing characteristic of single molecule magnets. $\text{Mn}_{12}$ substituted with gallate-derivatized ligands have also resulted in highly ordered mesophases. These molecules exhibit either smectic or 3D organized mesophases, and maintain their single molecule magnetic properties. The ligands enforce the assembly, and are stabilized by the tendency to preferentially align parallel to one another. Although these molecules have been used to form films, unfortunately both STM and AFM (probes of the monolayers) fail due to the molten character of the molecules. These ligands induce self-assembly, but inhibit topographic studies. By contrast the decanoic acid substituted clusters here, form stable monolayers easily observed by STM.

2.2 Experimental Section

2.2.1 General Information

$\text{Mn(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}$ and decanoic acid were purchased from Sigma-Aldrich Chemical Co. $\text{KMnO}_4$ was obtained from J.T. Baker Chemicals. All chemicals were used as received. The $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}$ was prepared according to published procedures. Infrared spectra were
measured in the range 450-4000 cm\(^{-1}\) as pressed pellets in KBr on a Nicolet 380 FT-IR. Thermal analysis was performed on a TGA Q50 TA instrument. TGA data were studied from samples in a platinum pan, from 20-500\(^\circ\)C with a heating rate of 10\(^\circ\)C/min. Elemental (C, H, N) analysis was performed using a Perkin Elmer 2400 Series II CHN/O Analyzer. X-ray powder diffraction patterns were obtained using a Rigaku Ultima IV X-Ray powder diffractometer with Cu K\(\alpha\) radiation and a scintillation counter. The grazing incidence attachment allowed for the attainment of x-ray patterns for thin films at varied incidence angles.

\[\text{Mn}_{12}\text{O}_{12}(\text{C}_{10}\text{H}_{19}\text{O}_2)_{16}, \text{ or Mn}_{12}\text{C}_{16}\]

was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Decanoic acid (0.6969 g, 4.05 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn\(_{12}\) solution under N\(_2\). The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with acetonitrile to remove excess decanoic acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm\(^{-1}\)): 3530 (m), 2957 (w), 2922 (s), 2851 (s), 1586 (s), 1505 (m), 1415 (s), 1112 (m), 720 (w), 638 (s), 541 (m). Anal. Calcd for Mn\(_{12}\)O\(_{12}\)(C\(_{10}\)H\(_{19}\)O\(_2\))\(_{16}\): C, 52.46; H, 8.58. Found: C, 52.23; H, 9.2. Percent yield 49%.

2.2.2 SANS & Neutron Reflectometry

Small angle neutron scattering (SANS) was performed on NG7 30m instrument at the NIST Center for Neutron Research. In order to increase the scattered intensity, five silicon wafers containing dropcast Mn\(_{12}\)(C\(_{10}\))\(_{16}\) were stacked. Room temperature scattering was
measured with detector settings of 9 m and 1 m-offset in order to cover a large Q range. Neutron Reflectometry experiments were performed on the PBR reflectometer at the NIST Center for Neutron Research with one silicon wafer containing dropcast $\text{Mn}_{12}(\text{C}_{10})_{16}$. A large Q range was covered to obtain higher order peaks.

2.2.3 STM

A drop of a saturated 1-phenyloctane solution containing the compound to be imaged was placed on freshly cleaved highly oriented pyrolytic graphite (HOPG, SPI-1 grade, Structure Probe, Inc.) to obtain a self-assembled monolayer. A Nanoscope E STM (Veeco) was used for all imaging. The tips were made from Pt/Ir wire (80/20%, California Fine Wire) by mechanical cutting, and the quality of the tips was verified by scanning bare HOPG prior to imaging. All images are unfiltered. Scanning Tunneling Microscopy (STM) imaging was performed under ambient conditions with setting of about 500 pA of current and 500 mV of bias voltage. Images were analyzed with and exported from NanoScope Analysis 1.40.

2.3 Results and Discussion

2.3.1 Synthesis and Characterization of $\text{Mn}_{12}(\text{C}_{10})_{16}$

The first steps in characterizing the $\text{Mn}_{12}(\text{C}_{10})_{16}$ clusters were to confirm the core remained intact and that full substitution was achieved. The characteristic Mn-O stretching frequency in FTIR analysis is present between 450 and 700 cm$^{-1}$ indicating that the core remained intact upon ligand exchange and elemental analysis also confirms that full substitution is reached. Mass spectroscopy experiments were conducted to more precisely determine substitution (see section 2.3.1.1).
It was also important to verify that the magnetic properties of the cluster maintained the characteristic SMM behavior, which was probed through ac susceptibility measurements. The out-of-phase peak in the ac susceptibility is the defining characteristic of an SMM, as observed in the Mn$_{12}$(C$_{10}$)$_{16}$ cluster (see Figure 2.1). The presence of phase dependent peaks confirms that the substituted cluster acts as an SMM. Additionally, the energy barrier and relaxation times were calculated to be 64.6K and $2.72 \times 10^{-8}$ s, respectively. Both these values fall within the range reported for other substituted Mn$_{12}$ SMMs of 60-70K and $10^{-10}$-$10^{-8}$ s. Further characterization of the magnetic properties of the clusters are detailed in chapters 2 and 3.

**Figure 2.1. AC susceptibility of Mn$_{12}$(C$_{10}$)$_{16}$.** The out-of-phase component of the AC susceptibility is frequency dependent, as is characteristic of SMMs.

### 2.3.1.1 Full Substitution

Though FTIR supported the presence of an intact core and CH stretches indicative of decanoic acid substitution, it is not sensitive enough to confirm full decanoic acid replacement.
We know that a loss of the peak in $\chi''$ vs. $T$ appears when less than 16 ligands are substituted, but mass spectroscopy provides a detailed description of the extent of ligand substitution.

Thus, investigation of the $\text{Mn}_{12}(\text{C}_{10})_{16}$ was performed with Electrospray Ionization-Mass Spectroscopy (ESI-MS). This technique involves dissolving the $\text{Mn}_{12}(\text{C}_{10})_{16}$ in a 90% acetonitrile solution and directly injecting it into the instrument. A high voltage is applied to form an aerosol out of the cluster, producing ions out of the molecule that are unlikely to fragment. As such, the resulting spectrum always displays the molecular ion.

![Figure 2.2. ESI-MS of less substituted cluster.](image)

This sample was synthesized by addition of $\text{Mn}_{12}$ dropwise to the ligand.

Here, ESI-MS was employed to determine the extent of substitution in solution of the cluster and how the equilibria varied with time. Samples that were synthesized with different methodical order, (1) the cluster was added to the ligand versus (2) ligand added to the cluster, were
investigated. Comparing the two, it is clear in Figure 2.3 that adding the ligand drop-wise to the clusters results in the most complete substitution (as compared to Figure 2.2). However, in both cases, less substituted clusters were also present, as well as extra decanoic acid.

**Figure 2.3. ESI-MS of more fully substituted cluster.** Ligand is added dropwise to the cluster in this sample.

Measurements were also taken of the same clusters in solution after remaining in the solution for at least a week, as shown in Figure 2.4. In this case, it appears that over time, the equilibrium favors Mn$_{12}$(C$_{10}$)$_{16}$, as the monosubstituted Mn$_{12}$(C$_{10}$)$_{15}$(C$_{2}$)$_{1}$ ratio decreased. These results suggest that although ligand substitution has been reported to occur rather quickly, multiple equilibria are present. Steric effects may kinetically slow down the addition of the final ligands in the clusters. Therefore, the synthesis of the fully substituted clusters was optimized by allowing it to remain in solution for longer times and driving the exchange with three toluene washes to take advantage of the toluene-acetic acid azeotrope.
Figure 2.4. ESI-MS of cluster after 1 week in solution. The sample of the more fully-substituted cluster where ligand was added to the Mn$_{12}$ was left in solution for 1 week.

2.3.2 Surface Organization

The key goal in investigating these clusters is to drive close-packing based on the size and spherical shape of the Mn$_{12}$ with long-chained alkyl groups. In order to determine whether the clusters form organized films, x-ray diffraction and neutron scattering experiments were performed on thick films, while STM was enlisted to image the monolayer.

2.3.2.1 X-ray Diffraction

The packing structure of the clusters were the biggest concern in this study. Bulk powders displayed a striking patter, which will be discussing in Chapter 3. Here x-ray diffraction (PXRD) measurements were conducted on films to determine the packing structure in the z-direction. Mn$_{12}$(C$_{10}$)$_{16}$ was dissolved in both toluene and hexanes to determine any solvent
effects, and deposited on the aluminum sample holders. Measuring the diffraction angle with the scintillation counter, a defined lamellar pattern, with identifiable (001), (002), and (003) peaks, was observed (Figure 2.5).

![Figure 2.5. PXRD comparison of solvent effects.](image)

Figure 2.5. PXRD comparison of solvent effects. Comparison of the PXRD pattern shows possible solvent effects, where hexanes produced broader, less intense lamellar peaks than did toluene.

This indicates ordering of the clusters into layers, with an interlayer separation of 2.76 nm and 2.82 nm when deposited in hexanes versus toluene, respectively. The higher order peaks observed for hexanes also appear broader, indicative of increased disorder than the films in toluene. The slight differences in these distances indicate that the packing is somewhat affected by the solvent. Solvent effects have been documented with molecular assemblies\textsuperscript{107}, most notably by Sessoli in efforts to prepare monolayers of Mn\textsubscript{12} on gold.\textsuperscript{108} Though the solvents had no effect on the morphology, they did impact the absorption kinetics of the clusters. Here, it is
possible that the larger boiling point of the toluene allows for a slower rate of evaporation than hexanes. Thus, the clusters have more time to assemble with less disorder, giving rise to the sharper diffraction peaks.

This diffraction pattern, however, does not provide information on the ordering across the surface in the x-y plane. As such neutron diffraction studies were employed to get a better understanding of the organization.

2.3.2.2 Neutron Diffraction

Neutron diffraction can provide information on the organization of clusters on surfaces, much like x-ray diffraction. Depending on the orientation of the sample in the neutron beam, different information can be determined. First, neutron reflectometry was performed on the PBR reflectometer at NIST Center for Neutron Research (NCNR). This method provides information about the film perpendicular to the substrate, in the z-direction. These experiments confirmed the ordering seen with the PXRD studies. A peak observed at the same d-spacing suggests that the neutrons and x-rays behave similarly. It was possible that the diffraction experiment could be affected by the ligand because neutrons are sensitive to different isotopes, especially hydrogen versus deuterium (the long chained alkyl ligands are abundant with hydrogen). The Mn_{12}(C_{10})_{16} was dissolved in toluene and dropcast onto silicon wafers to form a thick film.
Figure 2.6. Neutron reflectometry of Mn$_{12}$(C$_{10}$)$_{16}$. Here, Q1 corresponds to the (001) Bragg peak and Q2 corresponds to the (002).

Two clear superlattice peaks were observed with the reflectometry measurements, consistent with the lamellar pattern observed with PXRD (Figure 2.6). The Bragg peak appears at a d-spacing of 2.69 nm, in good agreement with the x-rays. This suggests that neutrons diffract off the sample in the same manner as x-rays.

In order to probe the organization of the Mn$_{12}$(C$_{10}$)$_{16}$ within a layer, parallel to the substrate, small-angle neutron scattering (SANS) was performed. Using the 30 meter SANS instrument (NG7) at NCNR we first probed the x-y plane. The Bragg peak was observed at a cluster-to-cluster spacing of 2.54 nm (Figure 2.7).
Figure 2.7. SANS of Mn$_{12}$(C$_{10}$)$_{16}$. This method displays the ordering of the cluster in the x-y plane.

The smaller distance in the x-y plane may be understood as caused by increased interdigitation of the ligand around the cluster. This effect is notably across the surface, whereas the greater interlayer distance suggests weaker interactions between the clusters.

2.3.2.3 Surface Imaging

Though SANS confirms ordering, it does not provide information as to the packing on the surface of a substrate. By depositing a monolayer of cluster on the surface of graphite, Scanning Tunneling Microscopy (STM) can be employed to image the surface and determine the packing structure at the liquid-solid interface. A drop of dilute solution of Mn$_{12}$(C$_{10}$)$_{16}$ in 1-phenyloctane was placed on the surface of HOPG for the imaging. The solvent 1-phenyloctane is historically used for STM studies due to its high boiling point, and slow evaporation. This is necessary for STM since the clusters must remain in solution to obtain tunneling measurements at the HOPG interface.
The bias voltage is an important factor in performing STM experiments. A positive voltage indicates a flow of electrons from the tip to the surface while a negative value represents an electron flow from surface to tip. Altering the bias also determines what components of the film are measured, i.e. the substrate or surface adsorbed layers. Here, the bias was set to -600 mV, typical for that of tunneling from the surface to the tip. The bright spots in the image are areas of high electron density, i.e. where the clusters are located.

![STM image of Mn_{12}(C_{10})_{16}. Organization represented at the 50 nm length scale (left) and 12.5 nm scale (right).](image)

At the larger length scale, a clear hexagonal close-packed organization is observed, where the clusters appear in the honeycomb-like pattern (Figure 2.8, left). Zooming in on the image, the clusters are more easily defined in the images (Figure 2.8, right). They appear slightly canted, which agrees with the calculation performed by Saywell on Mn_{12} on gold. The clusters were geometry optimized in a variety of orientations, with the lowest energy orientation being tilted on the surface. Rough geometry optimization performed with the Forcite module of Materials
Studio of localized clusters suggests similar behavior of Mn$_{12}$(C$_{10}$)$_{16}$. The ligands interdigitate, as seen in Figure 2.9 (left), and the cores appear canted (right image).

![Image of localized group of clusters](image)

**Figure 2.9. Geometry optimized model of localized group of clusters.** It is apparent that the ligands interdigitate (left). Removing the ligands for clarity, the cores appear canted (right).

In order to determine the average pattern and distances between clusters, a Fast Fourier Transform was performed on the zoomed out image. As seen in Figure 2.10, the average hexagonal pattern was confirmed. The distance that corresponds to the Q observed in SANS experiments is the distance between the clusters in the 1 and 5, or 2 and 4 positions marked in the image. Here the distance 2.56 nm matches well to that obtained from neutron scattering. This not only confirms that the scattering is due to the cluster separation in the x-y plane, but also provides the type of ordering.
In comparison, images of less substituted cluster, known through ESI-MS to have remaining acetate groups, were rendered. As Figure 2.11 illustrates, alternating narrow (0.684 nm width) and wide columns (1.95 nm width) appear, in stark contrast to the hexagonal close-packing of the fully substituted cluster. The narrow columns appear due to the clusters arranging more closely with the acetates than they do with the decanoates, representing the wider columns. Since these clusters did not exhibit ac susceptibility peaks, it is important to ensure synthesis of fully substituted cluster to achieve assembly of clusters and maintain SMM behavior.
2.4 Conclusion

This work has shown that ligand exchange of Mn$_{12}$ with long-chained carboxylates promotes organization of the clusters on a variety of surfaces. Our hypothesis is that decanoic acid ligand should make the SMM more spherical, to allow for the self-assembly while maintaining the characteristic SMM behavior. The ligands help to align the clusters, with a lamellar structure perpendicular to the substrate, though greater interdigitation occurring in the plane parallel to the substrate.

Though ordered films have been shown possible here through manipulation of the size and shape, the magnetism of the clusters has not been probed here. The following chapters investigate the ordering of additional clusters with varied chain lengths, as well as the magnetic properties on the surface.
CHAPTER 3. CONTROLLED ORGANIZATION OF $\text{Mn}_{12}$ THROUGH ALKYL CHAIN MODIFICATION

3.1 Introduction

The assembly of SMMs is an important goal in the SMM community, since it is necessary to form ordered, addressable films for application in device development. $\text{Mn}_{12}$ has been shown to aggregate on surfaces\textsuperscript{48}, so altering its size and shape for self-assembly has been a major undertaking in the past couple of decades.\textsuperscript{33}

Since $\text{Mn}_{12}$ has been shown to undergo ligand exchange reactions with other carboxylic acids in excess (Scheme 3.1), this method has been utilized for most investigations of this SMM.

\[
\text{Mn}_{12}\text{O}_{12}(\text{C}_2\text{H}_3\text{O}_2)_{16}\cdot4\text{H}_2\text{O} + 16\text{C}_n\text{H}_{2n}\text{O}_2 \rightarrow \\
\text{Mn}_{12}\text{O}_{12}(\text{C}_n\text{H}_{2n-1}\text{O}_2)_{16}\cdot4\text{H}_2\text{O} + 16\text{C}_2\text{H}_4\text{O}_2
\]  \hspace{1cm} (Scheme 3.1)

The key challenges are to ensure an intact core and full substitution of all acetates upon ligand exchange. Previous studies have shown that the ligands in the axial position preferentially exchange first, followed by the equatorial ligands depending on the pKa of the ligands.\textsuperscript{3,109} More basic, strong donor ligands favor the equatorial site, where stronger Mn-O bonds can be formed and stabilize the molecule. As such, careful exchange can be controlled through the stoichiometric ratios of ligand:cluster in the reaction to replace only the axial acetates. Christou has done much work in obtaining mixed ligands on $\text{Mn}_{12}$, investigating their magnetic properties.\textsuperscript{3,59,110,111} These clusters showed properties consistent with SMMs, with energy barrier values within the range of that reported for other $\text{Mn}_{12}$ derivatives of 60-70K.\textsuperscript{3}

Steric hinderance is another consideration that must be taken into account when performing ligand exchange reactions on $\text{Mn}_{12}$. For example, the bulky 9-anthracenecarboxylate, a luminescent ligand, was used to target an $\text{Mn}_{12}$ derivative that retained the magnetic character with added optical enhancements.\textsuperscript{112} However, the bulkiness of this ligand caused the core to
fragment, forming a trinuclear Mn$_3$ cluster. It is likely that there are multiple equilibria present and the bulky ligand stabilizes the small nuclearity due to steric factors. Therefore, ligands that are too bulky are not suitable for ligand exchange, as they stabilize smaller clusters. A way around this is to utilize tetradeutate ligands, such as anthracene-1,8-carboxylate derivatives. The double binding sites on these ligands allow for bridging of four Mn sites. This was attempted with a mixed ligand approach, where anthracene (functionalized with thiols) exhibited strong affinity for binding to the axial positions of the Mn$_{12}$ (Figure 3.1).\textsuperscript{113} The resulting cluster has the potential to direct assembly with the easy axis of the clusters oriented perpendicular to the surface.

![Figure 3.1. Structure of modified Mn$_{12}$ cluster. Anthracene-1,8-carboxylate ligands occupy axial positions. Reproduced with permission from The Royal Society of Chemistry.\textsuperscript{113}](image)

Tetracarboxylate ligands have therefore been shown to improve site selectivity of Mn$_{12}$, relying on the shape and chelate effect rather than basicity of the ligands to drive the exchange. The toluene azeotrope method has also been employed to carefully remove acetate. Toluene is
known to form an azeotrope with acetic acid in a 38:62 ratio, so performing the reactions in toluene pulls off the acetates, driving the reaction to the right.\textsuperscript{111,114} This is particularly useful for carboxylates with pKa values higher than acetic acid and provides pure product in high yields.\textsuperscript{32} Here the goal is to be able to control the ordering of the Mn\textsubscript{12} through ligand exchange reactions.

Through the many investigations, it has been clear that the size and shape of the Mn\textsubscript{12} is easily controlled with substitution of carboxylic acid ligands, which can be functionalized with other groups. For instance, thiol-terminated carboxylates have been studied for grafting Mn\textsubscript{12} onto gold surfaces by taking advantage of the gold-thiol interactions.\textsuperscript{35,48,63,102,106} These interactions are too weak, however, to form ordered films, showing that this chemistry does not have any advantage for self-assembly.

Many efforts to ligand exchange Mn\textsubscript{12} for the purposes of organization have resulted in disordered aggregates thus far, so new methods of assembly are necessary. As detailed in Chapter 2, we have utilized the longer chained decanoic acid in excess for ligand exchange with Mn\textsubscript{12}. Decanoic acid was first chosen because it is well known that self-assembled monolayers form the most ordered monolayers for chain lengths larger than C10. We expected that the shorter chain lengths would not benefit enough from van der Waals interactions to promote organization. The shorter organic chains also result in less spherical molecules. Therefore, we performed ligand exchange with a range of carboxylic acids, with alkyl chains ranging from C4 to C14 in order to investigate what chain length is required for the promotion of ordered films.
3.2 Experimental Section

3.2.1 General Information

Mn(CH$_3$COO)$_2$·4H$_2$O and all carboxylic acids were purchased from Sigma-Aldrich Chemical Co. KMnO$_4$ was obtained from J.T. Baker Chemicals. All chemicals were used as received. The Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$ was prepared according to published procedures.$^4$ Mn$_{12}$O$_{12}$(C$_{10}$H$_{19}$O$_2$)$_{16}$, or Mn$_{12}$(C$_{10}$), was prepared according to the procedure in chapter 2. Infrared spectra were measured in the range 450-4000 cm$^{-1}$ as pressed pellets in KBr on a Nicolet 380 FT-IR. Thermal analysis was performed on a TGA Q50 TA instrument. TGA data were studied from samples in a platinum pan, from 20-500°C with a heating rate of 10°C/min. Elemental (C, H, N) analysis was performed using a Perkin Elmer 2400 Series II CHN/O Analyzer. X-ray powder diffraction patterns were obtained using a Rigaku Ultima IV X-Ray powder diffractometer with Cu Kα radiation and a scintillation counter. The grazing incidence attachment allowed for the attainment of x-ray patterns for thin films at varied incidence angles.

Mn$_{12}$O$_{12}$(C$_4$H$_7$O$_2$)$_{16}$, or Mn$_{12}$(C$_4$)$_{16}$. Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$ (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Butyric acid (367 µL, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn$_{12}$ solution under N$_2$. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess butyric acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm$^{-1}$): 3414 (m), 2962 (w), 2929 (s), 2853 (w), 1720 (s), 1663 (s), 1462 (s), 1346 (s), 1244 (s), 1199 (s), 1114 (s), 1072 (s), 1025 (s), 886 (m), 826 (m), 799 (m), 749 (m), 699 (m), 606 (s), 560 (s), 526 (s), 465 (s).
2871 (s), 1615 (s), 1532 (m), 1390 (s), 1096 (m), 798 (w), 611 (s), 598 (m). Anal. Calcd for Mn$_{12}$O$_{12}$(C$_4$H$_7$O$_2$)$_{16}$: C, 33.18; H, 5.22. Found: C, 28.44; H, 4.68. Percent yield 49%.

Mn$_{12}$O$_{12}$(C$_5$H$_9$O$_2$)$_{16}$, or Mn$_{12}$(C$_5$)$_{16}$. Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$ (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Valeric acid (439 µL, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn$_{12}$ solution under N$_2$. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess valeric acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm$^{-1}$): 3525 (m), 2961 (w), 2934 (s), 2869 (s), 1611 (s), 1534 (m), 1422 (s), 1104 (m), 802 (w), 633 (s), 542 (m). Anal. Calcd for Mn$_{12}$O$_{12}$(C$_4$H$_7$O$_2$)$_{16}$: C, 37.81; H, 6.03. Found: C, 38.34; H, 5.98. Percent yield 67%.

Mn$_{12}$O$_{12}$(C$_6$H$_{11}$O$_2$)$_{16}$, or Mn$_{12}$(C$_6$)$_{16}$. Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$ (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Hexanoic acid (501 µL, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn$_{12}$ solution under N$_2$. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess hexanoic acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm$^{-1}$): 3525 (m), 2958 (w), 2927 (s), 2862 (s), 1583 (s), 1510 (m), 1420 (s), 1109 (m), 802 (w), 640 (s), 542 (m). Anal. Calcd for Mn$_{12}$O$_{12}$(C$_4$H$_7$O$_2$)$_{16}$: C, 41.69; H, 6.71. Found: C, 39.65; H, 6.43. Percent yield 49%.
**Mn_{12}O_{12}(C_7H_{13}O_2)_{16}, or Mn_{12}(C_7)_{16}.** Mn_{12}O_{12}(CH_3COO)_{16} (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Heptanoic acid (567 µL, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn_{12} solution under N_2. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess hexanoic acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm\(^{-1}\)): 3529 (m), 2956(s), 2927(s), 2858 (s), 1585(s), 1506 (m), 1415 (s), 1109 (m), 722 (w), 639 (s), 541 (m). Anal. Calcd for Mn_{12}O_{12}(C_7H_{13}O_2)_{16}: C, 44.99; H, 7.28. Found: C, 44.76; H, 7.08. Percent yield 46%.

**Mn_{12}O_{12}(C_8H_{15}O_2)_{16}, or Mn_{12}(C_8)_{16}.** Mn_{12}O_{12}(CH_3COO)_{16} (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Octanoic acid (634 µL, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn_{12} solution under N_2. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess octanoic acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm\(^{-1}\)): 3532 (m), 2956(s), 2925 (s), 2853(s), 1584 (s), 1505 (m), 1416 (s), 1109(m), 721 (w), 637 (s), 542 (m). Anal. Calcd for Mn_{12}O_{12}(C_8H_{15}O_2)_{16}: C, 48.90; H, 7.70. Found: C, 47.32; H, 7.61. Percent yield 33%.

**Mn_{12}O_{12}(C_9H_{17}O_2)_{16}, or Mn_{12}(C_9)_{16}.** Mn_{12}O_{12}(CH_3COO)_{16} (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into
another schlenk flask. Nonanoic acid (367 µL, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn$_{12}$ solution under N$_2$. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess Nonanoic acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm$^{-1}$): 3528(m), 2957 (w), 2924 (s), 2853 (s), 1585 (s), 1506 (m), 1419 (s), 1113 (m), 721 (w), 641 (s), 544 (m). Anal. Calcd for Mn$_{12}$O$_{12}$(C$_9$H$_{17}$O$_2$)$_{16}$: C, 51.35; H, 8.15. Found: C, 49.81; H, 8.15. Percent yield 47%.

Mn$_{12}$O$_{12}$(C$_{12}$H$_{23}$O$_2$)$_{16}$, or Mn$_{12}$(C$_{12}$)$_{16}$. Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$ (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Lauric acid (0.0801 g, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn$_{12}$ solution under N$_2$. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess lauric acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm$^{-1}$): 3529 (m), 2957 (w), 2921 (s), 2851 (s), 1584 (s), 1505 (m), 1417 (s), 1112 (m), 721 (w), 639 (s), 543 (m). Anal. Calcd for Mn$_{12}$O$_{12}$(C$_{12}$H$_{23}$O$_2$)$_{16}$: C, 56.08; H, 9.22. Found: C, 55.75; H, 9.37. Percent yield 37%.

Mn$_{12}$O$_{12}$(C$_{14}$H$_{27}$O$_2$)$_{16}$, or Mn$_{12}$(C$_{14}$)$_{16}$. Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$ (0.1286 g, 0.0624 mmol) was dissolved in acetonitrile (40 mL). The solution was stirred for 1 hour, then cannula filtered into another schlenk flask. Myristic acid (0.914 g, 4.0 mmol) was dissolved in acetonitrile (10 mL) and stirred for 5 minutes. This was transferred to the flask containing the Mn$_{12}$ solution
under N$_2$. The solution was stirred for 4 hours, then acetonitrile was vacuum pumped off. The resulting solid was dissolved in toluene and vacuum pumped off to remove acetate. This process was repeated 3 times and the resulting solid was washed with water to remove excess myristic acid. Fine, dark brown crystalline powder was obtained. IR (KBr, cm$^{-1}$): 3525 (m), 2957 (w), 2917 (s), 2850 (s), 1583 (s), 1505 (m), 1418 (s), 1109 (m), 721 (w), 640 (s), 543 (m). Anal. Calcd for Mn$_{12}$O$_{12}$(C$_{14}$H$_{27}$O$_2$)$_{16}$: C, 58.99; H, 9.72. Found: C, 59.92; H, 10.60. Percent yield 39%.

3.2.2 SANS

Small angle neutron scattering (SANS) was performed on NG7 30m instrument at the NIST Center for Neutron Research. In order to increase the scattered intensity, five silicon wafers containing dropcast Mn$_{12}$ clusters were stacked. Room temperature scattering was measured with detector settings of 9 m and 1 m-offset in order to cover a large Q range.

3.3 Results and Discussion

3.3.1 Synthesis of Mn$_{12}$ Substituted Clusters

Mn$_{12}$(acetate) was synthesized according to published procedure and used as the starting compound for preparing substituted clusters.$^4$ It has been shown that Mn$_{12}$ undergoes ligand exchange with other carboxylic acids when present in excess, as seen in Scheme 3.1. The clusters were washed with toluene after the reaction to ensure full substitution, by taking advantage of the 38:62 toluene:acetic acid azeotrope. Here, carboxylic acids with varying alkyl chain length were studied to determine if the clusters maintain SMM behavior upon full substitution and if the ligand length confers self-organization.
3.3.2 Characterization of Substitution

A key challenge was ensuring full substitution of all acetates with the carboxylic acid. Since adding longer carbon chains introduces many more degrees of freedom, the ligand substituted species do not form suitable single crystals for X-Ray Diffraction (XRD). Therefore, full substitution was confirmed through C/H/N elemental analysis, where all clusters agreed with expected values for fully substituted species within 1%, with the exception of Mn\textsubscript{12}(C\textsubscript{4})\textsubscript{16} as summarized in Table 3.1. Despite best efforts, pure Mn\textsubscript{12}(C\textsubscript{4})\textsubscript{16} was unable to be obtained at this time, either due to less substitution or solvent coordination to the clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Expt. %C</th>
<th>Expt. %H</th>
<th>Calc. %C</th>
<th>Calc.%H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{4})\textsubscript{16}</td>
<td>28.44</td>
<td>4.68</td>
<td>33.18</td>
<td>5.20</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{5})\textsubscript{16}</td>
<td>38.34</td>
<td>5.98</td>
<td>37.81</td>
<td>6.03</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{6})\textsubscript{16}</td>
<td>39.65</td>
<td>6.43</td>
<td>41.69</td>
<td>6.71</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{7})\textsubscript{16}</td>
<td>44.76</td>
<td>7.08</td>
<td>44.99</td>
<td>7.28</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{8})\textsubscript{16}</td>
<td>47.32</td>
<td>7.61</td>
<td>48.90</td>
<td>7.70</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{9})\textsubscript{16}</td>
<td>49.81</td>
<td>8.15</td>
<td>51.35</td>
<td>8.15</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{10})\textsubscript{16}</td>
<td>52.25</td>
<td>9.20</td>
<td>52.46</td>
<td>8.58</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{12})\textsubscript{16}</td>
<td>55.75</td>
<td>9.37</td>
<td>56.08</td>
<td>9.22</td>
</tr>
<tr>
<td>Mn\textsubscript{12}(C\textsubscript{14})\textsubscript{16}</td>
<td>59.92</td>
<td>10.60</td>
<td>58.99</td>
<td>9.72</td>
</tr>
</tbody>
</table>

It was also necessary to confirm that the core remained intact upon substitution. Mn\textsubscript{12} has a characteristic core stretching frequency for the Mn-O bonds between 550 and 750 cm\textsuperscript{-1}.\textsuperscript{115} FTIR spectroscopy was employed and identified that each substituted cluster displayed this feature (Figure 3.2). The alkane stretching frequencies are also indicative of the ordering of the ligand. Stretches at 2920 and 2850 cm\textsuperscript{-1} imply ordered chains, whereas 2928 and 2856 cm\textsuperscript{-1} represent disorder. As ligand chain length increased from 4 to 14, the chains were more ordered.
3.3.3 Thermal Properties

Thermogravimetric Analysis (TGA) is another measure on the substitution of the clusters and confirms that there are no solvents of crystallization. Figure 3.3 is a representative graph of the TGA, showing that the mechanism of decomposition remains the same with each cluster, with no significant difference in temperature.

**Figure 3.3.** TGA of Mn_{12}(C_{10})_{16}. The steps indicate decomposition of ligand and core.
The total weight loss from room temperature to 500°C is recorded in Table 3.2 and compared to that expected and corresponds to the decomposition of the ligands, as well as the core to Mn₃O₄, as confirmed through powder x-ray diffraction (PXRD) (Figure 3.4).

Table 3.2. TGA weight loss. Decomposition was followed from room temperature to 500°C.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Expt % loss</th>
<th>% Calc loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₁₂(C₇)₁₆</td>
<td>69.35</td>
<td>69.39</td>
</tr>
<tr>
<td>Mn₁₂(C₈)₁₆</td>
<td>69.59</td>
<td>71.53</td>
</tr>
<tr>
<td>Mn₁₂(C₉)₁₆</td>
<td>72.46</td>
<td>73.39</td>
</tr>
<tr>
<td>Mn₁₂(C₁₀)₁₆</td>
<td>73.85</td>
<td>75.02</td>
</tr>
<tr>
<td>Mn₁₂(C₁₂)₁₆</td>
<td>74.14</td>
<td>77.74</td>
</tr>
<tr>
<td>Mn₁₂(C₁₄)₁₆</td>
<td>78.66</td>
<td>79.93</td>
</tr>
</tbody>
</table>

Comparing the expected decomposition of Mn₁₂O₁₂(L)₁₆·4H₂O to Mn₃O₄ to the experimental percentage loss, the difference between the two falls within 5% for each cluster.

Figure 3.4. PXRD of cluster decomposed to Mn₃O₄. Each cluster displayed this pattern after TGA experiments.
3.3.4 Magnetic Properties

The defining characteristic of an SMM is the out-of-phase component of the AC susceptibility. The confirmation of this component in all clusters was important in clarifying that the ligand exchange reaction did not affect the SMM behavior of the materials. The measurement also allows for the calculation of the relaxation time and effective energy barrier for reversal of magnetization.

Figure 3.5. Out-of-phase ac susceptibility of Mn$_{12}$(C$_9$)$_{16}$. The peaks in this $\chi''$ vs. $T$ graph are frequency dependent and correspond to the relaxation of spins and energy barrier.

Figure 3.5 is a representative $\chi''$ vs. $T$ of Mn$_{12}$(C$_9$)$_{16}$, displaying frequency dependent peaks, which were observed for each cluster. From the peak maximum at different frequencies, an Arrhenius plot was constructed to determine the effective energy barrier, $U_{\text{eff}}$, and relaxation of spins, $\tau$ (Figure 3.6).
Figure 3.6. Arrhenius plot of Mn$_{12}$(C$_9$)$_{16}$. This was constructed from the AC susceptibility peaks.

The exponential plot fits to Equation 3.1, where the exponent is equal to $U_{\text{eff}}/kT$. $U_{\text{eff}}$ is the energy barrier that the spins must overcome to reverse the direction of magnetization and $k$ is the Boltzmann constant.

$$\tau_0 = \tau \cdot e^{U_{\text{eff}}/kT} \quad \text{(Equation 3.1)}$$

Table 3.3 summarizes the calculated $U_{\text{eff}}$ and $\tau$ for each cluster that was obtained from their respective Arrhenius plots. The reported $U_{\text{eff}}$ for Mn$_{12}$ SMMs have been reported to be in the range of 60 and 70K, with $\tau_0$ values on the order of $10^{-10}$ to $10^{-8}$ s. These substituted clusters fall within this range, however no noticeable correlation between ligand chain length and these values have been observed.
### Table 3.3. Energy barrier and relaxation times. Each was calculated from the Arrhenius plots.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$\tau \times 10^8$ s</th>
<th>$U$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{12}$(C$<em>4$)$</em>{16}$</td>
<td>4.14</td>
<td>65.5</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>5$)$</em>{16}$</td>
<td>3.93</td>
<td>64.0</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>6$)$</em>{16}$</td>
<td>3.32</td>
<td>67.2</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>7$)$</em>{16}$</td>
<td>2.73</td>
<td>67.1</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>8$)$</em>{16}$</td>
<td>3.29</td>
<td>65.0</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>9$)$</em>{16}$</td>
<td>3.61</td>
<td>64.4</td>
</tr>
<tr>
<td>Mn$<em>{12}$(C$</em>{10}$)$_{16}$</td>
<td>2.72</td>
<td>64.6</td>
</tr>
<tr>
<td>Mn$<em>{12}$(C$</em>{12}$)$_{16}$</td>
<td>1.67</td>
<td>65.0</td>
</tr>
<tr>
<td>Mn$<em>{12}$(C$</em>{14}$)$_{16}$</td>
<td>3.50</td>
<td>60.3</td>
</tr>
</tbody>
</table>

Constructing plots of the in-phase component ($\chi'$) of the susceptibility further shows the temperature where frequency dependency disappears and the clusters behave like paramagnets (Figure 3.7).

![Figure 3.7. In-phase susceptibility of Mn$_{12}$(C$_9$)$_{16}$. This $\chi'$ vs. T graph is used to calculate the Curie constant and Weiss temperature.](image)

48
The straight portion can be fit to the Curie-Weiss Law, where the slope is equal to the inverse of the Curie constant, C, and the y-intercept is Weiss temperature, \( \theta \), divided by \( C \), as in Equation 3.2.

\[
\frac{1}{\chi} = \left( \frac{1}{C} \right) T - \frac{\theta}{C}
\]

(Equation 3.2)

The values of \( C \) and \( \theta \) for each cluster are listed in Table 3.4.

**Table 3.4. Curie constant & Weiss temperature.** These were determined from \( 1/\chi' \) vs. \( T \) plots.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>( C ) (K)</th>
<th>( \theta ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mn}<em>{12}(C_4)</em>{16} )</td>
<td>21.7</td>
<td>-4.89</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C_5)</em>{16} )</td>
<td>27.0</td>
<td>-2.97</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C_6)</em>{16} )</td>
<td>38.5</td>
<td>-4.46</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C_7)</em>{16} )</td>
<td>43.5</td>
<td>-3.22</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C_8)</em>{16} )</td>
<td>74.1</td>
<td>-2.25</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C_9)</em>{16} )</td>
<td>52.6</td>
<td>-4.74</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C</em>{10})_{16} )</td>
<td>55.6</td>
<td>-4.61</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C</em>{12})_{16} )</td>
<td>30.3</td>
<td>-4.21</td>
</tr>
<tr>
<td>( \text{Mn}<em>{12}(C</em>{14})_{16} )</td>
<td>55.25</td>
<td>-3.93</td>
</tr>
</tbody>
</table>

It is apparent that the Curie constant increases with increasing chain length, with the exception of \( \text{Mn}_{12}(C_8)_{16} \) and \( \text{Mn}_{12}(C_{12})_{16} \), while \( \theta \) remains about the same for each cluster. The negative value for \( \theta \) reflects anti-ferromagnetic interactions between metals within the core.

The value of the ground spin state for each of the clusters can be calculated from the \( \chi'T \) vs. \( T \) plot, where the point where the curves converge can be used to calculate \( \mu \) and therefore \( S \) according to equations 3.3 and 3.4, where \( g=2 \). The spin states for each cluster is listed in Table 3.5.

\[
\mu = \sqrt{2.83 \cdot \chi T}
\]

(Equation 3.3)

\[
\mu = g \cdot \sqrt{s(s + 1)}
\]

(Equation 3.4)
Table 3.5. Calculated ground spin states. The larger clusters display larger spin states.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$\chi T$ (emu·K/mol)</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{12}$(C$<em>4$)$</em>{16}$</td>
<td>15.1</td>
<td>5.02</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>5$)$</em>{16}$</td>
<td>22.0</td>
<td>6.38</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>6$)$</em>{16}$</td>
<td>27.9</td>
<td>7.46</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>7$)$</em>{16}$</td>
<td>33.5</td>
<td>8.13</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>8$)$</em>{16}$</td>
<td>61.2</td>
<td>10.58</td>
</tr>
<tr>
<td>Mn$_{12}$(C$<em>9$)$</em>{16}$</td>
<td>39.2</td>
<td>8.65</td>
</tr>
<tr>
<td>Mn$<em>{12}$(C$</em>{10}$)$_{16}$</td>
<td>41.2</td>
<td>8.96</td>
</tr>
<tr>
<td>Mn$<em>{12}$(C$</em>{12}$)$_{16}$</td>
<td>23.6</td>
<td>6.60</td>
</tr>
<tr>
<td>Mn$<em>{12}$(C$</em>{14}$)$_{16}$</td>
<td>44.2</td>
<td>8.92</td>
</tr>
</tbody>
</table>

The same trend is observed here, where the ground spin state increases with increasing ligand chain length, again with the exceptions of Mn$_{12}$(C$_8$)$_{16}$ and Mn$_{12}$(C$_{12}$)$_{16}$.

3.3.5 X-ray Diffraction

Though it was not possible to grow crystals of suitable quality for single crystal x-ray diffraction, the powders obtained from the synthesis were crystalline, so the powder x-ray diffraction patterns were obtained for each cluster.

Figure 3.8. Bulk PXRD of Mn$_{12}$(C$_{10}$)$_{16}$. The lamellar pattern indicates a layered structure.
Each cluster displayed the same lamellar packing pattern that was observed for Mn_{12}(C_{10})_{16}, where identifiable (001), (002), and (003) peaks were present (Figure 3.8). Weak reflections were also present at d=1.21 and 1.12 nm; however, these did not correspond to known structures, so no other structural information about the clusters could be inferred. When comparing the patterns between different clusters, a clear systematic shift in d-spacing is observed. Clusters with longer carbon chains exhibited diffraction at lower angles, indicative of larger d-spacing (Figure 3.9).

![Figure 3.9. (001) peak of substituted clusters. Varying the chain lengths resulted in shifted peaks, and therefore changes in d-spacing.](image)

In fact, a linear correlation was found to exist between ligand chain length (x-axis) and d-spacing (y-axis), as seen in Figure 3.10, where the d-spacing can be predicted according to the following equation:

\[
y = 0.2515x + 0.3394
\]

(Equation 3.5)

This indicates that regardless of ligand chain length, the clusters show systematic ordering.
Figure 3.10. Correlation between ligand chain length and d-spacing. As ligand chain length increases, as does d-spacing in a linear relationship.

Further x-ray investigation probed films of clusters, where they were dissolved in toluene and drop-cast on to the surface of silicon wafers. These thick films were probed with GI-PXRD to see the differences in the packing of the clusters throughout the film. Applying a small incidence angle of 0.5° provides the structural information at the surface, whereas higher incidence angles display the structure deeper in the film, at the silicon interface.

For Mn$_{12}$(C$_{10}$)$_{16}$, the peaks in the pattern remain at the same position, with the only difference being a broadening at lower angles (Figure 3.11). This broadening is caused by averaging of a larger area across the surface as opposed to smaller areas at a larger depth for higher angles. In comparison, the smaller cluster Mn$_{12}$(C$_{6}$)$_{16}$ displays more peaks at the surface than the expected lamellar pattern seen deeper in the film (Figure 3.12).
Figure 3.11. GI-PXRD of Mn$_{12}$(C$_{10}$)$_{16}$. Changing the incidence angles probes different depths of the film.

Thus, there are mixed packing phases at the surface. These x-ray patterns only definitively provide the packing of the structure in the z-direction, but suggest that longer chained clusters are also ordered across the layer, while shorter chains are not. However, in order to get exact structural information for the clusters in the x-y plane, neutron diffraction techniques were employed.
3.3.6 Film Organization

The first neutron experiments we performed were to ensure that the diffraction observed with x-rays is identical to diffraction by neutrons. As such, the z-direction of the same dropcast films that were probed in x-rays were also investigated by neutrons, which is detailed for Mn$_{12}$(C$_{10}$)$_{16}$ in Chapter 2. Since the data corroborated well, we investigated the ordering of the clusters across layers via small angle neutron scattering (SANS).

SANS allowed for investigation of the ordering of the clusters on silicon surfaces, probing the packing parallel to the surface, i.e. in the x-y plane. It is clear that longer chained ligands aid in the ordering of the clusters, as Mn$_{12}$(C$_{9}$)$_{16}$ through Mn$_{12}$(C$_{12}$)$_{16}$ display defined Bragg peaks (Figure 3.13). Sharply defined peaks are indicative of long-range order of the sample across the surface. The peaks appear are smaller distances than expected based on the PXRD patterns, suggesting that the clusters are able to more closely pack across the layer. This
could be due to greater interdigitation in this direction, causing the clusters to behave more like hard spheres in the z-direction. Another possibility is simply weaker interactions down layers that cause them to be further apart.

![Figure 3.13. SANS of clusters with varied chain lengths.](image)

The ordering is lost for clusters with shorter ligands, as the peak disappears.

Investigation of shorter chained ligands, such as Mn$_{12}$(C$_7$)$_{16}$ and shorter, the Bragg peak is no longer clearly apparent. The little scattering where the Bragg peaks should be are due to short-range ordering where a few clusters organize, but the majority of the sample is disordered. The broad scattering and loss of a clear Bragg peak indicates a loss of ordering across the layer, which can be explained by the additional diffraction peaks observed with GI-PXRD.

This data suggests that the ordering of the clusters is highly dependent on their size and therefore shape. Longer chains result in aspect ratios closer to 1, indicative of more spherical materials. This spherical shape allows for the clusters to better close-pack uniformly throughout the film. The shorter clusters are not as spherical and thus the shape does not drive them to
hexagonally close pack across the layers. However, they are still able to order down the layers, perpendicular to the film.

3.4 Conclusion

We’ve shown that organization of SMM clusters is possible by controlling the shape. Ligand exchange allowed for placement of a variety of alkyl chains around the Mn-O core, while maintaining SMM behavior. The relaxation times and energy barrier were consistent with that reported for Mn$_{12}$ derivatives. Furthermore, regardless of chain length, ordering perpendicular to the substrate was observed independent of shape effects. The organization across layers, however, proved to rely on the ligand chain length, as only longer chains showed superlattice ordering. The shorter chain lengths, below C9, were disordered, indicating that the hexagonal close packing is indeed driven by the spherical shape of the clusters.
CHAPTER 4. MAGNETIC INVESTIGATION OF Mn$_{12}$ ORDERED FILMS

4.1 Introduction

A key aspect involved in the investigation of materials for device development is the characterization of their properties when grafted onto surfaces as films. In order for them to be applicable, they must retain the unique properties observed in the bulk powders. The previous chapters detailed the organization of Mn$_{12}$ single molecule magnet derivatives on surfaces, demonstrating the ability of clusters with longer chained ligands to organize on surfaces both as monolayers across the surface and down layers in thick films. However, magnetic studies using synchrotron radiation and neutron diffraction provides additional information about the magnetic ordering.

Polarized synchrotron radiation has allowed for the magnetic structure information of materials to be probed, specifically by employing x-ray absorption spectroscopy (XAS). XAS is an element and site specific tool that is used to study the unoccupied electronic density of states. If circularly polarized x-rays are employed in this technique, quantitative information about the spin and orbital angular momenta can be obtained. More specifically, it is the difference between the XAS signal of left and right circularly polarized x-rays that allows for understanding of the electronic and magnetic structure of samples, a technique that is known as X-ray Magnetic Circular Dichroism (XMCD). This relatively new approach has attracted much attention for the study of materials due to the strong $2p \rightarrow 3d$ transitions at the L edges that are dipole-allowed. An advantage that XMCD has over other methods is its sensitivity to oxidation state, allowing for the separation of contributions of mixed valent materials, like Mn$_{12}$. 
The shape of the spectra changes based on the magnitude of the contributions from each oxidation state, crystal field changes, and 3d spin-orbital coupling.\textsuperscript{116,118–120} Because Mn has weak spin-orbital coupling, the L\textsubscript{2,3} edges are mixed, so spin momentum cannot be determined.\textsuperscript{121} However, it is still possible to determine the contribution of each oxidation state to the signal through addition of the weighted expected signals if ferromagnetically aligned, or subtraction of them if antiferromagnetic.\textsuperscript{122}

While XMCD provides intra-cluster magnetic information, polarized beam neutron diffraction allows for inter-cluster magnetic structure by applying a \textsuperscript{3}He spin filter. The advantage of the \textsuperscript{3}He system is its ability to effectively polarize a broad wavelength band of neutrons, can polarize a large area of neutron beam, and polarization direction can be easily reversed.\textsuperscript{123} Polarized beam has only been applied to Small Angle Neutron Scattering (SANS) in the past decade to study magnetic nanoparticle assemblies.\textsuperscript{124,125} According to spin selection rules, only the magnetism perpendicular to the scattering wave vector, Q, contributes to the scattering. Furthermore, the spin-scattering is based on the direction of transmitted spins either parallel (+) or antiparallel (-) to the applied field. These respective spin scattering intensities are represented by the following equations:

\begin{align*}
I(+) &= I(++) + I(+-) \\
I(-) &= I(-+) + I(--),
\end{align*}

(Eq. 4.1) (Eq. 4.2)

where I(--), I(++) refer to non-spin flip, where the reversal of spin is conserved, and I(+-), I(-+) are spin flip, indicating of reversal of spin. These latter spin-flip scattering intensities are equal and due only to magnetic inter-particle correlations. On the other hand, non-spin flip
character is due to both nuclear and magnetic contrasts, giving rise to structural characteristics as well.

These components of the scattering can be taken advantage of to determine the magnetic interactions between clusters, giving rise to determination of magnetic ordering and whether aggregation occurs with application of an external field.\textsuperscript{126} This is especially useful for the characterization of films, to determine how the organized clusters interact with one another.

As such, we prepared thick films of Mn\textsubscript{12} in order to determine the magnetic properties of the clusters on surfaces. We were especially interested in how the interactions change between surface organization and bulk material, with the hope that the shape directed closed-packing detailed in the previous chapter retained the unique magnetization of SMMs.

4.2 Experimental Section

4.2.1 General Information

Mn\textsubscript{12}(C\textsubscript{10})\textsubscript{16} and Mn\textsubscript{12}(C\textsubscript{12})\textsubscript{16} were prepared according to the experimental procedures provided in Chapters 2 and 3.

4.2.2 SQUID

Superconducting Quantum Interference Device (SQUID) measurements were performed on a Quantum Design MPMS 3 SQUID Magnetometer at the University of South Carolina Department of Chemistry. Approximately 10mg of sample was loaded into a 2mm x 2.6 mm D cylinder. Five quadrant measurements were taken at 2K, while one quadrant measurements were obtained at 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, 10, and 20K. Zero-field cooled and field cooled measurements were obtained at 1000 Oe field.
4.2.3 XAS/XMCD

X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements were performed at beamline 4-ID-C of the Advanced Proton Source at Argonne National Laboratory. Mn$_{12}$(C$_{10}$)$_{16}$ samples were prepared in toluene (5mM) and dropcast onto both gold and silicon surfaces, with silver paint applied to the corner to enhance conductivity. The samples were mounted on a liquid He cryostat in a split-coil superconducting magnet with both the field and sample normal parallel to the incident x-ray beam. Each measurement was obtained for total electron yield (TEY) mode at 3.2K and 1T magnetic field.

4.2.4 SANS

Small angle neutron scattering (SANS) was performed on NG7 at the National Institute of Standards and Technology. In order to increase the scattered intensity, 5 silicon wafers containing thick films of dropcast Mn$_{12}$(C$_{10}$)$_{16}$ in toluene (5mM) were stacked in an aluminum foil packet with a cadmium mask. The Tritan magnet was used to apply and external magnetic field and a spin flipper was utilized to control which neutron spins passed through to the sample, which was under vacuum. Room temperature and low temperature scattering were measured with detector settings of 9 m and 1 m-offset in order to cover a large Q range. The same procedure was repeated for Mn$_{12}$(C$_{12}$)$_{16}$.

4.3 Results and Discussion

The structural organization of Mn$_{12}$ clusters with varied chain lengths is reported in chapter 3, where long-range ordering in the z direction for all ligand chain lengths was observed, but ordering in the x-y plane disappeared with the shorter chain lengths (C<8). So we focus now
on the longer chain lengths of C₁₀ and C₁₂ to probe whether magnetic ordering occurs along with the structural organization.

4.3.1 Magnetism of Bulk Powders

The AC susceptibility plots for Mn₁₂(C₁₀)₁₆ and Mn₁₂(C₁₂)₁₆ are shown in Chapter 3, indicating that the clusters possess an out-of-phase component of the magnetization, characteristic of SMMs. It is also important to obtain full magnetization data, i.e. M vs. H curve, on the clusters to add further information by providing the coercive field at about 20 Oe.⁵⁸,⁵⁹ Utilizing SQUID magnetometry on bulk powders, a hysteresis curve was observed for both Mn₁₂(C₁₀)₁₆ and Mn₁₂(C₁₂)₁₆ (Figure 4.1).

![Figure 4.1. Hysteresis curves at 2K. Mn₁₂(C₁₀)₁₆ curve (blue triangles) has a greater coercivity than Mn₁₂(C₁₂)₁₆ (black circles).](image)

C₁₂ had a slightly smaller coercive magnetization than C₁₀ but the blocking temperatures for each remain at ~3K, as observed through the remnant magnetization, as well as the field-cooled plots (Figures 4.2 and 4.3).
Figure 4.2. Remnant magnetization curves. \( \text{Mn}_{12}(\text{C}_{10})_{16} \) appears as black triangles and \( \text{Mn}_{12}(\text{C}_{12})_{16} \) as blue circles.

Irreversibility is observed below 3K, which is comparable to previous reports for \( \text{Mn}_{12} \).\(^{127}\) Steps in the hysteresis are present, which indicates quantum tunneling of magnetization, characteristic of SMMs. However, the smaller coercivity and weaker steps in the hysteresis could be due to the longer chain lengths causing the clusters to be too far for tunneling.
Figure 4.3. Field-cooled and zero-field-cooled measurement. Comparison between Mn$_{12}$(C$_{10}$)$_{16}$ and Mn$_{12}$(C$_{12}$)$_{16}$.

The isothermal magnetization plots depicted in Figure 4.4 show the temperature dependence of the magnetization of the clusters. As temperatures increase, the superparamagnetism is lost, becoming a simple paramagnet. This is most clear for the 20K curve where it loses the coercivity. It is clear that the clusters do maintain SMM behavior in the bulk, but the magnetic ordering and whether the clusters retain the magnetization in films require SANS and XMCD experiments to be performed.
Figure 4.4. Isothermal magnetization of Mn$_{12}$(C$_{12}$)$_{16}$. It is clear that the coercivity is lost at higher temperatures.

4.3.2 X-Ray Magnetism

XMCD provides information on two components of the system: oxidation state of the Mn and spin ordering. XMCD was performed at 3K, 1T field, on both gold and silicon surfaces to compare substrate effects, which gave a signal for the L$_{2,3}$ edge. Each oxidation state displays a characteristic pattern, based on the symmetry and crystal field. Measurements were obtained for both Mn$_{12}$ and Mn$_{12}$(C$_{10}$)$_{16}$ films to determine whether the ligand exchange affected the core. However, no significant difference was observed between the line shapes of the two clusters, nor was there any difference between gold and silicon substrates. As such, the substituted cluster behaves identically to the native Mn$_{12}$.

The expected signal for different oxidation states can be calculated according to the sum rules put forth, where the XMCD output is highly dependent on the magnetic field, spin-orbital coupling, symmetry, and strength of the crystal field.$^{121,128}$ van der Laan investigated a variety of
3d transition metals with variations of these parameters, calculating spectral changes (Figure 4.5). For d^5 Mn, subtle differences are observed by increasing the crystal field, or removing spin-orbit coupling.

![Figure 4.5. Calculated XMCD spectra for d^5 Mn.](image)

Since Mn_{12} is composed of two oxidation states in a 1:2 ratio of Mn^{4+} to Mn^{3+}, the simulated signal for each must calculated individually and then scaled appropriately to create the combined signal. The negative L_3 edge is primarily a result of the eight ferromagnetically coupled Mn^{3+} and the positive L_2 edge is attributed to the four Mn^{4+}, which are antiferromagnetic to the Mn^{3+}. Additionally, the antiferromagnetic alignment of the Mn atoms is signified through subtraction of Mn^{4+} from Mn^{3+}, whereas ferromagnetic alignment is the addition. An additional
consideration to be considered is the reduction of the outer Mn\(^{3+}\) to Mn\(^{2+}\), which has been observed in previous studies of Mn\(_{12}\) derivatives with XMCD.\(^{62,106,129}\)

The symmetry of the atoms can have a marked difference in the signals as well, so should be taken into account. Because of Jahn-Teller distortions, the Mn\(^{3+}\) should be calculated in D\(_{4h}\) symmetry, while simulating Mn\(^{4+}\) under O\(_h\) symmetry. We turned to the reported calculations of Mn\(_{12}\) XMCD spectra for comparison of line-shapes to obtain qualitative measures as to whether reduction occurs. Figure 4.6 is the experimentally determined signal of Mn\(_{12}\) bulk powder superimposed on the calculated signal as reported by Moroni.\(^{130}\) This signal is representative of the antiferromagnetic arrangement between Mn\(^{3+}\) and Mn\(^{4+}\).

![Figure 4.6. XMCD spectrum of Mn\(_{12}\). Here, the experimental spectrum is compared to calculations. Reproduced with permission from the American Physical Society.\(^{130}\)](image)

In comparison, we observed a slightly shifted signal, with changes in the line shape (Figures 4.7 and 4.8). Though the Mn\(^{3+}\) L\(_3\) edge and the higher energy the Mn\(^{4+}\) L\(_2\) edge
expected for Mn$_{12}$ are apparent, the multiplet signal observed in the experimental signal between 635 and 640 eV indicates that a reduction to Mn$^{2+}$ occurred as well.

![XMCD spectra of Mn$_{12}$ on gold and silicon](image)

**Figure 4.7.** XMCD spectra of Mn$_{12}$ on gold and silicon. No apparent substrate differences were observed.

Though previous reports attributed this reduction to Au-S interactions, our data suggests it is in fact beam damage since it was observed for each substrate with no thiol groups present. Other experiments have taken precautions to reduce the beam damage, but it may be unavoidable for Mn$_{12}$ since the measurements are taken by aiming an intense beam of electrons at the higher order Mn, which easily accepts the electron to be reduced to the 2+ state.
Figure 4.8. XMCD spectra of Mn_{12}(C_{10})_{16}. Again, no substrate differences between gold and silicon were observed.

Additionally, within a single cluster, Mn^{3+} and Mn^{4+} are antiferromagnetically aligned for both Mn_{12} and Mn_{12}(C_{10})_{16}. Therefore, we infer that the substituted clusters maintain the same spin ordering as the unsubstituted species. Since all clusters were prepared from Mn_{12} under identical conditions, we are confident that spins are aligned in the same fashion and Mn_{12}(C_{12})_{16} has antiferromagnetically aligned Mn^{3+} and Mn^{4+}.

4.3.3 Neutron Magnetism

In order to characterize cluster-to-cluster magnetization, polarized beam SANS experiments were performed on both Mn_{12}(C_{10})_{16} and Mn_{12}(C_{12})_{16} on the 30m NG7 instrument at NIST. Unfortunately, the scattering of Mn_{12}(C_{10})_{16} was outside the Q-range limits of the instrument, so we were unable to obtain data on this cluster. However, Mn_{12}(C_{12})_{16} fell within the limit, so the scattering at both 1m and 9m detector distances were measured to get a broad Q range. Measurements were obtained below the blocking temperature with applied external fields.
of 0T, 0.5T, and 1.5T and compared to observations at 40K and 0T in order to identify the magnetization of the clusters and field dependency. Since the expected scattering was weak, 5 wafers were stacked and placed in the beam.

The Bragg peak was observed for each measurement at a Q of 0.2 Å⁻¹, as seen in Figure 4.9, which corresponds to an cluster-to-cluster spacing of 3.1 nm, as expected from the previous room temperature SANS experiment reported in Chapter 3.

![Figure 4.9. SANS Bragg peak of Mn12(C12)16. The sharp peak corresponds to ordered material.](image)

Application of an external magnetic field should align the spins of the clusters, the direction and structure of which can be determined based on the scattering of the neutrons. The beamline set-up for a half pol experiment involves the use of a spin flipper located in front of the sample, which controls the spin direction of the neutrons that hit the sample. When it is set to ON (OFF), only spin down (up) electrons are allowed to pass through the spin flipper, the rest are scattered off before reaching the sample. Subtracting the scattering of OFF from that of ON tells
us the net magnetization coming from the material. According to the spin selection rules, only the magnetization that is perpendicular to Q participates in the scattering. Therefore, at the observed Bragg diffraction peak, maximum magnetic scattering occurs at 90° and 270°, while there is no scattering at 0°, 180°, and 360° (Figure 4.10). Since the scattering was observed at the Bragg peak, the clusters themselves are ferromagnetic at the low temperatures.

![Figure 4.10. SANS magnetism of Mn_{12}(C_{12})_{16} at Q=0.21 Å^{-1}. The maximum scattering occurs at 90° and 270°.](image)

Figure 4.10 illustrates the full magnetic scattering of the samples at 0.5T field. Note that the sector 0 refers to the magnetization parallel to Q and sector 90 is the magnetization perpendicular to Q, the latter’s features that are indicative of the model.
Figure 4.11. Magnetic scattering of Mn$_{12}$(C$_{12}$)$_{16}$ at 0.5 T field. The parallel and perpendicular components are compared.

The scattering can be fit to different models using SASView, providing a model of the magnetic structure of the clusters. Several models have been developed to fit to experimental data, however no one model fit the scattering we observed with the Mn$_{12}$(C$_{12}$)$_{16}$. Therefore, different models were combined to explain the ordering. It is most clear that there is a component of a power law to the fit, with additional character that is similar to a sphere (Figure 4.12). The power law indicates long range aggregation of spins, while in the short range region, the pattern is consistent with uncorrelated spheres. This suggests that the clusters exhibit individual magnetization, independent of their surroundings. However, in the longer-range, the spins of the clusters do align in some fashion.\textsuperscript{131} This could possibly be due to the alignment of the spins in a chain-like manner.
Interestingly, at intermediate fields magnetic scattering parallel to Q was also observed at 0.07 Å⁻¹ (Figure 4.13), where the maximum values of scattering are negative due to the direction in which spins are subtracted (ON minus OFF for consistency with previous measurements) and observed at 0, 180, and 360°. The flare observed in the image is due to this parallel component in the scattering and is slightly angled, at approximately 11°. According to the spin selection rules, this should not occur. However, we believe that this indicates a “spin-flop” of either the Mn³⁺ or Mn⁴⁺, which means that the spins of one of the oxidation states align parallel to the field, while the spins of the other are perpendicular to the field. The observed angle could be caused by canting of the spins, an effect previously observed in CoFe₂O₄ nanoparticles. This canting would be consistent with the observed tilt of the Mn₁₂(C₁₀)₁₆ clusters on HOPG, as shown in Chapter 2.
Figure 4.13. SANS magnetism of Mn$_{12}$(C$_{12}$)$_{16}$ at Q=0.07 Å$^{-1}$. The maximum scattering occurs at 0°, 180°, and 360°.

As seen with the XMCD, the spins are antiferromagnetically aligned at low fields, but applying larger fields may force the spins to align ferromagnetically. AC susceptibility measurements tell us there is a slow relaxation of spin, with an out-of-phase component. It’s probable that this out-of-phase component is what we are seeing at the low Q.

The fit of the low Q scattering is similar to that of the high Q Bragg peak seen in Figure 4.10, with obvious power law and spherical character (Figure 4.14). Though in this case it is observed parallel to the Q instead of the expected perpendicular direction. Nonetheless, this is indicative of long-range aggregation of the spins, where they are aligned in some manner.
Figure 4.14. Magnetic scattering of Mn_{12}(C_{12})_{16} at 1.5 T field. The 79° and 11° vectors are compared here.

Further modeling of these fits is necessary, however, in order to get a more accurate view of the how the clusters are truly interacting and magnetically behaving. In this regard, the system could benefit from additional SANS experiments, utilizing full polarization where the spin flip after scattering can be analyzed to determine the individual components of the neutron spins.

4.4 Conclusion

The magnetization of Mn_{12} substituted clusters was investigated to determine the effects of organization on surfaces. The bulk magnetism of powders displayed characteristic SMM behavior, with a weakly stepped hysteresis curve at low temperatures displaying the quantum tunneling of magnetization. The XMCD signal was comparable to antiferromagnetically aligned Mn^{3+} and Mn^{4+}, with apparent reduction to Mn^{2+} on the surface due to beam damage. Further experiments can attempt to reduce the damage by optimizing conditions,\textsuperscript{118,130} though it has been found that the bulk measurements are not indicative of that occurring at the monolayer, where
Mn$^{2+}$ accounted for about 20% of the composition. Further investigation of the inter-cluster interactions revealed short-range magnetic agglomeration but ferromagnetic long-range behavior similar to combined power law and spherical model. Additionally, we observed an apparent “spin-flop,” where a component of the magnetization is parallel to the Q instead of the expected perpendicular component. This may be due to the application of an external magnetic field forcing the antiferromagnetic spins to align ferromagnetically. Additional SANS experiments with full polarization instead of half may be able to separate this component by analyzing the direction of spins after scattering from the sample.
CHAPTER 5. LUMINESCENCE IN COPPER(I) HALIDE EXTENDED NETWORKS

5.1 Introduction

Luminescent materials have gained a great deal of attention because of potential applications including chemo-sensors, light-emitting diodes (LEDs), display devices and biological probes.\textsuperscript{133,134} There has long been interest in the study of univalent group 11 transition metal complexes because of their intriguing structural and photo-physical properties.\textsuperscript{135} Copper, which is abundant and inexpensive, is known to form both complexes and coordination polymers that are highly emissive even at room temperature.\textsuperscript{76–78} Recently, luminescent Cu(I) halide complexes have been found to produce efficient electroluminescence in thin film devices.\textsuperscript{77} In addition, the integration of organic-inorganic hybrids into thin film devices has been demonstrated for metal halide amine perovskite materials\textsuperscript{136} and successfully used in photovoltaic cells.\textsuperscript{138} Copper halides and pseudohalide have been of interest for vapochromism,\textsuperscript{139} and more recently for copper based organic LEDs materials.\textsuperscript{11} The interest is due to the thermally activated delayed fluorescence (TADF) which has been shown to give fast and efficient luminescence.\textsuperscript{72–74} The potential for novel devices is inspiring, and has renewed interest in the luminescent copper halide systems.

The structural chemistry of compounds formed from Cu(I), X (halide) and organo-amines is quite rich because of the lack of stereo-chemical preference of the $d^{10}$ electronic configuration.\textsuperscript{84,135} Cu(I) metal centers are particularly attractive due to their ability to assemble into coordination polymers and similar networks.\textsuperscript{84} The structure of these copper-organic frameworks largely depends on the nature of the organic ligand and the halide, but the synthetic conditions used (solvent and temperature) are also quite important. Although there are examples
where the halide has structure-directing abilities.\textsuperscript{140,141} The coordination properties of the organic ligands often control the dimensionality of the resulting polymer.\textsuperscript{76,142} We have found that for the same set of components (Cu(I), X, L), different compositions and structures can be stabilized depending on whether the synthesis is hydrothermal or from organic solvents. These building blocks have produced a wide range of polymeric structure types and have provided insight into the formation of network structures.\textsuperscript{84}

Despite the rich structural diversity, there are some commonly observed structures of copper(I) halides (Cu-X) in combination with mono- and bidentate ligands (L).\textsuperscript{84,135,143} Some frequently observed structural motifs for Cu-X include [CuXL]\textsubscript{4} tetramers, a single stranded polymer chain (zig-zag of \textendash CuX\textendash),\textsuperscript{144} and the double stranded ‘stair’ (-Cu\textsubscript{2}X\textsubscript{2}-) polymer.\textsuperscript{84,145,146} Clusters are more commonly found with monodentate ligands, while both chains and stairs can be formed with mono or bi-dentate ligands.\textsuperscript{147} We have previously investigated halide-pseudohalide copper polymer compounds using hydrothermal synthesis.\textsuperscript{141} We discovered novel structures such as a mixed halide and cyanide polymeric structure, [Cu\textsubscript{3}Cl\textsubscript{2}CN(pyrazine)]\textsubscript{n}, which exhibits three coordinate cyanide.\textsuperscript{141} This structure contrasts with the halide only polymer, [Cu\textsubscript{2}X\textsubscript{2}(pyrazine)]\textsubscript{n}, which exhibits the common double stranded ‘stair’ structure for X = Cl, Br, and I. This framework structure forms the basis for the compounds investigated here.

Of the luminescent copper halides, perhaps the most systematically studied system is the tetrameric cubane structure, [CuIL]\textsubscript{4}, for monodentate ligands, such as pyridine (py).\textsuperscript{146,148,149} This structure has been described as a Cu\textsubscript{4} tetrahedron with a larger I\textsubscript{4} tetrahedron surrounding it\textsuperscript{135} and is strongly luminescent as both a solid\textsuperscript{150} and in solution.\textsuperscript{151} The emissive state in this system is predominantly metal centered.\textsuperscript{135} Ford also investigated the luminescence of copper
halide polymers, demonstrating that both the chain and ladder structures are emissive and highlighting the role of the halogen in halogen-ligand charge transfer (XLCT) was thought to be significant. Ford argued that inorganic-organic hybrids that undergo this type of electron-transfer process are likely to exhibit non-linear optical properties, and demonstrated this for the first time in \([\text{CuI(acetyl-pyridine)}_2]_n\), chain polymer.\(^{135}\) By contrast, Araki discovered the ligand plays an important role in the luminescence properties of a series of mixed ligand, \(\text{Cu}_2\text{X}_2(\text{PPh}_3)L\) (where \(L=\text{aromatic amine}\)), dimeric complexes that form chains in the solid state.\(^{152}\) These compounds are luminescent through the full spectrum of color depending on the choice of aromatic organoamine. Thus, by modifying the double stranded \([\text{Cu}_2\text{X}_2L]_n\) stair structure and the \([\text{CuX(L)}]_n\) chain structure using select ligands from this series, we sought to determine whether the emission energy could be tuned analogously in the copper halide coordination polymers. Although less attention has been placed on the luminescence of coordination polymers,\(^{135,152,153}\) there are advantages of hybrid inorganic-organic materials due to enhanced thermal stability and emission tunability\(^{154}\) which makes them suitable for commercial applications.\(^{155}\)

In this investigation, we have synthesized a series of copper (I) iodide coordination polymers, and select bromide analogs and investigated their photophysical properties. The focus was on polymers with the -\(\text{Cu}_2\text{I}_2\)- double stranded ladder or stair backbone and include: \([\text{Cu}_2\text{I}_2L]_n\), for bidentate ligands \(L=\text{pyrazine (pyz, 1)}, \text{quinazoline (quinz, 2)}\), and \([\text{CuIL}]_n\) for monodentate ligands \(L=3\)-benzoylpyridine (3-bzpy, 3) and 4-benzoylpyridine (4-bzpy, 4). We were interested in elucidating the role of the halide by preparing bromide analogs of each compound, however, the analogous structure type was not always observed. In the case of \([\text{Cu}_2\text{X}_2 (\text{pyz})]\), this compound can be prepared for all of the halides \(X=\text{Cl, Br, I}\), and here we
report the luminescence properties of the Br and I systems. In the case of the copper bromide reaction with quinazoline formed a different structure type, with the single stranded 'zig-zag' chain of copper bromide, \( [\text{CuBr(quinz)}]_n \) (7). We include \( [\text{CuBr(pyz)}]_n \) (6) in order to compare the properties of the single stranded chain structures with the double stranded stair in the Cu-Br-pyz series. For this series of compounds, only two have unreported structures, so we include the crystal structures of \( [\text{Cu}_2\text{I}_2(\text{quinz})]_n \), (2) and \( [\text{CuI}(3\text{-bzpy})]_n \) (3). The luminescence at both room temperature and low temperature (77K), as well as the lifetime measurements are reported for all compounds. We explored the non-linear optical (NLO) properties for all compounds with non-centrosymmetric space groups, and found the \( [\text{CuBr(quinz)}]_n \) to have the most significant properties.

5.2 Experimental Section

5.2.1 General Information

Acetonitrile, copper(I) iodide, copper(I) bromide, quinazoline, pyrazine, dimethylaminopyridine, and 3-benzoylpyridine were obtained from Sigma Aldrich. 4-benzoylpyridine was obtained from Alfa Aesar. All materials were used as received. All the copper(I) halide polymers were characterized by IR and elemental analysis. Infrared spectra were measured in the range 450-4000 cm\(^{-1}\) as pressed KBr pellets on a Nicolet 380 FTIR spectrometer. Elemental analysis (C, H and N content) was performed on a Perkin Elmer 2400 microanalyzer, using acetonilide as standard. Phase purity was supported using powder x-ray diffraction using a Rigaku Ultima IV powder diffractometer with Cu K\( \alpha \) radiation, under a range of 20-80° 2\( \theta \).

\( [\text{Cu}_2\text{I}_2(\text{pyz})]_n \) (1). A solution of pyrazine (0.0400 g, 0.5 mmol) in CH\(_3\)CN (20 mL) was added to a CH\(_3\)CN (20 mL) solution of CuI (0.1904 g, 1.0 mmol). Yellow solid appeared upon
stirring, which was isolated by vacuum filtration. The product was washed with acetone and recrystallized in hot CH$_3$CN. The resulting yellow block crystals were found to emit a bright orange color under UV light. IR (cm$^{-1}$): 1637 (s), 1477 (m), 1416 (vs), 1157 (m), 1120 (m), 1049 (m), 804 (m), 451 (m). Anal. Calc’d. for C$_4$H$_4$N$_2$Cu$_2$I$_2$: C, 10.42; H, 0.87; N, 6.08; Found: C, 10.63; H, 0.83; N, 5.87. Percent yield 76%.

$[\text{Cu}_2\text{I}_2(\text{quinz})]_n$ (2). A solution of CuI (0.1904 g, 1.0 mmol) in CH$_3$CN (25 mL) was added to an CH$_3$CN solution (25 mL) of quinazoline (0.0650 g, 0.5 mmol). The resulting yellow solution was allowed to stand undisturbed overnight, upon which, red-orange needles slowly formed. The product was collected by vacuum filtration, washed with acetone and recrystallized from hot CH$_3$CN. The crystals were found to emit an orange color under UV light. IR (cm$^{-1}$): 1713 (s), 1617 (s), 1576 (s), 1561 (w), 1488 (s), 1378 (s), 1302 (m), 1208 (s), 1151 (w), 1137 (m), 1085 (m), 965 (m), 785 (s), 750 (s), 647 (m), 633 (m), 487 (m). Anal. Calc’d. for C$_8$H$_6$N$_2$Cu$_2$I$_2$: C, 19.0; H, 1.13; N, 5.29; Found: C, 18.79; H, 1.06; N, 5.43. Percent yield 83%.

$[\text{CuI}(3\text{-bzpy})]_n$ (3). A solution of CuI (0.1904 g, 1.0 mmol) in CH$_3$CN (10 mL) and a solution of 3-benzoylpyridine (0.1832 g, 0.5 mmol) in CH$_3$CN (5 mL) were added to form a fluffy, bright yellow powder. The product was collected by vacuum filtration and washed with acetone. Recrystallization in hot CH$_3$CN afforded the formation of fine, yellow needles that emit an intense yellow color under UV light. IR (cm$^{-1}$): 1662 (vs), 1593(s), 1577 (w), 1448 (m), 1418 (m), 1319 (s), 1286 (vs), 1195 (w), 1157 (w), 1031 (w), 941 (w), 927 (w), 827 (w), 790 (w), 744 (w), 707 (vs), 687 (w), 655 (m). Anal. Calc’d. for C$_{12}$H$_9$NOCuI: C, 38.57; H, 2.43; N, 3.75; Found: C, 38.34; H, 2.32; N, 3.71. Percent yield 63%.
[CuI(4-bzpy)]ₙ (4). To a CH₃CN (20 mL) solution of CuI (0.1904 g, 1.0 mmol), a solution of 4-benzoylpyridine (0.1832 g, 1.0 mmol) in CH₃CN (20 mL) was added. Immediate formation of an orange precipitate was observed upon stirring. The product was collected via vacuum filtration and washed with acetone. Recrystallization in hot CH₃CN resulted into the formation of orange needles that were found to emit red luminescence under UV light. IR (cm⁻¹): 1657 (vs), 1596 (w), 1446 (m), 1411 (vs), 1281 (vs), 946 (m), 747 (m), 694 (vs), 647 (s). Anal. Calc’d. for C₁₂H₉NOCuI: C, 38.57; H, 2.43; N, 3.75; Found: C, 38.38; H, 2.28; N, 3.62. Percent yield 91%.

[Cu₂Br₂(py)z]ₙ (5). CuBr (0.173 g, 1.2 mmol), pyrazine (0.048 g, 0.6 mmol), and 8 mL of HBr (0.26M) were combined in a hydrothermal bomb. After 5 h at 150°C, the reaction vessel was cooled at 0.2°C/min to room temperature. The yellow crystals were filtered off in air and washed with acetone. They were luminescent under UV light as a bright yellow color. IR (cm⁻¹): 1476 (m), 1409 (vs), 1156 (m), 1113 (m), 1047 (m), 800 (m), 448 (m). Anal. Calc’d. for C₄H₄N₂Cu₂Br₂: C, 13.09; H, 1.10; N, 7.63; Found: C, 13.34; H, 1.17; N, 7.61. Percent yield 53%.

[CuBr(py)z]ₙ (6). A solution of pyrazine (0.0400 g, 0.5 mmol) in CH₃CN (20 mL) was added to a CH₃CN (20 mL) solution of CuBr (0.143 g, 1.0 mmol). Orange solid appeared upon stirring, which was isolated by vacuum filtration. The product was washed with acetone and recrystallized in hot CH₃CN. The resulting orange block crystals were found to emit a bright red color under UV light. IR (cm⁻¹): 1477 (m), 1416 (vs), 1159 (m), 1117 (m), 1054 (m), 804 (m), 450 (m). Anal. Calc’d. for C₄H₄N₂CuBr: C, 21.49; H, 1.80; N, 12.53; Found: C, 19.65; H, 1.65; N, 10.71. Percent yield 78%.
[CuBr(quinz)]\(_n\) (7). A solution of CuBr (0.0717 g, 0.5 mmol) in CH\(_3\)CN (25 mL) was added to a CH\(_3\)CN (25 mL) solution of quinazoline (0.0651 g, 0.5 mmol). The metallic orange plate-like crystals that came out were isolated via vacuum filtration and washed with CH\(_3\)CN. The product was luminescent under UV light as a red color. IR (cm\(^{-1}\)): 1615 (s), 1572 (m), 1487 (s), 1384 (vs), 1306 (m), 1206 (w), 1155 (w), 928 (w), 791 (vs), 748 (vs), 648 (w), 633 (m), 486 (m). Anal. Calc’d. for C\(_8\)H\(_6\)N\(_2\)CuBr: C, 35.12; H, 2.21; N, 10.24; Found: C, 35.12; H, 2.18; N, 10.18. Percent yield 39%.

5.2.2 Photophysical Characterization

The photoluminescence data were obtained in a Fluorolog-3 spectrofluorimeter (Horiba FL3-22-iHR550), with 1200 grooves/mm excitation monochromator gratings blazed at 330 nm and 1200 grooves/mm emission monochromator gratings blazed at 500 nm. An ozone-free xenon lamp of 450 W (Ushio) was used as a radiation source. The excitation spectra corrected for instrumental function were measured between 250 and 600 nm. The emission spectra were measured in the range 450-850 nm in front face mode at 22.5°. All emission spectra were corrected for instrumental function. The emission decay curves were obtained using a TCSPC system and a Horiba NanoLED model N-370 (peak wavelength = 370 ± 10 nm, ~4 pJ/pulse) as excitation source. All spectra were measured on solid samples.

5.2.3 Non-linear Optical Properties

Approximately 200 mg of the powdered material was sieved into different particle size ranges (<20, 20-45, 45-63, 63-75, 75-90, and 90-125 µm) and subsequently placed in separate fused silica tubes. To compare with a known SHG material, a standard, α-SiO\(_2\), was also ground and sieved into the same particle size range. Powder SHG measurements
were carried out on a modified Kurtz-NLO56 system equipped with a pulsed Nd:YAG laser having an output of 1064 nm. Phase matching information was determined and the SHG efficiency of the sample was reported with respect to α-SiO₂.

5.2.4 Single Crystal X-ray Crystallography

A suitable needle-like crystal was mounted on a Mitegen micromount for single-crystal x-ray diffraction analysis. Intensity data were collected on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector using Mo Kα radiation (λ = 0.71073 Å). The data were integrated using the APEX2 suite of software and absorption corrections were calculated using SADABS/TWINABS. The structures were solved using direct methods and refined by full-matrix least squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located in calculated positions and refined isotropically. Crystallographic details can be found in the Supporting Information.

5.2.5 Computational Methods

Density functional theory (DFT) calculations were performed with the Gaussian 09/D.01 package, using the geometric parameters of [CuI(3-bzpy)]ₙ and [CuI(4-bzpy)]ₙ obtained from XRD analysis. The structures were extended to include at least two CuI units. Single point calculations were performed with B3LYP functional level of theory and 3-21G* basis set for all atoms. The HOMO and LUMO figures were generated with ChemCraft.
5.3 Results and Discussion

5.3.1 Synthesis of CuI Coordination Polymers

We have synthesized a series of Cu-I compounds with the ligands illustrated in Figure 5.1 under both hydrothermal and acetonitrile conditions.

These N-heteroatomic aromatic ligands were selected from those used in the previously reported series Cu$_2$X$_2$(PPh$_3$)(L), on the basis of the spectral range of emission, and their ability to form a polymer network (chains or stairs). Copper (I) halide coordination polymers have been reported from both hydrothermal synthesis$^{160-162}$ and from organic solvents.$^{84,142}$ Hydrothermal conditions are ideal for crystal growth, and aqueous Cu(I) can be stabilized under these conditions by the presence of organoamines. We have previously been unable to grow single crystals of [Cu$_2$I$_2$(pyz)]$_n$ hydrothermally, but the structure was reported from the hydrothermal synthesis of Cu(II) with pyrazine carboxylate by zur Loye.$^{163}$ We prepared this compound directly from CuI and pyrazine in acetonitrile, similar to most of the compounds reported here. In some systems both approaches form the same compounds, but frequently either the stair or the chain compound is exclusively found for a given method.

For most of our syntheses, whether hydrothermal or from organic solvents, the stoichiometry of reagents does not dictate the product stoichiometry. In most cases variation of
the metal:halide:ligand ratio did not change the product composition for either method. This is in contrast to the Cu:X system with the ligand 4, 4'-bipyridyl, in which the stoichiometry of the product, [CuXL] or [(CuX)_2L], could be controlled by the reagent ratio of CuX:L. The effect of the synthetic conditions can be illustrated by the two series of compounds where L includes the bidentate ligands pyrazine and quinazoline. In the series with pyrazine, using hydrothermal synthesis it was possible to form the stair structures, [Cu_2X_2(pyz)]_n, for X = Cl, Br, and I, but none of the chain compounds [CuX(pyz)]_n. Using acetonitrile as the solvent, the iodide also formed the stair structure [Cu_2I_2(pyz)]_n, but for bromide only the chain structure [CuBr(pyz)]_n could be prepared. In the case of quinazoline, we found that the stair compound [Cu_2I_2(quinz)]_n was also easily stabilized from either hydrothermal or organic solvents, but never the chain compound [CuI(quinz)]_n. For bromide with quinazoline, the chain compound [CuBr(quinz)]_n could only be formed from acetonitrile, and it was not possible to crystallize the stair structure [Cu_2Br_2(quinz)]_n using either method. In most general terms, we found that the chain compounds form under acetonitrile conditions while the stair compounds were more easily crystallized hydrothermally. We were, however, unable using any method to prepare: [CuI(pyz)]_n, [CuI(quinz)]_n, or [Cu_2Br_2(quinz)]_n, creating gaps in the series of compounds reported here. The inability to isolate these compounds suggests that the stair structure is more stable for the iodide complexes while the chain structure is more stable for the bromide. By contrast, using the monodentate ligands benzoylpyridine (bzpy), we were unable to isolate any chain compounds for the iodide or bromide using either method. Although we were able to prepare bromide analogs of the stair structures from acetonitrile with this ligand, they did not luminesce and are not included here.
5.3.2 Structure Determination

The focus of these studies is on two structure types, the 'stair' and the 'chain' compounds, which have been nicely summarized previously for mono and bi-dentate ligands. Inconveniently, the stoichiometry of the product does not indicate structure. In the case of monodentate ligands the metal:halide:ligand stoichiometry 1:1:1 could structurally be a dimer or stair type polymer (Cu$_2$X$_2$L$_2$), or tetramer (Cu$_4$X$_4$L$_4$). For example, pyridine can form either a cubane cluster [CuIpy]$_4$ or the stair polymer [CuIpy]$_n$ depending on the conditions (e.g. the tetramer is favored at low temperatures).

![Figure 5.2. Crystal structures of ladder compounds.](image)

[2, left] and [CuI(3-bzpy)]$_n$ (3, right) both have the bidentate amine bridging -Cu$_2$I$_2$- ladder, but the ligand is bidentate for quinz, and monodentate for 3-bzpy.

The structure of [CuIpy]$_n$ is quite similar to the double stranded stair structure with pendant monodentate ligands as illustrated in Figure 5.2 (right). For the copper halide organoamine complexes reported here there were only two different structure types, double stranded stair structure illustrated in Figure 5.2, and the zig-zag chain structure shown in Figure 5.3.
One advantage for the photophysical studies is that generally the structure can be preserved with different halides, while for the cluster compounds the structure can change substantially with a change in halide.\textsuperscript{135} It is possible to form either structure with monodentate or bidentate organoamine ligands as presented in Table 5.1.\textsuperscript{163} This table summarizes the structure type, bonding mode, Cu-Cu bond distance, aromatic ring distance, and space group for the known structures. All compounds were characterized by elemental analysis and powder x-ray diffraction to confirm the powders were single phased, and the patterns were matched with diffraction patterns generated from the single crystal structures.

Table 5.1. Structural information for copper compounds. Structural differences are apparent.

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Ligand bonding mode</th>
<th>Cu-Cu Bond (Å)</th>
<th>Aromatic Rings (Å)</th>
<th>Space Group</th>
<th>Refcode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$I$_2$(pyz)</td>
<td>Stair</td>
<td>bidentate</td>
<td>2.756 4.134</td>
<td>P-1</td>
<td>AGIYEU01\textsuperscript{42}</td>
</tr>
<tr>
<td>Cu$_2$I$_2$(quinz)</td>
<td>Stair</td>
<td>bidentate</td>
<td>2.739 3.486 2.654 4.207</td>
<td>P-1</td>
<td></td>
</tr>
<tr>
<td>CuI(3-bzpy)</td>
<td>Stair</td>
<td>monodentate</td>
<td>2.6819 4.064</td>
<td>C2</td>
<td></td>
</tr>
<tr>
<td>CuI(4-bzpy)</td>
<td>Stair</td>
<td>monodentate</td>
<td>2.818 4.178 2.895</td>
<td>P21/c</td>
<td>KALNOA\textsuperscript{43}</td>
</tr>
<tr>
<td>Cu$_2$Br$_2$(pyz)</td>
<td>Stair</td>
<td>bidentate</td>
<td>2.814 3.868</td>
<td>P-1</td>
<td>WOWYOW\textsuperscript{17}</td>
</tr>
<tr>
<td>CuBr(pyz)</td>
<td>Chain</td>
<td>bidentate</td>
<td>3.986 3.986 3.756 3.876</td>
<td>P c a 2</td>
<td>VEVFUX\textsuperscript{15}</td>
</tr>
<tr>
<td>CuBr(quinz)</td>
<td>Chain</td>
<td>bidentate</td>
<td>3.876 3.756 3.876</td>
<td>P c a 2</td>
<td>HUWCEH\textsuperscript{14}</td>
</tr>
</tbody>
</table>
For the two unreported structures we include select crystallographic information in Table 5.2. We found quinazoline compound \([\text{Cu}_2\text{I}_2(\text{quinz})]_n\) (2) to have the common double-stranded 'stair' structure with the stairs linked with the bidentate ligand as illustrated in Figure 5.2 (left). The copper is four-coordinate (to three iodine and the nitrogen of one ligand) in a distorted tetrahedral geometry. We also report the structure of benzoylpyrazine compound \([\text{CuI}(3\text{-bzpy})]_n\) (3). This compound is iso-structural with the previously reported \([\text{CuI}(4\text{-bzpy})]_n\) (4) shown in Figure 5.2 (right). Both have the same double stranded stair, with only monodentate coordination of the ligand. In the case of the \([\text{CuI}(3\text{-bzpy})]_n\) the two rings of the benzoyl pyridine are not co-planar, and form a herring bone stack between the ladders.

**Table 5.2. Crystallographic information.** We report the structures of compounds 2 & 3.

<table>
<thead>
<tr>
<th></th>
<th>([\text{Cu}_2\text{I}_2(\text{quinz})]_2)</th>
<th>([\text{CuI}(3\text{-bzpy})]_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space Group</strong></td>
<td>P-1</td>
<td>C2</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>4.2068(8)</td>
<td>15.744(3)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>8.8327(17)</td>
<td>4.0635(6)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>15.339(3)</td>
<td>18.279(4)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
<td>92.608(6)</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>91.696(6)</td>
<td>92.191(5)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>100.988(6)</td>
<td>90</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
<td>558.51(18)</td>
<td>1168.6(4)</td>
</tr>
<tr>
<td><strong>R_f</strong></td>
<td>0.0831</td>
<td>0.0318</td>
</tr>
</tbody>
</table>

Both compounds were found to have relatively short Cu-Cu bond lengths, less than the van der Waals radius of 2.85 Å (\([\text{Cu}_2\text{I}_2(\text{quinz})]_n\) had the shortest Cu-Cu distance of 2.65Å and \([\text{CuI}(3\text{-bzpy})]_n\) shortest distance was 2.68Å). Another structural feature relevant for the optical properties is the distance between the aromatic rings, which were in the weak limit of greater than 3.5Å. Quenching of emission could result from stacking, as reported for trans-stilbazole polymers with copper iodide.\(^{167}\)
5.3.3 Luminescence Studies

The emissive excited states observed in copper halide compounds include metal centered, metal-to-ligand charge transfer (MLCT) and halide-to-ligand charge transfer (XLCT). Previous luminescence studies of copper halide 'chains' and 'stair' compounds investigated by Ford found that the emission energy was influenced by the polarizability of the halide and the electronic properties of the ligand.\textsuperscript{167} By contrast, for cluster compounds a cluster-centered excited state of $d$-$s$ character ($^3CC$) was present and was found to be influenced by the Cu-Cu bond length.\textsuperscript{135}

Table 5.3. Luminescence data. The emissions & lifetimes of compounds 1-7 are reported.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure Type</th>
<th>$\lambda_{exc}$ (nm)</th>
<th>$\lambda_{em}$ 298K (nm)</th>
<th>$\lambda_{em}$ 77K (nm)</th>
<th>$\tau_{298,K}$\textsuperscript{[a]} (µs)</th>
<th>$\tau_{77,K}$\textsuperscript{[a]} (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 [Cu$_2$I$_2$(pyz)]</td>
<td>stair</td>
<td>400</td>
<td>676</td>
<td>621</td>
<td>0.944 ± 0.011 (0.32)</td>
<td>0.094 ± 0.011 (0.47)</td>
</tr>
<tr>
<td>2 [Cu$_2$I$_2$(quinz)]</td>
<td>stair</td>
<td>390</td>
<td>620</td>
<td>639</td>
<td>0.823 ± 0.017 (0.18)</td>
<td>0.121 ± 0.017 (0.20)</td>
</tr>
<tr>
<td>3 [CuI(3-bzpy)]</td>
<td>stair</td>
<td>390</td>
<td>556</td>
<td>553, 590 (sh)</td>
<td>1.051 ± 0.006 (0.64)</td>
<td>0.244 ± 0.007 (0.36)</td>
</tr>
<tr>
<td>4 [CuI(4-bzpy)]</td>
<td>stair</td>
<td>270</td>
<td>664</td>
<td>654, 716 (sh)</td>
<td>0.934 ± 0.033 (0.14)</td>
<td>0.194 ± 0.002 (0.86)</td>
</tr>
<tr>
<td>5 [Cu$_2$Br$_2$(pyz)]</td>
<td>stair</td>
<td>420</td>
<td>609</td>
<td>591</td>
<td>3.24 ± 0.03 (1.00)</td>
<td>15.6 ± 0.3 (1.00)</td>
</tr>
<tr>
<td>6 [CuBr(pyz)]</td>
<td>chain</td>
<td>390</td>
<td>682</td>
<td>729</td>
<td>1.19 ± 0.14 (0.33)</td>
<td>0.20 ± 0.03 (0.67)</td>
</tr>
<tr>
<td>7 [CuBr(quinz)]</td>
<td>chain</td>
<td>270</td>
<td>644</td>
<td>680</td>
<td>1.058 ± 0.002 (0.43)</td>
<td>0.183 ± 0.003 (0.49)</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} – The fractions of each lifetime are indicated between parenthesis. * - The decay of the compound was not observed.
Generally, all of the compounds investigated here exhibit luminescence due to XLCT (at room temperature and 77 K) in the range of 550-680 nm. In Table 5.3, we report the excitation, emission wavelengths, emission lifetimes, and Cu-Cu distances for compounds 1-7. Although [CuI(3-bzpy)]\textsubscript{n} has the highest energy emission and shortest Cu-Cu bond (2.68Å), collectively there is no trend between the copper-copper bond length and the emission energy, indicating a reduced role of metal centered bonding in the luminescence properties.

5.3.3.1 Bromide-vs-Iodide

To probe the role of the halide, we aimed to compare coordination polymers with the same structure and ligand, with either bromide or iodide. Our example is for the stair structure with pyrazine as the bridging ligand, and their emission spectra are shown in Figure 5.4.

![Figure 5.4. Emission spectra of CuX\textsubscript{2}(pyz). Room temperature (solid) and 77K (dashed) emission spectra where X = Br (5, green), and I (1, black). Room temperature solid lines and 77K dashed lines.](image)

After deconvolution, the 0-0 transition of [Cu\textsubscript{2}I\textsubscript{2}(pyz)]\textsubscript{n} is located at 663 nm and for [Cu\textsubscript{2}Br\textsubscript{2}(pyz)]\textsubscript{n} at 548 nm. The shift to lower energy for the heavier iodide analog is consistent with what one would expect based on polarizability, or alternatively electronegativity. This is in contrast to the emissive properties of two previously reported stair polymers with the monodentate ligand pyridine, [CuI(py)]\textsubscript{n} which shows an emission maximum at 437 nm, while the [CuBr(py)]\textsubscript{n} has a peak at 509 nm.\textsuperscript{81} The explanation for this reversal in trend is thought to be
due to the halide ionicity, or ligand field strength in the case of [CuX(dtpb)] (dtpb = 1,2-bis (o-
ditolylyphosphino)benzene). What is also notable here is that the luminescence appeared
weaker for bromide analogs, while in several cases the chloride analog lacked any observable
emission.

5.3.3.2 Chain-vs-Stair Structure

We anticipated that the structure, whether stair or chain polymer should influence the
luminescence properties. Thus we were interested in comparing systems with the same ligand
and the same halide but different structure type. The example from our work is for copper,
bromide and pyrazine, forming either the [Cu2Br2(pyz)]ₙ which has the stair structure type and
the 0-0 transition is at 586 nm, in contrast to the [CuBr(pyz)]ₙ with the chain structure that shows
its 0-0 transition at 648 nm. The emission spectra for these two compounds (as well as
[CuBr(quinz)]ₙ) are shown in Figure 5.5.

![Figure 5.5. Emission spectra of CuBr polymers. Room temperature spectra of compounds
[Cu2Br2 (pyz)]ₙ (5, green) [CuBr(quinz)]ₙ (7, blue), and [CuBr(pyz)]ₙ (6, black).
]

The emission at longer wavelengths for the chain structure can also be observed by
comparing the acetyl-pyridine (acpy) polymers with the stair structure, [CuI(acpy)]ₙ (emission
maximum at 612 nm), with the chain structure, [CuI(acpy)₂]ₙ (emission maximum at 700 nm).
We postulate, as discussed below, that the HOMO is based on a mix of the metal and halogen
orbitals, while the LUMO is dominantly $\pi^*$ ligand orbitals. The higher energy of the stair may be a result of stabilization of the HOMO due to delocalization through the stair structure increasing the energy separation between HOMO and LUMO.

5.3.3.3 Ligand Binding Mode

One approach to determining the effect of the ligand was to compare coordination polymers with the same structure, same halide and ligands differing only as to whether they are monodentate or bidentate. There are several possibilities, but our focus was on the comparison between pyridine and pyrazine. For the iodide example, the $[\text{CuI(py)}]_n$ with the stair structure was reported to have its emission maximum at 437 nm,\textsuperscript{135} whereas $[\text{Cu}_2\text{I}_2(\text{pyz})]_n$ also has a stair structure but with a bridging pyrazine and emission maximum at 676 nm. In the case of bromide for the same system, the previously reported $[\text{CuBr(py)}]_n$ with the stair structure has an emission maximum at 509 nm. However the $[\text{Cu}_2\text{Br}_2(\text{pyz})]_n$ also has a stair structure with the bridging pyrazine and shows its emission maximum at 609 nm. Both examples suggest that the bridging ligand has a shifted LUMO, or that potentially delocalization lowers the LUMO giving a lower energy emission for the bridged ligands.

5.3.3.4 Ligand Electronic Structure

Of all the components that affect the emission energy of the copper halide polymers, we found that the electronic structure of the ligand was most important. We selected the ligands based on the emission reported for the $[\text{Cu}_2(\mu-\text{Br})_2(\text{PPh}_3)_2(L)]_n$ complexes, which varied between ~579 nm and 707 nm. The energy of emission of these complexes decreased in the order 3-bzpy > quinz > 4-bzpy > pyz. The same energy of emission order was found for these ligands in the
[Cu$_2$I$_2$L]$_n$ series. The range of emission energies (556 nm-676 nm) is also close even though we would expect the iodide to be generally shifted compared with the bromide compounds.

![Figure 5.6. Emission spectra of CuI polymers. Room temperature (solid) and 77K (dashed) spectra of [CuI(3-bzpy)]$_n$ (3, green), [Cu$_2$I$_2$ (quinz)]$_n$ (2, blue), [CuI(4-bzpy)]$_n$ (4, black).](image)

Perhaps the most striking example of the ligand effect is for the closely related benzoyl-pyridine isomers 3-bzpy and 4-bzpy, which differ only in whether the non-coordinating benzoyl substitutes meta- or para- on the pyridine ring. In this example, [CuI(3-bzpy)]$_n$ has its 0-0 phonon transition at 539 nm, whereas the one of [CuI(4-bzpy)]$_n$ is red-shifted to ~637 nm (Figure 5.6). This is the strongest argument for the role of the ligand electronics in the emission spectra. For this particular pair, we have carried out the MO calculations to determine the properties of the HOMO and LUMO by the DFT method on Gaussian 09. The geometry was taken from the crystal structures, and the fragment included in the calculation was two –Cu-I—units and two ligands. The calculated energy levels were similar to those of previously investigated copper iodide complexes in that the HOMO is dominantly based on the copper 3$d$ and iodide 4$p$ orbitals, whereas the LUMO is primarily based on the $\pi^*$ of the aromatic amine (see Figure 5.7). The low overlap between the donating and accepting orbitals often leads to a low energy gap between $S_1$ and $T_1$ as observed by Steffen. For the two compounds compared here, the calculated HOMO-LUMO difference was 2.05 eV or 600 nm for [CuI(3-bzpy)]$_n$ compared with 539 nm.
experimentally, and 1.74 eV or 712 nm for CuI(4-bzpy)\textsubscript{n} compared with 637 nm observed experimentally.

![Molecular Orbital Diagram](image)

**Figure 5.7. Molecular orbital diagram and HOMO/LUMO representations.** The HOMO (upper left) orbitals illustrating the combination of metal and iodide, and the LUMO (upper right) orbitals illustrating the contribution of the π* aromatic amine orbitals. On the right, molecular orbital calculation for [CuI(3-bzpy)]\textsubscript{n} (left) and [CuI(4-bzpy)]\textsubscript{n} (right).

Both values are ~ 60 nm too low in energy, but the trend is consistent. These calculations are supported by studies by Araki, who found that the emission energy in the [(Cu\textsubscript{2}Br\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}(L\textsubscript{2})] for L = 3-bzpy, 4-bzpy also using DFT methods found similar frontier orbitals, where the excited state was due to charge transfer from the metal to the π* of the N-heteroaromatic ligand with mixing of the halogen adding XMLCT. Charge transfer to an antibonding LUMO should cause a geometrical change, involving bond change and large Stokes shift. Our shifts are < 7000-10000 cm\textsuperscript{-1} similar to that observed by Pike.\textsuperscript{165,169} Larger Stokes shifts (12000-14000 cm\textsuperscript{-1}) have been observed for tetranuclear clusters.\textsuperscript{165}
5.3.4 Luminescence Lifetime Measurements

The emission decay curves for the \([\text{Cu}_2\text{I}_2(\text{pyz})]_n\), \([\text{Cu}_2\text{I}_2(\text{quinz})]_n\) and \([\text{CuBr}(\text{quinz})]_n\) complexes (Table 5.3) show three lifetime components, with the shortest in the 1–50 ns range attributed to fluorescence. The longer lifetime components, with similar magnitudes as those observed for the \([\text{CuI}(\text{3-bzpy})]_n\), \([\text{CuI}(\text{4-bzpy})]_n\) and \([\text{CuBr}(\text{pyz})]_n\) complexes (Table 5.3) and for the \([\text{Cu}_2\text{Br}_2(\text{pyz})]_n\) complex (Table 5.1), are shorter than what would be expected for phosphorescence (10–1000 \(\mu\)s) and can be attributed to TADF (Thermally Activated Delayed Fluorescence) or singlet harvesting.\(^4\) In this process, after intersystem crossing (\(S_1 \rightarrow T\)) the \(S_1\) level is thermally repopulated if the singlet-triplet energy gap is approximately 1000 cm\(^{-1}\) (or 0.15 eV) as suggested by our calculations.\(^1\) For larger energy separations (10\(^3\) cm\(^{-1}\)), only triplet emission is observed at room temperature. The TADF mechanism also explains the overlap between excitation and emission, which is characteristic of “pure” fluorescence transitions accompanied by a relatively long fluorescence lifetime. TADF is very attractive for OLED applications due to the possibility of obtaining high electroluminescence efficiencies along with short, when compared to phosphorescent materials, emission lifetimes.\(^73,74,168,170\) The emission lifetime depends on the rigidity of the structure and the energy gap between the excited and ground states. In the present case, the rigidity of the structure is a factor that contributes to increase the emission lifetimes due to the polymeric nature of the complexes (Figures 5.2 and 5.3). The direct dependence of the emission lifetime on the energy gap between excited and ground states was demostred by Kato and co-workers.\(^171\) This dependence explains the shorter emission lifetimes values obtained with our compounds when compared with several reported
blue emitters.\textsuperscript{172,173} In addition, the lifetimes measured here are similar to those of orange and red emitters reported by Steffen and co-workers also attributed to TADF.\textsuperscript{11}

To confirm that TADF is responsible for the observed emission behavior, the excitation and emission spectra were obtained at 77 K (Figures 5.4 and 5.5). We note that we do not have temperature dependent structural information for any of these compounds to determine whether there are structural distortions or symmetry changes as a function of temperature. Two compounds, [Cu$_2$I$_2$(pyz)$_n$] and [Cu$_2$Br$_2$(pyz)$_n$], had emission energies with hypsochromic shift at low temperature (the energy difference between the room temperature and low temperature peaks is ~500 cm$^{-1}$), similar to that observed for the chains of dimers, {Cu$_2$X$_2$(PPh$_3$)(L)}.\textsuperscript{152} All other compounds exhibited a bathochromic shift, in the range 823-1,310 cm$^{-1}$ (the difference between the high and low temperature peaks is similar to that observed for the phosphine copper dimers reported by Deaton).\textsuperscript{73} In the case of the bzpy ligands is possible to observe the vibrational splitting in the spectra of both isomers [CuI(3-bzpy)$_n$] and [CuI(4-bzpy)$_n$] with energies of 1,134 cm$^{-1}$ and 1,324 cm$^{-1}$, respectively, which is close to one of the vibrational modes of these complexes (see experimental section). Finally, the decrease in temperature decreases the probability of the thermally activated $^3\text{T} \rightarrow ^1\text{S}_1$ conversion that is reflected in the increase of the lifetime up to tens of $\mu$s (Table 5.3), which is characteristic of phosphorescence.\textsuperscript{173} The energy shifts in combination with the lifetime measurements suggest there is more than one emission level, and they are close enough in energy for TADF.

5.3.5 Non-linear Optical Properties

Materials possessing non-centrosymmetric space groups have the potential to emit second harmonic generation (SHG) light upon laser irradiation.\textsuperscript{79,80} In addition to
structural constraints, the presence of a charge transfer transition has also been identified as an important electronic feature that leads to second-order NLO response. Alignment along a specific direction of related chromophores has been observed to increase SHG efficiencies in organic salts. Ford investigated the NLO properties of non-centrosymmetric \([\text{CuX(L)}]_n\) \((X = \text{Cl, Br, I, L= pseudoaromatic } \eta^1 \text{ nitrogen donor ligands})\) with single-stranded and ladder type structures to determine the structural and electronic properties that contribute to the SHG. Based on these studies, the conclusions were: 1) the SHG efficiencies do not follow the intensity of emissions, 2) the MLCT process alone does not control the second-order NLO activity, and 3) chain compounds appear to exhibit stronger NLO than ladders.

![Figure 5.8. SHG curve for CuBr(quinz). Phase matchable and ~150 times larger than α-SiO₂ for 45-63 µm particle size.](image)

We investigated the second order NLO of several compounds reported here, using an incident non-resonant wavelength of 1064 nm, taking quartz (α SiO₂) as the reference material.
The NLO values for copper halide polymers reported previously ranged from 23-45 times that of quartz. The strongest SHG we observed was for the [CuBr(quinz)]\textsubscript{n} (7). This compound crystallizes in the space group \textit{Pca2}\textsubscript{1} and emits in the red, with a \(\lambda_{\text{em}} = 644\) nm. The SHG was shown to be phase matchable, and \(\sim100\) times larger response compared to \(\alpha-\text{SiO}_2\). The structure type is similar to the chain structures reported previously, in which the copper is bonded to two ligands. The structures subtly differ in that the quinazoline compound reported here has ligands that bridge two chains. Nonetheless, our results are a modest improvement over those reported previously.

5.4 Conclusion

In this series of copper bromide and iodide organoamine coordination polymers we have reported the crystal structure of two new compounds, [Cu\textsubscript{2}I\textsubscript{2}(quinz)]\textsubscript{n} (2) and [CuI(3-bzpy)]\textsubscript{n} (3). Both coordination polymers have the frequently observed double stranded ‘stair’ formed by \(-\text{Cu}_2\text{I}_2-\) units. We have also investigated the luminescence properties of several ‘stair’ type coordination polymers, found that the emission is most likely due to a \((M+X)LCT\). While the structure and halide are important for the emission energies, it appears that the electronic structure of the ligand has the strongest impact. The copper iodides have the advantage of being air-stable and although we have not investigated the electroluminescent properties, these materials exhibit TADF and may be of potential interest in organic light-emitting diodes. In screening the non-centrosymmetric structures, we discovered one of the strongest NLO response observed in the copper halide organoamine systems in the chain structure [CuBr(quinz)]\textsubscript{n} (7).
CHAPTER 6. CONCLUSION

Both cluster and coordination materials were investigated here for the purpose of preparing ordered assemblies. This is a key concern for materials development in being able to apply the attractive magnetic and luminescent properties for application.

The ability of Mn$_{12}$ SMM clusters to self-assemble on a variety of surfaces has been demonstrated here by altering the size and shape through ligand exchange with long-chained carboxylates. Long chains, such as those C9 and longer, result in clusters with aspect ratios closer to 1. The more spherical material drives the hexagonal close-packing onto surfaces, without having to utilize gold-thiol interactions, as seen in the SANS measurements that displayed the superlattice peaks for these longer chained materials, but not for the shorter ones. All clusters retained their SMM behavior upon ligand exchange and displayed ordering perpendicular to the substrates. Probing of the magnetic behavior with XMCD revealed antiferromagnetic behavior between the Mn$^{3+}$ and Mn$^{4+}$ within clusters, however the beam proved too intense for hysteresis investigation, as reduction to Mn$^{2+}$ occurred. Further experiments should probe the magnetism on surfaces utilizing other methods. Thick films can be probed through SQUID measurements by placing a small enough sample in the holder. However, it is necessary to investigate the magnetism of monolayers to understand if the individual layers retain the magnetism and ordering, since thicker films act more like the bulk powders.

As far as the optical properties of materials, Cu(I) coordination polymers have displayed a range of luminescence through alteration of ligand, halide, and structure type of the complexes. These materials clearly displayed metal-to-ligand charge transfer, as seen through DFT calculations, where the HOMO was predominantly metal and halide character, while the LUMO...
consisted of ligand character. Additional experiments are ongoing to expand the range of luminescence through investigation of 3-coordinate Cu(I) materials. These compounds have the potential to expand the range of luminescence to the blue regime, which is highly sought after in order to be able to apply the materials to real applications.
REFERENCES


Germany, 1995.


Gatteschi, D.; Biagi, R.; Del Pennino, U.; De Renzi, V.; Gurevich, L.; Van der Zant, H. S.

(103) Martínez, R. V.; García, F.; García, R.; Coronado, E.; Forment-Aliaga, a.; Romero, F. M.;


(105) Terazzi, E.; Bourgogne, C.; Welter, R.; Gallani, J. L.; Guillon, D.; Rogez, G.; Donnio, B.


71 (3), 185–187.


(112) Taleb, N.; Richards, V. J.; Argent, S. P.; van Slageren, J.; Lewis, W.; Blake, A. J.;
Champness, N. R. Dalt. Trans. 2011, 40 (22), 5891.


Killarney, J. P.; McKinnon, M.; Murphy, C.; Henline, K. M.; Wang, C.; Pike, R. D.;


9667–9675.


(160) Ni, J.; Wei, K.-J.; Min, Y.; Chen, Y.; Zhan, S.; Li, D.; Liu, Y. Dalt. Trans. 2012, 41 (17),
5280.


