DESIGN AND SYNTHESIS OF SHAPE-PERSISTENT TERPYRIDINE-BASED METALLOMACROMOLECULES AND ARCHITECTURES

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DESIGN AND SYNTHESIS OF SHAPE-PERSISTENT TERPYRIDINE-BASED METALLOMACROMOLECULES AND ARCHITECTURES

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ABSTRACT

Self-assembly has grown into an important facet in the realm of supramolecular chemistry. Since its onset, the ability to construct intricate ensembles has become an area of intense research. Utilizing the <tpy-M$^{II}$-tpy> (tpy = 2,2′;6′,2″-terpyridine) coordinative interaction, many metallomacrocycles have been synthesized and isolated via both stepwise and self-assembled processes.

The study of constitutional isomers in supramolecular chemistry has been limited, due to the scarcity of explored systems for study. However, from different benzene-cored tetra$kisterpyridine$ ligands (1,2,3,4 vs. 1,2,4,5), two sets of novel isomers have been self-assembled with either Cd$^{II}$ or Zn$^{II}$, and their different drift times were ascertained using electrospray ionization mass spectrometry coupled with travelling wave ion mobility (ESI-TWIM-MS). Another set of isomeric metallomacrocycles were also synthesized from 60°- and 120°-oriented $bisterpyridine$ ligands. Molecular modeling and ESI-TWIM-MS on these constitutional isomers suggest extensive differences between the two systems.

By restricting the ability for self-assembly of geometrically-optimal ring systems, such as a triangle from a 60°-oriented ligand, has led to the isolation of a series of folded supramolecular tetramers or "Dondorff" rings. The
photochemistry of these systems reveals lifetimes on the 1-2 ns timeframe, as well as typical UV-vis and photoluminescence (PL) spectra. By applying gradient mass spectrometry (gMS\textsuperscript{2}), it was deduced that the order of bonding strength in the tetramers was Cd\textsuperscript{II} < Zn\textsuperscript{II} < Fe\textsuperscript{II} < Ru\textsuperscript{II}.

Near quantitative self-assembly of molecular triangles was achieved by the stoichiometric mixing of various substituted 60\textdegree-oriented \textit{bis}terpyridine ligands with either Cd\textsuperscript{II} or Zn\textsuperscript{II}. These triangles were characterized with \textsuperscript{1}H and \textsuperscript{13}C NMR, UV-vis, and PL spectroscopies, as well as ESI-TWIM-MS. The triangles were further assembled into nanofibers by layering with the hexavalent anion - sodium benzenehexacarboxylate. These fibers were analyzed with transmission electron microscopy (TEM) as well as selected area electron diffraction (SAXD), which revealed spacing values that correlated well with molecular modeling.

Use of a Moore-type dendron, as a molecular antenna, led to the synthesis of a new family of 120\textdegree-oriented \textit{bis}terpyridine ligands. Self-assembly of the ligands with Cd\textsuperscript{II} resulted in formation of supramolecular hexamers in high yields. The hexamers, characterized by ESI-TWIM-MS, as well as \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopies, were also studied for quantum yield values, which increased as a function of the increasing dendron generation attached to the metallomacrocycles.
DEDICATION

I would like to dedicate this work to all of the people who helped me become the person that I am today. My parents, Lyle and Elaine Schultz, taught me the value of a full day's work, which as it turns out, was a necessity in the completion of projects. My older siblings, Billie and Lyle, were excellent role models for the path to success, which kept me on the proper path. My wife, Jessica, has earned a degree herself, in patience. For all my long days, nights, and weekends, she never gave me a hard time, rather encouraged me when I was worried about projects successes, getting me back on track. And also to my colleagues here at The University of Akron, thank you for providing an outlet for research frustrations, as only you can understand at times. Without you, the time would have been much more stressful. I would like to acknowledge both Dr. Moorefield and Dr. Newkome for their guidance through the dark and bright times. They instilled in me the toolbox to become a successful Ph.D. chemist, and for that, thank you.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xiii</td>
</tr>
</tbody>
</table>

## CHAPTER

I. RECENT PROGRESS IN SHAPE-PERSISTENT SELF-ASSEMBLED METALLOMACROCYCLES ........................................ 1

1.1 Introduction ......................................................... 1

1.2 Square Planar-based Metallomacrocycles ................. 3

1.3 Octahedral-based Metallomacrocycles ....................... 33

1.4 Concluding Remarks ................................................. 53

II. STOICHIOMETRIC SELF-ASSEMBLY OF ISOMERIC, SHAPE-PERSISTENT SUPRAMOLECULAR BOWTIE AND BUTTERFLY STRUCTURES .... 55

2.1 Introduction ......................................................... 55

2.2 Results and Discussion ............................................. 57

2.3 Conclusions .......................................................... 67

2.4 Experimental ......................................................... 68

III. STABLE, TRINUCLEAR Zn\textsuperscript{II} AND Cd\textsuperscript{II}-METALLOCYCLES: TWIM-MS, PHOTOPHYSICAL PROPERTIES, AND NANOFIBER FORMATION ......................................................... 77

3.1 Introduction .......................................................... 77
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Drift times and collision cross sections for self-assembled products 10, 11, 12 and 13</td>
<td>63</td>
</tr>
<tr>
<td>3.1</td>
<td>Experimental Bragg angles ($\theta_e$) and distances ($d_e$), calculated Bragg angles ($\theta_c$) and distances ($d_c$), $hkl$ Miller Indices and 1D XRD maxima assigned in the patterns</td>
<td>88</td>
</tr>
<tr>
<td>4.1</td>
<td>$^1$H NMR shift summary (in ppm) for 4 – 8. All spectral data were acquired in CD$_3$CN on a 500 MHz NMR spectrometer</td>
<td>100</td>
</tr>
<tr>
<td>4.2</td>
<td>Photophysical Properties of Complexes 3 - 8[a]</td>
<td>104</td>
</tr>
<tr>
<td>5.1</td>
<td>Summary of ESI-TWIM-MS drift time data</td>
<td>124</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Examples of early work in supramolecular chemistry by A) Lehn, B) Cram, and C) Pederson, who were awarded the Nobel Prize for their efforts.</td>
</tr>
<tr>
<td>1.2</td>
<td>Cartoon depiction of typical Pt\textsuperscript{II}- and Pd\textsuperscript{II}-based metallomacrocycles</td>
</tr>
<tr>
<td>1.3</td>
<td>Study on the role of auxiliary ligand L on self-assembly, along with use of a fluorinated electron-deficient spacer to control the square-triangle equilibrium</td>
</tr>
<tr>
<td>1.4</td>
<td>Synthesis of endo- and exo-ferrocene substituted ligands and their corresponding self-assembly behavior</td>
</tr>
<tr>
<td>1.5</td>
<td>Summary of Fréchet-dendron modified metallomacrocycles</td>
</tr>
<tr>
<td>1.6</td>
<td>Metallomacrocycles 53 and 54 along with ordering of organic macrocycle 55 and 53 on HOPG (inset)</td>
</tr>
<tr>
<td>1.7</td>
<td>Metallo-macromolecular sensors 81-83</td>
</tr>
<tr>
<td>1.8</td>
<td>Modification of molecular rhomboids via [3+2] Huisgen-type cycloaddition</td>
</tr>
<tr>
<td>1.9</td>
<td>Dipyrazole polygons 95 and 96, and their crystal structures</td>
</tr>
<tr>
<td>1.10</td>
<td>Molecular boxes 115 and 116 with cartoon of differing orientations</td>
</tr>
<tr>
<td>1.11</td>
<td>A) Donors and acceptors utilized in the self-assembly of molecular squares, B) X-ray crystal structure of 117, and C) plot of effect on A-549 cancer cell line</td>
</tr>
<tr>
<td>1.12</td>
<td>Homometallic hexamers 118 and 119 and the isolation heterometallic hexamers 122-124 by step-wise syntheses</td>
</tr>
<tr>
<td>1.13</td>
<td>Synthesis of metallomacrocycles 134-140 utilizing ligands of a 60°-orientation</td>
</tr>
</tbody>
</table>
1.14 Images of Serpinski gasket 151 by A) AFM, B) TEM, and C) STM…………………………………………………………………..45
1.15 Formation of A) Oxi-SWNT composite with water - soluble hexamer 152 and B) AFM image of composite………………………………………………………………………………46
1.16 A) Formation of dendrimer-based nanocomposites with hexamer 153. B) Use of metallotriangles 154-159 in the self-assembly of nanofibers with benzenehexacarboxylate…………………………………………………………………………48
1.17 Spoked wheel 178 and corresponding ¹H NMR and ESI-MS……………52
1.18 Stoichiometric self-assembly of the spoked wheel derivatives 181-183……………………………………………………………………….53
2.1 Hexagonal spoked-wheel motif A) and isomeric triangular polygons (B and C) along with their corresponding terpyridine-based metallocyclic representations (counterions omitted for clarity)…………………………56
2.2 One dimensional ESI-MS of the mixture of 8 and 9, with pertinent charge states marked. Note: counterions (BF₄⁻) omitted for clarity……………………………………………………………………………..59
2.3 ¹H NMR spectrum of Ru²⁺ dimer 6………………………………………….60
2.4 ¹H NMR overlay of starting materials 5 (top) and 6 (bottom) with the Zn bowtie 10 in the center. Arrows depict assigned resonance shifts that occur upon complex formation…………………………………………………………………………61
2.5 A) ESI-MS and B) 2-D ESI-TWIM-MS plot (mass-to-charge ratio vs. drift time) of 10. The charge states of intact assemblies are marked…………………………………………………………………………62
2.6 ESI-MS and TWIM-MS plots for Cd²⁺-based bowtie 11…………………..63
2.7 ESI-MS and TWIM-MS data for Zn²⁺-based butterfly 12…………………..65
2.8 ESI-MS and TWIM-MS data for Cd²⁺-based bowtie 13…………………..66
2.9 Comparison of the estimated collision cross sections of bowtie 10 and butterfly 12 at different charge states, i.e., 4+ to 7+……………………………………67
3.1 Typical ¹H NMR spectrum of a bisterypyridine ligand and its corresponding Zn²⁺ and Cd²⁺ metallocycles……………………………………………………………80
3.2 GHSQC NMR spectrum of triangle 9………………………………………..81
3.3 A) ESI-MS, B) TWIM-MS, and C) gMS\(^2\) spectra for triangle 10........82

3.4 MALDI-MS for triangle 8...............................................................84

3.5 UV-vis A) and photoluminescence B) spectra of the H-, methyl-, and methoxy-substituted bis[terpyridines 5-7 and triangles 8-13 were obtained using spectrophotometric grade DMF, along with a photograph C) of the luminescence properties of 11-13. Excitation wavelength was 285 nm for ligands was 315 nm for complexes. Data were collected at a concentration of 5.0x10\(^{-5}\) M for ligands and 5.0x10\(^{-6}\) M for complexes, respectively.................................85

3.6 \(^1\)H, \(^19\)F, and \(^31\)P NMR data for filtrate from fiber growth of 12 with sodium benzenhexacarboxylate, confirming presence of PF\(_6\)................86

3.7 TEM images of fibers formed from triangles 13 (left), and 12 (right) with benzenhexacarboxylate (inset: SAXD diffraction pattern from trimer 12).................................................................87

3.8 Proposed packing model for triangle 12 in the fiber based on powder and selected area X-ray diffraction.........................................88

4.1 \(^1\)H NMR spectrum of dimer 3 and peak assignments in CD\(_3\)CN, where free resonances are italicized..................................................99

4.2 Stacked \(^1\)H NMR spectra overlay of 4 – 8, where Cd\(^{II}\) = yellow, Zn\(^{II}\) = green, Fe\(^{II}\) = purple, and Ru\(^{II}\) = red, respectively, measured in CD\(_3\)CN..100

4.3 Computer simulation of tetramer 4: A) Side view with the solvent-accessible surface area as blue shell; B) Lowest energy conformer of tetramer 4; and C) Stick model of the flattened, higher energy tetramer 4...........................................................................................................102

4.4 A) Conventional 1D ESI-MS spectrum for tetramer 7 with an enlargement of the 4+ isotope pattern; B) 2D TWIM-MS plot for 7, consistent with a single species; and C) strength comparison for 7 via gMS\(^2\) with collision energies ranging from 6 to 60 eV (set by varying the trap cell bias from 6 to 60 V)..................................................................103

4.5 A) Normalized UV-visible absorption spectra of 3 – 8 in MeCN; B) Corrected emission spectra of 3 – 7 using Ar\(^+\) ion laser excitation (488 nm, ~100 mW). The constant intensity Raman band of the MeCN solvent, located at 570 nm in these experiments, was used to normalize the emission spectra.........................................................105
5.1 \(^1\)H NMR spectra for the 60°-based constructs. Minor shift differences are observed for the 4,4"- and 5,5"-protons of macrocycles 3 and 4; whereas, a large upfield shift in the 6,6" resonances for 2 to 3 (or 2 to 4) is noted. Previously published 2 and 3 are shown for comparison.\(^{195}\) (*CHCl\(_3\))………………………………………………………………………………………………118

5.2 ESI-MS comparison of 3 and 4…………………………………………119

5.3 \(^1\)H NMR spectra for the 120°-based 6 - 8. As in rings 3 and 4, small differences in the spectra of 7 and 8 are seen, while the expected upfield shift for the 6,6" resonance in free ligand 6 compared to complex 7 (and 8) is observed. (*CHCl\(_3\))……………………………………………………122

5.4 \(^1\)H NMR spectra for 60° oriented hexamer 4 and 120° oriented hexamer 8. Red arrows indicate the difference in chemical shifts of the para-oriented protons attached to the corner benzene rings……………………123

5.5 A) 1D ESI mass spectra for 60° oriented hexamer 4 and 120° oriented hexamer 8, B) gMS\(^2\) plots of the 4+ peak from 4 and 8 at various activation collision energies (eV)………………………………125

5.6 Computer generated images of the metallomacrocycles 4, 8, 3, and 7 and their solvent accessible surfaces generated with a 1.4 Å probe………….126

6.1 \(^1\)H NMR of bis-terpyridine ligand 13 and corresponding metallomacrocycle 16………………………………………………………………………………………………139

6.2 Photophysical data for antenna modified compounds 12 – 17. A) UV-vis, acquired in DMF at a concentration of 5x10\(^{-5}\) M; B) PL spectral overlay, acquired in DMF at a concentration of 5x10\(^{-6}\) M, with an excitation wavelength of 305 nm; C) Tabulated summary of relevant data, including quantum yields, which were acquired on a Hamamatsu absolute PL quantum yield measurement system spectrophotometric grade DMF at 25 °C and an excitation wavelength of 305 nm……………………………………141

6.3 CV data for hexamer 16, samples were acquired in a 100 mM solution of Bu\(_4\)NPF\(_6\) in DMF at a scan rate of 100 mV/sec……………………………………143
## LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Recent work of Fujita, <em>et al.</em> reporting the first manipulation of the (&lt;\text{pyr-Pt}^{\text{II}}\text{-pyr}&gt;) coordinative bond in the self-assembly of metallomacrocycles</td>
</tr>
<tr>
<td>1.2</td>
<td>Isolation of bis(pyrollo)tetrathiafulvalene-based metallomacrocycles 10 and 11. Triangle 11 was shown to bind C(_{60}), whereas the corresponding square 10 was not</td>
</tr>
<tr>
<td>1.3</td>
<td>Ferrocene-substituted metallocubes 22-24, nitroaromatic-sensing metallosquare 25, and potential C(_{60})-encapsulating rhombus 26</td>
</tr>
<tr>
<td>1.4</td>
<td>Novel carborane-based metallomacrocycles 30-32, 37, and 38</td>
</tr>
<tr>
<td>1.5</td>
<td>Self-assembly of 2,6-di(4,4’-dipyridyl)-9-thiabicyclo[3.3.1]nonane (39) with various acceptors</td>
</tr>
<tr>
<td>1.6</td>
<td>Study of self-assembly of ligands 56, 58, and 60 with Pd(^{\text{II}}) (above) and 56-59 equilibrium Pt(^{\text{II}}) (below)</td>
</tr>
<tr>
<td>1.7</td>
<td>Self-assembly of asymmetric ligands 61 and 62 with acceptors 14 and 15, as well as molecular modeling for macrocycles 63-66</td>
</tr>
<tr>
<td>1.8</td>
<td>Self-assembly of sodium isonicotinate with Pd(^{\text{II}}) sources 68 and 69 and the corresponding self-sorted equilibrium</td>
</tr>
<tr>
<td>1.9</td>
<td>Self-assembly study on methyl- and chloro-bipyridines</td>
</tr>
<tr>
<td>1.10</td>
<td>Metallomacrocycles based on 78 with two potential open binding sites. In the inset: other potential structures (a) and their respective energies (b) by molecular modeling</td>
</tr>
<tr>
<td>1.11</td>
<td>Post-structural modification of metallomacrocycles 84 and 86 utilizing Co(CO)(_6) to transform the acetylene bond angle</td>
</tr>
<tr>
<td>1.12</td>
<td>Synthesis and crystal structure of Ni(^{\text{II}}) NHC-based molecular squares</td>
</tr>
<tr>
<td>1.13</td>
<td>Self-assembly of catalytically-active tetragon 98 from Tröger's base-derivative 97</td>
</tr>
</tbody>
</table>
1.14 Self-assembly of crown-ether substituted molecular bowl 100
1.15 Self-assembly of complexes 102 and 103 and crystal structures of their respective encapsulated analogues.................................30
1.16 Self-assembly of elongated hexamer 105 and congested hexamer 106…31
1.17 Utilization of HETPHEN approach in formation of metallo-macrocycles and –ladders.................................................................32
1.18 Use of modified HETPHEN approach in the self-assembly of highly complex architectures 112-114.................................................33
1.19 Isolation of linear species from a single one-pot reaction as well as cyclic structure 118...............................................................39
1.20 Synthesis and crystal structure of dinuclear metallomacrocycle 131.....40
1.21 Self-assembly and post-modification of metallohexamer 142..............43
1.22 Synthesis of A) polyfunctionalized metallomacrocycle 147 and B) exo-modified hexamer 150.........................................................44
1.23 A) Isolation and nanofiber growth of pentamer 161 and hexamer 162. B) Isolation of macrocycles 163-165 with ring sizes 5-7.................49
1.24 A) Formation of large metallomacrocycles 166-171. B) Synthesis of the bent 60°-oriented tetramers.......................................................51
2.1 Synthesis of 3, 5, 6, and 7. Ligands 3, 5, and 7 were synthesized from 2 or 4 with 1 and isolated in good yields........................................59
2.2 Suzuki coupling of aryl halides 1-3 and their subsequent cyclizations to form 8-13, respectively.....................................................79
3.1 Suzuki coupling of aryl halides 1-3 and their subsequent cyclizations to form 8-13, respectively.....................................................79
4.1 Synthesis of the folded squares 4 – 8. Reagents and conditions: i) H2O : toluene : t-BuOH (3:3:1 v/v/v), Na2CO3 (15 eq.), Δ, 48 h; ii) 1.05 eq. FeCl3·H2O, MeOH, Δ, 12 h; iii) 0.5eq. RuCl2(DMSO)4, MeOH : CHCl3 (1:1 v/v), Δ, 12 h; iv) M^2+, CHCl3 : MeOH (1:1 v/v), Δ or RT, 12-24 h. Counterions have been omitted for clarity........................................98

xiv
5.1 Synthesis of 2 - 4. Reagents and conditions: i) Ru(DMSO)$_4$Cl$_2$, MeOH:CHCl$_3$ (1:1 v/v), Δ; ii) FeCl$_2$·4 H$_2$O, MeOH:CHCl$_3$ (1:1 v/v), Δ. Also depicted are optimized models of tetramer 3 and multiple conformations (crown and basket) of hexamer 4.

5.2 Synthesis of compounds 5 - 8. Also depicted are side views of geometrically optimized structures for tetramer 7 and hexamer 8. Reagents and conditions: i) Ru(DMSO)$_4$Cl$_2$, MeOH:CHCl$_3$ (1:1 v/v), Δ; ii) FeCl$_2$·4 H$_2$O, MeOH:CHCl$_3$ (1:1 v/v), Δ.

6.1 Synthetic route to antenna 6 and iodo-modified bisterpyridine 11. Reagents and conditions: i) 2-methyl-3-butyne-2-ol, Pd(PPh$_3$)$_4$, CuI, NEt$_3$, reflux 12 h; ii) NaH, anhydrous toluene, distill; iii) Pd(PPh$_3$)$_4$, CuI, NEt$_3$, 4, reflux 12 h; iv) (a) HCl, NaNO$_2$, 0°C; (b) KI, I$_2$, reflux 1 h; v) BH$_3$·THF, THF, 25°C, 12 h; vi) PCC/Celite, CH$_2$Cl$_2$, 12 h; vii) 2-acetylpyridine, NaOH, EtOH, NH$_4$OH, 60°C, 8 h.

6.2 Self-assembly of antenna-functionalized ligands 13 and 14, followed by subsequent cyclization with Cd$^{II}$. Reagents and conditions: i) Pd(PPh$_3$)$_4$, CuI, NEt$_3$, reflux 12 h; ii) 1.00 eq Cd(NO$_3$)$_2$·4 H$_2$O, 3:2 CHCl$_3$:MeOH, 25 °C, 12 h.
CHAPTER I

RECENT PROGRESS IN SHAPE-PERSISTENT, SELF-ASSEMBLED,
METALLOMACROCYCLES

1.1 Introduction

Beginning with the inception of crown ethers,\textsuperscript{1} the field of supramolecular chemistry has blossomed to the forefront of chemical research. From modest beginnings,\textsuperscript{2-5} the eloquent, yet utilitarian, structures that have resulted are at times awe-inspiring.\textsuperscript{6-11} From Cram and Lehn's pioneering works with the advancement of crown ethers to cryptands\textsuperscript{4,12,13} and their inclusion complexes onward to Newkome and Tomalia's non-cyclic, tree-like architectures, such as: \(1 \rightarrow 3\) \textsuperscript{14-16} and \(1 \rightarrow 2\) \textsuperscript{17-19} branched dendrimers, respectively, there has been obvious advancement from dendrimer's 1985 birth. A simple keyword Scifinder search of \textit{dendrimer} in 2012 provides a mere 30,000 results for casual perusal, due to the plethora of their proposed and observed functions. The same trends can be observed in the publications surrounding the crown ethers and cryptands as well as from constructs that combine the two. The work in these early constructs, shown in Figure 1.1 led to the Nobel Prize in chemistry being awarded in 1987 to Pederson, Cram, and Lehn, in which Lehn defined the field of supramolecular chemistry as "chemistry beyond the molecule".\textsuperscript{20}
However, beginning with the self-assembly of the first metallogrid,\textsuperscript{21-24} the interest in self-assembly of metallomacrocyclic rings as well as higher ordered architectures has intensified over the years. The metallogrid relies on the utilization of a $<\text{L-M-L}>$ coordinative bond to hold the grid together, where L is an appropriate ligand, however, was commonly $N$- or $O$-based, and M is often zinc or some other divalent metal. The lability of the metal-ligand coordination is key to permitting equilibration until the most thermodynamically favored product is formed. Other strategies for self-assembly have included van der Waals interactions,\textsuperscript{25,26} hydrogen bonding,\textsuperscript{27-30} and hydrophilic/hydrophobic interactions,\textsuperscript{31-35} to name a few. Increased research has led to the assembly of asymmetric grids,\textsuperscript{36} onward to polygons from triangles to dodecagons,\textsuperscript{37-50} as well as other architectures, such as wheels,\textsuperscript{51-53} bowties,\textsuperscript{54-56} and cage-type structures.\textsuperscript{57-60} There are a variety of research groups exploring the role of these architectures in a variety of applications, from biomedical\textsuperscript{61-63} to solar\textsuperscript{64-66} and LED\textsuperscript{67,68} technologies. As more practical applications for these polymetalloassemblies are discovered, it can be anticipated that this field will
continue to increase as the use of different metal combinations are instilled into the organometallic infrastructure.

Within the field of metalloarchitectures, there are two major branches based on rigid and flexible ligands. Within our work, we have particular interest in the more rigid frameworks. The advantage of shape-persistent structures lies in their functional predictability. When a rigid ligand self-assembles, the resulting metalloarchitecture is often generated in high-yield, and also is homogenous in size. This results in a structural size that remains constant and lends itself to a variety of utilitarian applications from gas storage devices to more complex structures, such as catenanes and rotaxanes. Rigid self-assembled structures also play a pivotal role in solubilizing carbon nanotubes as well as Buckminster fullerenes due to their ability to interact via π-π stacking. The following sections will review the recent progress that has been made in the field of self-assembled, rigid, shape-persistent, metalloarchitectures and metallomacrocycles.

1.2 Square Planar-based Metallomacrocycles.

The most common type of macrocycle is the M\textsuperscript{II}-based triangles and squares, often with a <pyr-ML\textsubscript{2}-pyr> type connectivity, where L is amine or phosphine, as shown in Figure 1.2. Other macrocycles, such as rhomboids and hexagons, are also common, if the correct angle in the pyridine or phosphine is instilled. Interestingly, the majority of these types of complexes are metal-cornered macrocycles, instead of ligand-cornered. The equilibrium has been studied in depth over the past two decades, and won't be addressed here,
unless research is focused on controlling the aforementioned equilibration. Instead, the focus will be on reported structures and applications; however, there has been a plethora of research performed to shift this equilibrium to either side.\textsuperscript{87-89} This L group commonly has additional R groups attached, such as methyl or phenyl; in most circumstances the ligand donors are organic in nature. The metals most commonly incorporated are platinum and palladium, due to their well-known chemistry, relatively low cost, and desirable UV and photoluminescence (PL) properties.\textsuperscript{90-92} The X spacer, depicted in Figure 1.2, in the bipyridine spacer tailors the properties of the macrocycle, with varying the length of conjugation being the most common technique. The counterions [Z] have also been studied in depth for these systems and play a key role in shifting the equilibrium from square to triangle.\textsuperscript{85} These macrocycles have found countless applications, with sensors,\textsuperscript{45} biomedical,\textsuperscript{93} and potential LED\textsuperscript{94} technology to name but a few.

![Diagram of Pt\textsuperscript{II} and Pd\textsuperscript{II} based metallomacrocycles](image)

**Figure 1.2. Cartoon depiction of typical Pt\textsuperscript{II} and Pd\textsuperscript{II}-based metallomacrocycles.**

One of the first metallomacrocycles of this type was isolated by Fujita,\textsuperscript{95} but now his publications tend to primarily discuss the synthesis is of three-
dimensional assemblies.\textsuperscript{60,96-98} Recently he took advantage of the photolabilization of the thermally inert $\text{Pt}^{\text{II}}$-$\text{pyr}$ bond to drive to the formation of cages (not shown) and ring 3, shown in Scheme 1.\textsuperscript{99,100} Notable limitations involve the bipyridine-modified durene linear spacer 1 in which 1 was replaced with the analogous benzene ligand 4. The reaction did not proceed to give the expected macrocycle 5, presumably due to a combination of solubility problems as well as the twist angle, which is 90° for bipyridine 1, but only 36° analogue 4.

\begin{align*}
\text{Scheme 1.1. Recent work of Fujita, et al. reporting the first manipulation of the} \\
<\text{pyr-Pt}^{\text{II}}\text{-pyr}> \text{ coordinative bond in the self-assembly of metallomacrocycles.}
\end{align*}
The L group (See Figure 1.2) can play a key role in the equilibration of the triangle and square assemblies. Ferrer et al.\textsuperscript{100} reported the use of two different diamine ligands on the Pt\textsuperscript{II} and Pd\textsuperscript{II} corners, one flexible ethylenediamine and one rigid 2,2′-bipyridine, shown in Figure 1.3. Originally, the fluorinated spacer was designed to encapsulate electron-rich aromatics, but this was unsuccessful. So instead, they showed that for rigid bipyridine, there was a mixture of square (7, major) and triangle (6, minor). The role of counterions was also explored, using both triflate and nitrate. Interestingly, with the nitrate counterion, refluxing conditions were necessary for assembly, whereas with the triflate, assembly occurred at room temperature. However, neither counterion had an effect on the resultant metallomacrocyclic equilibrium. Using the flexible EDA ligand resulted in the formation of exclusively the square 8, likely a result of the smaller size. The fluorinated spacer also plays a key role in the equilibrium, as the corresponding non-fluorinated ligand results in a mixture of both triangle and square, although the reason for which is uncertain. These compounds, that were now water-soluble, began to act as encapsulating agents of aromatics under aqueous conditions.
Figure 1.3. Study on the role of auxiliary ligand L on self-assembly, along with use of a fluorinated electron-deficient spacer to control the square-triangle equilibrium.

Instead, use of electron-rich ligands, such as bis(pyrrolo)tetrathiafulvalene 9, in the self-assembly has demonstrated the ability to encapsulate electron-deficient aromatics, such as C\textsubscript{60}.\textsuperscript{67} This current hot topic in supramolecular chemistry, especially as the utilitarian applications of C\textsubscript{60} continue to be explored.\textsuperscript{11,101,102} This particular system, as shown in Scheme 1.2, led to the surprising precipitation of square 10 in only 31% yield; whereas, the remaining triangle 11 was isolated in 60% yield after simple solvent evaporation. The cavity size of 11 demonstrated a capability of binding C\textsubscript{60}, where the corresponding square 10 did not bind at all, suggesting that the interior pore size is the "sweet
spot" for triangle 11. This first reported example of use of a macrocycle for $C_{60}$ encapsulation rather than a cage, and Sallè, et al. are moving in the direction of a bis(pyrollo)tetrathiafulvalene cage in order to improve the binding capability.

A current trend in modification of metallomacrocycles has been the incorporation of ferrocene into the auxiliary ligand $[L]$. Ferrocene has been primarily investigated for its well-known redox capabilities; however, it has also been used in sensing and binding applications. In 2008, the work of Yang et al. reported the synthesis of three such exo-ferrocene-substituted macrocycles, based on ligand 12. Additionally, Ghosh, et al. report its endo-
substituted derivatives in 2012, depicted in cartoon form in Figure 1.4.\textsuperscript{110} The exo-substituted macrocycles designed with tailored pore sizes and utilizing bisorganoplatinum(II) ligands 13, 14, and 15 afforded the corresponding metallomacrocycles 16, 17, and 18, respectively.\textsuperscript{110} Molecular modeling of 16-18 suggests predicted pore sizes of 5.3, 1.6, and 3.3 nm, respectively. The endo-substituted ligand 19 was self-assembled with 120°-oriented bisorganoplatinum(II) ligand 15 as well as linear ligand 13 to afford the [3+3] hexagon 20 as well as [6+6] hexagon 21, which have interior pore diameters of 1.6 and 3.8 nm, respectively. Preliminary investigation of macrocycles 16-18, 20, and 21 are promising toward functional electroactive supramolecular architectures.

Figure 1.4. Synthesis of endo- and exo-ferrocene substituted ligands and their corresponding self-assembly behavior.
Zhao et al. synthesized other ferrocene-substituted cyclic structures including a series of three molecular triangles \(22-24\), which have six ferrocene moieties attached.\(^{111}\) The electrochemical properties of these ferrocenes were studied and were found to be electronically independent. The remaining ferrocene structures, depicted in Scheme 1.3, include nitro-aromatic sensing square \(25\)\(^{112}\) and \(C_{60}\)-encapsulating rhombus \(26\).\(^{102}\) These are unique to the other ferrocene-substituted macrocycles in that the ferrocene itself bridges the two phosphine moieties. Also shown in Scheme 1.3 is a molecular modeling by Zhao and coworkers simulation of the encapsulation complex of \(C_{60}\) in rhombus \(26\).

![Diagram](image)

Scheme 1.3. Ferrocene-substituted metallotriangles \(22-24\), nitroaromatic-sensing metallosquare \(25\), and potential \(C_{60}\)-encapsulating rhombus \(26\).
Although the branching core of metallomacrocycles is typically benzene-based, occasionally different cores can be utilized. In 2005, Jude et al., published a series of metallomacrocycles utilizing a carborane core.\textsuperscript{113} With practical applications such as liquid crystalline properties,\textsuperscript{113-115} non-linear optics (NLO),\textsuperscript{116,117} and thermally stable materials,\textsuperscript{118,119} carboranes provide a practical functionality allowing for metallomacrocycles that potentially enhance already desirable properties. Utilizing known Sonogashira methods, carborane 27 was synthesized and cyclized with organoplatinum(II) ligands 14, 28, and 29 to afford the corresponding metallotriangle 30, metallorectangle 31, and metallosquare 32, respectively, as shown in Scheme 1.4. Carborane bisorganoplatinum(II) 33 and 34 acceptors were also synthesized via Sonogashira coupling in modest yields and cyclized with pyridine donors 35 and 36. The resultant metallomacrocycles were much more soluble than most carborane-based polymers, which is the most common disadvantage to such systems.
Scheme 1.4. Novel carborane-based metallomacrocycles 30-32, 37, and 38.

Also utilizing a unique core other than benzene, recent work took advantage of the interior angle of 2,6-di(4,4’-dipyridyl)-9-thiabicyclo[3.3.1]nonane 39, as the branching point in a set of three metallomacrocycles. The sulfur at the bridgehead position was desirable due to the unique ability to act as a scaffold or different connector. When ligand 39 was combined with 60°-oriented acceptor 14, 120°-oriented acceptor 15, or elongated linear acceptor 40, resulted in near-quantitative isolation of metallomacrocycles 41-43, shown in Scheme 1.5. Even though donor ligand 39 is chiral, there was no observation of diastereomers; however, easy synthesis of
120°-oriented donor 39 (one step, >90% yield) makes it a practical ligand for further studies.

Scheme 1.5. Self-assembly of 2,6-di(4,4′-dipyridyl)-9-thiabicyclo[3.3.1]nonane (39) with various acceptors.

With dendrimers having found applications in nearly all aspects of modern day, supramolecular chemistry, from hydrophobic and hydrophilic coatings to biomaterial and sensing applications, it seems that there would be numerous examples of PdII- and PtII-based metallomacrocycles with dendritic auxiliary substituents. While this topic has not received intense interest, there have been several publications by Stang and coworkers in recent years, summarized in Figure 1.5. The dendritic ligands 44a-d (where a-d represents G0-G3, respectively) were always utilized as the donor, and a Fréchet-type dendron was chosen as the exterior modification. Starting with donors 13-15, three series of tailored dendrimer-functionalized metallomacrocycles 45-47
were formed. Also, a longer linear acceptor 40 was synthesized to give a larger [6+6] metallohexagon 48. In 2012, it was reported that a crown ether substituted acceptor 49 was utilized for a [3+3] type self-assembly of hexagon 50 in high yield. Post-modification of this hexamer with dibenzylammonium cations 51 resulted in the threaded metallomacrocycle 52. Interestingly, the size of the substituted dendron substantially decreased the rate of host – guest interaction $K_a$ by one order of magnitude.

Figure 1.5. Summary of Fréchet-dendron modified metallomacrocycles.

Controlling the order in which metallomacrocycles assemble is quickly becoming a booming tangent of self-assembly. As the field of self-assembly advances, it is natural for the expansion to more complex architectures for
advanced applications and nanodevices to become the next logical step. An
advantage is the ability to readily observe the degree-of-ordering via scanning
tunneling microscopy (STM). These beautiful arrays will hopefully lead to
miniaturization of current technology and information storage devices.$^{132,133}$
Highly ordered pyrolytic graphite (HOPG) is a common surface for STM. In
2010, it was reported that metallosquare 53 and metallorectangle 54 were able to
form bilayers on known arrays 55, as the pore sizes are similar.$^{75}$ Figure 1.6
depicts macromolecules 53-56, in addition to a STM image of 55/53 bilayer.
Another exploration into the depths of metallomacrocycles has been studied in depth by Brusilowskij et al. and involves the use of *bis*alkynylpyridines 56-60, which were synthesized with varying cores and subsequently self-assembled with Pd$^{\text{II}}$ or Pt$^{\text{II}}$. The cores, shown in Scheme 1.6, consist of a biphenyl core, a 2,2′-bipyridine core, and a much more rigid phenanthroline core.
Later, the position of the pyridine \textit{(para vs. meta)} was also studied. This work is extremely interesting, as the self-assembly provides some insight into the order that Pd\textsuperscript{II} and Pt\textsuperscript{II} bind with flexible ligand 56. This ligand prefers a transoid conformation; however, the first equivalent of Pd\textsuperscript{II} led to the formation of a [2+2] metallomacrocycle, followed then by generation of a complex possessing exterior 2,2′-bipyridines. Analysis of these ligands with Pt\textsuperscript{II}, as a metal linker, leads to a thermodynamic equilibrium between the cyclic polygons M\textsubscript{4}L\textsubscript{2} and M\textsubscript{6}L\textsubscript{3}. After several hours, the M\textsubscript{4}L\textsubscript{2} metallomacrocycle was determined to be the only product. This was confirmed by ESI-MS; however, the self-assembly behavior of \textit{meta}-substituted ligands is quite different. Even though the major product remains the M\textsubscript{4}L\textsubscript{2} metallomacrocycle, there are always traces of the M\textsubscript{6}L\textsubscript{3} metallomacrocycle present. In depth analysis \textit{via} tandem ESI-MS suggests that the M\textsubscript{4}L\textsubscript{2} self-assembled polygons of the \textit{meta}-substituted \textit{bisalkynyl} pyridines are much more strained than the analogous \textit{para}-substituted polygons.
Scheme 1.6. Study of self-assembly of ligands 56, 58, and 60 with Pd$^{\text{II}}$ (above) and 56-59 equilibrium Pt$^{\text{II}}$ (below).

Another method for the study of ligand binding involves using asymmetric ligands, as a probe. In 2009, Stang et al. synthesized the asymmetric ligands 61 and 62 and studied their self-assembly behavior with acceptors 14 and 15, as shown in Scheme 1.7. Linear donors 61 and 62 possess both a para- and meta-substituted pyridine ring, thus permitting the potential of multiple arrangements of cyclic hexagons 63 and 64 and rectangle 65 and 66, such as either geometrically matched or mismatched. Molecular modeling suggests that the parallelogram is the more stable of the possible bonding combinations, which was verified by X-ray crystallography and supported by $^{31}$P NMR spectroscopy and ESI-MS.
Scheme 1.7. Self-assembly of asymmetric ligands 61 and 62 with acceptors 14 and 15, as well as molecular modeling for macrocycles 63-66.

Ghosh and Mukherjee applied a similar strategy with the role of symmetry and auxiliary ligand on the self-assembly behavior with Pd$^{II}$. Shown in Scheme 1.8, sodium isonicotinate 67 was self-assembled with different Pd$^{II}$ sources 68 and 69. Envisioning several products, the group was surprised to find that there was only a single set of square / triangle equilibrated structures. The head-to-tail macrocycle 63 was verified by X-ray crystallography. The dynamic equilibrium was further evaluated by variable temperature $^1$H NMR spectroscopy, suggesting metallosquares 70 and 72 are favored at high temperatures, as would be expected.
Scheme 1.8. Self-assembly of sodium isonicotinate with \( \text{Pd}^{\text{II}} \) sources 68 and 69 and the corresponding self-sorted equilibrium.

More subtle alterations to the donor ligand have also been considered. By placing sterically hindering groups on one side of the pyridine donor 74, (Scheme 1.9), Stang et al. were able to control the formation of a single head-to-tail isomeric square 75.\(^{137}\) By switching from two methyl groups to single chlorine functionality, such as in ligand 76, or by moving the substituents from the \( \alpha \)- to \( \beta \)-position as in ligand 77 results in a distribution of isomers A-D in the corresponding macrocycles.
Scheme 1.9. Self-assembly study on methyl- and chloro-bipyridines.

By leaving open binding sites in the final self-assembled product, the option for post-modification becomes viable, or the macrocycle could potentially act as a sensor by additional coordination at that site. As shown in Scheme 1.10, a recent self-sorting study looked at the ability to form a single pair of macrocyclic products from *tris*pyridyl donor 78, even though there are multiple binding possibilities for *bis*organoplatinum(II) acceptors 14 and 15. Molecular modeling of the additional possible isomeric macrocycles suggests a large difference between the observed structures and other possible structures. Potential applications proposed by the authors for metallomacrocycles 79 and 80 include catalysis and guest encapsulation.
Scheme 1.10. Metallomacrocycles based on 78 with two potential open binding sites. In the inset: other potential structures (a) and their respective energies (b) by molecular modeling.

The ability to detect nitroaromatic compounds (NACs) has garnered increased interest over the past decade. The ability for metallomacrocycles 81 and 82 to act as sensors for electron-deficient compounds through fluorescence quenching, suggests that they are ideal candidates for NAC detection. Similarly, titration of Cu$^{II}$ and Ni$^{II}$ with metallorectangle 83 suggests that it may be a candidate for metal ion detection, shown in Figure 1.7. The detection was exclusive to $d_3$ transition metals; there was no observed quenching of the soft metal ions that were tested.
Another step for transitioning metallomacrocycles to utilitarian applications revolves around their ability to perform post-assembly modifications allowing metallomacrocycles to function as sensors and catalysts, or change pore sizes. Recently, cobalt hexacarbonyl was utilized, as a transformation reagent, to coordinate acetylene bonds, thus converting hexagon 84 to two smaller hexagons 85, Scheme 1.11. The coordination of Co(CO)₆ changes the bonding directionality of the acetylene from 180° to 120° resulting in a change in pore size post-assembly. Another example of this method uses square 86, which is in equilibrium between the triangular analogue due to flexibility of the organopalladium(II) acceptor, to afford exclusively the [2+2] rhomboidal structure 87. Efforts to expand this research to three-dimensional polyhedral are underway.
Scheme 1.11. Post-structural modification of metallomacrocycles 84 and 86 utilizing Co(CO)$_6$ to transform the acetylene bond angle.

With the intense interest in Huisgen-type [3+2] cycloadditions in recent years,$^{118,143-145}$ it is not surprising to find post-modification of metallomacrocycles involving copper(I) catalyzed "click" chemistry. Recently, Zhao et al. reported the synthesis of an exo-acetylene-modified donor 88. Self-assembly of 88 with acceptor 14, depicted in Figure 1.8, led to the formation of rhombus 89, whose structure was confirmed by $^{31}$P NMR spectroscopy and ESI-MS. Attachment of azides N3-1 – N3-3 under mild conditions resulted in the isolation of metallorhomboids 90-92, which have various potential applicability due to their potential functionalities, e.g., multimeric biotin structure 92. The variety of macrocycles isolated could act as sensors or enhance sensitivities of current immunoassays.
Although the majority of square planar motifs revolve around the use of Pt$^{II}$ and Pd$^{II}$ with acetylene-based linkers in the formation of metallomacrocycles, there are examples of different linkers in the formation of squares. In 2008, Hepp et al. reported the synthesis of a bis-carbene Ni$^{II}$ complex, as a starting acceptor, for synthesis of a metallosquare.$^{146}$ With the wide applicability of $N$-heterocyclic carbenes (NHCs) in catalytic$^{147-149}$ and biomedicinal$^{150}$ chemistry, the authors originally attempted to use Pd$^{II}$ and Pt$^{II}$ as metals for cyclization; however, their reactivity with NHCs did not lead to the desired complexes. Thus, when switching to nickelocene, as a metal source, the linear dinickel complex 93 was obtained. Introduction of 4,4'-bipyridine led to the self-assembly of molecular square 94 (Scheme 1.12), which was proven by X-ray crystallography.
Scheme 1.12. Synthesis and crystal structure of Ni$^{II}$ NHC-based molecular squares.

A limitation to the traditional molecular polygons is their marginal solubility in aqueous media. For most sensors, this is a necessity; however, examples of water-soluble metallomacrocycles are rare.$^{112,139}$ Recent publications by Yu et al. demonstrated two such compounds 95 and 96, shown in Figure 1.9,$^{151,152}$ possessing dipyrazole linkers that seem to have a positive effect on aqueous solubility, and the resultant macrocycles are even soluble under strongly acidic conditions. Metallocycle 96 displayed selectivity of thiocyanate ions in aqueous DMSO media.
Due to its shape-persistent V-shape, the use of Tröger's base has increased in the field of separation\textsuperscript{153,154} and molecular tweezer\textsuperscript{155} chemistry. As shown in Scheme 1.13, ligand 97, a known compound consisting of Tröger's base possessing two pyrazoles moieties, self-assembles to afford molecular tetragon 98 upon stoichiometric reaction of PdCl$_2$(MeCN)$_2$ under ambient conditions. The authors then studied its catalytic activity towards Mizoroki-Heck coupling and observed a strong\textsuperscript{156} selectivity towards the formation of trans-stilbenes.
Scheme 1.13. Self-assembly of catalytically-active tetragon 98 from Tröger's base-derivative 97.

Yu et al. have also utilized various crown ether substituted phenanthrolines, such as 99, as ligands for self-assembly. Combination with a benzo- or naphthimidazole resulted in the formation of a molecular bowl 100, shown in Scheme 1.14.157 The formation of the metallomacrocycles was tracked by $^1$H NMR spectroscopy and the products were characterized via ESI-MS. Single crystals were obtained; their X-ray data confirm the bowl-like structure suggesting applications such as anion sensing as well as organocatalysts.
Another mode of connectivity for square planar complexes is \(<\text{pyr-M}^{II}\text{-tpy}>\), where the metal source can be either \(\text{Pt}^{II}\) or \(\text{Pd}^{II}\). This complex results in an extended planar \(\pi\)-system that could potentially stack with electron-rich aromatics. The work of Nabeshima et al. has focused on just that.\(^{158-160}\)

Bifunctional ligand 101 was readily synthesized in moderate yields via a three-step synthesis, and then was readily dimerized in near-quantitative yield with \(\text{Pd(cod)(BF}_4)_2\) at ambient conditions to afford the corresponding metallomacrocycle 102. The cavity of 102 has proven to be extremely selective, binding various diphenols. The affinity of binding decreases as the substitution of the diphenol changes from \(\text{para} > \text{meta} > \text{ortho}\). Also, fused terpyridines afforded macrocycle 103, which displayed selective affinity towards haloarenes with increasing \(K_a\) values from chloro- < bromo- < iodoarenes. Crystal structures of these host-guest complexes were also solved for the catechol-encapsulated analogue of 102 and \(\text{o-diiodobenzene-encapsulated analogue of 103}\). Crystal
structures are shown in Scheme 1.15. The o-diiodobenzene-encapsulating dimer possesses perfect symmetry in the binding with contact distances of 3.4 and 3.8 Å, respectively, due to the distortion caused by the iodine-aromatic repulsion.

Scheme 1.15. Self-assembly of complexes 102 and 103 and crystal structures of their respective encapsulated analogues.

Perera et al. reported the self-assembly of a Pd\textsuperscript{II}-based hexameric metallomacrocycle in 2010\textsuperscript{161,162}. Isolation and characterization of bis-Pd\textsuperscript{II} acetonitrile adduct 104 created a 120°-orientation that when combined with 4,4\textsuperscript{'}-bipyridine led to the high-yield assembly of hexamer 105, depicted in Scheme 1.16. The same strategy was employed in the self-assembly of sterically congested hexamer 106, which unexpectedly self-assembled in near-quantitative yields. Utilization of variable temperature \textsuperscript{1}H NMR spectroscopy and ESI-TWIM-MS aided in structure characterization of hexamers 105 and 106.
Schmittel et al. reported the use of Cu$^+$, as a metal source, for the self-assembly of phenanthroline-based metallo tweezer 107, which also possessed two pendant porphyrin moieties, depicted in cartoon form in Scheme 1.17.$^{163}$ Once in hand, the tweezers were used as synthons in the higher-ordered self-assembly of metallomacrocycles 108. By varying the length of the bipyridine spacer, ladder-type assemblies 109 and 110 were also isolated by incorporation of 4,4$'$-bipyridine and DABCO into the porphyrin tweezers, respectively. The structures were characterized by $^1$H NMR spectroscopy as well as ESI-MS.
Scheme 1.17. Utilization of HETPHEN approach in formation of metallo-
macrocycles and -ladders.

Modified versions of this heteroleptic *bis*phenanthroline (HETPHEN) approach were utilized in the self-assembly of trapezoid 111, scalene triangle 112, isosceles triangle 113, and spoked wheel 114. Their level of complexity is awe-inspiring, with triangle 112 consisting of *nine* components. The intricacy of these asymmetric systems has led to increased exploration in the formation of advanced structures by similar methods, shown in Scheme 1.18. By spending time in creating a combinatorial library for both terpyridine and phenanthroline binding preferences with various metals, the authors were able to capitalize on extremely complex self-sorting behavior in metallomacrocycles and other architectures.
Scheme 1.18. Use of modified HETPHEN approach in the self-assembly of highly complex architectures 112-114.

1.3 Octahedral-based Metallomacrocycles

Although the majority of metallomacrocycles are of the square planar variety, increased research in the last 15 years has led to numerous publications involving octahedral metals, as the coordinative core for cyclization. The most common connectivity is the <tpy-M\textsuperscript{II}-tpy> type, recent work has utilized the pyridine rather than terpyridine connectivity, leaving non-coordinating ligands in the remaining available metal binding sites. These macrocycles can be chemically robust, if metals such as Ru\textsuperscript{II} or Fe\textsuperscript{II} are used; they can also be dynamic systems, in the case of Cd\textsuperscript{II} and Zn\textsuperscript{II}. Utilitarian applications have
been shown as sensors, bioactive molecules,\textsuperscript{93} LEDs,\textsuperscript{167} and solar devices,\textsuperscript{168} and show promise in the formation of higher ordered architectures.

Würthner \textit{et al.} recently reported the synthesis of molecular boxes \textbf{115} and \textbf{116}, shown in Figure 1.10.\textsuperscript{169} These boxes consist of a linear porphyrin dimer with an available zinc atom for binding to another linear component. For the assembly, these authors chose a pyridine-substituted porphyrin and perylene \textit{bisimide}, as the linear synthon. Molecular boxes \textbf{115} and \textbf{116} displayed very interesting photophysical properties, as a mere change of the bay position substituent drastically changed the UV-vis and PL spectra. From crystal structure data, the bulky –R groups in \textbf{115} distort the alignment of the box, thus decreasing the photophysical properties. These boxes could serve as potential hosts for aromatic guests, as well as potential three-dimensional architectures with the available chlorides on the Ru\textsuperscript{II} connectivity sites.
Figure 1.10. Molecular boxes 115 and 116 with cartoon of differing orientations.

Stang et al. recently utilized a similar mode of connectivity to create a variety of molecular boxes.\textsuperscript{90,112,170-172} Figure 1.11 shows the molecular structures of pyridine donors and Ru\textsuperscript{II} acceptors, used in the self-assembly process, which was conducted under refluxing conditions resulting in rectangles of \( \geq 70\% \) yield. In some instances, interlocked noncatenane-type complexes have been isolated, and their single crystal structures solved.\textsuperscript{172} The rectangles have been tested as catalysts, sensors, and potential hosts; however, the most promising application of such squares is the ability to act as anti-cancer agents. Tests of metallorectangle
117 (Figure 1.11B) against the HTC-15 and SK-hep-1 cancer cell line show IC\textsubscript{50} values of 3.7 and 4.2 µM, compared to the values of 5.6 and 6.3 for cisplatin, respectively. Shown in Figure 1.11C is the effect of the donor and acceptor of 117 (denoted D\textsubscript{117} and A\textsubscript{117}, respectively) compared with 117 on the A-549 cancer cell line. These studies were expanded to include additional cancer cell lines, including HeLa and AGS, with similar results.

Figure 1.11 A) Donors and acceptors utilized in the self-assembly of molecular squares, B) X-ray crystal structure of 117, and C) plot of effect on A-549 cancer cell line.

The utilization of <tpy-M\textsuperscript{II}-tpy> connectivity in the self-assembly of metallomacrocycles began in 1999 by Newkome and coworkers and since then
has been a key research area in functional materials as well as more recently dynamic self-assembly processes. After isolation of the first homometallic metallohexamers 118 and 119, work began on heterometallic macrocycles. In 2004, their work was published utilizing the linear species 120 and 121 and their self-assembly with Fe$^{II}$, shown in Figure 1.12. While ruthenium is slow to react with the bis-terpyridine ligands, allowing for good yields of linear dimer 120 and trimer 121, Fe$^{II}$ is faster reacting making it a viable ring-closure step. Isolation of hexamers 122 and 123 was achieved by column chromatography in moderate yields. Step-wise self-assembly also allows for the introduction of different functionalities on the periphery of the hexamers, and this will be addressed later. Also isolated, utilizing the step-wise method, was metallohexamer 122, which possesses five Ru$^{II}$ ions and a single Fe$^{II}$ ion. The electrochemical properties of these compounds are promising as potential catalysts or molecular batteries, as each hexamer is capable of accepting 12 electrons.
Figure 1.12. Homometallic hexamers 118 and 119 and the isolation heterometallic hexamers 122-124 by step-wise syntheses.

Until 2006, the linear hexamers were synthesized by stepwise techniques. In a shotgun attempt to isolate longer chain oligomers, a one-step synthesis gave rise to mixture of small linear synthons.\textsuperscript{176} As shown in Scheme 1.19, bispterpyridine 125 and adduct 126 (containing a trace 127) were refluxed under reducing conditions for 12 h, after which, preparative chromatography resulted in the isolation of hexamer 118 as well as linear structures 120, 121, and 128-130, which were all characterized by $^1$H NMR spectroscopy. Further, the reactions of the proper length oligomers, such as dimer 120 with tetramer 128 with RuCl$_3$ under reducing conditions led to the isolation of hexamer 118 in good yields. This technique of using oligomeric complexes, as starting materials, would
become a common technique for the synthesis of increasingly complex metallomacrocycles and architectures.

Scheme 1.19. Isolation of linear species from a single one-pot reaction as well as cyclic structure 118.

120, 121, 128, 129, 130 (n = 2-6)

Scheme 1.19. Isolation of linear species from a single one-pot reaction as well as cyclic structure 118.
Since heterometallic metallomacrocycles had been isolated in good yields, focus turned to applying this knowledge to new structures. Molecular clip 131 was dimerized with Fe$^{II}$ to afford the very congested macrocycle 132 in high yields, and was characterized by X-ray crystallography (see Scheme 1.20). The crystals were grown using 1,2,4,5-benzenetetracaboxylate, as a monomeric counterion, a technique that would be utilized again for higher ordered growth.

Scheme 1.20. Synthesis and crystal structure of dinuclear metallomacrocycle 131.

By changing the angle-of-orientation about the benzene-cored ligand, it was easy to envision a 60°-oriented bisterpyridine ligand. In 2005, Hwang et al.
reported utilization of Sonogashira coupling in the synthesis of ligand 133. Using the previously described methods for cyclization, triangular architectures 134-136 were readily isolated in good yields.\textsuperscript{179} Li et al. isolated a series of elongated ligands, which readily cyclized in the presence of FeCl\textsubscript{2} to form the trimeric hexamers 137-140 (Figure 1.13).\textsuperscript{47} Minor differences in the electrochemical and photophysical properties suggested some stacking behavior in the planar metallomacrocycles 137 and 138 that may not be present in the substituted macrocycles, such as trimeric hexamers 139 and 140.

![Figure 1.13. Synthesis of metallomacrocycles 134-140 utilizing ligands of a 60°-orientation.](image)

With multiple macrocycles available, focus turned to the modification of the periphery of the metallomacrocycles. Synthesis of bisolefin modified ligand
141 led to cyclization with Fe$^{II}$ to form hexamer 142, as shown in Scheme 1.21, which possessed terminal alkenes in close proximity, making it an ideal candidate for Grubbs metathesis. Once connected, reversibility of the <tpy-Fe$^{II}$-tpy> connectivity under basic conditions resulted in covalently-bonded hexamer 143, which was further modified by reduction of the olefins and hexamer reformation. The ether linkages between the bisterypyridines acted as a template for the reassembly of the hexamer in an 80% yield, which is better than most iron-based self-assembly procedures. Also removed from ethereal-linked hexamer 143 was the phenol modified bisterypyridine via catalytic hydrogenation to give all-organic macrocycle 144. The reversibility of the <tpy-Fe$^{II}$-tpy> linkage was utilized later in the assembly of modified gold-nanorods.
An additional post-complexation synthetic route was published by Eryazici et al., in which the iodo-modified ruthenium complex 145, shown in Scheme 1.22A, was used as a reagent in a Suzuki cross-coupling reaction to form the asymmetric trimer 146. This trimer was reacted with FeCl₂ to afford the corresponding hexamer 147. The 4,4″ modification with carboethoxy groups as well as two pendant bromo-groups provides a chance for additional cross
coupling chemistry. Additionally, the diiodo-modified *bisterpyridine* complex 148 was coupled *via* a Sonogashira reaction to form free ligand 149, which after subsequent cyclization resulted in the isolation of a chair-like hexamer 150, which was easily observed by TEM, as shown in Scheme 1.22B.69

Scheme 1.22. Synthesis of A) polyfunctionalized metallomacrocycle 147 and B) exo-modified hexamer 150.

New thresholds opened in 2006 with the report of the synthesis of the first molecular fractal, termed the novel Serpinski gasket 151.183 This work was a
direct result of the stepwise methods that were highlighted earlier. As shown in Figure 1.14, this molecular fractal could be observed via AFM, TEM, and cryogenic STM, leaving no doubt to the presence of the desired fractal architecture.

Figure 1.14. Images of Serpinski gasket 151 by A) AFM, B) TEM, and C) STM.

The incorporation of the hexameric macrocycles into higher ordered architectures began with the synthesis of water-soluble hexamer 152. Wang, et
*al.* reported the functionalization of \( m-[(\text{bis(terpyridyl)}\text{)}\text{phenol with tris-3,4,5-} \) (tetraethylenglycol)-substituted benzene. The corresponding *bisterpyridine was cyclized to afford 152, which readily associated with oxidized single-wall carbon nanotubes (Oxi-SWNTs), as shown in Figure 1.15A. The composite was further characterized by AFM (Figure 1.15B), which showed the nanotube with added hexamers of 4 - 5 nm width and 0.6 – 0.9 nm in height; values that are consistent with molecular modeling. Addition of excess competing anions, such as PF\(_6^-\) resulted in the disassembly of the composite at ambient conditions, which was measurable through both UV-vis as well as XPS spectroscopies. The use of this composite, as a potential solar device has shown promise because of the ability of hexamer 152 to store a high density of electrons.

![Figure 1.15. Formation of A) Oxi-SWNT composite with water-soluble hexamer 152 and B) AFM image of composite.](image)
The use of multivalent anions aided in the growth of crystal formation of single crystals of metallomacrocycle 131. Using this, Wang, et al. reported the formation of a dendrimer-metallomacrocycle composite nanofiber in 2008.\(^{184}\) Layering MeCN solution of 12\(^+\) charged hexamer 153 with the sodium salt with a 12\(^-\) charge of the first generation Newkome-type dendrimer\(^{14}\) resulted in slow growth of red nanofibers, as shown in Figure 1.16A. Selected area electron diffraction (SAED) provided \(d\)-spacing data that was totally consistent with the molecular simulations of 3.85 nm along the long axis of the fiber. When the third generation Newkome-type dendrimer was utilized in this process, aggregate formation resulted, as would be expected with the high negative charge (108\(^-\)), thus requiring the presence of multiple hexamers 153 to balance the charge. Similarly, Schultz et al. used a series of triangles 154-159 of a hexavalent charge paired with benzenehexacarboxylate (see Figure 1.16B) in the formation of nanofiber composites.\(^{178}\) Again, SAED was used, along with molecular modeling, to simulate the aforementioned fibers. Modeling suggests that the hexacarboxylate anion acts as the mononuclear counterion; however, due to the poor solubility of the fibers, this was not confirmed. The fibers possessed slight solubility in DMSO and the \(^{31}\)P and \(^{19}\)F NMR confirmed the absence of any PF\(_6\)^\(^-\) in the composite, consistent with ion exchange. Variable temperature studies on the triangles themselves showed good thermal stability of the metallomacrocycles.
While working with the classic 120°-oriented component systems, there was always a trace amount of a compound that was never fully characterized until 2010, when Chan et al., reported the isolation of traces of compacted pentameric metallomacrocycle from the self-assembly of sugar-modified bisterpyridine 160 with FeCl$_2$.$^{185}$ Although the pentamer 161 was a minor product with nearly
identical $^1$H NMR to its hexameric analogue 162, the structure was ultimately elucidated via ESI-MS. Due to the carbohydrate functionality, both macrocycles readily formed nanofibers, as shown in Scheme 1.23A, that were observable by TEM. Proving the formation of 161 led to isolation of macrocycles with a series of Newkome-type dendrons appended; the substituted macrocycles 163-165 were isolated with ring sizes 5-7. These macrocycles, shown in Scheme 1.23B, were isolated by very patient chromatography techniques and potentially could provide a set of negatively charged complexes, rather than positively charged, given removal of the pendant $t$-butyl groups.

Scheme 1.23. A) Isolation and nanofiber growth of pentamer 161 and hexamer 162. B) Isolation of macrocycles 163-165 with ring sizes 5-7.
Linear synthons 120 and 121, when cyclized with FeCl₂, led to 166-168 possessing 8-, 9-, and 10-membered rings being isolated in minor yields, as well as the expected hexamers 169 and 170 and all Ru\textsuperscript{II} hexamer 171, shown in Scheme 1.24A.\textsuperscript{50,187} These larger rings were primarily characterized by ESI-MS, as the \textsuperscript{1}H NMR, revealing subtle differences between the various rings. The cross-sectional values of the ionic states were calculated from the ESI-TWIM-MS data, and the experimental values were as expected from the values calculated, with an increase in cross-section from hexamer progressing to the decamer. The utilization of DOSY NMR of the nonamer 168 was useful in further supporting the larger ring size, as the analogous hexamer was detected to be smaller. Both macrocycles were consistent with the diameters of simulated metallomacrocycles. Also isolated was a series of tetramers 172-176, shown in Scheme 1.24B, from the 60°-oriented starting ligand 177.\textsuperscript{188} The Ru\textsuperscript{II} dimer 178 derived from 177 was the starting reagent for the self-assembly to generate tetramers 172-175, with tetramer 176 isolated as a minor product from the cyclization of 177 with FeCl₂. The photophysical properties of these tetramers were studied, along with transient absorption, which provided lifetimes on the 1 - 2 nanosecond timescale. Comprehensive ESI-MS data were also collected, including gradient MS-MS (gMS\textsuperscript{2}), which allowed for acquisition of the relative strength of the tetramers, indicating 172 < 173 < 174 < 175, which is consistent with previous studies\textsuperscript{166} on the strength of <tpy-M\textsuperscript{II}-tpy> coordination.

Stoichiometric self-assembly of higher complex architectures has been well-established in the platinum and palladium chemistry, but it has not been explored in the bis(terpyridine) connectivity. In 2011, Wang et al., published the synthesis of the symmetric spoked wheel 178 by three-component self-assembly. This molecular wheel was isolated in near quantitative yields, as shown in Figure 1.17, relying on a hexa(terpyridine) core and a 1,2,3-tri(terpyridyl) exterior. When mixed in a 1:6:12 L\textsubscript{1}:L\textsubscript{2}:M\textsuperscript{II} molar ratio, where the metal is Zn or Cd, L\textsubscript{1} is the core hexa(terpyridine) and L\textsubscript{2} is the periphery tri(terpyridine), respectively, high yields of the spoked wheel were obtained. The ESI-MS of 178 was pristine, as was the \textsuperscript{1}H NMR spectroscopy, verifying
successful synthesis of the structure. The basic size of 178 was also captured via TEM, with the diameter of ca. 6 nm consistent with molecular simulation calculations.

Figure 1.17. Spoked wheel 178 and corresponding $^1$H NMR and ESI-MS.

From wheel 178, it is possible to see three smaller triangular-based architectures within the large spoked wheel, depicted in cartoon form in Figure 1.18. One is a molecular rhombus 179, which was recently synthesized by Lu et al. via the stoichiometric assembly of 1,2,3-tristerpyridyl ligand 180 with the 60°-oriented ligand 181 using Cd$^{II}$ or Zn$^{II}$ in a precise 1:1:5 ratio. Removal of the central terpyridyl ligand 180 resulted in a dynamic equilibrium between the homoleptic self-assembly of 181 and the desired rhomboidal structure. The additional <tpy-M$^{II}$-tpy> complex in 179 results in a much more thermodynamically stable end-product, which accounts for the near quantitative assembly. The other two possible structures that arise from 178 are bowtie- 182
and butterfly-shaped molecule 183. These were examples of supramolecular constitutional isomers. Studies on their drift times using ESI-TWIM-MS were significantly different, as were their calculated cross-sectional values. These compounds are the beginning of ongoing research in the area of stoichiometric terpyridine-based self-assembly of higher ordered architectures.

Figure 1.18. Stoichiometric self-assembly of the spoked wheel derivatives 181-183.

1.4 Concluding Remarks

Shape-persistent metallomacrocycles provide a unique opportunity to have precise control over molecular size, shape, and design; as well as obtain products in near quantitative yields. This mode of assembly allows for a plethora of utilitarian applications, including sensors, anti-cancer treatments, LEDs, and solar devices to name a few. Recent advances in shape-persistent metallomacrocycles have focused on application, and the next phase appears to be geared toward more
complex systems, which will hopefully give rise to an increased insight and control over macromolecular architectures. The following chapters are a summation of the past five years of my research in the field of shape-persistent terpyridine chemistry.
CHAPTER II

STOICHIOMETRIC SELF-ASSEMBLY OF ISOMERIC, SHAPE PERSISTENT, SUPRAMOLECULAR BOWTIE AND BUTTERFLY STRUCTURES

2.1 Introduction

The last 20 years have led to major advances in the field of supramolecular chemistry. Lehn, Stang, Fujita, Schmittel, and others have reported numerous examples of novel macromolecules that rely on <ligand-M-ligand> connectivity, as a driving force for assembly. While homoleptic self-assembly is typically quite facile; heteroleptic self-assembly is often more difficult. Typically, directed and self-assembly techniques are combined in the synthesis of large metallocycles, rectangles, and other polygons. These recent developments enhanced the insights into molecular self-assembly of higher ordered superstructures. Of the numerous examples, several have utilized <tpy-M<sup>+</sup>-tpy> (tpy = terpyridine) connectivity as a means of constructing multi-component systems.

In particular, we recently reported utilizing <tpy-M<sup>+</sup>-tpy> connectivity for the facile construction of a hexagonal, spoked wheel, represented by Figure 2.1A, which is composed of six individual triangles with shared sides that exhibit
isomeric patterns, such as end-to-end triangles 2.1B and 2.1C possessing differing orientations about a mutual point. This is an example of discrete control over the supramacromolecular self-assembly of bicyclic, polygonal constitutional isomers; notably, monocyclic stereo-, syn-anti-, linkage-, and supramolecular-isomers along with isomeric nanobaskets have been reported. We herein report the synthesis of novel bis- and tetrakisterpyridine ligands and their use in the construction of isomeric, triad-based, bicyclic architectures.

Figure 2.1. Hexagonal spoked-wheel motif A) and isomeric triangular polygons (B and C) along with their corresponding terpyridine-based metallocyclic representations (PF$_6^-$ counterions omitted for clarity).

Recent advances in mass spectrometry (MS) have been key factors in better understanding the principles of supramolecular construction. The use of
traveling wave ion mobility (TWIM)-MS coupled with electrospray ionization (ESI)-MS has afforded mass, charge, and size differentiation in the characterization of these species by allowing the observation of the higher charge states without fragmenting the labile metal-ligand connections of the self-assembled product.\textsuperscript{10,161,196}

Prior to this technique, it was often impossible to get acceptable MS data,\textsuperscript{196,210,211} and in cases where there were multiple components, the \textsuperscript{1}H NMR spectra would often be extremely complex and inconclusive. Also, if there were undesirable side products resulting from kinetic instability, their structural characterization could be difficult.

2.2 Results and Discussion

The critical bisterpyridine ligand 3 was successfully synthesized (Scheme 2.1) by the Suzuki cross-coupling of 4,5–dibromo–1,2–bis-carbomethoxybenzene (2)\textsuperscript{212} with excess 4′-(4-boronatophenyl)–2,2′:6′,2″–terpyridine (1) in a H\textsubscript{2}O:toluene:t-BuOH mixture (3:3:1 v/v/v) for 48 h; column chromatography (Al\textsubscript{2}O\textsubscript{3}, CHCl\textsubscript{3}) followed by recrystallization afforded (51%) bisterpyridine 3. Characterization included pertinent \textsuperscript{1}H NMR resonances such as, a singlet at 8.71 ppm and a doublet at 8.65 ppm assigned to the 3′,5′- and 6,6″-tpyH\textsubscript{s}, respectively; all other resonances were readily assignable. An ESI-MS peak at m/z 809.2, consistent with [M+H]\textsuperscript{1+}, also supported the structural assignment. Ligand 3 maintained the \textsuperscript{1}H NMR marker resonance (CO\textsubscript{2}CH\textsubscript{3}) at 4.0 ppm, allowing for structural comparisons.
Alkoxy–modified, tetraalkylterpyridine 5 was prepared (84%, Scheme 2.1) from 1 and 4 using a similar protocol to that of 3. The $^1$H NMR spectrum of 5 (Figure 2.4) exhibited a single set of resonances for the terpyridine moieties that was nearly identical to that of 3, as well as the expected symmetrical resonances for the aryl core; an ESI-MS peak for [M+H]$^{1+}$ at m/z 1508.0 corroborated the assignment. Initial attempts to obtain the desired bowtie 9 using 3, 5, and Cd$^{2+}$ (or Zn$^{2+}$), in a 4:1:6 stoichiometry, respectively, gave a triangle 8, as the major component, along with bowtie 9 as shown by both ESI-MS (Figure 2.2) and NMR analyses. Notably, prior attempts using this procedure and the methoxy–modified analog of bisligand 3 (3-OMe, See Experimental) led to more favorable, but yet, similar undesirable mixtures.

Modifications aimed at eliminating the formation of trimer 8 focused on restricting the degrees-of-freedom. Thus, a Ru$^{ll}$ dimer was targeted to instill a non-reversible complex between the two outer 60° ligands. Dimer 6 was prepared (40%) from the stoichiometric reaction of bisligand 3 with RuCl$_2$(DMSO)$_4$ in a refluxing CHCl$_3$:MeOH mixture (1:1 v/v) followed by column chromatography (Al$_2$O$_3$, CHCl$_3$ → MeCN:H$_2$O: sat KNO$_3$(aq) 25:1:1 v/v/v); small oligomers were also isolated (22%), based on $^1$H NMR spectroscopy. Dimer 6 was characterized by the expected two sets of resonances ($^1$H NMR) with an integration ratio of 1:1 for the complexed and metal-free terpyridine ligands (Figure 2.3). The MALDI-MS was consistent with dimer formation, exhibiting a peak at m/z of 1843.91.
Scheme 2.1. Synthesis of 3, 5, 6, and 7. Ligands 3, 5, and 7 were synthesized from 2 or 4 with 1 and isolated in good yields.

Figure 2.2. One dimensional ESI-MS of the mixture of 8 and 9, with pertinent charge states marked. Note: counterions (BF$_4^-$) omitted from structures for clarity.
Figure 2.3. $^1$H NMR spectrum of Ru$^{II}$ dimer 6.

Reaction of the bisterpyridine dimer 6 with the alkyl-modified tetrakisterpyridine 5 and Zn(BF$_4$)$_2$ in a 2:1:4 stoichiometric ratio afforded the heterometallic bowtie polygon 10 (Scheme 2.2) with no observable tetrameric starting material; the $^1$H NMR spectrum of 10 exhibited peaks in the expected 6:1 ratio corresponding to the -CO$_2$CH$_3$:OCH$_2$R moieties. Although this creates the potential for self-assembly of 6 and the meta substituted terpyridines of 5, the steric strain of this type of bonding would be enthalpically disfavored over the depicted structure in Scheme 2.2.

COSY analysis simplified assignment of all resonances in the aromatic region of the $^1$H NMR. Notable attributes of the $^1$H NMR spectrum (Figure 2.4) include three discernible sets of 3',5' resonances, two of which partially overlap, but exhibit an ideal 1:2 integration; the 3,3" and 6,6" resonances displayed the desired downfield and upfield trends, respectively. Results from ESI-MS and
TWIM-MS (Figure 2.5 and Figure 2.6) showed that bowtie 10 with either Zn\textsuperscript{II} or Cd\textsuperscript{II} was the predominant component. Based on the sharp drift time distribution of the different charge states, no other component was detected in TWIM-MS, reflecting the highly rigid, shape-persistence of this bowtie-type architecture. Additionally, Zn\textsuperscript{II} and Cd\textsuperscript{II} give complexes of the same size, as the corresponding drift times of each charge state are nearly identical (Table 2.1).

Figure 2.4. \textsuperscript{1}H NMR overlay of starting materials 5 (top) and 6 (bottom) with the Zn bowtie 10 in the center. Arrows depict assigned resonance shifts that occur upon complex formation.
Figure 2.5. A) ESI-MS and B) 2-D ESI-TWIM-MS plot (mass-to-charge ratio vs. drift time) of 10. The charge states of intact assemblies are marked.
Figure 2.6. ESI-MS and TWIM-MS plots for Cd$^{II}$-based bowtie 11.

Table 2.1. Drift times and collision cross sections for self-assembled products 10, 11, 12 and 13.
In view of this result, can one discern the difference between two isomeric structures, for example, via differences in MS drift times or collision cross sections? This was tested by preparing the related butterfly motif 12 by the self-assembly of ligands 7 [accessed by Suzuki coupling of 1,2,3,4-tetrabromo-5,6-bis-hexoxybenzene (4, Scheme 2.1) to the terpyridine boronic acid 1] and 6 (Scheme 2.2). The tetrakis[terpyridyl] product revealed two distinct sets of resonances that are easily differentiable. Based on modeling of isomers 10 and 12, there is a difference in size or theoretical cross section value for the two species, thus one would expect a difference between these isomers in the TWIM-MS.

Butterfly 12 was readily assembled, resulting in a nearly identical 1D ESI-MS (Figure 2.7) to that of 10 (Figure 2.5); however, the TWIM-MS drift times were different at low charge states, e.g., 4+ to 6+. Notably, the bowtie complex 10 has a significantly larger collision cross section than that of its butterfly-shaped isomer 12 (Figure 2.7). As the charge increases, both isomers have very similar drift times or cross sections (Table 2.1). Thus, the charge distribution affects the sizes of these two complexes at low charge states; whereas, once the +7 charge state is reached, there are marginal differences between the two.
Scheme 2.2. Synthesis of bowtie 10 and butterfly 12 from 6 with 5 or 7.

Figure 2.7. ESI-MS and TWIM-MS data for Zn$^{	ext{II}}$-based butterfly 12.
Figure 2.8. ESI-MS and TWIM-MS data for Cd$^{II}$-based bowtie 13.
Figure 2.9. Comparison of the estimated collision cross sections of bowtie 10 and butterfly 12 at different charge states, \(i.e.,\) 4+ to 7+.

2.3 Conclusion

In summary, two novel supramolecular isomers have been isolated \textit{via} a three component self-assembly procedure. These bowtie and butterfly-type structures were predesigned to utilize \(<\text{tpy-M}^{+2}\text{-tpy}>\) connectivity where \(\text{M}^{+2}\) is either \(\text{Cd}^{+2}\) or \(\text{Zn}^{+2}\). Initial attempts provided a mixture of a small triangle as well as the desired structure; whereas, restriction of the components' degrees-of-freedom by preparation of a \(\text{Ru}^{+2}\) dimer led to the isolation of a pure \(\text{bis}\)-triangular supramolecular structures that were elucidated by \(\text{^1H}\) and COSY NMR spectroscopy, as well as ESI-TWIM-MS. While the one-dimensional ESI-MS data were identical for the isomers, the TWIM-MS data revealed notable differences regarding detailed size and structure information. Comparison of the drift times of the two isomers showed a significant difference in the low charge states for the two isomers, whereas the drift times of the higher charge states remained nearly
identical. Further utilitarian studies of these isomers and related materials are ongoing.

2.4 Experimental Section

**General Procedures.** Chemicals were purchased from Fisher Scientific, Sigma/Aldrich, or VWR, checked by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al$_2$O$_3$ (IB-F) or SiO$_2$ (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al$_2$O$_3$, Brockman Activity I (60-325 mesh) or SiO$_2$ (60-200 mesh) from Sorbent Technologies. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra were recorded on either a Varian Mercury 300 or Varian NMR 500 spectrometer, using CD$_3$CN (B) for complexes and CDCl$_3$ (A) for ligands, and referenced to 1.94 and 7.27 ppm, respectively. Mass spectra were obtained on a Bruker Esquire electrospray ion trap mass spectrometer (ESI-MS). Traveling wave ion mobility mass spectrometry (TWIM-MS) experiments were performed using a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer. The TWIM device is located between the Q and ToF mass analyzers and consists of three parts, a trap cell, an ion mobility (IM) cell, and a transfer cell. The trap and transfer cells can be used for conventional tandem MS experiments via collisionally activated dissociation (CAD). The ion mobility cell is used in IM separations. Generally, the following parameters were used in TWIM-MS experiments: ESI capillary voltage, 1.5 kV; sample cone voltage, 15 V; extraction cone voltage, 3.2 V; desolvation gas flow, 800 L/h (N$_2$); trap collision energy (CE), 2 eV; transfer CE,
1 eV; trap gas flow, 1.5 mL/min (Ar); IM gas flow, 22.7 mL/min (N₂); sample flow rate, 10 μL/min; source temperature, 30 °C; desolvation temperature, 40 °C; IM traveling wave velocity, 350 m/s. The IM traveling wave heights were set at 7.5 V. In the tandem MS experiments, the trap CE was varied within 6-23 eV to cause fragmentation. The sprayed solution was prepared by dissolving ~1 mg of sample (1 mL) of MeCN/MeOH (3:2) solvent mixture.

4′-(4-Boronatophenyl)-2,2′:6′,2″-terpyridine (1): To a round bottom flask, a mixture of 4–formylphenylboronic acid (3.36 g, 20 mmol), 2-acetylpyridine (5.32 g, 44 mmol), absolute EtOH (150 mL), and powdered NaOH (4.80 g, 120 mmol) were added. After stirring at 23 °C for 5 h, the solution’s color changed from a yellow to red, after which the mixture was heated at 65 °C for 12 h to give a dark yellow solution with a colorless precipitate. The precipitate was filtered in vacuo and washed with Me₂CHOH and CHCl₃ to give (63%) 1, as a near colorless solid; 4.5 g. m.p. = >300°C; ¹H NMR (300 MHz, CD₃OD): δ 8.70-8.63 (m, 6H, 6,6″-tpyH, 3′,5′-tpyH, 3,3″-tpyH), 8.00 (dd, 2H, J = 7.8 Hz, 5,5″-tpyH), 7.75 (dd, 4H, J = 7.8 Hz, ArH), 7.47 (dd, 2H, J = 6.3 Hz, 4,4″-tpyH); ¹³C NMR (300 MHz, d-MeOH): 118.17, 121.64, 123.91, 124.61, 133.77, 134.07, 137.38, 148.62, 151.80, 155.52, 156.12 ppm; ESI/MS 354.0 [M+H].

1,2,4,5-Tetrabromo-3,6-bishexoxybenzene (4): To a stirred solution of MeOH (100 mL) and KOH (1.90 g, 47.5mmol), 1-bromohexane (7.4 g, 45.0 mmol) and 1,2,4,5-tetrabromohydroquinone (3.53 g, 7.8 mmol) was added. The mixture was refluxed for 24 h, then concentrated in vacuo, followed by column chromatography (SiO₂, hexanes Rₑ = 0.71) to afford 6, as a colorless oil: 4.0 g,
86%. $^1$H NMR (300 MHz, A): $\delta$ 3.96 (t, 4H, OCH$_2$R, $J$ = 5.4 Hz), 1.86 (pentet, 4H, OCH$_2$CH$_2$R, $J$ = 6.9 Hz), 1.54 (m, 4H, alkylCH$_2$), 1.36 (m, 8H, alkylCH$_2$), 0.93 (t, 6H, alkyl CH$_2$, $J$ = 6.6 Hz); $^{13}$C NMR (300 MHz, A): $\delta$ 14.1, 22.6, 25.5, 29.9, 31.6, 73.6, 105.0, 121.4, 152.0.

**1,2,3,4-Tetrabromo-5,6-bishexoxybenzene**: To a stirred solution of MeCN (500 mL), K$_2$CO$_3$ (7.70 g, 56.3 mmol), 1-bromohexane (9.3 g, 56.3 mmol), and 1,2,3,4-tetrabromocatechol (4.0 g, 9.3 mmol) was added. The mixture was refluxed for 24 h, then concentrated *in vacuo*, followed by column chromatography (SiO$_2$, hexanes $R_f$ = 0.71) to afford 1,2,3,4-tetrabromo-5,6-bishexoxybenzene, as a colorless oil: 4.0 g, 72%; $^1$H NMR (300 MHz, A): $\delta$ 3.98 (t, 4H, OCH$_2$R, $J$ = 6.6 Hz), 1.80 (pentet, 4H, OCH$_2$CH$_2$R, $J$ = 7.2 Hz), 1.48 (m, 4H, alkylCH$_2$), 1.34 (m, 8H, alkylCH$_2$), 0.90 (t, 6H, alkylCH$_2$, $J$ = 6.9 Hz); $^{13}$C NMR (300 MHz, A): $\delta$ 14.0, 22.7, 25.7, 30.1, 31.7, 74.2, 121.9, 123.3, 150.8; MALDI-MS = 617.0 [M+Na].

**General Coupling Procedure:**

To a 3-necked round bottom flask, the initial aryl halide, 4’–(4-boronatophenyl)-2,2’:6’2”-terpyridine (1.5 equiv. per halide), Na$_2$CO$_3$ (6 equiv.), and water:Me$_3$COH:toluene (3:1:3) were added. The system was freeze-pump-thawed (3x) and backfilled with argon or nitrogen, after which PdCl$_2$(PPh$_3$)$_2$ (6 mol% per halide) was added. The biphasic system was refluxed for 48 h resulting in a red aqueous layer and a tan organic layer. The aqueous layer was extracted with CHCl$_3$, the combined organic extract was dried (MgSO$_4$), and concentrated *in vacuo* to give a residue, which was dissolved in few milliliters of toluene,
followed by precipitation with MeOH to give an off-white solid, which was column chromatographed (Al$_2$O$_3$) eluting with CHCl$_3$ to give pure title compound, as a colorless solid.

**1,2,4,5-Tetakis(4′-terpyridyl-p-phenyl)-p-dihexoxybenzene (5):** Using the general procedure, the following were used in the specified quantities: 1,2,4,5-tetrabromo-3,6-dihexoxybenzene (600 mg, 1.01 mmol), 4′-(4-boronatophenyl)-2,2′:6′,2″-terpyridine (2.14 g, 6.06 mmol), Na$_2$CO$_3$ (150 mg, 12 mmol), water (36 mL), t-butyl alcohol (12 mL), and toluene (36 mL), PdCl$_2$(PPh$_3$)$_2$ (150 mg, 199 µmol) to afford 5: 2.13 g (90%); m.p. = >300 °C; $^1$H NMR (500 MHz, A): δ 8.73 (s, 8H, 3′,5′-tpyH), 8.68 (d, 8H, $J = 4.0$ Hz, 6,6″-tpyH), 8.62 (d, 8H, $J = 8.0$ Hz, 3,3″-tpyH), 7.84 (m, 16H, 5,5″-tpyH, Ar′H), 7.47 (d, 8H, $J = 8.0$ Hz, ArH), 7.33 (t, 8H, $J = 6.0$ Hz, 4,4″-tpyH, Ar′H), 3.07 (t, 4H, $J = 6.0$ Hz, OCH$_2$), 0.94 (m, 8H, alkylCH$_2$), 0.78 (m, 8H, alkylCH$_2$), 0.68 (t, 6H, $J = 7.5$ Hz, alkyl CH$_3$); $^{13}$C NMR (500 MHz, A): 13.9, 22.5, 25.3, 29.7, 31.3, 73.2, 118.7, 121.2, 123.8, 126.4, 131.9, 135.7, 136.3, 137.9, 149.0, 150.1, 151.1, 155.8, 156.4; MALDI [M+H] = 1504.3.

**3,4-Bis(4′-terpyridyl-p-phenyl)-o-dicarbomethoxybenzene (3)** was prepared using the general procedure: 3,4-dibromo-1,2-biscarbomethoxybenzene (1.0 g, 2.9 mmol), 4′-(4-boronatophenyl)-2,2′:6′,2″-terpyridine (3.1 g, 8.6 mmol), Na$_2$CO$_3$ (300 mg, 24 mmol), water (90 mL), t-butyl alcohol (30 mL), and toluene (90 mL), PdCl$_2$(PPh$_3$)$_2$ (215 mg, 290 µmol) to give 3, as a colorless solid: 1.2 g (51%); m.p. > 300 °C; $^1$H NMR (CDCl$_3$, 300 MHz, A): δ 8.71 (s, 4H, 3′,5′-tpyH), 8.64-8.66 (d, 4H, $J = 4.8$ Hz, 6,6″-tpyH), 8.60-8.63 (d, 4H, $J = 8.1$ Hz, 3,3″-
tpyH), 7.87 (s, 2H, ArH), 7.80-7.85 (m, 8H, 5,5″-tpyH, Ar′H), 7.27-7.33 (m, 8H, 4,4″-tpyH, Ar′H), 3.95 (s, 6H, CO₂Me); ¹³C NMR (300 MHz, A): 167.74, 156.03, 155.79, 149.45, 148.96, 142.83, 140.24, 137.55, 136.97, 131.08, 130.19, 127.32, 123.82, 121.38, 118.88, 53.93; ESI/MS (m/z): [C₅₂H₃₆N₆O₄+H]⁺: 809.2.

[(3)₂Ru⁺²][NO₃]⁻ (6): To a 1L round bottom flask, 3 (200 mg, 250 µmol), RuCl₂(DMSO)₄ (40 mg, 83 µmol), and 1:1 CHCl₃:MeOH (200 mL) were added after refluxing for 48 h, the reaction was concentrated in vacuo to give a red powder that was purified by column chromatography (Al₂O₃, CHCl₃ → 1:1:25 H₂O:sat KNO₃(aq):MeCN upon removal of free 3) to afford 6, as a red powder: 83 mg, 54%; m.p. > 300°C; ¹H NMR (500 MHz, 1:1 CD₃OD:CDCl₃): δ 9.13 (s, 4H, complexed 3′,5′-tpyH), 8.76 (s, 4H, J = 8.0 Hz, free 3,3″-tpyH), 8.76 (m, 12H, free and complexed 3′,5′-tpyH, free 6,6″-tpyH), 8.17 (d, 4H, J = 8.0 Hz, Ar′H), 7.96-7.91 (m, 10H, 5,5″-tpyH, ArH), 8.18 (d, 4H, J = 8.0 Hz, Ar′H), 7.58 (d, 4H, J = 8.0 Hz, Ar′H), 7.42 (d, 4H, J = 8.0 Hz, Ar′H), 7.41 (t, 4H, J = 6.0 Hz, complexed 4,4″-tpyH), 7.38 (d, 4H, J = 5.0 Hz, complexed 6,6″-tpyH), 7.21 (t, 8H, J = 6.5 Hz, complexed, 4,4″-tpyH), 3.99 (s, 6H, OCH₃), 3.98 (s, 6H, OCH₃); ¹³C NMR (300 MHz, 1:1 CD₃OD:CDCl₃): 168.0, 167.9, 157.9, 155.9, 155.8, 155.3, 151.7, 149.6, 148.7, 148.4, 142.9, 142.4, 141.9, 140.4, 138.4, 137.6, 137.4, 135.5, 131.4, 131.2, 131.1, 130.9, 130.4, 127.9, 127.7, 127.1, 124.9, 124.2, 121.9, 121.4, 118.6, 52.7; MALDI - MS: m/z = 1843.91 [M+H]. Also isolated were longer chain oligomers accounting for an additional 24% of the overall yield.

1,2,3,4-Tetakis(4′-terpyridyl-p-phenyl)-o-dihexoxybenzene (7) was prepared using the general procedure: 1,2,3,4-tetrabromo-5,6-dihexoxybenzene
(1.0 g, 1.67 mmol), 4′-(4-boronatophenyl)-2,2′:6′,2″-terpyridine (3.55 g, 10.0 mmol), Na₂CO₃ (708 mg, 6.68 mmol), water (72 mL), t-butyl alcohol (24 mL), and toluene (72 mL), PdCl₂(PPh₃)₂ (800 mg, 668 µmol): 1.0 g (40%); m.p. = >300 °C; ¹H NMR (500 MHz, A): 8.70 (s, 4H, 3′,5′-tpyH), 8.66 (d, J = 4.0 Hz, 4H, 6,6″-tpyH), 8.59 (d, J = 8.0 Hz, 4H, 3,3″-tpyH), 8.55 [s(br), 8H, 3′,5′-tpyH, 6,6″-tpyH], 8.50 (d, J = 8 Hz, 4H, 3,3″-tpyH), 7.83 (t, J = 6.0 Hz, 4H, 5,5″-tpyH), 7.78 (d, J = 8.5 Hz, 4H, Ar′H), 7.75 (t, J = 6.0 Hz, 4H, 5,5″-tpyH), 7.53 (d, J = 8.5 Hz, 4H, Ar′H), 7.36 (d, J = 8.5 Hz, 4H, Ar′H), 7.30 (t, J = 6.0 Hz, 4H, 4,4″-tpyH), 7.21 (t, J = 6.0 Hz, 4H, 4,4″-tpyH), 7.04 (d, J = 8.5 Hz, 4H, Ar′H), 3.89 (t, 4H, OCH₂), 0.94 (m, 8H, alkylCH₂), 0.79 (m, 8H, alkylCH₂), 0.67 (t, J = 6.5 Hz, 6H, alkyl CH₃); ¹³C NMR (500 MHz, A): 14.0, 22.6, 25.6, 30.2, 31.6, 73.8, 117.6, 117.7, 118.6, 118.8, 121.0, 121.1, 123.4, 123.4, 123.6, 123.6, 125.6, 125.9, 126.0, 126.2, 131.5, 131.7, 132.1, 132.2, 135.2, 136.0, 136.2, 136.5, 136.7, 138.3, 147.9, 148.1, 150.0, 155.8, 155.8, 156.3 ppm; MALDI 1508.4 [M+H].

**General Self-assembly Procedure:**

To a stirred solution of 5 or 7 (4.1 mg, 2.7 µmol) in CHCl₃:MeOH (3:2; v/v) was delivered 6 (10.0 mg, 5.4 µmol) and M⁺² (10.9 µmol) via a syringe (1 mg/mL). The red solution was stirred at ambient conditions for 4 h, followed by precipitation with NH₄PF₆ to afford the desired compound, as a red powder, which was washed with copious amounts of MeOH.

**Zn Bowtie (10)** was prepared from the general procedure to afford 10, as a red powder: 16.8 mg (81%). ¹H NMR (500 MHz, B): δ 9.06 [s, 12H, 3′,5′-tpyH(Ru)], 9.03 [s, 12H, 3′,5′-tpyH(Zn)], 8.77 (d, 12H, J = 8.0 Hz, 3,3″-tpyH),
8.69 (d, 12H, \( J = 8.0 \) Hz, 3,3'-tpyH), 8.26-8.21 (m, 24H, ArH, 5,5'-tpyH), 8.16-8.08 (m, 24H, ArH, 5,5'-tpyH), 7.87 (d, 12H, \( J = 8.0 \) Hz, ArH), 7.82 (d, 12H, \( J = 8.0 \) Hz, 6,6'-tpyH), 7.46 (d, 12H, \( J = 4.5 \) Hz, 6,6'-tpyH), 7.38 (m, 20H, 5,5'-tpyH, 6,6'-tpyH, ArH), 7.17 (m, 12H, 5,5'-tpyH, ArH), 4.01 (s, 24H, CO\(_2\)Me), 3.34 (s (br), 4H, OCH\(_2\)R), 1.31 (m, 8H, C\(_\text{alkyl}\)H\(_2\)), 1.12-1.01 (m, 24H, C\(_\text{alkyl}\)H\(_2\)), 0.72 (t, 6H, \( J = 7.5 \) Hz, alkyl CH\(_3\)); \(^{13}\)C NMR (500 MHz, B): 173.3, 173.1, 158.2, 155.5, 152.4, 149.8, 148.0, 147.8, 141.2, 138.0, 131.1, 128.0, 127.7, 127.5, 124.8, 124.2, 68.4, 63.5, 32.3, 27.6, 24.8, 19.9, 18.0; ESI/MS: (m/z) 1589.6 \([M-4PF_6^-]^4+\) (calcd m/z = 1589.7), 1242.7 \([M-5PF_6^-]^5+\) (calcd m/z = 1242.8), 1011.4 \([M-6PF_6^-]^6+\) (calcd m/z = 1011.4), 846.2 \([M-7PF_6^-]^7+\) (calcd m/z = 846.2), 722.3 \([M-8PF_6^-]^8+\) (calcd m/z = 722.3), 626.0 \([M-9PF_6^-]^9+\) (calcd m/z = 626.0), 548.8 \([M-10PF_6^-]^{10+}\) (calcd m/z = 548.9), 485.7 \([M-11PF_6^-]^{11+}\) (calcd m/z = 485.7), 433.2 \([M-12PF_6^-]^{12+}\) (calcd m/z = 433.2).

**Cd Bowtie (11)** was prepared via the general procedure to afford 11, as a red powder: 17.1 mg (88%); \(^1\)H NMR (500 MHz, B): \( \delta \) 8.95 (s, 24H, 3',5'-tpyH), 8.64 (d, 24H, \( J = 8.0 \) Hz, 3,3''-tpyH), 8.16-8.03 [m, 120H, ArH, 5,5''-tpyH, 6,6''-tpyH (Cd)], 7.78 [d, 24H, \( J = 4.0 \) Hz, 6,6''-tpyH (Ru)], 7.67 (s, 8H, Ar'R), 7.47 (t, 24H, \( J = 7.0 \) Hz, 4,4''-tpyH), 4.00 (s, 24H, CO\(_2\)CH\(_3\)), 3.36 (s (br), 4H, OCH\(_2\)R), 1.32 (m, 8H, alkyl CH\(_2\)), 1.12 (m, 8H, alkyl CH\(_2\)), 0.92 (m, 16H, alkyl CH\(_2\)), 0.72 (t, 6H, \( J = 7.5 \) Hz, alkyl CH\(_3\)); \(^{13}\)C NMR (500 MHz, B): 173.2, 173.0, 158.2, 154.6, 153.3, 150.2, 148.2, 147.8, 140.8, 137.9, 131.2, 128.0, 127.2, 126.9, 68.2, 63.0, 32.8, 27.8, 24.4, 19.5, 18.0; ESI/MS: (m/z) 1638.8 \([M-4PF_6^-]^4+\) (calcd m/z = 1638.7), 1282.0 \([M-5PF_6^-]^5+\) (calcd m/z = 1282.0), 1044.2 \([M-6PF_6^-]^6+\) (calcd m/z = 1044.2).
$= 1044.1$, $874.3$ [M-7PF$_6^{-}$]$^{7+}$ (calcd $m/z = 874.4$), $748.9$ [M-8PF$_6^{-}$]$^{8+}$ (calcd $m/z = 748.9$).

**Zn Butterfly (12)** was prepared via the general procedure to afford 12, as a red powder; 16.3 mg (78%); $^1$H NMR (500MHz, B): $\delta$ 9.06-9.00 (m, 36H, 3′,5′-tpyH), 8.75 – 8.65 (m, 36H, 3,3″-tpyH), 8.30 – 7.70 (m, 72H, 5,5″-tpyH, ArH), 7.51 – 7.32 (m, 24H, 6,6″-tpyH), 7.22 – 7.09 (m, 20H, 5,5″-tpyH, ArH), 4.05 (s(br), 4H, OCH$_2$R), 4.01 (s, 24H, CO$_2$C$_3$), 1.31 (m, 8H, alkyl CH$_2$), 1.12-1.01 (m, 24H, alkyl CH$_2$), 0.72 (t, 6H, $J = 7.5$ Hz, alkyl CH$_3$); $^{13}$C NMR (500 MHz, B): 173.3, 173.1, 158.3, 155.7, 151.9, 149.5, 148.2, 147.9, 144.5, 143.2, 141.2, 138.7, 128.1, 127.7, 127.5, 121.9, 120.8, 67.4, 64.8, 33.1, 27.6, 24.8, 19.4, 18.4; ESI/MS: ($m/z$) 1589.6 [M-4PF$_6^{-}$]$^4+$ (calcd $m/z = 1589.7$), 1242.7 [M-5PF$_6^{-}$]$^5+$ (calcd $m/z = 1242.8$), 1011.4 [M-6PF$_6^{-}$]$^6+$ (calcd $m/z = 1011.4$), 846.2 [M-7PF$_6^{-}$]$^7+$ (calcd $m/z = 846.2$), 722.3 [M-8PF$_6^{-}$]$^8+$ (calcd $m/z = 722.3$), 626.0 [M-9PF$_6^{-}$]$^9+$ (calcd $m/z = 626.0$), 548.8 [M-10PF$_6^{-}$]$^{10+}$ (calcd $m/z = 548.9$), 485.7 [M-11PF$_6^{-}$]$^{11+}$ (calcd $m/z = 485.7$), 433.2 [M-12PF$_6^{-}$]$^{12+}$ (calcd $m/z = 433.2$).

**Cd Butterfly (13)** was prepared via the general procedure to afford 13, as a red powder: 16.7 mg (82%); $^1$H NMR (500 MHz, B): $\delta$ 9.06-8.94 (m, 36H, 3′,5′-tpyH), 8.34 – 8.65 (m, 36H, 3,3″-tpyH), 8.26 – 7.65 (m, 72H, 5,5″-tpyH), 7.51 – 7.32 (m, 24H, 6,6″-tpyH), 7.18 – 7.09 (m, 20H, 5,5″-tpyH, ArH), 4.07 (s(br), 4H, OCH$_3$R), 4.00 (s, 24H, CO$_2$C$_3$), 1.33 (m, 8H, alkyl CH$_2$), 1.12-1.01 (m, 24H, alkyl CH$_2$), 0.75 (t, 6H, $J = 7.5$ Hz, alkyl CH$_3$); $^{13}$C NMR (500 MHz, B): 173.2, 173.1, 158.4, 155.5, 154.8, 153.4, 151.6, 150.8, 148.6, 147.1, 140.2, 137.2, 131.9, 128.9, 127.5, 126.3, 68.0, 63.5, 32.9, 27.3, 24.1, 19.0, 18.8; ESI/MS: ($m/z$) 1638.8
[M-4PF$_6$]$^{4+}$ (calcd $m/z = 1638.7$), 1282.0 [M-5PF$_6$]$^{5+}$ (calcd $m/z = 1282.0$),
1044.2 [M-6PF$_6$]$^{6+}$ (calcd $m/z = 1044.1$), 874.3 [M-7PF$_6$]$^{7+}$ (calcd $m/z = 874.4$),
748.9 [M-8PF$_6$]$^{8+}$ (calcd $m/z = 748.9$).
CHAPTER III

STABLE, TRINUCLEAR Zn\textsuperscript{II}- AND Cd\textsuperscript{II}-METALLOCYCLES: TWIM-MS, PHOTOPHYSICAL PROPERTIES, AND NANOFIBER FORMATION

3.1 Introduction

Self-assembly of predesigned architectures has attracted much attention in recent years\textsuperscript{60,214-218}. Crystal engineering\textsuperscript{219-221} as practiced with non-covalent structural control, provides insight into the use of supramolecular synthons for the generation of highly ordered structures. With few exceptions, ionic interactions provide a superb pathway to ordered, stable assemblies, and networks. Whereas, complex polyionic interactions have played critical roles in the development of novel materials that include rotaxanes\textsuperscript{222} porphyrins\textsuperscript{223} and dendrimers\textsuperscript{224}; with one exception\textsuperscript{184} there has been limited reports in the area of nanofiber formation. Nanofibers prepared by traditional methods have found application in gene delivery\textsuperscript{225} photonics and electronics\textsuperscript{226} and offer new avenues to functional materials. We herein report the creation and characterization of nanoscale fibers, based on the polyionic-mediated assembly of metallomacrocycles, constructed from \textit{bis}(2,2′:6′,2″-terpyridinyl) ligands possessing a 60° orientation.
3.2 Results and Discussion

Three ligands (5-7; Scheme 3.1) possessing 60° directionality were synthesized by Suzuki coupling with known aryl halides 1-3 and 4-terpyridinylphenylboronic acid (4) by refluxing in 3:3:1 toluene:water:t-butanol mixture for 48 hours. The previously unreported ligands were readily purified by either column chromatography or simple recrystallization from the reaction mixture to give the bisteryridines in good yields. These ligands were identified by their characteristic $^1$H NMR spectra (Figure 3.1) as well as their ESI-MS (Figure 3.3A). When these ligands were mixed stoichiometrically with either Zn(BF$_4$)$_2$ or Cd(NO$_3$)$_2$ followed by precipitation with NH$_4$PF$_6$, a series of six triangular metallomacrocycles (8-13) was generated in 80 - 92% yield.
Scheme 3.1. Suzuki coupling of aryl halides 1-3 and their subsequent cyclizations to form 8-13, respectively.

The triangles exhibited $^1$H NMR spectra indicative of their equilateral symmetry that facilitates easy structure elucidation. Characteristic upfield shifts (Figure 3.1) for the terpyridinyl 6,6” protons from ~8.7 ppm for the free ligand to ~8.1 and ~7.8 ppm for the cadmium and zinc triangles, respectively, are indicative of $<M^{2+}>$ (where, $< =$ terpyridine) octahedral complex formation. The $^{13}$C-$^1$H and $^1$H-$^1$H COSY NMR spectra, shown in Figure 3.2 of the products are also consistent with the triangular structures.
Figure 3.1. Typical $^1$H NMR spectrum of a bisteryridine ligand and its corresponding Zn$^{II}$ and Cd$^{II}$ metallocycles.
Electrospray ionization mass spectrometry (ESI-MS) coupled with traveling-wave ion mobility-mass spectrometry (TWIM-MS), a variant of ion mobility mass spectrometry, were employed to aid in the characterization of these triangular architectures. A typical ESI-MS spectrum for the triangles is shown in Figure 3.3A, which exhibits the charges for the methoxy-substituted, Cd-based triangle ranging from $Z = +2$ to $+6$ as well as the theoretical and experimental isotope patterns for the $+4$ charge state. Analysis by ESI-TWIM-MS ensured that there were no superimposed isomers or conformers within the sample as corroborated by the single, regular step-like spectrum (Figure 3.3B) and only minor fragments at low drift times; hence, the
intact triangle was the primary species observed. Subsequently, the triangle stability for 10 was examined using gradient tandem mass spectrometry (gMS², Figure 3.3C) by analyzing the +4 charge state (m/z=722) and subjecting it to collisionally activated dissociation prior to ion mobility separation at collision
energies ranging from 6 to 32V. At an ion trap voltage 32V, the +4 complex completely disappears, corresponding to a center-of-mass collision energy ($E_{cm}$) of 0.45 eV.

All triangles 8-13 displayed similar spectra. In contrast, previous studies on +4 ions of hexacadmium macrocycles exhibited a $E_{cm}$ value of 0.19 eV. Notably, a MALDI MS was also obtained for the triangle 8 (Figure 3.4); this technique was typically useful for the characterization of the more stable bisterpyridine-Ru$^{2+}$ complexes. Terpyridine-based Cd$^{2+}$ and Zn$^{2+}$ complexes have been observed to be much weaker than the Ru$^{2+}$ counterparts resulting in inconclusive spectra. Note that for the first time, intact terpyridine-based supramolecular macrocycles with Cd$^{2+}$ were observed in MALDI. This suggests that the triangular rigid geometry could be playing an important role in self-assembly and stability in concert with that of the metal ion-terpyridine effects.
The UV-visible and photoluminescence (PL) spectra of the free ligands 5-7 and the corresponding Cd- and Zn-based triangles were recorded. A red shift is observed in the UV absorptions (Figure 3.5A) of the ligands 5-7 that is attributed to the increasing electron-donating capability of the peripheral groups (*i.e.*, H-, Me-, and MeO-) of the corner benzene rings. While, UV absorption in the metallocycles 8-13 shows little difference, due presumably to the $d_{10}$ metals inhibition of the MLCT bands. However, the PL spectra of the H- and Me-modified trigonal complexes 8, 9, 11, and 12 exhibit a significant bathochromic shift from 467 to 499 nm (Cd-based) and 474 to 510 nm (Zn-based), respectively. For both triangles 10 and 13 possessing a methoxy substituent, nearly complete quenching of the photoluminescence is observed.
Figure 3.5. UV-vis A) and photoluminescence B) spectra of the H-, methyl-, and methoxy-substituted bis-terpyridines 5-7 and triangles 8-13 were obtained using spectrophotometric grade DMF, along with a photograph C) of the luminescence properties of 11-13. Excitation wavelength was 285 nm for ligands was 315 nm for complexes. Data were collected at a concentration of 5.0x10\(^{-5}\) M for ligands and 5.0x10\(^{-6}\) M for complexes, respectively.

Attempts to investigate the utility of the macrocycles to self-assemble into ordered arrays resulted in the formation of composite nanofibers. Pairing the hexavalent positively charged metallotriangles with benzenehexacarboxylate afforded ion-paired nanofibers as observed by transmission electron microscopy. The linear, hair-like fibers were obtained using a mixed solvent system prepared from dilute solutions (~1 mM) of metallocycle in MeCN and sodium benzenehexacarboxylate in water. Fiber formation began at the solvent interface
24 hours after layering and was complete in 6 days, filtered, then washed with water and MeCN. The filtrate was analysed by $^1$H, $^{31}$P, and $^{19}$F NMR spectroscopies and revealed that no terpyridine resonances were present, but the presence of PF$_6^-$, consistent with counterion exchange. The fibers of 12 were slightly soluble in MeOH, and possessed signals from terpyridine cyclics; however, there was no phosphorus in the $^{31}$P-NMR spectrum (See Figure 3.6).

![NMR Spectra](image)

Figure 3.6. $^1$H, $^{19}$F, and $^{31}$P NMR data for filtrate from fiber growth of 12 with sodium benzenehexacarboxylate, confirming presence of PF$_6^-$.  

Fibers were drop cast onto carbon-coated copper TEM grids. Large bundled structures were observed (~300 nm in diameter, Figure 3.7), composed of smaller organized fibers with diameters of 20 nm closely corresponding to the triangular side length, as determined by molecular modeling. Selected area X-ray
diffraction (SAXD) of the Zn-based triangle 12 gave a \( d \)-spacing value of 0.589 nm, as seen in Figure 3.7. Notably, control experiments with sodium benzenehexacarboxylate and Cd(NO\(_3\))\(_2\) or Zn(OTf)\(_2\) gave no fiber growth under identical conditions.

Figure 3.7 TEM images of fibers formed from triangles 13 (left), and 12 (right) with benzenehexacarboxylate (inset: SAXD diffraction pattern from trimer 12).

Powder XRD (X-ray diffraction) data obtained from microcrystalline regions within the fibers supports the SAXD data and provide insight into the long range order in the fibers; orthorhombic unit cell dimensions of 39.82, 8.38, and 49.14 Å for \( a \), \( b \), and \( c \), respectively, were found. Based on these data, a packing model for the triangles in the fiber was derived from molecular modeling (Figure 3.8). The counterions have been omitted from this model, and further studies are on-going to determine the exact location of the benzenehexacarboxylate. A tabulated summary of the SAXD for the microcrystals (Table 3.1) gives all unit cell and theoretical data.
Table 3.1: Experimental Bragg angles ($\theta_e$) and distances ($d_e$), calculated Bragg angles ($\theta_c$) and distances ($d_c$), $hkl$ Miller Indices and 1D XRD maxima assigned in the patterns.

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Figure 3.8. Proposed packing model for triangle 12 in the fiber based on powder and selected area X-ray diffraction.

3.3 Conclusions

In conclusion, new bis-terpyridine ligands possessing a 60° interior angle with respect to the ligating moieties have been synthesized and their facile self-assembly with cadmium and zinc afforded high yields of the corresponding metallotriangles. TWIM-MS and gMS$^2$ show the triangular motif to be
unexpectedly stable and the PL properties can be engineered to generate good candidates for electronic applications, such as in LEDs. The potential to self-assemble offers avenues to higher ordered supramacromolecular materials.

3.4 Experimental

**General Procedures.** Chemicals were purchased from Fisher Scientific, Sigma/Aldrich, or VWR, confirmed by $^1$H and $^{13}$C NMR spectroscopies, and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al$_2$O$_3$ (IB-F) or SiO$_2$ (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al$_2$O$_3$, Brockman Activity I (60-325 mesh) or SiO$_2$ (60-200 mesh) from Sorbent Technologies. $^1$H and $^{13}$C NMR spectra were recorded on either a Varian Mercury 300 or Varian NMR 500 spectrometer using CD$_3$CN (A) for complexes and CDCl$_3$ (B) for ligands, and referenced to 1.94 and 7.27 ppm, respectively. Mass spectra were obtained on a Bruker Esquire electrospray ion trap mass spectrometer (ESI-MS). Traveling wave ion mobility-mass spectrometry (TWIM-MS) experiments were performed using a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer. The TWIM device is located between the Q and ToF mass analyzers and consists of three parts, a trap cell, an ion mobility (IM) cell, and a transfer cell. The trap and transfer cells can be used for conventional tandem MS experiments via collisionally activated dissociation (CAD). The ion mobility cell is used in IM separations. Generally, the following parameters were used in TWIM-MS experiments: ESI capillary voltage, 1.5 kV; sample cone voltage, 15 V; extraction cone voltage, 3.2 V;
desolvation gas flow, 800 L/h (N₂); trap collision energy (CE), 2 eV; transfer CE, 1 eV; trap gas flow, 1.5 mL/min (Ar); IM gas flow, 22.7 mL/min (N₂); sample flow rate, 10 μL/min; source temperature, 30 °C; desolvation temperature, 40 °C; IM traveling wave velocity, 350 m/s. The IM traveling wave heights were set at 7.5 V. In the tandem MS experiments, the trap CE was varied within 6-32 eV to cause fragmentation. The sprayed solution was prepared by dissolving ~1 mg of sample (1 mL) of MeCN/MeOH (3:2) solvent mixture. X-ray diffraction experiments were conducted on a Rigakua 18 kW rotating anode X-ray generator using Cu Ka radiation (0.1542 nm) in transmission mode visualized with an R-AXIS-IV image plate system, using an exposure time of 30 minutes. The peak positions were calibrated using silicon crystals, with background scattering subtracted from the sample pattern. Transmission electron microscopy (TEM, Philips Tecnai) was used to observe the crystal morphology under a bright field imaging mode at an accelerating voltage of 120 kV. The selected area electron diffraction was obtained under a diffraction mode by inserting and centering the selected area aperture. The d-spacing of electron diffraction spots were calibrated with thallous chloride diffraction standards. Molecular modeling and analysis of the diffraction patterns were performed using the Cerius2 package of Accelrys.

4′-(4-Boronatophenyl)-2,2′:6′,2″-terpyridine (4). (see Chapter 2)

**General Coupling Procedures:**

To a 3-necked round bottom flask, the initial aryl halide, 4′–(4-boronatophenyl)-2,2′:6′,2″-terpyridine (1.5 equiv. per halide), Na₂CO₃ (6 equiv.), and water:γ-butyl alcohol:toluene (3:1:3 v/v/v) were added. The system was
freeze-pump-thawed 3x and backfilled with argon or nitrogen, after which PdCl$_2$(PPh$_3$)$_2$ (6 mol% per halide) was added. The biphasic system was refluxed for 48 hours resulting in a red aqueous layer and a tan organic layer. The aqueous layer was extracted with CHCl$_3$ (3x100 mL), the resulting organic layers were combined, dried (MgSO$_4$), and concentrated in vacuo to give a dark residue, which was dissolved in a minimal volume of toluene, followed by precipitation from MeOH to give an off-white solid, which was column chromatographed (Al$_2$O$_3$) eluting with CHCl$_3$ to give pure title compound, as a colorless solid.

**o-Bis(4′-terpyridyl-p-phenyl)benzene (5)** was prepared using the general procedure: 1,2-Diodobenzene (I; 1.65 g, 5.0 mmol), 4′-(4-boronatophenyl)-2,2′:6′,2″-terpyridine (4.0 g, 11.3 mmol), Na$_2$CO$_3$ (730 mg, 60 mmol), water (180 mL), t-buty alcohol (60 mL), and toluene (180 mL), PdCl$_2$(PPh$_3$)$_2$ (660 mg, 1.72 mmol) to afford 5, as a colorless solid; 2.80 g (82 %); m.p. 257.3-258.5 °C; $^1$H NMR (300 MHz, B): δ 8.74 (s, 4H, 3′,5′-tpyH), 8.68 (d, 4H, $J = 3.9$ Hz, 6,6″-tpyH), 8.64 (d, 4H, $J = 7.8$ Hz, 3,3″-tpyH), 7.84 (m, 8H, 5,5″-tpyH, Ar′H), 7.51 (m, 4H, ArH), 7.33 (m, 8H, 4,4″-tpyH, Ar′H); $^{13}$C NMR (300 MHz, B): δ 118.76, 121.28, 123.72, 127.04, 127.85, 130.41, 130.72, 136.53, 136.78, 139.97, 142.24, 149.08, 149.72, 155.85, 156.26 ppm; ESI/MS 693.2 [M+H].

**3,4-Bis(4′-terpyridyl-p-phenyl)-o-xylene (6)** was prepared from the general procedure: 4,5-dibromo-1,2-dimethylbenzene (2: 1.30 g, 5.0 mmol), 4′-(4-boronatophenyl)-2,2′:6′,2″-terpyridine (4.2 g, 11.5 mmol), Na$_2$CO$_3$ (740 mg, 60 mmol), water (180 mL), t-buty alcohol (60 mL), and toluene (180 mL), PdCl$_2$(PPh$_3$)$_2$ (640 mg, 1.72 mmol) to give 6, as a colorless solid: 2.40 g (66%);
m.p. 236.0-237.1 °C; \(^1\)H NMR (300 MHz, B): δ 8.74 (s, 4H, 3′,5′-tpyH), 8.68 (d, 4H, \(J = 4.5\) Hz, 6,6"-tpyH), 8.64 (d, 4H, \(J = 8.1\) Hz, 3,3″-tpyH), 7.84 (m, 8H, 5,5″-tpyH, Ar′H), 7.51 (m, 4H, ArH), 7.33 (m, 8H, 4,4″-tpyH, Ar′H); \(^{13}\)C NMR (300 MHz, B): δ 156.28, 155.83, 149.79, 149.08, 142.30, 137.42, 136.76, 136.33, 136.27, 131.99, 130.42, 126.98, 123.70, 121.28, 118.74, 19.52 ppm; ESI/MS 721.3 [M+H].

**3,4-Bis(4′-terpyridyl-p-phenyl)-o-dimethoxybenzene (7)** was prepared from the method described in Chapter II.

**General Procedure for Cyclization:**

In a round bottom flask, a stirred mixture of (5-7) (1.00 eq), and M\(^{12}\) (1.00 eq) was dissolved in DMF (80 mL), and maintained at 25°C for 24 h, after which excess NH\(_4\)PF\(_6\) was added to the clear solution. After 3 hours, MeOH was added to give an off-white precipitate that was filtered affording the desired molecular triangle.

[(5)\(_3\)Cd\(_{3}^{+}\)][6PF\(_6\)\(^{−}\)] (8) was prepared from the general procedure using 5 (100 mg, 144 μmol), Cd(NO\(_3\))\(_2\) · 4H\(_2\)O (44.6 mg, 144 μmol) in DMF (80 mL): 131 mg (82%); m.p. >300°C; \(^1\)H NMR (300 MHz, A): δ 8.95 (s, 12H, 3′,5′-tpyH), 8.76 (d, 12H, \(J = 7.8\) Hz, 3,3″-tpyH), 8.16-8.08 (m, 36H, 5,5″-tpyH, 6,6″-tpyH, Ar′H), 7.75-7.62 (m, 24H, ArH, Ar′H), 7.46 (t, 12H, \(J = 6.1\) Hz, 4,4″-tpyH); \(^{13}\)C NMR (300 MHz, A): δ 154.66, 150.25, 149.67, 148.76, 144.19, 141.24, 139.46, 134.62, 131.14, 130.89, 128.65, 127.74, 127.32, 123.71, 121.71 ppm; ESI/MS:
m/z = 1497.7 [M-2PF₆⁻]⁺², 950.16 [M-3PF₆⁻]⁺³, 676.3 [M-4PF₆⁻]⁺⁴, 512.10 [M-5PF₆⁻]⁺⁵.

[(6)₃Cd₃⁺⁶][6PF₆⁻] (9) was prepared from the general procedure using 6 (109 mg, 146 μmol), Cd(NO₃)₂·4H₂O (44.9 mg, 146 μmol) in DMF (80 mL): 146 mg (91%); m.p. > 300°C; ¹H NMR (500 MHz, A): δ 8.94 (s, 12H, 3′,5′-tpyH), 8.75 (d, 12H, J = 7.8 Hz, 3,3″-tpyH), 8.16-8.10 (m, 36H, 5,5″-tpyH, 6,6″-tpyH, Ar′H), 7.63 (d, 12H, J = 7.8 Hz, Ar′H), 7.46 (t, 12H, J = 3.9 Hz, 4,4″-tpyH), 7.22 (s, 2H, ArH), 2.56(s, 18H, C₃H₈); ¹³C NMR (500MHz, A): δ 18.57, 121.62, 123.70, 127.28, 131.10, 134.31, 136.85, 137.28, 141.21, 144.32, 144.46, 148.71, 148.86, 150.32, 154.74 ppm; ESI/MS: m/z = 1541.0 [M-2PF₆⁻]⁺² (calc. m/z = 1547.1), 979.0 [M-3PF₆⁻]⁺³ (calc. m/z = 979.1), 697.7 [M-4PF₆⁻]⁺⁴ (calc. m/z = 697.8), 529.0 [M-5PF₆⁻]⁺⁵ (calc. m/z = 529.0), 416.7 [M-6PF₆⁻]⁺⁶ (calc. m/z = 416.7).

[(7)₃Cd₃⁺⁶][6PF₆⁻] (10) was prepared from the general procedure using 7 (109 mg, 146 μmol), Cd(NO₃)₂·4H₂O (44.9 mg, 146 μmol) in DMF (80 mL): 137 mg (84%); m.p. = >300 °C; ¹H NMR (500 MHz, A): δ 8.94 (s, 12H, 3′,5′-tpyH), 8.75 (d, 12H, J = 7.8 Hz, 3,3″-tpyH), 8.16-8.10 (m, 36H, 5,5″-tpyH, 6,6″-tpyH, Ar′H), 7.63 (d, 12H, J = 7.8 Hz, Ar′H), 7.46 (t, 12H, J = 3.9 Hz, 4,4″-tpyH), 7.22 (s, 2H, ArH); ¹³C NMR (500MHz, A): δ 56.84, 115.32, 122.66, 124.76, 128.35, 128.70, 132.32, 132.94, 135.30, 142.27, 145.30, 149.85, 150.35, 150.69, 151.31, 155.78 ppm; ESI/MS: m/z = 1588.5 [M-2PF₆⁻]⁺² (calc. m/z = 1588.5), 1010.3 [M-3PF₆⁻]⁺³ (calc. m/z = 1010.3), 721.5 [M-4PF₆⁻]⁺⁴ (calc. m/z = 721.5), 548.2 [M-5PF₆⁻]⁺⁵ (calc. m/z = 548.2), 432.7 [M-6PF₆⁻]⁺⁶ (calc. m/z = 432.6).
[(5)$_3$Zn$_3$]$^+6$][6PF$_6^-$(11)] was prepared from the general procedure using 5 (150 mg, 216 μmol), Zn(BF$_4$)$_2$·8H$_2$O (64.1 mg, 216 μmol) in DMF (80 mL): 170 mg (75%); m.p. >300 °C; $^1$H NMR (500 MHz, A): δ 8.99 (s, 12H, 3′,5′-tpyH), 8.73 (d, 12H, $J = 7.8$ Hz, 3,3″-tpyH), 8.16 (d, 12H, $J = 8.4$ Hz, Ar′H), 8.09 (t, 12H, $J = 3.9$ Hz, 5,5′-tpyH), 7.85 (d, 12H, $J = 2.7$ Hz, 6,6″-tpyH) 7.75-7.69 (m, 12H, ArH), 7.65 (d, 12H, $J = 8.4$ Hz, Ar′H), 7.38 (t, 12H, $J = 4.5$ Hz, 4,4″-tpyH); $^{13}$C NMR (500MHz, A): δ 121.54, 121.72, 123.34, 123.57, 127.54, 127.91, 128.09, 131.29, 131.51, 134.82, 139.69, 141.44, 144.53, 148.09, 150.01, 155.96 ppm; ESI/MS: m/z = 1426.8 [M-2PF$_6^-$(calc. m/z = 1426.7), 903.2 [M-3PF$_6^-$(calc. m/z = 903.3), 641.2 [M-4PF$_6^-$(calc. m/z = 641.2), 484.0 [M-5PF$_6^-$(calc. m/z = 484.1), 479.1 [M-6PF$_6^-$(calc. m/z = 479.1).

[(6)$_3$Zn$_3$]$^+6$][6PF$_6^-$(12)] was prepared from the general procedure using 6 (150 mg, 208 μmol), Zn(BF$_4$)$_2$·8H$_2$O (61.78 mg, 208 μmol) in DMF (80 mL): 178 mg (80%); m.p. >300 °C; $^1$H NMR (500 MHz, A): δ 8.95 (s, 12H, 3′,5′-tpyH), 8.77 (d, 12H, $J = 7.8$ Hz, 3,3″-tpyH), 8.13 (d, 12H, $J = 7.8$ Hz, Ar′H), 8.07 (t, 24H, $J = 4.8$ Hz, 5,5′-tpyH), 7.82 (d, 24H, $J = 3.0$ Hz, 6,6″-tpyH) 7.59 (d, 12H, $J = 7.8$ Hz, Ar′H), 7.49 (s, 6H, ArH), 7.35 (t, 24H, $J = 4.2$ Hz, 4,4″-tpyH), 2.60 (s, 18H, Ar-CH$_3$); $^{13}$C NMR (500 MHz, A): 18.6, 121.3, 123.2, 127.5, 127.7, 131.2, 131.9, 134.3, 136.9, 137.4, 141.2, 144.5, 147.9, 148.0, 149.8, 155.8 ppm; ESI/MS: m/z = 1469.5 [M-2PF$_6^-$(calc. m/z = 1469.4), 931.3 [M-3PF$_6^-$(calc. m/z = 931.3), 662.0 [M-4PF$_6^-$(calc. m/z = 661.9), 500.4 [M-5PF$_6^-$(calc. m/z = 500.4), 393.3 [M-6PF$_6^-$(calc. m/z = 393.3).
[(7)$_3$Zn$_{3+6}$] [6PF$_6$]$^-$ (13) was prepared from the general procedure using 7 (150 mg, 199 μmol), Zn(BF$_4$)$_2$·8H$_2$O (59.1 mg, 199 μmol) in DMF (80 mL): 171 mg (79%); m.p. >300 °C; $^1$H NMR (500 MHz, A): δ 8.99 (s, 12H, 3′,5′-tpyH), 8.73 (d, 12H, $J = 8.0$ Hz, 3,3″-tpyH), 8.14 (d, 12H, $J = 8.5$ Hz, Ar'H), 8.10 (t, 12H, $J = 8.0$ Hz, 5,5″-tpyH), 7.85 (d, 12H, $J = 5.0$ Hz, 6,6″-tpyH), 7.64 (d, 12H, $J = 8.5$ Hz, Ar'H), 7.38 (t, 12H, $J = 5.5$ Hz, 4,4″-tpyH), 7.26 (s, 6H, ArH), 4.04 (s, 18H, OCH$_3$); $^{13}$C NMR (500 MHz, A): δ 55.8, 114.2, 121.3, 123.4, 127.5, 127.7, 131.3, 131.9, 134.2, 141.2, 144.4, 147.9, 148.0, 149.4, 149.8, 155.8 ppm; ESI/MS: m/z = 1517.0 [M-2PF$_6$]$^{+2}$ (calc. m/z = 1517.1), 963.0 [M-3PF$_6$]$^{+3}$ (calc. m/z = 963.1), 686.1 [M-4PF$_6$]$^{+4}$ (calc. m/z = 686.0), 519.8 [M-5PF$_6$]$^{+5}$ (calc. m/z = 519.8), 409.1 [M-6PF$_6$]$^{+6}$ (calc. m/z = 409.1).

**Nanofiber formation:** An aqueous solution of sodium benzenehexacarboxylate (4.7 mg, 1 μmol) was layered with an MeCN solution metalloctriangle (1 mmol, 5mL) via syringe delivery. Within 6 hours, fibers began to form at the interface. The mixture was allowed to set undisturbed for 2 weeks. The fibers were filtered and washed with MeCN and water. They were insoluble in most common organic solvents. TEM grids were prepared by dropcasting the fiber solution directly onto carbon-coated copper grids. While the three zinc triangles 11-13 formed large quantities of fibers, the cadmium triangles formed mostly powder, but after 3 weeks of sitting, a few small fibers began to form.
CHAPTER IV

DONORFF RINGS: SYNTHESIS, ISOLATION, AND PROPERTIES OF 60°-
DIRECTED BISTERPYRIDINE-BASED FOLDED TETRAMERS

4.1 Introduction

Over the past decades, extensive work in the field of self-assembly has led to isolation of many interesting as well as complex structures.\textsuperscript{46,60,230,231} These intricate ensembles have revolutionized the field of supramolecular chemistry. The work of Lehn,\textsuperscript{190,232} Stoddart,\textsuperscript{233,234} Schmittel,\textsuperscript{37,164,195} and others\textsuperscript{79,187,235-243} continues to introduce increased complexity into multi-component systems; however, most self-assembled techniques rely on the target compound possessing the most thermodynamic stability leading to the predesigned structure. Less stable products must be synthesized by kinetic control, utilizing structural factors such as steric or ionic effects to achieve the desired macromolecular targets.

The equilibrium between such structures has been a topic of discussion for several years. For example, the Pd\textsuperscript{II}- and Pt\textsuperscript{II}-based equilibrium from triangle to tetramer has been extensively studied by Stang and others.\textsuperscript{86,88,244,245} These compounds exist as a thermodynamic equilibrium with the square being the enthalpically favored structure. Newkome and Wesdemiotis et al.\textsuperscript{228} also reported the presence of larger, unexpected rings when a labile $<$tpy-Zn\textsuperscript{II}-tpy$>$ (tpy =

\begin{equation}
\end{equation}
terpyridine) connectivity was combined with a 120°-oriented ligand. Another technique leading to the synthesis of desired, yet unfavored, metalloycles is to remove the potential for the formation of the enthalpically favored structure. Structures possessing \(<\text{tpy-Ru}^{\text{II}}\text{-tpy}>\) connectivity are very robust complexes,\(^{166,246}\) being strong enough to prohibit scrambling of ligands to achieve maximum enthalpic gain. We have recently reported the formation of large polygons isolated from a kinetic process utilizing \(<\text{tpy-Ru}^{\text{II}}\text{-tpy}>\) connectivity in their construction.\(^{50,187}\)

This chapter reports the utilization of a 60°-directed bisligand and its transformation to a corresponding Ru\(^{\text{II}}\)-based dimer, which was used for the self-assembly of novel \(\text{hetero-}\) and \(\text{homo-metallo}\) tetramers possessing folded shapes that resemble manta rays of the family Mobulidae, specifically of genus \(\text{Manta}\). These Dondorff-shaped tetramers, aptly named after the first to describe the manta ray,\(^{247}\) were characterized by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy as well as electrospray ionization traveling wave ion mobility mass spectrometry (ESI TWIM-MS);\(^{162,186,196}\) their photophysical and electrochemical properties were also studied.

4.2 Results and Discussion

\(\text{Bisterpyridine ligand 2}\) was synthesized by a Suzuki coupling\(^{227}\) of commercially available 4,5-dibromoveratrole and readily accessible 4′-boronatophenyl-2,2′:6′,2″-terpyridine \(\text{1}\) \textit{via} the Kröhnke synthesis\(^{248}\) and has been published elsewhere.\(^{54}\)
Scheme 4.1. Synthesis of the folded squares 4 – 8. Reagents and conditions: i) \( \text{H}_2\text{O} : \text{toluene} : \text{-BuOH} (3:3:1 \text{ v/v/v}), \text{Na}_2\text{CO}_3 (15 \text{ eq.}), \Delta, 48 \text{ h}; \) ii) 1.05 eq. \( \text{FeCl}_2\cdot \text{H}_2\text{O}, \text{MeOH}, \Delta, 12\text{h}; \) iii) 0.5eq. \( \text{RuCl}_2(\text{DMSO})_4, \text{MeOH} : \text{CHCl}_3 (1:1 \text{ v/v}), \Delta, 12 \text{ h}; \) iv) \( \text{M}^{2+}, \text{CHCl}_3 : \text{MeOH} (1:1 \text{ v/v}), \Delta \text{ or RT, 12-24 h}. \) Counterions have been omitted for clarity.

Ligand 2 was dimerized by a stoichiometrically controlled reaction with \( \text{RuCl}_2(\text{DMSO})_4 \) in \( \text{CHCl}_3 : \text{MeOH} (1:1 \text{ v/v}) \) for 24 h to afford (28%) the target dimer 3 (Scheme 4.1). Along with consistent MALDI-MS data for the \([\text{M-NO}_3^-]\) m/z value of 1668.0, the \(^1\text{H NMR spectrum provided readily assignable resonances (Figure 4.1). The dimer 3 possesses two distinct 3',5' resonances at}}
9.01 and 8.74 ppm, respectively, as well as two –OCH\textsubscript{3} resonances at 4.02 and 3.99 ppm both with the desired integration ratio of 1:1.

![Figure 4.1. \textsuperscript{1}H NMR spectrum of dimer 3 and peak assignments in CD\textsubscript{3}CN, where the free terpyridine resonances are italicized.](image)

Dimer 3 (Scheme 4.1) was readily cyclized with Cd\textsuperscript{II}, Zn\textsuperscript{II}, Fe\textsuperscript{II}, and Ru\textsuperscript{II} to give the corresponding tetramers. Purification in the cases of Cd\textsuperscript{II} and Zn\textsuperscript{II} consisted of simple counterion exchange with NH\textsubscript{4}PF\textsubscript{6} to afford the target tetramers 4 and 5, respectively, in good yields. Using Fe\textsuperscript{II} and Ru\textsuperscript{II}, the respective tetramers 6 and 7 were purified \textit{via} column chromatography in moderate yields. Following a one-pot reaction of \textit{bisterpyridine} 2 with FeCl\textsubscript{2}·4H\textsubscript{2}O, the Fe\textsuperscript{II} tetramer 8 was isolated as a minor product (8%), and the expected trimer was isolated as the predominant product (29%) after chromatography.
Figure 4.2. Stacked $^1$H NMR spectra of 4 – 8, where Cd$^{II}$ = yellow, Zn$^{II}$ = green, Fe$^{II}$ = purple, and Ru$^{II}$ = red, respectively, measured in CD$_3$CN.

<table>
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<tr>
<th>Compound</th>
<th>M$^{+2}$</th>
<th>3′,5′</th>
<th>3,3″</th>
<th>Ar′H</th>
<th>4,4″</th>
<th>ArH</th>
<th>6,6″</th>
<th>5,5″</th>
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Table 4.1. $^1$H NMR shift summary (in ppm) for 4 – 8. All spectral data were acquired in CD$_3$CN on a 500 MHz NMR spectrometer.
The $^1$H NMR spectra for metallocycles 4 – 6 (Figure 4.2), where the color denotes the respective metals, display two resonances for each assignable proton, all integrating 1:1; whereas, the spectra for 7 and 8 exhibit only a single set of resonances due to increased symmetry inherent in identical \textit{<tpy-M}^{II}-tpy\textit{>} connectivity. A summary of the assigned peaks can be found in Table 1. A general trend in the spectra is a progressive upfield shifts for the 6,6$''$ protons from 8.2 to 7.9 to 7.5 to 7.2 ppm as the metal changes from Cd$^{II}$ to Zn$^{II}$ to Ru$^{II}$ to Fe$^{II}$, respectively. As expected, there is no significant change in the ruthenium complex resonances throughout the series.

Preliminary molecular modeling (see Experimental Section 4.4 for parameters) of the Dondorff rings provided insight into their structural configuration. Figure 3A illustrates a slightly folded structure of 4, wherein the folding alleviates the strain placed on the 60$^\circ$ angles of the \textit{bisterpyridinyl} substituents in a flattened conformation. Figure 3B depicts the lowest energy conformer that is optimally folded; Figure 3C shows a high energy flattened stick model of 4. Ample space within the ring (~9.0 Å) suggests a host-guest potential.

The cyclic tetramers 4 – 8 were further characterized \textit{via} ESI-MS coupled with TWIM mass spectrometry. A typical ESI-MS spectrum is shown in Figure 4A for tetramer 7. All charges from +3 to +8 are readily identified by their isotope patterns, as shown for the +4 state in the inset. TWIM-MS (Figure 4B) confirmed the presence of a single species by a typical step-like spectrum with minor peaks at low m/z range, which correlate to fragments of the tetramer. In addition, gradient tandem MS (gMS$^2$, Figure 4C) spectra for tetramer 7, whereby
the +4 state ion was exposed to collisional-activated dissociation at increasing collision energy,\textsuperscript{211} revealed good stability at energies up to 55 eV.

Figure 4.3. Computer simulated images of tetramer 4: A) Side view with the solvent-accessible surface area as blue shell; B) Lowest energy conformer of tetramer 4; and C) Stick model of the flattened, higher energy tetramer 4.
Figure 4.4. A) Conventional 1D ESI-MS spectrum for tetramer 7 with an enlargement of the 4+ isotope pattern; B) 2D TWIM-MS plot for 7, consistent with a single species; and C) strength comparison for 7 via gMS² with collision energies ranging from 6 to 60 eV (set by varying the trap cell bias from 6 to 60 V).
At a trap voltage of 60V, the +4 charge state almost disappeared, corresponding to a center-of-mass (COM) collision energy of 2.31 eV. The remaining tetramers in the +4 charge states were also studied by gMS\(^2\) resulting in COM values of 1.53, 1.64, 1.77, and 1.67 for 4, 5, 6, and 8, respectively, where these values provide structural stability information for these particular charge states, with the stabilities of 4 and 5 being approximately the same, followed by 6 and 8, and lastly 7. This result indicates the stability order of \(<\text{tpy-M}^\text{II}-\text{tpy}>\) as \(\text{Cd}^\text{II} < \text{Zn}^\text{II} < \text{Fe}^\text{II} < \text{Ru}^\text{II}\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\lambda_{\text{abs}} (\varepsilon \times 10^{-3} \text{ M}^{-1}\text{cm}^{-1}))</th>
<th>(\lambda_{\text{em}}(\text{nm})^{[b]})</th>
<th>(\tau (\text{ns})^{[c]})</th>
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<td>286 nm (223), 311 nm (187), 494 nm (57.6)</td>
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<tr>
<td>5</td>
<td>286 nm (238), 311 nm (194), 494 nm (62.5)</td>
<td>663</td>
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<tr>
<td>6</td>
<td>286 nm (310), 311 nm (268), 494 nm (98.4), 571 nm (63.7)</td>
<td>[d]</td>
<td>[d]</td>
</tr>
<tr>
<td>7</td>
<td>286 nm (318), 311 nm (330), 494 nm (155)</td>
<td>674</td>
<td>1.7</td>
</tr>
<tr>
<td>8</td>
<td>286 nm (305), 311 nm (311), 571 nm (76.2)</td>
<td>[d]</td>
<td>[d]</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Measured in degassed MeCN; \(^{[b]}\) Corrected emission maxima after 488 nm excitation; \(^{[c]}\) Error in lifetime measurements ±10%; and \(^{[d]}\) No detectable emission.

Table 4.2. Photophysical Properties of Complexes 3 - 8\(^{[a]}\).

The UV-vis absorption spectra of 2 – 8 in MeCN are presented in Figure 4.5A. Ligand 2 exhibits the typical \(\pi \rightarrow \pi^*\) bands at 285 and 330 nm localized on the tpy-Ph subunits. Upon complexation with Ru\(^\text{II}\) in the case of dimer 3, a new metal-to-ligand charge transfer (MLCT) band forms at 483 nm. The spectra for tetramers 4, 5, and 7 are all similar in nature due to their structural resemblance, but differ substantially in oscillator strength depending on the number of CT
active metal centers (Ru$^{\text{II}}$ and Fe$^{\text{II}}$). Tetramer 6, however, possesses a second MLCT band at 575 nm, arising from the characteristic Fe$^{\text{II}}$-tpy absorption band; whereas, 8 only possesses the band at 575 nm. Table 4.2 summarizes all absorption and photoluminescence data obtained for 3 – 8. Photoluminescence spectra of tetramers 3 – 5 and 7 when using 488 nm laser excitation were all nearly identical; however, 6 and 8 display no detectable photoluminescence, as would be expected in the case of Fe$^{\text{II}}$ MLCT complexes (Figure 4.5B).

Figure 4.5. A) Normalized UV-visible absorption spectra of 3 – 8 in MeCN; B) Corrected emission spectra of 3 – 7 using Ar$^+$ ion laser excitation (488 nm, ~100 mW). The constant intensity Raman band of the MeCN solvent, located at 570 nm in these experiments, was used to normalize the emission spectra.

Due to the low photoluminescence intensity of these complexes (on the order of the Raman scattering of the solvent), it was necessary to use a laser excitation source, rather than the more traditional lamp, to obtain well-resolved
emission spectra. Based on the inherently low quantum efficiencies associated with Ru-tpy complexes, attempts to measure photoluminescence quantum yields were unsuccessful. Notably, the associated excited-state lifetimes of the luminescent molecules as determined by time-correlated single photon counting (TCSPC) measurements were all between 1 - 2 ns (Table 2).

4.3 Conclusion

In conclusion, five metallomacrocyclic tetramers have been synthesized employing a novel bisterpyridinyl ligand. Access to these tetragons possessing unique folded architecture is facilitated by (1) the properties inherent in the building blocks that include 60°-juxtaposed coordination sites, linear <tpy-metal-tpy> connectivity and the ability to form complexes with different metal ions, and (2) the strong <tpy-RuII-tpy> coordination that circumvents triangular macrocycle formation. Characterization by NMR spectroscopy, MS, UV-vis spectroscopy, photoluminescence spectroscopy, and computer simulation confirm the structures and suggest a highly stable motif.

4.4 Experimental Section

**General Procedures.** Chemicals were purchased from Fisher Scientific, Sigma-Aldrich or VWR, confirmed by 1H and 13C NMR, and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al2O3 (IB-F) or SiO2 (IB2-F) and visualized by UV light where necessary. Column chromatography was conducted using basic Al2O3, Brockman Activity I (60-325 mesh) or SiO2 (60-200 mesh) from Sorbent Technologies. 1H and 13C NMR spectra were recorded on either a Varian
Mercury 300 or Varian 500 NMR spectrometer using either (A) CD$_3$CN or (B) CDCl$_3$, as a solvent for complexes and ligands, and referenced to 1.94 and 7.27 ppm, respectively. Mass spectra (MS) were obtained on a Bruker HCT electrospray ion trap mass spectrometer (ESI-MS). Traveling wave ion mobility mass spectrometry (TWIM-MS) experiments were performed using a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer. The TWIM device, located between the Q and ToF mass analyzers, consists of trap, ion mobility (IM), and transfer cells. The trap and transfer cells can be used for conventional tandem MS experiments via collisionally activated dissociation (CAD). The ion mobility cell is used in IM separations. Generally, the following parameters were used in TWIM-MS experiments: ESI capillary voltage, 1.5 kV; sample cone voltage, 15 V; extraction cone voltage, 3.2 V; desolvation gas flow, 800 L/h (N$_2$); trap collision energy (CE), 2 eV; transfer CE, 1 eV; trap gas flow, 1.5 mL/min (Ar); IM gas flow, 22.7 mL/min (N$_2$); sample flow rate, 10 μL/min; source temperature, 30 °C; desolvation temperature, 40 °C; and the IM traveling wave velocity, 350 m/s. The IM traveling wave heights were set at 7.5 V. In the gradient tandem MS (gMS$^2$) experiments, CAD was performed in the trap cell at collision energies varied within 6-60 eV. The sprayed solution was prepared by dissolving the sample (1 mg/1 mL) in a MeCN/MeOH (3:2) solvent mixture. Computer simulation obtained using the Forcite Plus module in Materials Studio version 4.2 from Accelrys Software, Incorporated. Forcite Anneal Dynamics were applied using the Accelrys Universal Forcefield and Group-based summations; parameters: annealing cycles = 5, initial and mid-cycle temperatures
were 300 to 500 K, respectively, heating ramps per cycle = 5, dynamics steps per ramp = 500, total number of steps = 2500, using the NVE ensemble with random initial velocities and a time step of 1.0 fs. Geometry optimization was used after each of the Anneal dynamics steps. Geometry optimization parameters: The Smart optimization algorithm was used with convergent tolerances set to $1.0 \times 10^{-4}$ kcal/mol for energy, $5 \times 10^{-3}$ kcal/mol/Å for force, and $5 \times 10^{-5}$ Å for displacement. Maximum iterations = 5000 for each geometry optimization step. All spectra were collected in spectrophotometric grade MeCN in 1 cm$^2$ quartz anaerobic cells. Samples for photoluminescence and lifetime measurements were degassed with argon for 30 minutes. Absorption spectra were measured with a Cary 50 Biospectrophotometer accurate to ±2 nm. Corrected photoluminescence spectra were recorded on a PTI Instruments spectrofluorimeter (QM-4/2006-SE) equipped with a R928 PMT detector. The 488 nm line of an Ar$^+$ laser (Coherent, Innova 300) was isolated using a bandpass filter and used as the excitation source. The laser power for all measurements was 100 mW, as measured by Nova II/PD300-UV power meter/detector head from Ophir. Time resolved emission experiments were accomplished using a time correlated single photon counting (TCSPC) spectrometer (Edinburgh Instruments, LifeSpec II), which has been described previously.$^1$ An excitation wavelength of 470 nm was used. The resulting kinetic traces were fit with a single exponential decay in IGOR Pro to determine the lifetimes.

**4′-(4-Boronatophenyl)-2,2′:6′,2″-terpyridine (1).** See Chapter II.
3,4-Bis(4′-terpyridyl-p-phenyl)-o-dimethoxybenzene (2). See Chapter III.

\[(3)_2\text{Ru}^{2+} (\text{NO}_3^-)_2 (3)\]. To a single necked 1L round bottom flask was added 3 (750 mg, 1.00 mmol), RuCl\(_2\)(DMSO)\(_4\) (162 mg, 333 µmol), and 1:1 CHCl\(_3\) : MeOH (700 mL). After refluxing for 48 h, the reaction mixture was concentrated in vacuo to give a red powder that was column chromatographed (Al\(_2\)O\(_3\)) eluting with CHCl\(_3\) then to a solvent mixture [(1:1:25) H\(_2\)O:sat. KNO\(_3\):MeCN] to remove the uncomplexed 3 then to afford 4, as a red powder: 148 mg (26%); m.p. > 300 °C; \(^1\)H NMR (300 MHz, 1:1 CD\(_3\)OD:CDCl\(_3\)): δ 9.01 (s, 4H, complexed 3′,5′-tpyH), 8.74 (s, 4H, free 3′,5′-tpyH), 8.67 (m, 12H, free and complexed 3,3″-tpyH, free 6,6″-tpyH), 8.14 (d, 4H, J = 7.8 Hz, Ar′H), 7.92 – 7.82 (m, 8H, 4,4″-tpyH), 7.56 (d, 4H, J = 7.8 Hz, Ar′H), 7.49 – 7.35 (m, 20H, 5,5″-tpyH, 6,6″-tpyH, Ar′H), 7.17 – 7.10 (m, 8H, 4,4″-tpyH, ArH), 4.02 (s, 6H, OCH\(_3\)), 3.99 (s, 6H, OCH\(_3\)); \(^13\)C NMR (300 MHz, 1:1 CD\(_3\)OD:CDCl\(_3\)): 173.4, 157.8, 155.9, 155.0, 151.7, 149.5, 149.0, 148.7, 148.6, 148.5, 143.9, 142.3, 138.3, 137.1, 136.1, 166.9, 132.4, 131.9, 131.3, 130.6, 127.9, 127.5, 126.9, 125.1, 124.0, 121.4, 118.4, 116.6, 113.7, 56.2, 56.1; MALDI-MS: \(m/z = 1668.01\) [M-\text{INO}_3^-]\. Also isolated were longer chain oligomers accounting for an additional 40% of the overall yield.

**General Cyclization Procedure:** In a round bottom flask, a mixture of 3 (1.00 eq) and M\(^{2+}\) (1.00 eq) was dissolved in MeOH (80 mL), and maintained at 25 °C or refluxed, as specified, for 12 h with stirring. The reaction was
subsequently concentrated \textit{in vacuo} and the product purified by column chromatography (SiO$_2$) eluting with H$_2$O:sat. KNO$_3$:MeCN (1:1:16 v/v/v), where necessary, to afford the desired molecular tetramer. Following counterion exchange with NH$_4$PF$_6$, filtering, and washing with copious amounts of MeOH, the MeCN soluble product was obtained.

$[(3)_2\text{Cd}_2^{+8}](\text{PF}_6^-)_8$ (4) was prepared using the general procedure with 3 (9.7 mg, 6 µmol), Cd(NO$_3$)$_2 \cdot 4\text{H}_2\text{O}$ (1.7 mg, 6 µmol) at 25 °C. Pure 4 was obtained with simple ion exchange and no column chromatography as a red powder: 10 mg (73%); m.p. > 300 °C; $^1$H NMR (500 MHz, A): $\delta$ 9.02 (s, 8H, Ru 3′,5′-tpyH), 8.95 (s, 8H, Cd 3′,5′-tpyH), 8.76 (d, 8H, $J = 7.8$ Hz, Ru 3,3″-tpyH), 8.64 (d, 8H, $J = 7.8$ Hz, Cd 3,3″-tpyH), 8.16 (m, 32H, Cd and Ru Ar′H, Ru 4,4″-tpyH, Cd 6,6″-tpyH), 7.93 (dd, 8H, $J = 7.8$ Hz, 6.9 Hz, Cd 4,4″-tpyH), 7.66 (d, 16H, Ru and Cd Ar′H), 7.43 (m, 16H, 6,6″-Ru tpy, Ru 5,5″-tpyH), 7.21 (s, 8H, Cd and Ru ArH), 7.14 (dd, 8H, $J = 6.9$ Hz, 5.7 Hz, Cd 5,5″-tpyH), 4.02 (s, 12H, OCH$_3$), 4.01 (s, 12H, OCH$_3$); $^{13}$C NMR (500 MHz, A): $\delta$ 55.8, 121.3, 121.5, 123.8, 124.5, 127.3, 127.4, 127.5, 127.6, 131.3, 131.9, 132.0, 134.8, 138.1, 141.2, 143.7, 144.5, 147.6, 148.8, 149.6, 150.3, 152.4, 155.4, 158.2; ESI-MS: m/z 1387.9 [M-3PF$_6^-$]$^{3+}$ (calcd m/z = 1388.0), 1004.6 [M-4PF$_6^-$]$^{4+}$ (calcd m/z = 1004.7), 774.7 [M-5PF$_6^-$]$^{5+}$ (calcd m/z = 774.8), 621.4 [M-6PF$_6^-$]$^{6+}$ (calcd m/z = 621.5), 511.8 [M-7PF$_6^-$]$^{7+}$ (calcd m/z = 511.9), 430.1 [M-8PF$_6^-$]$^{8+}$ (calcd m/z = 430.0).

$[(3)_2\text{Zn}_2^{+8}](\text{PF}_6^-)_8$ (5) was prepared from the general procedure using 3 (20 mg, 12 µmol), and Zn(OTf)$_2$ (4.2 mg, 12 mmol). Pure product 5 was obtained with simple ion exchange and no column chromatography, as a red powder: 22
mg (81%); m.p. > 300 °C; \(^1\)H NMR (500 MHz, A): δ 9.10 (s, 8H, Ru 3’,5’-tpyH), 9.05 (s, 8H, Zn 3’,5’-tpyH), 8.78 (d, 8H, \(J = 8.0\) Hz, Ru 3,3’-tpyH), 8.72 (d, 8H, \(J = 8.0\) Hz, Zn 3,3’-tpyH), 8.20 (d, 16H, Zn and Ru Ar’H), 8.12 (dd, 8H, \(J = 8.0\) Hz, Ru 5,5’-tpyH), 7.90 (dd, 8H, \(J = 8.0\) Hz, Zn 5,5’-tpyH), 7.85 (d, 8H, \(J = 6.0\) Hz, Ru 6,6’-tpyH), 7.66 (d, 16H, \(J = 6.0\) Hz, Ru and Zn Ar’H), 7.44 (d, 8H, \(J = 6.0\) Hz, Zn 6,6’-tpyH), 7.37 (t, 8H, \(J = 7.0\) Hz, 6.0 Hz, Ru 5,5’-tpyH), 7.23 (s, 8H, Zn and Ru ArH), 7.15 (dd, 8H, \(J = 7.0\) Hz, 6.0 Hz, Zn 5,5’-tpyH), 4.02 (s, 12H, OC\(_2\)H\(_3\)), 4.01 (s, 12H, OC\(_2\)H\(_3\)); \(^{13}\)C NMR (500 MHz, A): δ 56.0, 121.5, 124.1, 124.8, 127.4, 127.6, 127.7, 131.5, 131.6, 132.2, 132.2, 134.8, 135.0, 138.1, 138.8, 144.0, 144.3, 147.8, 149.4, 149.9, 152.5, 153.2, 155.6, 158.2, 158.4, 160.5; ESI-MS: \(m/z\) 1356.1 [M-3PF\(_6\)\(^-\)]\(^{3+}\) (calcd \(m/z\) =1356.2), 981.8 [M-4PF\(_6\)\(^-\)]\(^{4+}\) (calcd \(m/z\) = 981.8), 755.8 [M-5PF\(_6\)\(^-\)]\(^{5+}\) (calcd \(m/z\) = 755.9), 605.7 [M-6PF\(_6\)\(^-\)]\(^{6+}\) (calcd \(m/z\) = 605.8), 498.5 [M-7PF\(_6\)\(^-\)]\(^{7+}\) (calcd \(m/z\) = 498.6).

\([(3)\text{Fe}_2\text{Fe}^+8](\text{PF}_6\text{)}^-\)_8 (6) was prepared from the general procedure using 3 (123 mg, 71 µmol) and FeCl\(_2\)·4H\(_2\)O (9.6 mg, 59 µmol). Pure product was obtained through column chromatography to give 6, as a purple solid: 71mg (54%); m.p. > 300 °C; \(^1\)H NMR (500 MHz, A): δ 9.20 (s, 8H, Fe 3’,5’-tpyH), 9.02 (s, 8H, Ru 3’,5’-tpyH), 8.64 (d, 8H, \(J = 7.8\) Hz, 3,3”-Ru tpyH), 8.60 (d, 8H, \(J = 7.8\) Hz, Fe 3,3”-tpyH), 8.29 (d, 8H, \(J = 7.8\) Hz, Fe Ar’H), 8.19 (d, 8H, \(J = 7.8\) Hz, Ru Ar’H), 7.81 (dd, 8H, \(J = 7.8\) Hz, 6.9 Hz, 3.3 Hz, Ru 4,4”-tpyH), 7.84 (dd, 8H, \(J = 7.8\) Hz, 3.3 Hz, Fe 4,4”-tpyH), 7.69 (d, 8H, \(J = 8.4\) Hz, Fe Ar’H), 7.66 (d, 8H, \(J = 8.4\) Hz, Ru Ar’H), 7.39 (d, 8H, \(J = 3.3\) Hz, Ru 6,6”-tpyH), 7.24 (s, 4H, Ru ArH), 7.22 (s, 4H, Fe ArH), 7.15 (d, 8H, \(J = 3.3\) Hz, Fe 6,6”-tpyH), 7.06 (t, 8H, \(J = 7.8\) Hz, Fe 6,6”-tpyH).
= 6.9 Hz, Ru 5,5″-tpyH), 7.03 (t, 8H, J = 6.9 Hz, Fe 5,5″-tpyH), 4.024 (s, 12H, OCH₃), 4.016 (s, 12H, OCH₃); ¹³C NMR (500 MHz, A): δ 167.7, 159.6, 159.4, 156.9, 154.4, 153.8, 151.1, 150.7, 149.0, 145.6, 145.29, 140.1, 140.0, 136.1, 136.0, 133.5, 133.4, 132.8, 132.8, 128.9, 128.8, 128.7, 126.0, 125.3, 122.7, 122.6, 115.9, 57.2, 57.2; ESI-MS: m/z 1350.2 [M-3PF₆]⁺ (calcd m/z = 1350.2), 976.4 [M-4PF₆]⁺ (calcd m/z = 976.4), 752.1 [M-5PF₆]⁺ (calcd m/z = 752.2), 602.6 [M-6PF₆]⁺ (calcd m/z = 602.6), 495.8 [M-7PF₆]⁺ (calcd m/z = 495.8), 415.7 [M-8PF₆]⁺ (calcd m/z = 415.7).

[(3)₂Ru₂⁺⁸(PF₆⁻)₈ (7)] was prepared from the general procedure using 3 (52 mg, 30 µmol) and RuCl₂(DMSO)₄ (12.1 mg, 25 µmol). The pure product was obtained through column chromatography to give 7, as a red solid: 22 mg (32%); m.p. > 300 °C; ¹H NMR (500 MHz, A): δ 9.01 (s, 8H, 3′,5′-tpyH), 8.64 (d, 8H, J = 8.1 Hz, 3,3″-tpyH), 8.18 (d, 8H, J = 8.4 Hz, Ar′H), 7.88 (dd, 8H, J = 8.4 Hz, 6.9 Hz, 4,4″-tpyH), 7.67 (d, 8H, J = 8.4 Hz, Ar′H), 7.41 (d, 8H, J = 4.8 Hz, 6,6″-tpyH), 7.21 (s, 4H, ArH), 7.12 (dd, 8H, J = 6.9 Hz, 4.8 Hz, 5,5″-tpyH), 4.01 (s, 12H, OCH₃); ¹³C NMR (500 MHz, A): δ 49.7, 114.7, 121.4, 124.8, 127.5, 127.6, 131.5, 132.2, 135.1, 138.2, 144.2, 147.8, 149.4, 152.6, 155.6, 158.4; ESI-MS: m/z 1380.5 [M-3PF₆]⁺ (calcd m/z = 1380.5), 999.1 [M-4PF₆]⁺ (calcd m/z = 999.1), 770.3 [M-5PF₆]⁺ (calcd m/z = 770.3), 617.8 [M-6PF₆]⁺ (calcd m/z = 617.8), 508.8 [M-7PF₆]⁺ (calcd m/z = 508.8), 427.1 [M-8PF₆]⁺ (calcd m/z = 427.0).

[(2)₂Fe₄⁺⁸(PF₆⁻)₈ (8)]. To a solution of 2 (400 mg, 5.32 mmol) in 1:1 MeOH:CHCl₃ (v/v) was added FeCl₂·4H₂O (72 mg, 4.43 mmol). The resulting deep purple solution was refluxed for 5 h and the counterion exchanged with
NH₄PF₆ to afford a purple solid that was purified by column chromatography (SiO₂) eluting with H₂O:sat KNO₃(aq):MeCN (1:1:17, v/v/v) to give 8, as a purple solid: 40 mg (8%); m.p. > 300 °C; ¹H NMR (500 MHz, A): δ 9.21 (s, 8H, 3',5'-tpyH), 8.62 (d, 8H, J = 8.1 Hz, 3,3"-tpyH), 8.30 (d, 8H, J = 8.4 Hz, Ar'H), 7.86 (t, 8H, J = 8.1 Hz, 6.9 Hz, 4,4"-tpyH), 7.73 (d, 8H, J = 8.4 Hz, Ar'H), 7.25 (s, 4H, ArH), 7.17 (d, 8H, J = 5.1 Hz, 6.6"-tpyH), 7.01 (t, 8H, J = 6.9 Hz, 5.1 Hz, 5,5"-tpyH), 4.03 (s, 12H, OCH₃); ¹³C NMR (500 MHz, A): δ 160.5, 158.2, 153.2, 138.9, 127.5, 121.4, 114.5, 56.0; ESI-MS: m/z 1319.9 [M-3PF₆⁻]³⁺ (calcd m/z = 1319.8), 953.6 [M-4PF₆⁻]⁴⁺ (calcd m/z = 953.6), 733.9 [M-5PF₆⁻]⁵⁺ (calcd m/z = 733.9), 587.4 [M-6PF₆⁻]⁶⁺ (calcd m/z = 587.4), 482.8 [M-7PF₆⁻]⁷⁺ (calcd m/z = 482.8), 404.3 [M-8PF₆⁻]⁸⁺ (calcd m/z = 404.3). Also isolated was pure trimer: 140 mg (29%).
CHAPTER V

SELF-ASSEMBLY AND CHARACTERIZATION OF THREE-DIMENSIONAL METALLOMACROCYCLES: A STUDY OF SUPRAMOLECULAR CONSTITUTIONAL ISOMERS

5.1 Introduction

Initial examples of supramolecular chemistry have included the creation of a large variety of intricate and complex structures, \(^{59,60,102,164,192,195,230}\) predicated on the work of Lehn, who paved the way for others to advance the field. \(^{251}\) This research has been inspired by the beauty observed macroscopically in Nature, in naturally occurring in self-assembled supramolecules, such as DNA. In most cases, thermodynamic equilibria provide the principle driving force for product creation. \(^{10,11,252,253}\) This often can result in an inability for separation or purification of the compounds due to their fragile architectures that are being held together by multiple non-covalent interactions. As a result, isolation of isomers of such molecules has been rare. \(^{54,57}\) Although isolation of single isomers is uncommon, observance of mixtures is not - several examples have, however, been characterized. \(^{85,137,209,254-257}\)

We recently reported the formation of novel supramolecular "bowtie" and "butterfly" constitutional isomers, each prepared from core ligands with unique
geometries resulting in constructs possessing different cross-sectional areas.\textsuperscript{54} Access to these materials relied on the synthetic design; however, traditional purification presented challenges due to the labile nature of the $<\text{tpy-}M^{\text{II}}\text{-tpy}>$ coordination complexes, where tpy $= 2,2':6',2''$-terpyridine and $M^{\text{II}} = \text{Cd}^{\text{II}}$ or $\text{Zn}^{\text{II}}$.\textsuperscript{10,162,258} Other work has demonstrated that cyclization of a 120\degree-oriented bisterpyridine ligand can lead to varying ring sizes under the proper reaction conditions;\textsuperscript{50,186,187} these rings result from kinetic control during $<\text{tpy-}M^{\text{II}}\text{-tpy}>$ coordination complex formation. More recently, 60\degree-oriented bisterpyridine ligands have been shown to form cyclic tetramers.\textsuperscript{188} As these results indicate, sets of isomers based on the directivity of the bisligands can be envisioned.

Electrospray ionization mass spectrometry, in particular high resolution ESI-MS, has been a key technique in the characterization of self-assembled macrocycles in recent years. It revealed both the mass-to-charge ratio ($m/z$) and isotope pattern of several charge states of the self-assembled structure, from which the corresponding molecular weight and composition can be unequivocally determined.\textsuperscript{90,259,260} ESI is a soft ionization technique, allowing for the characterization of weakly bonded or labile constructs and, thus, access to previously difficult-to-analyse compounds. As well, ESI-MS coupled with travelling wave ion mobility (TWIM) technology enables separation by geometrical shape, which has resulted in numerous publications concerning self-assembled products of both labile and robust connectivity. Examples include the differentiation of linear versus cyclic structures,\textsuperscript{196} various polygon mixtures,\textsuperscript{228,261} as well as \textit{cis} and \textit{trans} isomers.\textsuperscript{262}
In this chapter, we focus on the synthesis of a new set of supramolecular constitutional isomers, utilizing \(<\text{tpy-M}^{\text{II}}\text{-tpy}>\) connectivity, in which the hexameric isomers exhibit drastically different architectures. The difference in shape was readily discernible with ESI-TWIM-MS, with the most pronounced difference at low charge states. The current work concerns easily isolated, robust \textit{bisterpyridine}-based complexes using Fe\textsuperscript{II} or Ru\textsuperscript{II}. Rings of varying sizes were readily separated in pure form \textit{via} column chromatography, an option unavailable for the more labile Zn\textsuperscript{II} and Cd\textsuperscript{II} complexes, and characterized in depth by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopies, as well as ESI-TWIM-MS and molecular modelling.

5.2 Results and Discussion

\textit{Bisterpyridine} 1 was readily synthesized \textit{via} Suzuki coupling\cite{227} from 4-boronatophenyl-2,2′:6′,2″-terpyridine\cite{263} and 4,5-dibromoveratrole\cite{264} and, as reported elsewhere, the dimerization of 1 in the presence of Ru(DMSO)$_4$Cl$_2$ affords 2.\cite{213} Cyclization of 2 (Scheme 5.1) with FeCl$_2$·4 H$_2$O led to a mixture of two cyclic structures, tetramer 3\cite{188} and, unexpectedly, the folded 3D hexamer 4, which were both readily separated \textit{via} column chromatography, eluting with 1:1:16 H$_2$O:KNO$_3$(sat):MeCN (v/v/v) and isolated in 54 and 13% yields, respectively. It is expected that hexamer 4 exists in multiple orientations, \textit{e.g.}, a basket and crown form, shown below in Scheme 5.1. Although there are multiple forms, molecular modeling, shown later, revealed no significant energetic difference between them.
Scheme 5.1. Synthesis of 2 - 4. Reagents and conditions: i) Ru(DMSO)$_4$Cl$_2$, MeOH:CHCl$_3$ (1:1 v/v), Δ; ii) FeCl$_2$·4 H$_2$O, MeOH:CHCl$_3$ (1:1 v/v), Δ. Also depicted are optimized models of tetramer 3 and multiple conformations (crown and basket) of hexamer 4.

The $^1$H NMR spectra of tetramer 3 and hexamer 4, shown in the stacked plots of Figure 5.1, reveal two nearly identical spectra. The only noticeable differences between the spectra are minor differences in the chemical shifts of the
4,4″- and 5,5″-terpyridyl proton resonances ($\Delta\delta_{4,4''} = 0.18$ ppm and $\Delta\delta_{5,5''} = 0.16$ ppm). All other readily assignable resonances occur at identical chemical shifts. Also, the chemically instilled -OCH$_3$ marker is readily identifiable as two overlapping singlet resonances in the $^1$H NMR spectrum. It should be noted that given a high energy difference between the crown and basket form, one would expect a complicated spectrum, but the $^1$H NMR spectrum of hexamer 4 suggests that the conformational change happens rapidly at room temperature.

Figure 5.1. $^1$H NMR spectra for the 60°-based constructs. Minor shift differences are observed for the 4,4″- and 5,5″-protons of macrocycles 3 and 4; whereas, a large upfield shift in the 6,6″ resonances for 2 to 3 (or 2 to 4) is noted. Previously published 2 and 3 are shown for comparison.$^{188}$ (*CHCl$_3$)

118
Subsequent ESI-MS characterization revealed a significant difference between the two structures (Figure 5.2). Although some ions with the same \( m/z \) value are observed from 3 and 4, for example both the 6\(^+\) ion from 3 and the 9\(^+\) ion from 4 appear at \( m/z \) 602.2 amu, the corresponding isotope patterns are noticeably different. These data, along with the assignment of all other peaks within the mass spectrum, confirm the existence of two separate species, consistent with the structures of tetramer 3 and hexamer 4.

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Figure 5.2. ESI-MS comparison of 3 and 4.

Bisligand 5 was synthesized from 2,4-dimethoxy-1,5-dibromobenzene\(^{264}\) according to known procedures\(^{263}\) and was isolated in 51\% yield after column chromatography. Characterization \( \text{via} \) \(^1\)H NMR spectroscopy revealed the expected characteristic singlet resonance at 8.81 ppm assigned to the 3,5-protons, as well as doublets at 8.74 and 8.68 ppm for the 6,6- and 3,3-protons, respectively. All other NMR resonances were as anticipated; ESI-MS analysis supported the structure with a signal at \( m/z \) 753.4 amu attributed to \([\text{M+H}]^+\). This
ligand was subsequently dimerized with Ru(DMSO)$_4$Cl$_2$ to afford 6 in a 27% yield. The $^1$H NMR spectrum of 6 (Figure 5.3) is consistent with a dimer, with two sets of terpyridyl resonances, each integrating 1:1. Also, the ESI-MS of dimer 6 revealed peaks corresponding to the 1+ and 2+ charge states at $m/z$ 1092.0 and 803.2 amu, respectively.

Scheme 5.2. Synthesis of compounds 5 - 8. Also depicted are side views of geometrically optimized structures for tetramer 7 and hexamer 8. Reagents and conditions: i) Ru(DMSO)$_4$Cl$_2$, MeOH:CHCl$_3$ (1:1 v/v), Δ; ii) FeCl$_2$·4 H$_2$O, MeOH:CHCl$_3$ (1:1 v/v), Δ.

i) Ru(DMSO)$_4$Cl$_2$, MeOH:CHCl$_3$ (1:1 v/v), Δ; ii) FeCl$_2$·4 H$_2$O, MeOH:CHCl$_3$ (1:1 v/v), Δ.
Dimer 6 was cyclized with FeCl$_2$·4 H$_2$O and purified by column chromatography, affording two maroon bands (See Scheme 5.2). These bands were first characterized via $^1$H NMR, which exhibited two very similar spectra. Both products contain noticeably shifted 6,6″-proton absorptions compared to 6, as expected upon complex formation. More subtle changes include slight shifts in the 3′,5′ resonances from 9.24 to 9.30 ppm and 9.07 to 9.13 ppm, respectively (See Figure 5.3). Similarly, the 3,3″-proton resonances shift slightly downfield from 8.68 to 8.73 ppm in the ruthenium complex and from 8.64 to 8.69 ppm for the iron complex. The proton most affected by a change in ring size is the proton on the central benzene connector sandwiched between the two terpyridyl moieties. In this case, a downfield shift from 7.56 to 7.71 ppm is observed, indicative of two different ring sizes as observed in other reported cases of homologous metallomacrocycles; $^{50,187}$ as well, earlier work has resulted in the isolation of a pentameric structure from a similar 120°-directed ligand when using solely monomer 5. $^{185,186}$
Figure 5.3. $^1$H NMR spectra for the 120°-based 6 - 8. As in rings 3 and 4, small differences in the spectra of 7 and 8 are seen, while the expected upfield shift for the 6,6″ resonance in free ligand 6 compared to complex 7 (and 8) is observed. (*CHCl$_3$)

Stacked $^1$H NMR spectra of each of the hexameric species are markedly different, as shown in Figure 5.4. All terpyridine resonances in the more planar ring 8 are shifted significantly downfield in contrast to the same proton signals observed for the 3D, folded construct 4. Also hexamers possess distinctive absorptions attributed to the protons attached to the corner benzene rings. In the 60° case, two singlets are observed very close together at ~2.25 ppm; whereas in the 120° case, the two protons resonate noticeably apart at 7.84 and 7.15 ppm. A similar pattern is observed for the tetramers 3 and 7.
Identification of the ring sizes by providing accurate molecular weights of 7 and 8 was ascertained using ESI-MS. Tetramer 7 revealed m/z values consistent with its assignment, although a cyclic tetramer was unanticipated due to the >90° terpyridine directivity in the dimeric building block. However, peaks at m/z 1350.3, 976.5, 752.2, 602.7, 495.9, and 415.8 amu were observed, values that couple with the respective theoretical isotope patterns, are consistent with those calculated for the 3+ through 8+ charge states of 7. The 1D-ESI mass spectrum of hexamer 8 is nearly identical to that of 4 (Figure 5.5A), which is expected for two structural isomers. Analysis of the 4+ charge state of hexamers 4 and 8 by gradient tandem mass spectrometry (gMS², 5.5B) revealed a large difference in ion stability. Activation of the assemblies afforded dissociation values (eV) under
increasingly energetic collisions.\textsuperscript{211} The planar hexamer 8 completely fragmented at 22 eV collision energy; whereas, its three dimensional counterpart 4 was stable up to 40 eV.

<table>
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Table 5.1. Summary of ESI-TWIM-MS drift time data.
Figure 5.5. A) 1D ESI mass spectra for 60° oriented hexamer 4 and 120° oriented hexamer 8; B) gMS² plots of the 4+ peak from 4 and 8 at various activation collision energies (eV).
Further support for the different architectures was provided by comparing the two sets of isomers via TWIM-MS; a difference in the shapes correlate well with the recovered drift times observed for the two sets of isomers (Table 5.1). A general trend is seen for the drift times of the 60°-based tetramer 3 and hexamer 4 where they are smaller in comparison to those observed for their 120°-based counterparts, indicating that tetramer 7 and hexamer 8 occupy more space (i.e., they have more extended architectures). With rings 3 and 4 having to fold for alleviation of the potential ring strain, this result is reconciled.

Figure 5.6. Computer generated images of the metallomacrocycles 4, 8, 3 and 7 and their solvent accessible surfaces generated with a 1.4 Å probe.
Molecular modelling of the metallomacrocycles corroborates the ESI-TWIM-MS drift time results, shown in Figure 5.6. Both geometry-optimized tetramers 3 and 7 exhibit squared structures; although, 60°-based 3 possesses a more pronounced, folded (Dondorff\textsuperscript{188}) architecture, with bisecting metal-to-metal distances of \textit{ca.} 22 Å. The less pronounced folding of tetramer 7 gives it a slightly more open structure with the same measured distances of \textit{ca.} 24 Å.

The fold in 3 reduces the cross-sectional area and explains the different drift time compared to tetramer 7 observed in the ESI-TWIM-MS. The same phenomenon is observed when comparing the basket-like hexamer 4 to the classical hexameric structure of 8 with bisecting metal-to-metal distances of \textit{ca.} 26 and 40 Å, respectively. It should be noted that the energy minima of the crown configuration mirrored that of the basket configuration ($\Delta E_{\text{min}} < 4$ kcal). The metal-to-metal distances between the two forms are nearly identical with bisecting distances of 22 – 24 Å as well as 12 – 14 Å distances for adjacent metal atoms. Energy calculation of an intermediate, flattened, transition state was determined to also be similar ($\Delta E_{\text{min}} < 11$ kcal), due presumably to octahedral coordination distortion along with bond torsions. This relative ease of conformational transition between the basket and crown forms is consistent with only observing a single set of $^1$H NMR peaks, as well as TWIM-MS data, as has previously been observed in other systems with multiple configurations.\textsuperscript{187} The rigidity of 4 may explain its increased stability based on activation collision energies (Figure 5.5B). Finally, solvent accessible surface area calculations reveal a trend of slightly less surface area for the folded hexamer 4 and tetramer 3 (5304 and 3536 Å, respectively)
when compared to the classical hexamer 8 and tetramer 7 (5326 and 3551 Å, respectively).

5.3 Conclusions

The synthesis and characterization of a new set of supramolecular constitutional isomers have been demonstrated. These isomers are comprised of 60°- and 120°-oriented bisterpyridine ligands, which were dimerized with Ru\textsuperscript{II} and subsequently cyclization with Fe\textsuperscript{II} to afford two sets of cyclic tetramers and hexamers, after column chromatography, with identical molecular weights. With only subtle differences in the \textsuperscript{1}H NMR spectra, ESI-MS was utilized for identification of ring size. Although the 1D-ESI-MS data for the metallomacrocycles were identical, TWIM-MS revealed drastic differences between the isomers. This difference in cross-section size was verified by molecular modeling, which showed results consistent with the TWIM-MS data. Based on this work, the use of new monomers for supramolecular self-assembly is expected to generate new architectures possessing exciting structural constraints.

5.4 Experimental

**General Procedures.** Chemicals were purchased from Fisher Scientific, Sigma/Aldrich or VWR, confirmed with \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopies, and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al\textsubscript{2}O\textsubscript{3} (IB-F) or SiO\textsubscript{2} (IB\textsubscript{2}-F) and visualized by UV light. Column chromatography was conducted using basic Al\textsubscript{2}O\textsubscript{3}, Brockman Activity I (60-325 mesh) or SiO\textsubscript{2} (60-200 mesh) from Sorbent Technologies. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on either a
Varian Mercury 300 or Varian NMR 500 spectrometer using CD$_3$CN (A) for complexes and CDCl$_3$ (B) for ligands, and referenced to 1.94 and 7.27 ppm, respectively.

Mass spectra were obtained on a Bruker Esquire electrospray ion trap mass spectrometer (ESI-MS). Traveling wave ion mobility mass spectrometry (TWIM-MS) experiments were performed using a Waters Synapt HDMS quadrupole/time-of-flight (Q/ToF) tandem mass spectrometer. The TWIM device is located between the Q and ToF mass analyzers and consists of three cells: a trap, an ion mobility (IM), and a transfer. The trap and transfer cells can be used for conventional tandem MS experiments via collisionally activated dissociation (CAD). The ion mobility cell is used in IM separations. Generally, the following parameters were used in TWIM-MS experiments: ESI capillary voltage, 1.5 kV, sample cone voltage, 15 V, extraction cone voltage, 3.2 V; desolvation gas flow, 800 L/h (N$_2$); trap collision energy (CE), 2 eV; transfer CE, 1 eV; trap gas flow, 1.5 mL/min (Ar); IM gas flow, 22.7 mL/min (N$_2$); sample flow rate, 10 μL/min; source temperature, 30 °C; desolvation temperature, 40 °C; and the IM traveling wave velocity, 350 m/s. The IM traveling wave heights were set at 7.5 V. In the gMS$^2$ tandem MS experiments, the trap CE was varied within 6-60 eV to cause fragmentation. The sprayed solution was prepared by dissolving the sample (1 mg/1 mL) of MeCN/MeOH (3:2) solvent mixture.

3,4-Bis(4′-terpyridyl-p-phenyl)-o-dimethoxybenzene. See Chapter II.

[(3)$_2$Ru$^{+2}$]2NO$_3^−$. See Chapter IV
Procedure for isolation of 3 and 4. In a round bottom flask, a stirred solution of 2 (123 mg, 71 µmol) and FeCl$_2$ • 4 H$_2$O (9.6 mg, 59 µmol) in a MeOH:CHCl$_3$ solvent mixture (350 mL, 1:1 v/v) was refluxed for 12 h. The reaction mixture was concentrated *in vacuo* to give a maroon residue that was purified by column chromatography (SiO$_2$), eluting with a solvent mixture of sat KNO$_3$:H$_2$O:MeCN (1:1:16 v/v/v), and subjected to counterion exchange with solid NH$_4$PF$_6$ to afford tetramer 3: 71 mg (54%), and hexamer 4: 17 mg, (13%).

**Tetramer 3.** See Chapter IV

**Hexamer 4.** m.p. > 300 °C; $^1$H NMR (500 MHz, A): $\delta$ 9.22 (s, 12H, Fe 3',5'-tpyH), 9.06 (s, 12H, Ru 3',5'-tpyH), 8.67 (d, 12H, $J = 7.5$ Hz, Ru 3,3''-tpyH), 8.63 (d, 12H, $J = 7.5$ Hz, Fe 3,3''-tpyH), 8.32 (d, 12H, $J = 7.5$ Hz, Fe ArH), 8.22 (d, 12H, $J = 7.5$ Hz, Ru ArH), 7.83 (dd, 12H, $J = 6.5$ Hz, Ru 4,4''-tpyH), 7.80 (dd, 12H, $J = 6.5$ Hz, Fe 4,4''-tpyH), 7.73 (d, 12H, $J = 7.5$ Hz, Fe ArH), 7.70 (d, 12H, $J = 7.5$ Hz, Ru ArH), 7.42 (d, 12H, $J = 4.5$ Hz, Ru 6,6''-tpyH), 7.27 (s, 6H, Ru ArH), 7.25 (s, 6H, Fe ArH), 7.19 (d, 12H, $J = 4.5$ Hz, Fe 6,6''-tpyH), 7.09 (dd, 12H, $J = 6.5$ Hz, $J' = 4.5$ Hz, Ru 5,5''-tpyH), 7.01 (dd, 12H, $J = 6.5$ Hz, $J' = 4.5$ Hz, Fe 5,5''-tpyH), 4.02 (s, 18H, OC$_3$H$_7$), 4.01 (s, 18H, OC$_3$H$_7$); $^{13}$C NMR (500 MHz, A): $\delta$ 160.2, 158.2, 158.0, 155.4, 153.0, 152.3, 149.7, 149.3, 147.6, 144.1, 143.8, 138.6, 137.9, 134.8, 134.6, 132.0, 132.0, 131.4, 131.3, 127.5, 127.4, 127.2, 124.6, 123.9, 121.3, 121.2, 114.4, 55.8; ESI/MS: $m/z$ 1200.6 [M-5PF$_6$]$_{5+}$ (calcd $m/z = 1200.6$), 976.3 [M-6PF$_6$]$_{6+}$ (calcd $m/z = 976.4$), 816.2 [M-7PF$_6$]$_{7+}$ (calcd $m/z = 816.2$), 695.9 [M-8PF$_6$]$_{8+}$ (calcd $m/z = 696.0$), 602.6 [M-9PF$_6$]$_{9+}$ (calcd $m/z = 602.6$), 527.8 [M-10PF$_6$]$_{10+}$ (calcd $m/z = 527.9$), etc.
466.7 $[\text{M-11PF}_6^-]^{11+}$ (calcd $m/z = 466.7$), 415.7 $[\text{M-12PF}_6^-]^{12+}$ (calcd $m/z = 415.7$).

$[(\text{5})_2\text{Ru}^{+2}] 2\text{NO}_3^- \ (6)$. To a 500 mL round bottom flask was added 5 (300 mg, 399 µmol), RuCl$_2$(DMSO)$_4$ (64 mg, 133 µmol), and MeOH:CHCl$_3$ (300 mL, 1:1 v/v), then the mixture was refluxed for 17 h. The reaction was concentrated in vacuo to give a red powder that was column chromatographed (Al$_2$O$_3$, CHCl$_3$) changing to 1:1:40 H$_2$O:sat KNO$_3$:MeCN v/v/v upon removal of uncomplexed 5, to afford 6, as a red powder: 85 mg (27 %); m.p. > 300 °C; $^1$H NMR (300 MHz, 3:2 CD$_3$OD:CDCl$_3$) δ 9.21 (s, 4H, complexed 3′,5′-tpy$_H$), 8.83 (d, 4H, $J = 8.2$ Hz, complexed 3,3″-tpy$_H$), 8.68 (m, 12H, free 3′,5′-tpy$_H$, free 3,3″-tpy$_H$, 6,6″-tpy$_H$), 8.25 (d, 4H, $J = 7.8$ Hz, Ar$_H$), 7.99 (m, 18H, Ar$_H$, Ar′$_H$, complexed and free 4,4″-tpy$_H$), 7.78 (d, 4H, $J = 7.8$ Hz, Ar$_H$), 7.48 (m, 9H, Ar′$_H$, complexed 6,6″-tpy$_H$, free 5,5″-tpy$_H$), 7.29 (dd, 4H, $J = 8.2$ Hz, $J' = 5.6$ Hz, complexed 5,5″-tpy$_H$), 6.87 (s, 1H, Ar′$_H$), 4.01 (s, 4H, OCH$_3$), 3.99 (s, 4H, OCH$_3$); $^{13}$C NMR (300 MHz, 3:2 CD$_3$OD:CDCl$_3$) δ 159.2, 158.2, 157.6, 155.7, 155.6, 155.4, 152.1, 149.0, 148.6, 138.4, 137.9, 134.4, 132.3, 130.6, 130.1, 127.8, 127.2, 126.7, 124.3, 122.1, 121.9, 121.2, 118.7; ESI-MS: $m/z$ 803.2 [$\text{M-2NO}_3^-]^{12+}$ (calcd $m/z = 803.2$).

Procedure for isolation of 7 and 8: In a round bottom flask, a stirred solution of 7 (57 mg, 33 µmol) and FeCl$_2$ · 4H$_2$O (5.9 mg, 36 µmol) in MeOH:CHCl$_3$ (200 mL 1:1 v/v) was refluxed for 14 h. The reaction mixture was concentrated in vacuo and purified by column chromatography (SiO$_2$, 1:1:12 sat KNO$_3$:H$_2$O:MeCN v/v/v), and subjected to counterion exchange with solid
NH₄PF₆ to afford tetramer 7: 13 mg (18 %), and hexamer 8: 19 mg, (26 %), as maroon powders.

**Tetramer 7:** m.p > 300 °C; ¹H NMR (500 MHz, A): δ 9.24 (s, 8H, 3’,5’-tpyH), 9.07 (s, 8H, 3’,5’-tpyH), 8.68 (d, 8H, J = 8.0 Hz, 3,3”-tpyH), 8.64 (d, 8H, J = 8.0 Hz, 3,3”-tpyH), 8.38 (s, 8H, J = 7.5 Hz, ArH), 8.28 (d, 8H, J = 7.5 Hz, ArH), 8.07 (d, 8H, J = 7.5 Hz, ArH), 8.03 (d, 8H, J = 7.5 Hz, ArH), 7.97 (t, 8H, J = 8.0 Hz, 4,4”-tpyH), 7.91 (t, 8H, J = 8.0 Hz, 4,4”-tpyH), 7.56 (s, 4H, ArH), 7.20 (m, 16H, 5,5″-tpyH, 6,6″-tpyH), 7.10 (t, 8H, J = 7.5 Hz, 5,5”-tpyH), 7.01 (s, 4H, ArH), 4.01 (s, 12H, OCH₃), 4.00 (s, 12H, OCH₃); ¹³C NMR (500 MHz, A): δ 160.3, 158.0, 157.9, 156.2, 155.5, 140.4, 138.8, 138.0, 135.8, 134.6, 134.5, 130.7, 130.6, 127.6, 127.5, 127.4, 127.2, 124.4, 123.7, 122.9, 119.7, 119.6, 55.9; ESI/MS: m/z 1350.3 [M-3PF₆¯]³⁺ (calcd m/z = 1350.2), 976.5 [M-4PF₆¯]⁴⁺ (calcd m/z = 976.4), 752.2 [M-5PF₆¯]⁵⁺ (calcd m/z = 752.2), 602.7 [M-6PF₆¯]⁶⁺ (calcd m/z = 602.6), 495.9 [M-7PF₆¯]⁷⁺ (calcd m/z = 495.8), 415.8 [M-8PF₆¯]⁸⁺ (calcd m/z = 415.7).

**Hexamer 8:** m.p. > 300 °C; ¹H NMR (500 MHz, A): δ 9.30 (s, 12H, 3’,5’-tpyH), 9.13 (s, 12H, 3’,5’-tpyH), 8.73 (d, 12H, J = 7.5 Hz, 3,3”-tpyH), 8.69 (d, 12H, J = 8.0 Hz, 3,3”-tpyH), 8.43 (d, 12H, J = 8.0 Hz, ArH), 8.32 (d, 12H, J = 8.0 Hz, ArH), 8.08 (d, 12H, J = 8.0 Hz, ArH), 8.05 (d, 12H, J = 8.0 Hz, ArH), 8.00 (t, 12H, J = 7.5 Hz, 4,4”-tpyH), 7.94 (t, 12H, J = 7.5 Hz, 4,4”-tpyH), 7.71 (s, 6H, ArH), 7.49 (d, 12H, J = 4.5 Hz, 6,6”-tpyH), 7.24 (m, 24H, 6,6”-tpyH, 5,5”-tpyH), 7.01 (s, 6H, ArH), 4.07 (s, 18H, OCH₃), 4.06 (s, 18H, OCH₃); ¹³C NMR (500 MHz, A) δ 160.3, 158.3, 158.0, 155.5, 150.6, 138.6, 138.7, 138.0, 135.3, 134.8,
134.2, 130.8, 130.7, 127.6, 127.5, 127.3, 124.6, 123.9, 121.5, 121.4, 98.4, 58.4;

ESI/MS: \( m/z \) 1200.7 \([\text{M-5PF}_6^–]^{5+}\) (calcd \( m/z \) = 1200.6), 976.4 \([\text{M-6PF}_6^–]^{6+}\) (calcd \( m/z \) = 976.4), 816.3 \([\text{M-7PF}_6^–]^{7+}\) (calcd \( m/z \) = 816.2), 696.0 \([\text{M-8PF}_6^–]^{8+}\) (calcd \( m/z \) = 696.0), 602.7 \([\text{M-9PF}_6^–]^{9+}\) (calcd \( m/z \) = 602.6), 527.8 \([\text{M-10PF}_6^–]^{10+}\) (calcd \( m/z \) = 527.9), 466.8 \([\text{M-11PF}_6^–]^{11+}\) (calcd \( m/z \) = 466.7), 415.8 \([\text{M-12PF}_6^–]^{12+}\) (calcd \( m/z \) = 415.7).
CHAPTER VI

SYNTHESIS, PHOTOCHEMICAL, AND ELECTROCHEMICAL PROPERTIES OF ANTENNA FUNCTIONALIZED CADMIUM HEXAMERIC METALLOMACROCYCLES

6.1 Introduction

In recent years, self-assembly of pre-designed molecular architectures has become a topic of particular interest. Lehn\textsuperscript{265}, Stang\textsuperscript{266-268}, Schmittel\textsuperscript{164,195,269} and others\textsuperscript{270,271} have published numerous articles on the successful assembly of two and three dimensional structures. As well as these, the generation of terpyridine-based metallomacrocycles, in which a 60°-, 105°-, or 120°-oriented bisterpyridine building block was utilized to synthesize cyclic structures with a variety of bivalent metals (Fe\textsuperscript{II}, Ru\textsuperscript{II}, and Zn\textsuperscript{II}) via $<$tpy-$\mathrm{M}^{\text{II}}$-tpy$>$ connectivity and functionality have been reported.\textsuperscript{173-175,272} Some projected uses for such structures include solar devices, rigid architectures, and OLED devices. Along with other metals, recent work in our lab has focused on the labile $<$tpy-Cd$^{+2}$-tpy$>$ bond, utilizing an equilibrium to facilitate the formation of the enthalpically favored cyclic structure.\textsuperscript{10} This thermodynamic approach to materials has led to the formation of a novel, three component system in high yield.\textsuperscript{10}
Antennas for collection of light energy have also been found to enhance photochemical effects of photoactive compounds. These antennas have been used to mimic photosynthesis, improve emission properties, and act as markers. In particular, Moore-type, phenylacetylene dendrons have displayed significant enhancement of these properties, and would be a suitable antenna for these hexameric structure. Herein, this chapter describes the synthesis and characterization of phenylacetylene dendrons functionalized bisterpyridine ligands and their use in the self-assembly of hexameric cadmium metallomacrocycles; their photochemical along with electrochemical properties are also discussed.

6.2 Results and Discussion

The antenna-functionalized bisterpyridine ligands 13 and 14 were synthesized via palladium-catalyzed Sonogashira cross-coupling of iodo-modified bisterpyridine 11 and acetylene-terminated dendrons 3 and 6 (Scheme 6.1). The iodo-modified bisterpyridine 11 is readily accessible from 5-aminoisophthalic acid 7 via Sandmeyer reaction to give 8. Borane reduction of 8 affords the dialcohol 9, characterized by formation of the methylene –CH₂ in the 1H NMR spectrum. Subsequent PCC oxidation of 9 gave the 1,3-bisformyl-5-iodobenzene, which was identified by the disappearance of the aforementioned methylene protons and appearance of a formyl singlet at 10.1 ppm. This dialdehyde can be
Scheme 6.1. Synthetic route to antenna 6 and iodo-modified *bisterpyridine* 11.

Reagents and conditions: i) 2-methyl-3-butyne-2-ol, Pd(PPh₃)₄, Cul, NEt₃, reflux 12 h; ii) NaH, anhydrous toluene, distill; iii) Pd(PPh₃)₄, Cul, NEt₃, 4, reflux 12 h; iv) (a) HCl, NaNO₂, 0°C, (b) KI, I₂, reflux 1 h, v) BH₃·THF, THF, 25°C, 12 h; vi) PCC/Celite, CH₂Cl₂, 12 h; vii) 2-acetylpyridine, NaOH, EtOH, NH₄OH, 60°C, 8 h.
directly to the corresponding bis-terpyridine via aldol condensation and Michael addition with 2-acetylpyridine under basic. Aromatization with aqueous ammonia gave the target bis-terpyridine 11 in ca. 70% yield. Modified terpyridine 11 can be readily identified by a characteristic 3',5' proton singlet at 8.77 ppm as well as the characteristic peaks resulting from the 3,3", 6,6", 4,4", and 5,5". The Moore dendron was synthesized by a slight modification (Experimental Section 6.4) to the established literature procedures\textsuperscript{277,278} (See Scheme 6.1). Propagation of the known acetylene 3 with the dibromo-substituted propagator 4 yielded the desired protected G2 dendron 5. In our hands, it was found to be easier to perform the deprotection with NaH to give 6 rather than the standard deprotection method.\textsuperscript{277}
Scheme 6.2. Self-assembly of antenna-functionalized ligands 13 and 14, followed by subsequent cyclization with Cd$^{II}$. Reagents and conditions: i) Pd(PPh$_3$)$_4$, CuI, NEt$_3$, reflux 12 h; ii) 1.00eq Cd(NO$_3$)$_2$·4H$_2$O, 3:2 CHCl$_3$:MeOH, 25°C, 12 h.

Upon successful Sonogashira cross coupling with 11 to afford 13 and 14, nearly quantitative yields of the desired hexamers 16 and 17 were obtained by stoichiometric reaction of the desired ligand with cadmium nitrate to afford cream colored solids, (See Scheme 2) which were soluble in a mixed solvent system of 3:2 MeOH/CHCl$_3$ as well as DMF. It should be noted that ligand 12 and
metallomacrocycle 15 have been reported elsewhere,\textsuperscript{196} and their synthesis will not be discussed here. The structures were identified initially by the characteristic downfield shift of the 6,6” terpyridyl resonances, indicative of a \textit{bisterpyridine} complex, as shown in Figure 6.1. Further evidence for a sole product can be given \textit{via} the single \textit{t}-butyl type protons in each of the macrocycles, as well as the single set of 3’,5’ resonances. Also, there is a single Ar-\textit{H} proton resonance from the proton in between the two terpyridyl moieties, which has been shown to be extremely sensitive to ring size.\textsuperscript{50}

![Figure 6.1](image)

Figure 6.1. $^1$H NMR of \textit{bisterpyridine} ligand 13 and corresponding metallomacrocycle 16.

The $^{13}$C NMR spectrum displayed two acetylenic carbons for 16 at 86.6 and 92.8 ppm and a single \textit{t}-butyl resonance at 30.7 ppm, further supporting the assignment; whereas, 17 shows four acetylenic carbons at 92.0, 90.4, 88.6, and 86.3 ppm and again a single \textit{t}-butyl resonance at 31.2 ppm. These cyclic
structures were interpreted via ESI-MS, UV-vis spectroscopy, photoluminescence, as well as cyclic voltammetry.

The absorption emission spectra of 12-17 were nearly identical for each ligand as well as its corresponding macrocycle, as seen in Figure 6.2. As the dendron generation increases, there is the distinct formation of a shoulder at 310 nm, a result of the increasing conjugation of the appended antenna. There is also a peak at ca. 278 nm for each of the complexes and ligands, which remains nearly identical regardless of structure. All observed transitions are $\pi \rightarrow \pi^*$ from the ligand, as to be expected in the presence of cadmium, as its $d^{10}$ nature prevents metal-to-ligand charge transfer.
Figure 6.2. Photophysical data for antenna modified compounds 12 – 17. A) UV-vis, acquired in DMF at a concentration of 5x10⁻⁵ M; B) PL spectral overlay, acquired in DMF at a concentration of 5x10⁻⁶ M, with an excitation wavelength of 1, 12

<table>
<thead>
<tr>
<th></th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; absorption [nm]</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; emission [nm]</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>282 (0.39), 315 (0.15)</td>
<td>361</td>
<td>16.5±0.2%</td>
</tr>
<tr>
<td>13</td>
<td>282 (0.53), 315 (0.17)</td>
<td>372</td>
<td>27.0±0.3</td>
</tr>
<tr>
<td>14</td>
<td>282 (0.78), 295 (0.81), 313 (0.41)</td>
<td>357</td>
<td>41.1±0.4%</td>
</tr>
<tr>
<td>15</td>
<td>286 (1.84), 326 (0.58)</td>
<td>358</td>
<td>7.1±0.2%</td>
</tr>
<tr>
<td>16</td>
<td>286 (2.05), 313 (1.01)</td>
<td>373</td>
<td>23.8±0.3%</td>
</tr>
<tr>
<td>17</td>
<td>284 (0.78), 295 (0.81), 313 (0.67)</td>
<td>357</td>
<td>36.2±0.4%</td>
</tr>
</tbody>
</table>
305 nm; C) Tabulated summary of relevant data, including quantum yields, which were acquired on a Hamamatsu absolute PL quantum yield measurement system spectrophotometric grade DMF at 25°C and an excitation wavelength of 305 nm.

The photoluminescence spectrum exhibits a similar pattern, again as a result of the cadmium center forbidding charge transfer between the metal and ligand. There is a main emission from the ligand at ca. 360 nm from the ligand, as well as secondary emission at 510 nm, a consequence of intraligand charge transfer (ILCT). The quantum yield data are consistent with an antenna-type effect in that there is a progression of 7.1% to 23.8% to finally 36.2% for 15-17, respectively. This trend is entirely ligand based in that there are near identical values for the quantum yields of the non-complexed 12-14, although they were a little higher, presumably due to the cadmium creating a more probable triplet energy state. Summaries of all photochemical are presented in Table 1.

The electrochemical properties of 15-17 were analyzed via cyclic voltammetry in DMF with Ag/AgNO$_3$ as a reference electrode (Figure 3). All three complexes display similar electrochemical processes with a two quasi-reversible or irreversible single electron reductions at -1.65V and -2.41V. These reductions are consistent with the ability of the terpyridine ligand to accept two electrons. Also in each complex, there is a non-reversible oxidation process, due to the cadmium center. These values are similar with other terpyridine-cadmium metallocycles. There is no visible oxidation of the cadmium(II) metal species, presumably due to its $d^{10}$ electron configuration, as depicted in the cyclic voltammogram obtained for 16, shown in Figure 6.3.
6.3 Conclusions

In summary, novel bisterpyridine ligands functionalized with Moore-type, phenylacetylene antenna have been synthesized through the second generation. The cadmium-based hexameric macrocycles of these ligands have been characterized by $^1$H and $^{13}$C NMR spectroscopies as well as TWIM mass
spectrometry. Relative strengths of the complexes were also explored by MS. The metal complexes were also explored in great detail via both photo and electrochemistry. Quantum yields of the complexes were enhanced by the increased generation of the antenna, although there was no enhancement of this effect from the complexation with cadmium.

6.4 Experimental

**General Procedures.** Chemicals were purchased from Fisher Scientific, Sigma/Aldrich, or VWR, confirmed by $^1$H and $^{13}$C NMR spectroscopies, and used without further purification. Compounds 1-10 were synthesized via slight modifications to known procedures, and their $^1$H and $^{13}$C NMR spectra were identical to known structures. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al$_2$O$_3$ (IB-F) or SiO$_2$ (IB$_2$-F) and visualized by UV light. Column chromatography was conducted using basic Al$_2$O$_3$, Brockman Activity I (60-325 mesh) or SiO$_2$ (60-200 mesh) from Sorbent technologies. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 300 or 500 MHz spectrometer using CDCl$_3$ and referenced to 7.27 ppm, except where noted. Mass spectra were obtained on a Bruker Esquire electrospray ion trap mass spectrometer (ESI-MS), as described in detail elsewhere. Cyclic voltammetry was conducted on an Epsilon Electrochemical Workstation. Fluorescence spectra were collected on a Perkin-Elmer Fluorimeter in spectrophotometric grade DMF at 25°C. UV-vis spectra were collected on a Varian UV-vis spectrometer. Quantum yields were measured on a Hamamatsu absolute PL quantum yield.
measurement system spectrophotometric grade DMF at 25°C and an excitation
wavelength of 305 nm.

2-Methyl-3-butyne-4-(3',5'-di-tert-butylphenyl)-2-ol (2). A solution of
3,5-di-tert-butylbromobenzene (5.0 g, 18.6 mmol), 2-methyl-3-butyne-2-ol (1.81
mL, 18.6 mmol), Pd(PPh₃)₄ (200 mg, 150 µmol), CuI (1.9 mg, 10 µmol), and Et₃N
(85 mL) was freeze-pump-thawed (3X) and then refluxed for 24 hours, after
which the reaction was filtered through a silica plug, concentrated in vacuo, and
column chromatographed (SiO₂, CHCl₃, Rᵢ = 0.31) to give (69%) alcohol 2, as a
fluffy white solid: 3.7g; mp 102.3-102.7 °C; ¹H NMR: δ  1.3 (s, 18H, CH₃), 1.64
(s, 6H, CH₃), 7.28(s, 2H, ArH), 7.37 (s, 1H, ArH); ¹³C NMR: δ 31.53, 31.81,
34.98, 65.89, 84.43, 92.69, 121.88, 122.87, 126.09, 150.98.

3,5-Di-tert-butylphenylacetylene (3). A mixture of 2 (250 mg, 910
µmol), NaH (60% in mineral oil 320 mg, 8 mmol), and anhydrous toluene (50
mL) under argon was distilled until the temperature reached 110 °C (ca. 20 mL).
The remaining suspension was filtered and concentrated in vacuo to give 3 (51%),
as a white solid: 100 mg; mp 88.2-89.1°C (lit.²⁸¹ mp 87-88.5°C); ¹H NMR: δ 1.33
(s, 18H, CH₃), 3.04 (s, 1H, ≡CH), 7.37 (s, 2H, ArH), 7.43 (s, 1H, ArH); ¹³C
NMR: δ 31.31, 34.88, 72.92, 82.48, 120.92, 123.75, 126.78, 150.01.

3,5-Bis[(3',5'-di-tert-butyl)phenylacetylene]-3',3'-dimethyl-3'-hydroxy-
phenylacetylene (5). A mixture of 3 (380 mg, 1.77 mmol), 4 (255 mg, 710
µmol), Pd(PPh₃)₄ (93 mg, 74 µmol), CuI (15 mg, 7.8 µmol), and Et₃N (70 mL) in
THF (200 mL) was freeze-pump-thawed (3X) and then refluxed, After 24 h, the
mixture was filtered through a silica plug, concentrated in vacuo, and column chromatographed (SiO$_2$) eluting with a solvent mixture of EtOAc:hexanes (1:10) to give (72%) 5, as a white solid: 300 mg; $R_f$ = 0.19; mp 106.5-106.9 °C; $^1$H NMR: $\delta$ 1.36 (s, 36H, C$_{3}$H$_{3}$), 1.64 (s, 6H, CH$_{3}$), 2.07 (s, 1H, O$_{H}$), 7.38 (s, 4H, Ar$_{H}$), 7.42 (s, 2H, ArH), 7.57 (s, 2H, ArH), 7.63 (s, 1H, ArH); $^{13}$C NMR: $\delta$ 31.62, 31.79, 35.10, 73.13, 82.69, 89.46, 121.13, 122.64, 122.79, 123.96, 126.15, 127.00, 151.00, 152.22.

3,5-Bis[(3',5'-di-tert-butyl)phenylacetylene]phenylacetylene (6). A mixture of 5 (650 mg, 1.11 mol), NaH (60% in mineral oil, 400 mg, 10.4 mmol), and anhydrous toluene (50 mL) was distilled under argon until the temperature reached 110 °C (ca. 25 mL was distilled). The remaining suspension was filtered and concentrated in vacuo to give a brown oil that was column chromatographed (SiO$_2$) eluting with a solvent mixture of hexane:CH$_2$Cl$_2$ (4:1) to give (77%) pure 6, as a colorless film: 450 mg; $R_f$ = 0.68; mp 128-129 °C; $^1$H NMR: $\delta$ 1.43 (s, 18H, C$_{3}$H$_{3}$), 3.16 (s, 1H, ≡CH), 7.49 (s, 4H, Ar$H$), 7.51 (s, 2H, ArH), 7.72 (s, 2H, ArH), 7.83(s, 1H, ArH); $^{13}$C NMR: $\delta$ (ppm) 31.16, 34.76, 78.30, 82.24, 86.58, 91.92, 121.83, 122.89, 123.19, 124.38, 126.04, 134.39, 134.74, 150.98.

5-Iodoisophthalic Acid (8). To a stirred mixture of aqueous HCl (20 mL, 25%) and 5-aminoisophthalic acid (2.01 g, 11 mmol) cooled to 5° C, was added an aqueous solution (10 mL) of NaNO$_2$ (760 mg, 11 mmol) dropwise, keeping the temperature below 8°C. This mixture was stirred at 5 °C for 35 min. after which an aqueous solution (10 mL) of I$_2$ (150 mg, 11 mmol) and KI (1.83 g, 11.1 mmol) was added dropwise. The brown solution was stirred at 25 °C for 1.5 h, followed
by reflux for 1 h. The residual iodine was quenched with aq. NaHSO₃. The resulting cream solid was filtered and washed with water to give (64%) acid 8, as an off-white powder: 2.0 g; mp 284.1 – 285.0 °C (lit.²⁷⁹ mp 288-289 °C; ¹H NMR (DMSO-d₆): δ 7.35 (s, 2H, ArH), 7.64 (s, 1H, ArH); ¹³C NMR (DMSO-d₆): δ 95.51, 129.80, 133.78, 142.12, 165.94.

**3,5-Bis(hydroxymethyl)iodobenzene (9).** To a stirred solution of 8 (7.17 g, 25 mmol) in THF (100 mL) at 0 °C, was added BH₃·THF (1 M, 100 mL) dropwise then maintained at 25 °C for 12 h. The resulting solution was concentrated *in vacuo* and CHCl₃ (100 mL) was added. This organic mixture was extracted with aqueous K₂CO₃ (3 x 40 mL) and then satd. aqueous NaCl (3 x 40 mL). The combined organic layer was dried (MgSO₄), then concentrated *in vacuo* to give (96%) 9, as an off white solid: 6.3 g; mp = 126.1 – 127.0 °C; ¹H NMR: δ (ppm) 4.62 (s, 4H, CH₂), 7.38 (s, 1H, ArH), 7.70 (s, 2H, ArH); ¹³C NMR: δ 62.72, 95.10, 124.42, 133.80, 145.72.

**3,5-Diformyliodobenzene (10).** A mixture of 9 (5.27 g, 20.02 mmol), PCC (20.64 g, 95.8 mmol) mixed with Celite (21 g), and anhydrous CH₂Cl₂ (500 mL) was stirred mechanically for 5 h, after which the Celite/PCC was filtered and the filtrate was concentrated *in vacuo* to give a brown solid, which was flash chromatographed (SiO₂) eluting with CH₂Cl₂ to give (70%) pure 10, as a white solid: 3.62 g; Rₜ = 0.73; mp 122-122.5 °C (lit.²⁸² mp 117-119 °C); ¹H NMR: δ 8.32 (s, 1H, ArH), 8.44 (s, 2H, ArH), 10.02 (s, 2H, CHO); ¹³C NMR: δ 95.20, 129.79, 138.34, 143.12, 189.42.
3,5-**Bis(2,2′:6',2″terpyridyl)iodobenzene** (11). A mixture of 10 (1.5 g, 5.8 mmol), 2-acetylpyridine (3.11 g, 25.7 mmol), NaOH (1.39 g, 34.8 mmol), EtOH (100 mL), and 30% aqueous NH₃ (40 mL) was refluxed. After 8 h, the mixture was cooled to 25 °C, then filtered to give an off-white solid that was washed with EtOH to give (61%) 11, as a white solid: 2.3 g; mp 289-290 °C; ¹H NMR: δ 7.37 (t, 4H, *J* = 6.2 Hz, 5,5″-py), 7.90 (t, 4H, *J* = 8.1 Hz, 4,4″-tpy), 8.28 (s, 1H, ArH), 8.30 (s, 2H, ArH), 8.69 (d, 4H, *J* = 8.1 Hz, 3,3″-tpy), 8.75 (d, 4H, *J* = 3.6 Hz, 6,6″-tpy), 8.77 (s, 4H, 3′,5′-tpy); ¹³C NMR: δ 95.30, 119.07, 121.42, 123.95, 125.75, 136.64, 136.89, 141.54, 148.68, 149.15, 155.97, 156.17.

**G0 Bis**terpyridine 12 was published elsewhere.¹⁹⁶

**G1 Bis**terpyridine 13. A mixture of 11 (1.0 g, 1.5 mmol), 3 (645 mg, 3.0 mmol), Pd(PPh₃)₄ (104 mg, 90 µmol), CuI (34 mg, 180 µmol), NEt₃ (20 mL), and THF (200 mL) was freeze-pump-thawed (3X) and then refluxed for 24 h. The resulting brown suspension was filtered through Celite and concentrated *in vacuo* to give a tan solid that was recrystallized from CHCl₃/MeOH to give 13, as a white powder: 1.0 g, 90%; mp = 162-163 °C; ¹H NMR: δ 1.36 (s, 18H, CH₃), 7.37 (t, 4H, *J* = 6.0 Hz, 5,5″-tpy), 7.47 (s, 1H, ArH), 7.53 (s, 2H, ArH), 7.91 (t, 4H, *J* = 8.1 Hz, 4,4″-tpy), 8.19 (s, 2H, ArH), 8.29 (s, 1H, ArH), 8.72 (d, 4H, *J* = 7.8 Hz, 3,3″-tpy), 8.76 (d, 4H, *J* = 4.2 Hz, 6,6″-tpy), 8.84 (s, 4H, 3′,5′-tpy); ¹³C NMR: δ 31.62, 35.14, 87.70, 92.13, 119.42, 121.71, 122.12, 123.25, 124.17, 125.46, 125.96, 126.38, 131.26, 137.20, 140.05, 149.34, 149.76, 151.12, 156.27; ESI-MS m/z=753.5 [M+H].

148
**G2 Bisterpyridine 14.** A mixture of 11 (384 mg, 575 µmol), 6 (350 mg, 664 µmol), Pd(PPh₃)₄ (67 mg, 58 µmol), CuI (11 mg, 58 µmol), NEt₃ (20 mL), and THF (150 mL) was freeze-pump-thawed (3X) and then refluxed for 24 h. The resulting brown suspension was filtered through Celite and concentrated *in vacuo* to give a tan solid that was recrystallized from CHCl₃/MeOH to afford (65%) 14, as a white powder: 400 mg; mp 177.1-178.4 °C; ¹H NMR: δ 1.36 (s, 36H, CH₃), 7.34 (t, 4H, J = 6.0 Hz, 5,5''-tpyH), 7.47 (s, 4H, ArH), 7.74 (s, 1H, ArH), 7.80 (s, 2H, ArH), 7.87 (t, 4H, J = 8.1 Hz, 4,4''-tpyH), 8.16 (s, 2H, ArH), 8.31 (s, 1H, ArH), 8.72 (d, 4H, J = 7.8 Hz, 3,3''-tpyH), 8.76 (d, 4H, J = 4.2 Hz, 6,6''-tpyH), 8.84 (s, 4H, 3',5'-tpyH); ¹³C NMR: δ 31.4, 34.9, 86.8, 89.2, 89.7, 91.8, 119.1, 121.4, 121.9, 123.1, 123.7, 123.9, 124.4, 124.5, 126.0, 126.2, 131.1, 134.0, 134.3, 136.8, 140.0, 149.2, 149.2, 151.0, 156.1, 156.1; MALDI-MS = 1065.54 (M + H).

**G0 hexamer 15:** Published elsewhere

**G1 hexamer 16.** A stirred mixture of 13 (100.0 mg, 133.0 µmol) and Cd(NO₃)₂·4H₂O (41.0 mg, 133.0 µmol) in a solvent mixture of CHCl₃:MeOH (3:2, 25 mL). The solution was stirred at 25 °C for 12 h. and then concentrated *in vacuo* to give 16, as a cream solid: 127.0 mg; 98%; mp = >300 °C; ¹H NMR [CD₃OD:CDCl₃ (2:3)]: δ 1.34 (s, 108H, CH₃), 7.35 (s, 6H, ArH), 7.43 (t, 12H, J = 6.0 Hz, 5,5''-tpyH), 8.05-8.12 (m, 36H, 6,6''-tpyH; 4,4''-tpyH; ArH), 8.27 (s, 12H, ArH), 8.75 (s, 6H, ArH), 8.81 (d, 12H, J = 8.1 Hz, 3,3''-tpyH), 9.04 (s, 12H, 3',5'-tpyH); ¹³C NMR δ 30.7, 34.6, 86.6, 92.8, 121.6, 122.0, 123.3, 124.0, 125.8, 126.4, 127.2, 132.3, 138.4, 141.2, 149.3, 151.1; MS: m/z = 2906.2 [6L-2NO₃⁻]⁺², [3L-1NO₃⁻]⁺¹ (calcd m/z = 2906.1), 1916.8 [6L-3NO₃⁻]⁺³, [2L-1NO₃⁻]⁺¹ (calcd
$m/z=1916.7)$, 1422.11 $[6L-4NO_3^{-}]^{+4}$, $[3L-2NO_3^{-}]^{+2}$ (calcd $m/z=1422.1$), 927.4, $[6L-6NO_3^{-}]^{-6}$, $[3L-3NO_3^{-}]^{-3}$, $[2L-2NO_3^{-}]^{-2}$, $[1L-1NO_3^{-}]^{+1}$ (calcd $m/z=927.4$).

**G2 hexamer 17.** A stirred solution of 13 (100.0 mg, 93.0 µmol) and Cd(NO$_3$)$_2$·4H$_2$O (29.0 mg, 93.0 µmol) in a solvent mixture CHCl$_3$:MeOH (3:2; 25mL) was maintained at 25 °C for 12 h. and then concentrated *in vacuo* to give 17, as a cream solid: 127.0 mg; 98%; mp >300 °C; $^1$H NMR [CD$_3$OD:CDCl$_3$(2:3)]: δ 1.33 (s, 216H, CH$_3$), 7.39 (s, 24H, ArH), 7.43 (s, 6H, ArH), 7.46 (s, 12H, ArH), 7.58 (t, 12H, $J = 6.3$ Hz, 5,5''-tpyH), 8.20-8.29 (m, 24H, 6,6''-tpyH; 4,4''-tpyH), 8.44 (s, 12H, ArH), 8.81 (d, 18H, $J = 7.8$ Hz, 3,3''-tpyH, ArH overlapping), 9.22 (s, 12H, 3',5'-tpyH); $^{13}$C NMR: δ 31.2, 34.8, 86.3, 88.6, 90.4, 92.0, 121.6, 122.2, 123.1, 123.9, 124.6, 125.6, 125.9, 127.3, 132.2, 133.8, 134.8, 138.4, 141.1, 149.3, 151.0; ESI-MS: $m/z= 1890.7$ $[6L-4NO_3^{-}]^{+4}$, $[3L-2NO_3^{-}]^{+2}$ (calcd $m/z = 1890.7$), 1500.3 $[6L-5NO_3^{-}]^{+5}$, $[2L-1NO_3^{-}]^{+1}$ (calcd $m/z=1500.2$), 1239.5, $[6L-6NO_3^{-}]^{-6}$, $[3L-3NO_3^{-}]^{-3}$, $[2L-2NO_3^{-}]^{-2}$ (calcd $m/z=1239.8$).
CHAPTER VII

SUMMARY

Three sets of constitutional supramolecular isomers have been isolated utilizing a <tpy-M\textsuperscript{II}-tpy> connectivity. The first set of isomers relied on a stoichiometric self-assembly process for near quantitative yield of bowtie and butterfly-type compounds. The second two sets of isomers utilized the rapid rate of formation the <tpy-Fe\textsuperscript{II}-tpy> bisterpyridine kinetic complex. The resulting robust complexes consisted of one thermodynamically stable isomer and one folded or strained isomer. These macroarchitectures were studied in depth utilizing various ESI-MS techniques coupled with molecular modeling to elucidate the structure dynamics of the undesirable isomer.

Utilizing the robust <tpy-Ru\textsuperscript{II}-tpy> connectivity, a series of novel folded tetramers, or Dondorff rings, were self-assembled and isolated. Outside of traditional characterization, in-depth photophysical studies were performed on the resulting tetramers, including transient absorption spectroscopy, resolving lifetimes on the order of 1-2 ns. ESI-TWIM-MS was used to verify the presence of a single species. The use of gMS\textsuperscript{2} confirmed the relative strengths of the metallomacrocycles, with the order being Cd\textsuperscript{II} < Zn\textsuperscript{II} < Fe\textsuperscript{II} < Ru\textsuperscript{II}, a trend consistent with previously calculated data.
The thermodynamic terpyridine equilibrium methodology was used in the synthesis of six novel rigid terpyridine-based metallotriangles. These triangles were characterized by 1D and 2D NMR techniques, as well as ESI-TWIM-MS. The MS data provided pristine isotope patterns consistent with expected values. Furthermore, pairing the hexavalent metallomacrocycles with a benzene hexacarboxylate anion resulted in the formation of nanofiber bundles that were responsive to SAXD, and when coupled with molecular simulations, afforded expected spacing values for the proposed fiber. Removal of counterions was verified by $^{31}$P and $^{19}$F NMR spectroscopies.

Moore-type molecular antennae were synthesized and used in the modification of a 120°-modified bisterpyridine ligand. This family of ligands was cyclized with Cd$^{II}$ to form the corresponding hexamers in near quantitative yields, as confirmed via $^1$H NMR and ESI-MS. Determination of the quantum yields of the hexamers elucidated a trend of enhancement as a result of increased generation.
PUBLICATIONS


7. Newkome, G. R.; Wang, J. L.; Li, X; Wesdemiotis, C; Lu, X; Schultz, A; Sarkar, R; Stoichiometric Self-Assembly of Symmetric Supramolecular Complexes Polymer Preprints 2011, 52(2), 922-923
REFERENCES


160


282. Liu, Y.; Lahti, P. M. Molecules 2004, 9, 725-745.