TERPYRIDINE-BASED, COORDINATION-DRIVEN, 2D AND 3D SUPRAMOLECULAR ARCHITECTURES

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ABSTRACT

Beyond traditional molecular chemistry, supramolecular self-assembly focuses on generating highly complicated and well-defined structures by non-covalent interactions. [2,2':6',2"]-Terpyridine (tpy) ligand and <tpy-M\textsuperscript{II}-tpy> (M = metal) connectivity have been widely used to construct different shapes in this area. One-step and stepwise self-assemblies are of great importance to construct precise architectures.\textsuperscript{[1]-[3]} In metal-coordination, using different transition metals can form different complexes sometimes due to different coordination effects.

Four novel 2D and 3D terpyridine-based macromolecules have been designed and synthesized: a 2D hydrophilic bowl-like metallotriangle, a 2D bowtie-shaped complex, a 3D metallotriangle, and a 3D isomeric square-shaped nanocage. These supramolecules consist of terpyridine-based multidentate ligands and transition metal ions, which included: Ru\textsuperscript{II}, Zn\textsuperscript{II}, and Cd\textsuperscript{II}. Characterization was accomplished by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, 2D correlation NMR spectroscopy (COSY), 2D nuclear Overhauser effect NMR spectroscopy (NOESY), matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS), electrospray ionization traveling wave ion mobility mass spectrometry (ESI-TWIM-MS), transmission electron microscope (TEM), and molecular modeling.
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CHAPTER I
INTRODUCTION

Since the discovery of the double-layer organic light-emitting diode (OLED) in 1987,[4] research has been focused towards the development of full color displays and white light devices. Coordination compounds are of considerable importance to fabricating these devices,[5][6] because of their high stability and flexibility.[7]-[10] Over the past decades, the self-assembly of metallo-supramolecules has attracted attention in this particular arena. Among various metal complexes, [2,2':6',2"]-terpyridine-based (tpy) metal-organic hybrids are found to be important due to their unique electrochemical and photophysical properties.[11]-[13] Terpyridine can coordinate diverse metal ions (RuⅡ, CdⅡ, FeⅡ, and ZnⅡ) through stable ligand-metal-ligand connectivity,[14]-[19] they have been shown to offer great potential in this field. As for example, RuⅡ, with the filled electron shell, has application in the development of new photoluminescent (PL) or electroluminescent (EL) devices, as well as sensor materials.[20]-[21] Moreover, by coordinating different metal ions or attaching polymer chains, the photophysical behavior of these organic ligands can be tuned to show enhanced performance.[22]-[23]

There are many elegant examples that have been demonstrated by Lehn,[24-28] Stang,[29-31] Fujita,[32-33] Mirkin,[34-36] Newkome,[37-39] and others.[40-46] In order to the study the structures of supramolecules, electrospray ionization mass spectrometry (ESI-MS) is a very useful tool to characterize a wide range of discrete metallo-supramolecules of differe-
nt size and shape.\textsuperscript{[23]} The basic mechanism for ESI-MS is that it leaves only the unaltered and stable species, which reflects the stability of the complex.\textsuperscript{[47]} ESI-MS shows a set of regular peaks if one complete structure was formed. According to the number of peaks, we can calculate the total mass and confirm the final complex. To complement the ESI-MS, traveling wave ion mobility mass spectrum (TWIM-MS) affords a chromatography approach to separate ions by their charge and shape/size in the TWIM region and by m/z in the following mass analyzer. In order to further distinguish between isomeric structures, NMR and X-ray act as useful complementary instruments. Isomers show different patterns in the 1D NMR spectrum and X-ray analysis can offer data to model the exact structure, based on three-dimension coordinate system. NOESY NMR and COSY NMR are often used to determine through-space \textsuperscript{1}H-\textsuperscript{1}H interactions and assign connectivity of adjacent hydrogen, in order to pinpoint the position of each hydrogen in 1D NMR. Moreover, transmission electron microscope (TEM) images provide an insight into the structures' size, geometry, and aggregation pattern.

In my thesis, Chapter 1 discusses some basic concepts about supramolecules and supramolecular chemistry. Also some typical 2D and 3D metallo-supramolecules and coordinated metals are introduced in this Chapter. Chapter 2 provides the relevant data to support the formation of each structure. It also provides the analysis and explanation for each structure. Chapter 3 introduces how to synthesize each ligand and their final complexes in specific details. Chapter 5 summarizes the major results of these projects.
CHAPTER II

BACKGROUND

2.1 Development in metallo-supramolecular complex

This term, supramolecule, was initially introduced in 1937. In 1987, the French scientist, J.-M. Lehn was awarded the Nobel Prize for his part in introducing the concept "supramolecular chemistry to the world." And he said: "The supramolecular chemistry exists in molecular assemblies and molecular aggregation." In this research area, according to different degrees-of-strength, orientation, and nature of bonding, intermolecular interactions can be divided into: the coordination bond, hydrogen bond, π-π accumulation, electrostatic interactions, and hydrophobic interactions and so on. Following the supramolecular self-assembly principles, using the intermolecular interaction force, as a tool, new molecules can be assembled from multiple designer building blocks monomers. And these new macromolecules still maintain single, molecular unique properties.

When a metallo-supramolecular self-assembly occurs in solution, a metal ion can generally react with multiple ligands to form stable coordination bonds. The final structure of these supramolecules relies on the chemical composition of the system, temperature, concentration, and the equilibrium constant. When the molar ratio of metal ions to ligands is 1:1, the system could form a polymer chain; at higher concentration, the higher degree-of-polymerization will happen. In order not to form a polymer, it is necessary to maintain proper concentration during self-assembly.
Chan et al.\textsuperscript{[50]} reported the facile assembly of macrocycles (98%) using a bis-tpy ligand with Cd(NO$_3$)$_2$·4H$_2$O in dilute solution, however, increasing the concentration results in the formation of a polymeric material under same reaction condition (Figure 2.1.1). So different structures can be formed under different concentration.

### 2.2 2D Metallo-supramolecules

Self-assembly is an important tool to generate biomolecules, such as DNA, proteasomes, etc. In this field, coordination-driven assembly has large potential in the pursuit of biological system complexity. In this regard, [2,2′:6′,2″]-terpyridine had been widely used to construct these macromolecules due to its ability to bind diverse metal ions.

Sarkar et al.\textsuperscript{[51]} reported the formation of first-generation Sierpiński triangle, using tpy-Cd$^{II}$-tpy connectivity. This was the first Sierpiński triangle synthesized using tailored
tpy building blocks, since Waclaw Sierpiński\textsuperscript{[52]} formulated an equilateral triangular fractal in 1915. A 1:1 ratio of tetrakis(terpyridine) and bis(terpyridine) was coupled with precisely three equivalents of Cd\textsuperscript{II} to form the desired architecture. The triangle was characterized by NMR, ESI-MS, ESI-TWIM-MS, and TEM. This fascinating result opens a door to self-assembly of higher generation Sierpiński triangles.

Schultz \textit{et al.}\textsuperscript{[53]} synthesized the novel isomeric molecular butterfly and bowtie, which are typical examples of discrete control of supramolecular self-assembly (Figure 2.2.1). Their two structures show the same charge state pattern in ESI-MS spectrum, but can easily be distinguished with the aid of TWIM-MS and collision cross section, the molecular ions have different drift times and the bowtie complex has a larger collision cross section than that butterfly-shaped isomer. Both of the structures were confirmed by ESI-MS, TWIM-MS, and \textsuperscript{1}H NMR.

![Figure 2.2.1 Synthesis of the Zn\textsuperscript{II} analogues of the bis triangles 10 and 12 with 2 equiv of 6 (25 °C, 1 h) [reprinted with permission from \textit{J. Am. Chem. Soc.} \textbf{2012}, \textit{134}, 7672–7675. Copyright 2012 American Chemical Society].}
Inspired by this first generation, two-dimensional Sierpiński triangle,\(^{[51]}\) Chakraborty\(^{[54]}\) et al. reported the design and synthesis of a bimetallic metallotriangulane using a programmed step-wise synthetic protocol. The structure consists of two different metal ions: Ru\(^{II}\) and Zn\(^{II}\), with nine metal ions in total. The pure structure was well-characterized. The success of synthesizing the bimetallic architecture gives a new route to synthesize three or more metallo-centers supramolecules in the future.

2.3 3D Cages

Nowadays, there are still only a few 3D structures constructed through metal coordination\(^{[55-56]}\) due to the limited access to tailored building blocks and to many unexpected coordination possibilities, especially oligomers of polymeric products. Designer terpyridine-based 3D architectures are very appealing in view of the potential to address special issues that are tailored to the specific need.

Xie et al.\(^{[57]}\) reported the first terpyridine-based, kinetically controlled, highly symmetric supramolecular nanosphere. Four tridentate terpyridinyl building blocks

![Figure 2.3.1 Synthesis of the Ru\(^{II}\)-based, metallo-nanosphere using Ru(DMSO)\(_4\)Cl\(_2\) [reprinted with permission from J. Am. Chem. Soc. 2014, 136, 8165–8168. Copyright 2014 American Chemical Society].]
reacted with six Ru\textsuperscript{II} to form this complex (Figure 2.3.1) in moderate (35%) yield. This reaction is not under thermodynamic control, relying instead on kinetic control. As Ru\textsuperscript{II} is a non-labile metal ion, so the self-assembly is non-reversible. This nanosphere exhibits excellent stability in the presence of both strong acid and strong base, such as concentrated nitric acid and sodium hydroxide, and is also stable at high temperature.

Chakraborty \textit{et al.}\textsuperscript{[58]} reported the formation of one nanosphere and two temperature-dependent irreversible isomeric 3D nanocages using a \textit{tristerpyridine} ligand. The nanocage has potential for biomedical and optoelectronic applications. To introduce rigidity, \textit{tristerpyridine} monomer was converted to the corresponding monoRu\textsuperscript{II}-dimer, then the dimer assembled with Fe\textsuperscript{II} to construct the nanocage (Figure 2.3.2). The interesting part for this research is the influence of temperature. At 25 °C, only nanocage 6 was formed in high yield; however, upon 65 °C, two nanocages (6 and 7) formed and can be separated by column chromatography. The treatment of \textit{tristerpyridine} ligand with Ru\textsuperscript{II} results in the formation of nanosphere 4, as the only discrete architecture. The structure of nanosphere 4 was confirmed by single crystal X-ray analysis. The molecules packed together in a unique pattern, which look like three adjacent rings trapped within each other (Figure 2.3.3).
Figure 2.3.2  Synthesis of molecular nanosphere 4 and stepwise assembly of nanoarchitectures 6, 7, and 8 [reprinted with permission from J. Am. Chem. Soc. 2017, 139, 3012-3020. Copyright 2017 American Chemical Society].

Figure 2.3.3  a) Single crystal structure of nanosphere 4; b) The packing of four molecules of 4 showing ball-like stacking, which is based on an X-ray analysis [reprinted with permission from J. Am. Chem. Soc. 2017, 139, 3012-3020. Copyright 2017 American Chemical Society].
2.4 Coordinated metal ions

In self-assembly of terpyridine based macromolecules, Ru\textsuperscript{II}, Fe\textsuperscript{II}, Zn\textsuperscript{II}, and Cd\textsuperscript{II} are often used as coordinating metals to connect the two tpy ligands. There are two kinds of driving force: kinetic and thermodynamic. Reacting with labile metals, such as Cd\textsuperscript{II} and Zn\textsuperscript{II}, the reaction is reversible under thermodynamic controls,\textsuperscript{[59]} however, in case of non-labile metal ions, such as Ru\textsuperscript{II} and Fe\textsuperscript{II}, the reaction is non-reversible under kinetic control. The formation of terpyridine-based nanostructures is decided by both kinetic and thermodynamic control; previous studies showed an order of kinetically dominated complexation increase as Cd\textsuperscript{II}<Zn\textsuperscript{II}<Fe\textsuperscript{II}<Os\textsuperscript{II}<Ru\textsuperscript{II}.\textsuperscript{[60]} Recently, Ludlow \textit{et al.}\textsuperscript{[61]} reported that the formation of different structures by using labile and non-labile metals. With metals (\textit{e.g.} Fe\textsuperscript{II}) that can form strong coordinative bonds, the main product is triangle by creation of irreversible \textless tpy-Fe\textsuperscript{II}-tpy\textgreater complexes; in contrast, with metals (\textit{e.g.} Zn\textsuperscript{II}) capable of forming more labile coordinative bonds, the reaction finally reaches a dynamic equilibrium between the entropically favored dimer and the enthalpically favored trimer.
CHAPTER III

SELF-ASSEMBLY AND CHARACTERIZATION OF HYDROPHILIC BIMETALLIC METALLOTRIANGLE

3.1 Introduction

Although the stepwise self-assembly is a widely used strategy to overcome certain entropically disfavored limitation and to form complicated functional architectures, it is still a big challenge to well-design suitable building blocks and to utilize their coordination sequence to fabricate specific supramolecules. Herein, we report high yield preparation of a bimetallic metallotriangle through <tpy-MII-tpy> (M = RuII, ZnII) connectivity, which is a bowl-like structure. This structure was constructed by using both synthesis and self-assembly protocols.

3.2 Results and discussion

The bisterpyridine 1 was synthesized through a Suzuki coupling\textsuperscript{[62]} of 1,2-tetraethylene glycol-4,5-dibromobenzene\textsuperscript{[66]}, which was structurely confirmed by $^1$H NMR (Figure 3.2.1), and $^{13}$C NMR (Figure 3.2.1). In $^1$H NMR spectrum, the aromatic region of ligand 1 showed one set of distinctive terpyridine peaks, and aromatic phenyl-spacer peaks. Two sharp singlets existed at 8.72 and 7.08 ppm assigned to 3',5'-tpyH and PhH, respectively. The bisterpyridine "V" precursor 1 with hydrophilic long chain was reacted with Ru(DMSO)\textsubscript{4}Cl\textsubscript{2}\textsuperscript{[64]} to generate the hydrophilic RuII-dimer 2, which was well-characterized by $^1$H NMR (Figure 3.2.3), $^{13}$C NMR (Figure 3.2.5), and COSY NMR (Figure
3.2.4). It clearly showed two kinds of 3',5'-typyH singlets, one was at 9.19 ppm, another was at 8.65 ppm for coordinate and non-coordinate units, respectively. This hydrophilic RuII-dimer 2 with chloride counterions was converted to the corresponding RuIII-adduct 3 by reacting with RuCl₃·3H₂O. Then this RuIII-adduct 3 was treated with "X" monomer 4 to generate mono-capped terpyridine 5 in a CHCl₃ and MeOH mixed solvent (Scheme 3.2.1). The compound 5 was confirmed by ¹H NMR (Figure 3.2.6) and COSY NMR (Figure 3.2.7). There are four sets of 3',5'-typyH peaks in ¹H NMR spectrum, which is in consistent with this structure. And the upfield shift of coordinated 6,6'-typyH from 7.43 ppm to 7.18 ppm further suggested the metal-coordination. Furthermore, structure 5 was confirmed by ESI-MS spectrum (Figure 3.2.8). A series of expected peaks correspond to compound 5 with charge state from 4+ to 6+ can be observed, which was in full agreement with the theoretical pattern.

Scheme 3.2.1 Synthesis of monocapped-terpyridine 5.
Figure 3.2.1 $^1$H NMR spectra (500 MHz, 300K) of 1,2-tetraethylene glycol-4,5-bisterpyridine 1 in CDCl$_3$.

Figure 3.2.2 $^{13}$C NMR spectra (125 MHz, 300K) of 1,2-tetraethylene glycol-4,5-bisterpyridine 1 in CDCl$_3$. 
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Figure 3.2.5 $^{13}$C NMR spectra (125 MHz, 300K) of hydrophilic Ru$^{II}$-dimer 2 in CD$_3$OD.

Figure 3.2.6 $^1$H NMR spectra (500 MHz, 300K) of hydrophilic mono-capped terpyridine 5 in CD$_3$OD and CDCl$_3$ (3:1, v/v).
Figure 3.2.7  2-D NOESY NMR spectra (500 MHz, 300 K) of hydrophilic mono-capped terpyridine 5 in CD$_3$OD and CDCl$_3$.

Figure 3.2.8  ESI mass spectra for the hydrophilic mono-capped terpyridine 5.
A precise 1:1 ratio of ligand 5 and Zn(NO$_3$)$_2$·6H$_2$O in a mixture of CHCl$_3$ and MeOH (1:1; v/v) at 25 °C gave the desired hydrophilic bowl 6, in quantitatively yield, following by exchange of counterions with PF$_6^-$ (Scheme 3.2.2). The final bowl-like structure 6 was confirmed by $^1$H NMR (Figure 3.2.9) and 2D NOESY NMR (Figure 3.2.10). In $^1$H NMR spectrum, distinguishing features of four sharp singlets at 9.04, 9.03, 9.01, and 9.02 ppm were included because compound 6 was comprised of four non-equivalent terpyridine moieties. The drastic downfield shift of the 3',5'-tpyH from 8.61 ppm to 9.02 ppm compared to uncoordinated mono-capped terpyridine strongly supported the formation of Zn$^{II}$ complex.

Structure 6 was confirmed by ESI-MS spectrum (Figure 3.2.11). A series of expected peaks correspond to hydrophilic bowl 6 with charge state from 8+ to 15+ can be observed. The experimental isotope pattern of each peak was in full agreement with the theoretical pattern. The structure was further confirmed by ESI-TWIM-MS. In the 2D TWIM-MS plot, it showed charge states from 12+ to 18+, which displayed single and narrow bands with the expected step pattern (Figure 3.2.12).
Scheme 3.2.2  Synthesis of hydrophilic bowl complex 6.

Figure 3.2.9  $^1$H NMR spectrum (500 MHz, 300 K) of hydrophilic bowl 6 in CD$_3$CN.
Figure 3.2.10 2-D NOESY NMR spectra (500 MHz, 300 K) of hydrophilic bowl 6 in CD$_3$CN.

Figure 3.2.11 ESI mass spectra for the hydrophilic bowl 6.
3.3 Conclusion

Under thermodynamic control, a giant, hydrophilic, nanobowl was generated successfully through programmed step-wise procedures in high yield without further purification. Characterization was accomplished by NMR and ESI-TWIM-MS. The aggregation behavior of this hydrophilic metallotriangle will be studied using TEM in organic and aqueous solution mixture in near future.

3.4 Experimental section

**General procedures.** Solvents were commercially purchased from Sigma-Aldrich with 99% purity. RuCl$_3$·3H$_2$O,$^{[63]}$ RuCl$_2$(DMSO)$_4$,$^{[64]}$ Pd(PPh$_3$)$_2$Cl$_2$,$^{[65]}$ 1,2-tetraethylene glycol-4,5-dibromobenzene,$^{[66]}$ and 4’-(4-boronatophenyl)[2,2’:6’,2’”]terpyridine$^{[70]}$ were made by previous lab colleagues.

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 Al₂O₃, Brockman Activity I (60-325 mesh). ¹H and ¹³C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA). Data analyses were collected using the MassLynx 4.1 and DriftScope 2.1 programs provided by Waters. Energy minimization of the supramolecular assembly was conducted with the Materials Studio version 8.0 program, using Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. The geometry was optimized after each cycle and all optimizations used a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters.

1,2-Tetraethylene glycol-4,5 bisterpyridine 1: To a 1 L 3-necked round flask, 1,2-tetraethylene glycol-4,5-dibromobenzene⁶⁶ (1.97 g, 3.2 mmol), 4′-(4-boronatophenyl) [2,2′:6′,2″]terpyridine⁷⁰ (3.23 g, 9.5 mmol), Na₂CO₃ (1.36 g, 12.8 mmol), and Pd(PPh₃)₂Cl₂⁶⁵ (0.52 g, 0.64 mmol) were added. Then a solvent mixture of water (120 mL), toluene (200 mL), and ethanol (80 mL) was added under a nitrogen atmosphere. The system was refluxed at 100 °C for 48 hours. After cooling to 25 °C, the reaction mixture was extracted with CHCl₃ (3×100 mL). The combined extract was collected and dried by anhydrous MgSO₄ for 6 hours, then concentrated in vacuo to give a solid, which was column chromatographed (Al₂O₃) eluting with CH₂Cl₂/MeOH (35:1) to give 1: 1.38 g
(40%); m.p. > 250 °C; $^1$H NMR (500 MHz, CDCl$_3$, ppm) δ 8.72 (s, 4H, 3',5'-tpyH), 8.68 (d, $J$ = 10 Hz, 4H, 3,3''-tpyH), 8.64 (d, $J$ = 8 Hz, 4H, 6,6''-tpyH), 7.86 (dd, $J$ = 8 Hz, 4H, 4,4''-tpyH), 7.83 (d, $J$ = 8 Hz, PhH$^a$), 7.36 – 7.29 (m, 8H, 5,5''-tpyH and PhH$^b$), 7.10 (d, $J$ = 8 Hz, 4H, PhH$^a$), 4.31 (t, $J$ = 5 Hz, 4H, $2 \times$ CH$_2$), 3.94 (dd, $J$ = 6 Hz, $2 \times$ CH$_2$), 3.80 (dd, $J$ = 6 Hz, 4H, $2 \times$ CH$_2$), 3.72 (dd, $J$ = 6 Hz, 4H, $2 \times$ CH$_2$), 3.69 – 3.63 (m, 8H, $4 \times$ CH$_2$), 3.60 (t, $J$ = 5 Hz, 4H, $2 \times$ CH$_2$); $^{13}$C NMR (125 MHz, CDCl$_3$, ppm) δ 156.26, 155.83, 149.76, 149.05, 142.05, 136.89, 136.27, 133.26, 130.46, 126.99, 123.77, 121.39, 118.76, 117.13, 72.64, 70.87, 70.68, 70.30, 69.85, 69.24, 61.68, 50.81.

$\text{[Ru}^{II}\text{](1)z(Cl}^-\text{)z]}$ 2. To a 500 mL round bottom flask, 1,2-tetraethylene glycol-4,5-bisterpyridine 1 (1.00 g, 0.9 mmol) and Ru(DMSO)$_4$Cl$_2$[64] (146 mg, 0.3 mmol) were added into a solvent mixture of CHCl$_3$ (150 mL) and MeOH (150 mL). Then the system was stirred at 80 °C for 36 hours. The reaction mixture was cooled to 25 °C and concentrated in vacuo to give a red powder, which was then column chromatographed (Al$_2$O$_3$) eluting with CHCl$_3$/MeOH (10:1; v/v) to give 2: 370 mg (36%); m.p. > 300 °C; $^1$H NMR (500 MHz, CD$_3$OD, ppm) δ 9.19 (s, 4H, coordinated 3',5'-tpyH), 8.80 (d, $J$ = 8 Hz, 4H, coordinated 3',5'-tpyH), 8.68 (s, $J$ = 2 Hz, 4H, free 3',5'-tpyH), 8.66 (d, $J$ = 2 Hz, 4H, free 3,3''-tpyH), 8.64 (dd, $J$ = 5 Hz, 4H, coordinated 6,6''-tpyH), 8.14 (d, $J$ = 8 Hz, 4H, coordinated-PhH$^a$), 8.04 – 7.91 (m, 8H, 4,4''-tpyH), 7.89 (d, $J$ = 8 Hz, 4H, free PhH$^a$), 7.56
(d, \( J = 8 \) Hz, 4H, coordinated PhH\(^b\)), 7.41 – 7.44 (m, 12H, coordinated 6,6"-tpyH and free 5,5"-tpyH), 7.27 – 7.14 (d, \( J = 13 \) Hz, 4H, free 5,5"-tpyH), 4.45 – 4.26 (m, 8H, 4 \( \times \) CH\(_2\)), 4.05 – 3.90 (m, 8H, 4 \( \times \) CH\(_2\)), 3.77 – 3.61 (m, 40 H, 20 \( \times \) CH\(_2\)), 3.62 – 3.54 (m, 8H, 4 \( \times \) CH\(_2\)); \(^{13}\)C NMR (125 MHz, CD\(_3\)OD, ppm) \( \delta \) 158.64, 154.09, 152.11, 151.97, 151.10, 147.56, 145.57, 145.05, 144.70, 144.52, 144.44, 139.52, 138.23, 134.47, 133.02, 132.19, 129.89, 129.28, 128.87, 127.24, 126.64, 123.98, 123.85, 122.91, 121.91, 119.98, 117.87, 117.45, 114.48, 113.47, 112.92, 73.34, 73.09, 72.83, 68.75, 68.69, 66.84, 66.81, 66.64, 66.62, 66.30, 65.83, 65.39, 65.12, 57.56, 57.42.

[(Ru\(^{III}\))\(_2\)(Ru\(^{II}\))(2)(Cl\(^-\))]\(_8\) 3. To a 100 mL round bottom flask, Ru\(^{II}\)-dimer-1,2-tetraethylene glycol-4,5-bisterpyridine 2 (300 mg, 0.12 mmol), RuCl\(_3\)·3H\(_2\)O\(^{[63]}\) (61 mg, 0.29 mmol), and EtOH (50 mL) were added. The system was refluxed at 80 °C for 36 hours. The reaction mixture was cooled to 25 °C, filtered, and washed with EtOH (100 mL) for three times and then dried in vacuo to give a deep brown product 3 without further purification: 320 mg (98%). m.p. > 350 °C.
[(RuII)₂(2,3,6,7-Tetrakis(4-terpyridinylphenyl)-9,10-dimethyl-9,10-ethan anthracene) (Cl⁻)] 5. To a 500 mL round flask, adduct 3 (46 mg, 18 µmol), 2,3,6,7-tetrakis(4-terpyridinylphenyl)-9,10-dimethyl-9,10-ethan anthracene (tetraterpyridine) 4[69] (33 mg, 22 µmol), and a solvent mixture of CHCl₃/MeOH (300 mL, 1:1) were added. Then 4-ethylmorpholine (100 µL) was added into the solution slowly. The reaction was refluxed at 70 °C for 36 hours. After cooled to 25 °C, the reaction mixture was concentrated in vacuo to give a deep red solid, which was column chromatographed (Al₂O₃) eluting with a mixture of CHCl₃/MeOH (40:1; v/v) firstly to remove the trace monomer and fluorescent component 5, then CHCl₃/CH₃OH (18:1; v/v) to collect the product 5: 24 mg (33%); m.p. > 400 °C; ¹H NMR (500 MHz, CD₃OD, ppm) δ 9.20 (s, 12H, complexed 3',5'-tpyH), 8.86 – 8.88 (m, 12H, complexed 3,3''-tpyH), 8.58 – 8.61 (m, 12H, free 3',5'-tpyH, free 3,3''-tpyH and free 6,6''-tpyH), 8.15 – 8.16 (m, 12H, complexed PhH), 7.82 – 7.87 (t, 12H, complexed 4,4''-tpyH), 7.77 – 7.81 (d, 4H, J = 8 Hz, free PhH), 7.63 (s, 2H, free PhH), 7.52 – 7.54 (m, 12H, complexed PhH), 7.42 (m, 4H, free 6,6''-tpyH), 7.38 (m, 4H, free PhH), 7.36 (m, 4H, free 4,4''-tpyH), 7.19 – 7.21 (t, 12H, complexed 5,5''-tpyH), 7.16 (s, 6H, complexed PhH), 4.42 – 4.28 (m, 8H, 4 × CH₂), 3.80 – 3.96 (m, 8H, 4 × CH₂), 3.76 – 3.62 (m, 40H, 20 ×
CH₂), 3.58 (m, 8H, 4 × CH₂). ESI-MS (m/z): 998.6183 [5-4Cl⁻]^{4+} (calcd m/z =998.5449), 791.4839 [5-5Cl⁻]^{5+} (calcd m/z = 791.4390), 653.5742 [5-6Cl⁻]^{6+} (calcd m/z =653.5402).

[(Ru^{II})_{9}(Zn^{II})_{3}(4)(PF_{6}^-)_{24}] hydrophilic bowl 6. To a solution of ligand 4 (10 mg, 2.6×10^{-3} mmol) in a mixture of CHCl₃/MeOH (12 mL, 1:1), a solution of Zn(NO₃)₂·6H₂O (121 µg, 4×10^{-3} mmol) in MeOH (400 µL) was added slowly. The reaction was stirred for 12 hours at 25 °C, then aqueous solution of excess NH₄PF₆ was added to obtain a red precipitate, which was filtered and washed three times with MeOH and water to remove excess NH₄PF₆, then dried in vacuo to give the final complex 6, as red solid; m.p. > 400 °C; ¹H NMR (500 MHz, CD₃CN, ppm) δ 9.02 – 9.04 (m, 48H, complexed 3',5'-tpyH), 8.65 – 8.66 (m, 48H, complexed 3,3''-tpyH), 8.02 – 8.20 (m, 72H, complexed PhH^a, Zn coordinated PhH^c, Ru coordinated PhH^c without long alkyl chain), 7.86 – 7.88 (m, 48H, complexed 4,4''-tpyH), 7.68 (d, J = 3 Hz, 12H, Zn coordinate 6,6''-tpyH), 7.62 – 7.64 (m, 48 H, PhH^b), 7.44 (d, J = 5 Hz, 12H, Ru coordinated 6,6''-tpyH without alkyl long chain), 7.34 (m, 24H, Ru coordinated PhH^c with long alkyl chain), 7.16 (m, 48H, complexed 5,5''-tpyH), 4.40 (t, J = 6 Hz, 24 H, 12 × CH₂), 3.96 (t, J = 6 Hz, 24 H, 12 × CH₂), 3.84 – 3.73 (m, 120 H, 60 × CH₂), 3.74 (t, J = 5 Hz, 24H, 12 × CH₂). ESI-MS (m/z): 1784.4124 [6-8PF_{6}^-]^{8+} (calcd m/z = 1784.3676), 1570.6903 [6-9PF_{6}^-]^{9+} (calcd
$m/z = 1570.6613$, 1398.5297 $[\text{6-10PF}_6^-]^{10+}$ (calcd $m/z = 1398.5995$), 1258.2872 $[\text{6-11PF}_6^-]^{11+}$ (calcd $m/z = 1258.2762$), 1141.6007 $[\text{6-12PF}_6^-]^{12+}$ (calcd $m/z = 1141.5927$), 1042.6348 $[\text{6-13PF}_6^-]^{13+}$ (calcd $m/z = 1042.6273$), 957.8521 $[\text{6-14PF}_6^-]^{14+}$ (calcd $m/z = 957.8657$) and 884.3257 $[\text{6-15PF}_6^-]^{15+}$ (calcd $m/z = 884.3437$).
CHAPTER IV

SELF-ASSEMBLY AND CHARACTERIZATION OF A BOWTIE-SHAPED STRUCTURE

4.1 Introduction

Enlightened by the observation that crown ethers can change shapes depending on temperature and cation, the use of a crown ether monomer to construct the supramolecule, which can potentially open the door to a temperature-sensor molecular device. Herein, we report a non-reversible, self-assembly to construct a new bowtie-shaped structure. The RuII-dimer reacted with 24-crown-8 tetraterpyridine in 2:1 stoichiometric ratio to generate an interesting bent architecture with high flexibility (Scheme 4.2.1).

4.2 Results and discussion

The bisterpyridine 1 was synthesized by the treatment of 1,2-dibromo-4,5-bis(hexyloxy)benzene67 via a Suzuki Coupling.62 The 1H NMR of ligand 1 displayed one set of characteristic peaks and a triplet at 4.10 ppm, which corresponds to OCH2 linkage of alkyl chain (Figure 4.2.1). The bisterpyridine 1 was reacted with Ru(DMSO)4Cl264 to form the RuII-dimer 2. The 1H NMR data exhibit a singlet at 9.03 ppm and a doublet at 8.62 ppm assigned to the 3′,5′-tpyH and 6,6″-tpyH, for the coordinated terpyridine and non-coordinated terpyridine partion, respectively (Figure 4.2.2). This RuII-dimer 2 was converted to RuIII-adduct 3 by treatment with RuCl3·3H2O63 in EtOH solution. The self-assembly of RuIII-adduct 3 with crown ether monomer 4 genera-
te a bowtie-like complex 5 in a solvent mixture of CHCl₃ and MeOH at 25 °C. The final complex 5 was purified by column chromatography (SiO₂) in moderate yield (Scheme 4.2.1). The complex 5 was characterized by ¹H NMR (Figure 4.2.3) and all of the peaks are assigned with the aid of COSY NMR (Figure 4.2.6). The ¹H NMR exhibits three sharp singlets at 9.03, 9.04, and 9.05 ppm assigned to the 3',5'-tpyH of three non-equivalent terpyridine units.

The structure 5 was further characterized by ESI-MS analysis (Figure 4.2.4). A series of expected peaks with charge state from 4+ to 8+ can be observed and is in full agreement with the theoretical pattern. Isotope pattern for charged state 6+ was clearly resolved, which agrees well with theoretical isotope distribution. In the 2D TWIM-MS plot, charge states from 4+ to 9+ were observed, which show one set of bands with the expected step pattern (Figure 4.2.5), again this is in consistent with NMR result.

Scheme 4.2.1  Synthesis of bowtie-like complex 5.
Figure 4.2.1 $^1$H NMR (300 MHz, 300 K) of $4',4'''$-(4',5'-bis(hexyloxy)-[1,1':2',1"]-terphenyl]-4,4"-diyl}di-[2,2':6',2"]-terpyridine 1 in CDCl$_3$ and CD$_3$OD (3:1, v/v).

Figure 4.2.2 $^1$H NMR spectrum (500 MHz, 300 K) of Ru$^{III}$-dimer with alkyl chain 3 in CDCl$_3$ and CD$_3$OD (2:1, v/v).
Figure 4.2.3  $^1$H NMR spectrum (500 MHz, 300 K) of bowtie-like complex 4 in CD$_3$CN.

Figure 4.2.4  ESI mass spectra for the bowtie-like complex 4.
Figure 4.2.5  2D ESI-TWIM-MS plot for bowtie-like complex 4. The charge states of the intact assemblies are marked.

Figure 4.2.6  2-D COSY NMR spectra (500 MHz, 300 K) of bowtie-like complex 4 in CD$_3$CN.
4.3 Conclusion

The crown ether-based, bowtie-shaped architecture was successfully synthesized using multiple terpyridine-based building blocks through step-wise synthetic protocols. The final product was purified by column chromatography and fully-characterized by \(^1\)H NMR, COSY NMR, and ESI-TWIM-MS. The compound will be subjected to the TEM characterization to obtain further insight about shape, size, and geometry of the single molecule.

4.4 Experimental Section

**General procedures.** Solvents were commercially purchased from Sigma-Aldrich with 99% purity. \(\text{RuCl}_3 \cdot 3\text{H}_2\text{O}\),\(^{[63]}\) \(\text{RuCl}_2(\text{DMSO})_4\),\(^{[64]}\) \(\text{Pd}(\text{PPh}_3)_2\text{Cl}_2\),\(^{[65]}\) 1,2-dibromo-4,5-\(\text{bis}(\text{hexyloxy})\)benzene,\(^{[67]}\) 4’-(4-boronatophenyl)[2,2’:6’,2”]terpyridine\(^{[70]}\) were made by previous lab colleagues.

Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with \(\text{Al}_2\text{O}_3\) (IB-F) or \(\text{SiO}_2\) (IB2-F) and visualized by UV light. Column chromatography was conducted using basic \(\text{Al}_2\text{O}_3\), Brockman Activity I (60-325 mesh) or \(\text{SiO}_2\) (60-200 mesh) from Fisher Scientific. \(^1\)H and \(^{13}\)C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA). Data analyses were conducted using the MassLynx 4.1 and DriftScope 2.1 programs provided by Waters. Energy minimization of the supramolecules was conducted with the Materials Studio version 8.0 program, using Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. The geometry was optimized after each cycle and all optimizations used a
universal force field with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters.

4',4''''-[4',5''-Bis(hexyloxy)-[1,1':2',1''-terphenyl]-4,4''-diyl]di-[2,2':6',2'']-terpyridine, bis-terpyridine 1. To a 1 L 3-necked round flask, 1,2-dibromo-4,5-

bis(hexyloxy)benzene\(^{67}\) (3g, 6.87 mmol), 4'-(4-boronatophenyl)[2,2':6',2'']terpyridine\(^{70}\) (7.29 g, 0.02 mol), Na\(_2\)CO\(_3\) (2.86 g, 0.027 mol), and Pd(PPh\(_3\))\(_2\)Cl\(_2\)\(^{65}\) (1.11 g, 1.375 mmol) were added. Then a solvent mixture of water (120 mL), toluene (200 mL), and ethanol (80 mL) was added under a nitrogen atmosphere. The system was refluxed at 100 °C for 48 hours. After cooling to 25 °C, the reaction mixture was extracted with CHCl\(_3\) (3×100 mL). The combined extract was collected and dried over anhydrous MgSO\(_4\) for 6 hours. After concentration in vacuo, the residue was column chromatographed (Al\(_2\)O\(_3\)) eluting with hexane/CHCl\(_3\)/EtOAc (10:1:1; v/v/v) to afford yellow product 1: 1.8g (60%); m.p. > 250 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm) \(\delta\) 8.75 (s, 4H, 3',5'-tpy\(H\)), 8.70 (d, \(J = 8\) Hz, 4H, 3,3''-tpy\(H\)), 8.65 (d, \(J = 8\) Hz, 4H, 6,6''-tpy\(H\)), 7.88 (d, \(J = 8\) Hz, 4H, 4,4''-tpy\(H\)), 7.82 (d, \(J = 8\) Hz, 4H, Ph\(H^a\)), 7.33 (dd, \(J_1 = 7\) Hz, \(J_2 = 5\) Hz, 8H, 5,5''-tpy\(H\) and Ph\(H^b\)), 7.03 (d, \(J = 8\) Hz, 4H, Ph\(H^c\)), 4.12 (t, \(J = 7\) Hz, 4H, 2 \(\times\) OCH\(_2\)) 1.87 (t, \(J = 7\) Hz, 4H, 2 \(\times\) CH\(_2\)), 1.25 – 1.48 (m, 12 H, 6 \(\times\) CH\(_2\)), 0.91 (t, \(J = 7\) Hz, 6H, 2 \(\times\) CH\(_3\)).
[(Ru$^{III}$)(1)2(Cl$^-$)2] 2. To a 1 L round flask, bis-terpyridine 1 (3.07 g, 3.43 mmol), Ru(DMSO)$_4$Cl$_2$ [56] (555 mg, 1.14 mmol), and a solvent mixture of CHCl$_3$/MeOH (600 mL, 1:1) were added. This system was refluxed for 24 hours at 70 °C. After cooling to 25 °C, the solvent was removed in vacuo to give a red powder, which was column chromatographed (Al$_2$O$_3$) eluting with CHCl$_3$/MeOH (40:1; v/v) firstly to remove the fluorescent part, then CHCl$_3$/MeOH (35:1; v/v) to give the product 2: 1 g (60%); m.p. > 300 °C; $^1$H NMR (500 MHz, CD$_3$OD, ppm) δ 9.03 (s, $J = 2$ Hz, 4H, coordinated 3,5-tpyH), 8.72 (d, $J = 8$ Hz, 4H, coordinated 3',5'-tpyH), 8.66 (s, 2H, free 3',5'-tpyH), 8.63 (d, $J = 6$ Hz, free 3',3''-tpyH), 8.62 (d, $J = 5$ Hz, 4H, coordinated 6,6''-tpyH), 8.05 (d, $J = 8$ Hz, 4H, coordinated-Ph$^a$H), 7.99 – 7.87 (m, 8H, 4H, free Ph$^a$H), 7.83 (d, $J = 8$ Hz, 4H, free Ph$^a$H), 7.45 (d, $J = 8$ Hz, 4H, coordinated Ph$^a$H), 7.38 – 7.42 (m, 12H, coordinated 6,6-tpyH and free 5,5''-tpyH), 7.35 Hz, 4H, free Ph$^a$H), 4.13 (m, 8H, 4 × CH$_2$), 1.87 (m, 8H, 4 × CH$_2$), 1.52 (m, 8H, 4 × CH$_2$), (m, 4H, coordinated 5,5''-tpyH), 7.05 (d, $J = 2$ Hz, 4H, coordinated Ph$^a$H), 7.04 (d, $J = 2$ 1.36 (m, 8H, 4 × CH$_2$) 1.29 – 1.34 (m, 16 H, 8 × CH$_2$), 0.90 (d, $J = 2$ Hz, 12H, 6 × CH$_2$).
[(Ru^{III})_2(Ru^{II})(2)(Cl^-)]_8 3. To a 100 mL round bottom flask, dimer 2 (300 mg, 0.16 mmol), RuCl_3·3H_2O^{[63]} (72 mg, 0.35 mmol), and EtOH (50 mL) were added. The system was refluxed at 80 °C for 36 hours. The reaction mixture was cooled to 25 °C and filtered. The reaction residue was washed with EtOH (100 mL) for three times and dried in vacuo to afford the black solid 3, which was used without further purification: 340 mg (95%); m.p. > 350 °C.

[(Ru^{II})_6(1)_2(4)(PF_6^-)]_12 bowtie-like complex 5. To a 250 mL round flask, the ligand 3 (100 mg, 47 µmol) and crown ether monomer 4 (40 mg, 23.9 µmol) were added in a solvent mixture of CHCl_3 (50 mL) and MeOH (50 mL). Then 4-ethylmorpholine (150 µL) was added into the solution slowly. And the reaction was refluxed at 70 °C for two days. The reaction residue was cooled to 25 °C and concentrated in vacuo, which was flash column chromatographed (SiO2) eluting with [H_2O/MeCN/sat.KNO_3(aq), 1/18/1; v/v/v] to give a
red powder (NO$_3^-$). The counterions were exchanged upon treatment with aqueous solution of excess NH$_4$PF$_6$ to give a red precipitate, which was filtered, washed repeatedly with MeOH to remove excess NH$_4$PF$_6$, and then dried in vacuo to give complex 5, as deep red solid; m.p. > 400 °C; $^1$H NMR (500 MHz, CD$_3$CN, ppm) δ 9.20 – 8.95 (m, 24H, 3',5'-tpyH), 8.66 – 8.68 (m, 24 H, 3,3''-tpyH), 8.16 – 8.17 (m, 24 H, Ph$^a$H), 7.97 – 7.81 (m, 24H, 4,4''-tpyH), 7.64 – 7.65 (m, 24H, Ph$^b$H), 7.43 – 7.44 (m, 24 H, 6,6''-tpyH), 7.33 – 7.36 (m, 24 H, 5,5''-tpyH), 7.15 (d, $J = 7$ Hz, 8H, Ph$^c$H in crown ether), 4.45 (t, $J = 4$ Hz, 8H), 4.25 (m, 16H), 4.04 (t, $J = 7$ Hz, 8H, 4 × CH$_2$), 1.58 – 1.61 (m, 16H, 8 × CH$_2$), 1.53 – 1.38 (m, 64 H, 32 × CH$_2$), 1.00 (t, $J = 7$ Hz, 16 H, 8 × CH$_2$); ESI-MS (m/z): 1754.6747 [5-4PF$_6^-$]$^{4+}$ (calcd m/z = 1754.6479), 1374.3845[5-5PF$_6^-$]$^{5+}$ (calcd m/z = 1374.3298), 1121.6678[5-6PF$_6^-$]$^{6+}$ (calcd m/z = 1121.6115), 940.5483 [5-7PF$_6^-$]$^{7+}$ (calcd m/z = 940.5325), 804.4344 [5-8PF$_6^-$]$^{8+}$ (calcd m/z = 804.4674).
CHAPTER V

SELF-ASSEMBLY AND CHARACTERIZATION OF DOUBLE TRIANGLE STRUCTURE

5.1 Introduction

One paper reported by Xie et al.\textsuperscript{[57]} the author used 18-crown-6 tetraterpyridine to construct superimposed-bistriangle, octahedron, and cuboctahedron cages by a one-pot reaction. Inspired by this project, we report a one-step, self-assembly of a 3D "double triangle." 24-Crown-8 tetraterpyridine self-assembled with Zn\textsuperscript{II} in a precise ratio of 1:2 to generate this complex (Scheme 5.2.1). The structure consists of two triangles connected to each other along three vertices and it was named as a "double triangle."

5.2 Results and discussion

24-Crown-8 tetraterpyridine 1 was prepared by the four-fold Suzuki coupling\textsuperscript{[62]} of 4,4',5,5'-tetrabromodibenzo-24-crown-8\textsuperscript{[68]} with 4'- (4-boronatophenyl)-[2,2':6',2"]-terpyridine\textsuperscript{[70]}. The product was characterized by \textsuperscript{1}H NMR (Figure 5.2.1) and \textsuperscript{13}C NMR (Figure 5.2.2). In the \textsuperscript{1}H NMR spectrum, it showed only one set of terpyridine peaks and a sharp singlet at 8.72 ppm assigned to 3',5'-tpy\textit{H}. The self-assembly of monomer 1 with Cd\textsuperscript{II} results in the formation of the double triangle 2. The Cd\textsuperscript{II} complex 2 was initially characterized by \textsuperscript{1}H NMR (Figure 5.2.3) with the aid of COSY NMR (Figure 5.2.6) and \textsuperscript{13}C NMR (Figure 5.2.7).
Compared to monomer 1, the $^1$H NMR spectrum clearly showed that 3',5'-tpy$H$ shifted downfield from 8.72 ppm to 8.87 ppm and 6,6''-tpy$H$ shifted upfield from 8.67 ppm to 7.94 ppm, which suggests the occurrence of metal-coordination.

Scheme 5.2.1  Synthesis of double triangle 2.

Figure 5.2.1  $^1$H NMR spectrum (300 MHz, 300 K) of crown ether monomer 1 in CDCl$_3$. 

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Figure 5.2.2 $^{13}$C NMR spectra (125 MHz, 300K) of 24-crown-8 tetrerpyridine 2 in CDCl$_3$.

Figure 5.2.3 $^1$H NMR spectrum (500 MHz, 300 K) of double triangle 2 in CD$_3$CN.
The double triangle was further confirmed by ESI mass spectrometry (Figure 5.2.4). A series of dominant peaks was observed at $m/z = 1717.46, 1344.74, 1096.44, 919.09, 786.07, \text{ and } 682.51$ corresponding to the theoretical calculated charge states from 5+ to 9+, respectively, due to the consecutive loss of $\text{PF}_6^-$ counterions. The isotope pattern was clearly resolved for charge state 7+ and is in agreement with theoretically predication. The structure was further characterized by TWIM-MS. In the 2D TWIM-MS plot (Figure 5.2.5), it showed charge states from 6+ to 9+ displaying single and narrow band, further confirming the presence of single structure in solution.

![Figure 5.2.4  ESI spectra of double triangle 2.](image)
Figure 5.2.5  2D ESI-TWIM-MS plot (m/z vs. drift time) for double triangle 2. The charge states of the intact assemblies are marked.

Figure 5.2.6  2-D COSY NMR (500 MHz, 300 K) of double triangle 2 in CD$_3$CN.
Transmission electron microscopy (TEM) afforded a visualization of the double triangle 2, directly revealing both the size and shape of individual molecules upon deposition of a dilute MeCN/H$_2$O ($10^{-5}$ M, 5:1, v/v) solution of 2 with PF$_6^-$ counterions on carbon-coated grids (Cu, 400 mesh; Figure 5.2.8). The particles with clear triangular shape and clear edges were observed. The average distance (5 nm) between the vertices fits well with the size obtained from the optimized molecular model. At higher magnification, the image clearly shows that many triangular particles aggregate into each small group, which disperse uniformly.
Figure 5.2.8 Low-magnification TEM image shows a proper size triangular particle and a uniform aggregate. The high-magnification TEM image clearly exhibits a picture of proposed aggregate.

5.3 Conclusions

The 3D double triangle 2 was constructed by one-pot self-assembly in high yield. The coordination between Cd$^{II}$ ions with 24-crown-8 tetraterpyridine leads to the formation of an extremely pure double triangle according to $^1$H NMR and ESI-MS spectrum. The interesting aggregation pattern was clearly observed under TEM characterization, many small triangles pack together and disperse uniformly.

5.4 Experimental section

**General procedures.** Solvents were commercially purchased from Sigma-Aldrich with 99% purity. RuCl$_3$·3H$_2$O,$^{63}$ RuCl$_2$(DMSO)$_4$,$^{64}$ Pd(PPh$_3$)$_2$Cl$_2$,$^{65}$ 4,4',5,5'-tetrabromodibenzo-24-crown-8,$^{68}$ 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine$^{70}$ were made by previous lab colleagues.
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 Fisher Scientific. $^1$H and $^{13}$C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA). Data analyses were conducted using the MassLynx 4.1 and DriftScope 2.1 programs provided by Waters. Energy minimization of the supramolecules was conducted with the Materials Studio version 8.0 program, using Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. The geometry was optimized after each cycle and all optimizations used a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals parameters. For the TEM investigation, the solutions were drop cast onto a carbon-coated copper grid and the extra solution was absorbed by filter paper to avoid aggregation. The TEM images of the drop cast samples were taken with a Jeol JEM-1230 transmission electron microscope.

![Chemical Structure](image)

**24-Crown-8 tetraterpyridine 1.** To a 500 mL 3-necked round flask, 4,4',5,5'-tetrabromodibenzo-24-crown-8$^{[68]}$ (200 mg, 0.26 mmol), 4'-(4-boronatophenyl)-[2,2':6',2'']...
terpyridine\textsuperscript{[70]} (550 mg, 1.56 mmol), Na$_2$CO$_3$ (220 mg, 2.08 mmol), and Pd(PPh$_3$)$_2$Cl$_2$\textsuperscript{[67]} (84 mg, 0.104 mmol) were added. Then a solvent mixture of water (60 mL), toluene (100 mL), and EtOH (40 mL) was added under a nitrogen atmosphere. The system was refluxed at 100 °C for 48 hours. After cooling to 25 °C, the reaction mixture was extracted with CHCl$_3$ (3×100 mL). The combined liquid was collected and dried over anhydrous MgSO$_4$ for 6 hours. Concentration in vacuo gave the brown solid, which was column chromatographed (Al$_2$O$_3$) eluting with hexane/CHCl$_3$/EtOAc (6:1:1; v/v/v) to afford 1, as white yellow solid: 190 mg (60%); m.p. > 400 °C; $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 8.72 (s, 8H, 3',5'-tpyH), 8.67 (d, $J = 5$ Hz, 8H, 6,6"-tpyH), 8.63 (d, $J = 8$ Hz, 8H, 3,3"-tpyH), 7.85 (d, $J = 8$ Hz, 8H, 4,4"-tpyH), 7.79 (d, $J = 9$ Hz, 8 H, Ph$^f$), 7.31(d, $J = 8$ Hz, 8 H, 5,5"-tpyH), 7.05 (d, $J = 5$ Hz, 8 H, Ph$^p$), 4.31 (t, $J = 8$ Hz, 8 H), 4.01 (t, $J = 8$ Hz, 8 H), 3.92 (t, $J = 8$ Hz, 8 H); $^{13}$C NMR (125 MHz, CDCl$_3$, ppm) δ 156.31, 155.83, 149.77, 149.04, 148.53, 142.09, 136.73, 136.35, 133.14, 130.44, 126.99, 123.63, 121.27, 118.79, 116.56, 77.18, 71.39, 69.86.

**Double Triangle 2.** To a solution of crown ether monomer 1 (10 mg, 6×10$^{-3}$ mmol) in CHCl$_3$ (10 mL), a methanolic solution (7 mL) of Cd(NO$_3$)$_2$·4H$_2$O (367 µg, 0.012 mmol) was added slowly without any precipitation. The solution was stirred for 12 hours at 25 °C,
then half of the solution was treated with aqueous solution of excess NH₄PF₆ to obtain a yellow precipitate, which was filtered and washed three times with MeOH and water to remove any surplus NH₄PF₆, dried *in vacuo* to give quantitatively Cd²⁺ complex 2, as deep yellow solid. The other half of the solution was treated with aqueous solution of excess NaSbF₆ to obtain a yellow precipitate, which was also filtered and washed three times with MeOH and water to remove any excess NaSbF₆, dried *in vacuo* to give the final complex 2, which was dissolved in DMF (1 mL) and filtered to give a clean and bright solution. Then the solution was transferred into a long and thin tube and put in a 1 L rectangular bottle with EtOAc (100 mL), waiting for the crystals to grow; m.p. > 400 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 16H, 3',5'-tpyH), 8.63 (d, J = 8 Hz, 16H, 3,3''-tpyH), 8.09 (d, J = 8 Hz, 16H, PhH), 7.96 (d, J = 5 Hz, 16H, 6,6''-tpyH), 7.83 (t, J = 8 Hz, 16H, 4,4''-tpyH), 7.57 (d, J = 8 Hz, 16H, PhH), 7.21 (d, J = 8 Hz, 16H, PhH), 7.09 (t, J = 8 Hz, 16H, 5,5''-tpyH), 4.43 (t, J = 9 Hz, 8 H), 4.29 (d, J = 10 Hz, 8 H), 4.01 (t, J = 10 Hz, 8 H), 3.97 – 3.87 (m, 16H) 3.73 (t, J = 8 Hz, 8 H); ¹³C NMR (125 MHz, CD₃CN, ppm) δ 154.61, 152.48, 150.21, 149.68, 148.79, 141.21, 140.78, 134.25, 127.63, 127.25, 127.01, 123.75, 121.60, 117.26, 24.01, 19.59; ESI-MS (m/z): 1717.4487 [2-4PF₆⁻]⁴⁺ (calcd m/z = 1717.5255), 1344.7296 [2-5PF₆⁻]⁵⁺ (calcd m/z = 1344.6274), 1096.4320 [2-6PF₆⁻]⁶⁺ (calcd m/z = 1096.5287), 919.2258 [2-7PF₆⁻]⁷⁺ (calcd m/z = 919.1725), 786.7114 [2-8PF₆⁻]⁸⁺ (calcd m/z = 786.7813), 682.8486 [2-9PF₆⁻]⁹⁺ (calcd m/z = 682.8182).
6.1 Introduction

24-Crown-8 ethers can accommodate ions larger or smaller depending on their cavity size, which can be used as ion-selective electrodes for the determination of metal ions and neutral carrier molecules. Inspired by this, 24-crown-8 ether monomer was self-assembled with Ru\textsuperscript{II} in 2:1 ratio to form monoRu\textsuperscript{II}-dimer of 24-crown-8 tetraterpyridine, then the monoRu\textsuperscript{II}-dimer reacted with Zn\textsuperscript{II} in 1:3 ratio to generate the cis-tetramer and trans-tetramer in solution.

6.2 Results and discussion

The crown ether monomer 1 was treated with Ru\textsuperscript{II} to generate the monoRu\textsuperscript{II}-dimer 2, which was characterized by \textsuperscript{1}H NMR (Figure 6.2.2), COSY NMR (Figure 6.2.4), \textsuperscript{13}C NMR (Figure 6.2.5), and mass spectrometry (Figure 6.2.3). There was observed one sharp peak in the MALDI-MS spectrum at m/z = 3600.11, which matches with theoretical calculated mass for ligand 2 with one PF\textsubscript{6}\textsuperscript{−} counterion. Then the dimer 2 was self-assembled with Zn\textsuperscript{II} to form tetramer 3. The final structure 3 was firstly characterized by ESI-MS analysis (Figure 6.2.6), and a series of dominant peaks was observed at m/z = 730.11, 817.58, 924.56, 1058.11, and 1230.08 corresponding to the theoretical calculated charge states from 7+ to 11+, respectively, due to the consecutive loss of PF\textsubscript{6}\textsuperscript{−} counterions. There was
also another group of four regular peaks above the peak of charge state 7+. It was because the Na\textsuperscript{+} ions, which existed in the instrument would chelate with core part of the crown ether monomer 1 via dπ-π* bonding. The structure was further characterized by TWIM-MS. In the 2D TWIM-MS plot (Figure 6.2.7), it showed charge states from 7+ to 10+, which display single and narrow bands with the expected step pattern. Moreover, the complex was characterized by \textsuperscript{1}H NMR (Figure 6.2.9) with the aid of COSY NMR (Figure 6.2.11). In \textsuperscript{1}H NMR spectrum, there were two sets of peaks, which are not consistent with proposed single one structure. According to molecular modeling, there were two possibilities for tetramer 3. One is cis-structure, another is trans-structure (Figure 6.2.1). This mixed structure can not be separated by column chromatography due to the very close polarity. So, now attempt to grow a single crystal by diffusing EtOAc into a DMF solution of tetramer at room temperature using different counterions are being conducted, in order to characterize the actual structure of the tetramer by single crystal X-ray analysis (Figure 6.2.10).
Figure 6.2.1  The modeling structure of tetramer 3.

Scheme 6.2.1  The synthetic route of tetramer 3.
Figure 6.2.2  $^1$H NMR spectrum (500 MHz, 300 K) of monoRu$^{II}$-dimer of 24-crown-8 tetraterpyridine 2 in CD$_3$CN.

Figure 6.2.3  MALDI-MS spectrum of monoRu$^{II}$-dimer of 24-crown-8 tetraterpyridine 2.
Figure 6.2.4 2-D NOESY NMR (500 MHz, 300 K) of monoRu\textsuperscript{II}-dimer of 24-crown-8 tetraterpyridine 2 in CD\textsubscript{3}CN.

Figure 6.2.5 \textsuperscript{13}C NMR spectra (125 MHz, 300K) of monoRu\textsuperscript{II}-dimer of 24-crown-8 tetraterpyridine 2 in CDCl\textsubscript{3}.
Figure 6.2.6  ESI spectrum of tetramer 3.

Figure 6.2.7  Theoretical and experimental isotope distribution of charge states 8+ for tetramer 3.
Figure 6.2.8  ESI-TWIM-MS plot for tetramer 3 [(b) m/z vs drift time] with the charge states of intact assemblies marked.

Figure 6.2.9  $^1$H NMR spectrum (500 MHz, 300 K) of tetramer 3 in CD$_3$CN.
Figure 6.2.10  Diffusing EtOAc into a DMF solution of tetramer 3.

Figure 6.2.11  2-D COSY NMR (500 MHz, 300 K) of tetramer 3 in CD$_3$CN.
6.3 Conclusion

Novel 3D isomeric nanocages were formed in a high yield. The structural composition was supported by ESI-TWIM-MS. The $^1$H NMR spectrum is complicated and can not be easily resolved in order to analyse each tpy pattern. X-ray analysis will be useful to determine the complex. Further characterization will be accomplished, using TEM, gMS$^2$, and DOSY NMR.

6.4 Experimental Section

**General procedures.** Solvents were commercially purchased from Sigma-Aldrich with 99% purity. RuCl$_3$·3H$_2$O,$^{[63]}$ RuCl$_2$(DMSO)$_4$,$^{[64]}$ Pd(PPh$_3$)$_2$Cl$_2$,$^{[65]}$ 4,4’,5,5’-tetrabromodibenzo-24-crown-8,$^{[68]}$ 4’-(4-boronatophenyl)[2,2’:6’,2’”]terpyridine$^{[70]}$ were made by previous lab colleagues.

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) from Fisher Scientific. $^1$H and $^{13}$C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA). Data analyses were conducted using the MassLynx 4.1 and DriftScope 2.1 programs provided by Waters. Energy minimization of the supramolecules was conducted with the Materials Studio version 8.0 program, using Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). The counterions were omitted. The geometry was optimized after each cycle and all geometry optimizations used a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and van der Waals.
24-Crown-8 ether monomer 1. To a 500 mL 3-necked round flask, 4,4',5,5'-tetra-bromodibenzo-24-crown-8\[^{[68]}\] (200 mg, 0.26 mmol), 4'-{(4-boronatophenyl)-[2,2':6',2'\textsuperscript{\textprime\textprime}]}-terpyridine\[^{[70]}\] (550 mg, 1.56 mmol), Na\textsubscript{2}CO\textsubscript{3} (220 mg, 2.08 mmol), and Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}\[^{[67]}\] (84 mg, 0.104 mmol) were added. Then a solvent mixture of water (60 mL), toluene (100 mL), and EtOH (40 mL) was added under a nitrogen atmosphere. The system was refluxed at 100 °C for 48 hours. After cooling to 25 °C, the reaction mixture was extracted with CHCl\textsubscript{3} (3\times 100 mL). The combined liquid was collected and dried over anhydrous MgSO\textsubscript{4} for 6 hours. Concentration in vacuo gave the brown solid, which was column chromatographed (Al\textsubscript{2}O\textsubscript{3}) eluting with hexane/CHCl\textsubscript{3}/EtOAc (6:1:1; v/v/v) to afford 1, as white yellow solid: 190 mg (60%); m.p. > 400 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, ppm) \delta 8.72 (s, 8H, 3',5'-tpy\textsuperscript{H}), 8.67 (d, J = 5 Hz, 8H, 6,6''-tpy\textsuperscript{H}), 8.63 (d, J = 8 Hz, 8H, 3,3''-tpy\textsuperscript{H}), 7.85 (d, J = 8 Hz, 8H, 4,4''-tpy\textsuperscript{H}), 7.79 (d, J = 9 Hz, 8H, Ph\textsuperscript{H}), 7.31 (d, J = 8 Hz, 8H, 5,5''-tpy\textsuperscript{H}), 7.05 (d, J = 5 Hz, 8H, Ph\textsuperscript{H}), 4.31 (t, J = 8 Hz, 8H), 4.01 (t, J = 8 Hz, 8H), 3.92 (t, J = 8 Hz, 8H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, ppm) \delta 156.31, 155.83, 149.77, 149.04, 148.53, 142.09, 136.73, 136.35, 133.14, 130.44, 126.99, 123.63, 121.27, 118.79, 116.56, 77.18, 71.39, 69.86.
[(RuII)(1)2(Cl−)2] monoRuII-dimer 2. To a 500 mL flask, the crown ether monomer 1 (150 mg, 89 µmol), Ru(DMSO)4Cl2 [64] (144 mg, 29.8 µmol), and a solvent mixture of CHCl3/MeOH (300 mL, 1:1) were added. The system was refluxed at 80°C for 36 hours. After cooling to 25°C, the reaction residue was concentrated in vacuo to give a red powder, which was column chromatographed (Al2O3) eluting with CHCl3/MeOH (15:1; v/v) to give the red product 2: 50 mg (34%); m.p. > 400°C; 1H NMR (500 MHz, CD3CN, ppm) δ 8.50 (s, 6H), 8.46 (d, J = 11 Hz, 7H), 8.41 (s, 5H), 8.38 (d, J = 8 Hz, 3H), 8.34 (d, J = 8 Hz, 4H), 7.85 – 7.76 (m, 8H), 7.61 (s, 10H), 7.45 (d, J = 8 Hz, 7H), 7.41 (d, J = 8 Hz, 5H), 7.31 – 7.22 (m, 12H), 7.21 (s, 6H), 7.17 (d, J = 7 Hz, 5H), 7.12 (d, J = 8 Hz, 6H), 4.39 (s, 7H), 4.27 (d, J = 3 Hz, 13H), 3.98 (d, J = 2 Hz, 9H), 3.91 (s, 7H), 3.86 (s, 6H), 3.80 (s, 8H); 13C NMR (125 MHz, CDCl3, ppm) δ 158.06, 156.17, 155.77, 148.98, 136.82, 130.46, 127.78, 126.97, 123.70, 121.32, 118.76, 77.18, 77.09, 76.83, 71.38, 69.98; MALDI-MS (m/z): 3600.11 [2-PF6−] (calcd m/z = 3600.17).
[(Ru\textsuperscript{II})\textsubscript{2}(Zn\textsubscript{6}(2)(PF\textsubscript{6})\textsubscript{16}] tetramer 3. To a solution of monoRu\textsuperscript{II}-dimer 2 (10 mg, 3×10\textsuperscript{-3} mmol) in CHCl\textsubscript{3} (6 mL), a methanolic solution (6 mL) of Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (253 µg, 8×10\textsuperscript{-3} mmol) was added slowly. The solution was stirred for 15 hours at 25 °C, then treated with aqueous solution of excess NH\textsubscript{4}PF\textsubscript{6} to obtain a red precipitate, which was filtered and washed with MeOH and water for three times to remove any surplus NH\textsubscript{4}PF\textsubscript{6}, then dried in vacuo to give a deep red solid.

To a solution of monoRu\textsuperscript{II}-dimer 2 (10 mg, 3×10\textsuperscript{-3} mmol) in CHCl\textsubscript{3} (6 mL), a methanolic solution (6 mL) of Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (253 µg, 8×10\textsuperscript{-3} mmol) was added slowly. The solution was stirred for 15 hours at 25 °C, the solution was treated with aqueous solution of excess NaSbF\textsubscript{6} to obtain a red precipitate, which was filtered and washed with MeOH and water for three times to remove any excess NaSbF\textsubscript{6}, then dried in vacuo to give the final complex. Then, this Zn\textsuperscript{II} complex was dissolved in DMF (1 mL) and filtered to become a clean and bright solution. Then the solution was transferred into a long and thin tube and put in a 1 L rectangular bottle with EtOAc (100 mL), waiting for the crystals to grow; m.p. > 400 °C; \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN, ppm) δ 9.01 (s, 3H), 8.97 (s, 8H), 8.70 (d, \textit{J} = 8 Hz, 9H), 8.57 (s, 6H), 7.82 (s, 7H), 7.63 (dd, \textit{J} = 8 Hz, 20H), 7.23 (d, \textit{J} = 7 Hz,
10H), 5.86 (s, 3H), 4.42 (s, 7H), 4.30 (s, 7H), 4.03 (d, \( J = 12 \) Hz, 12H), 3.94 (s, 12H), 3.78 (d, \( J = 2 \) Hz, 12H), 3.31 (s, 11H); ESI-MS (m/z): 1230.2632 \([3-7PF_6^-]^7^+\) (calcd \( m/z = 1230.2411 \)), 1058.5862 \([3-8PF_6^-]^8^+\) (calcd \( m/z = 1058.5875 \)), 924.5559 \([3-9PF_6^-]^9^+\) (calcd \( m/z = 924.5269 \)), 817.8528 \([3-10PF_6^-]^{10^+}\) (calcd \( m/z = 817.8770 \)), 730.1803 \([3-11PF_6^-]^{11^+}\) (calcd \( m/z = 730.1669 \)).
In conclusion, a series of supramolecules has been successfully prepared through one-step or stepwise self-assemblies: bowtie-shaped complex, hydrophilic bowl, tetramer, and double triangle. These complexes were characterized by a combination of 1D NMR (\(^1\)H, \(^{13}\)C), 2D COSY and NOESY NMR, TEM, ESI-MS, and TWIM-MS. The application of ligands with complementary directivity to synthesize higher generation metallo-supramolecules and assembling more metallo-centers architecture are currently under way.
REFERENCES


