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Stepwise, Multicomponent Assembly of a Molecular Trapezoid Possessing Three Different Metals

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A novel terpyridine-based, trapezoidal architecture was synthesized by a coordination-driven multicomponent assembly and features three different tpy-M^{2+}-tpy bonds (M^{2+} = Ru^{2+}, Fe^{2+}, and Zn^{2+}) in the macrocyclic ring. This trimetallic macrocycle introduces the construction of polymetallosupramolecular assemblies possessing multiple, differing metal centers in an ordered, predetermined pattern. Characterization was accomplished by NMR spectroscopy, mass spectrometry, and UV-Vis spectroscopy.

Over the past two-decades, diverse examples of supramolecular constructs have attracted attention in biology[1] as well as many other fields, including supramolecular catalysis,[2-5] molecular electronics,[6-10] and chemical sensing.[11, 12] To mimic and simulate the naturally occurring assemblies, coordination-driven molecular assembly has paved the way for constructing numerous abiological supramolecular 2D and 3D architectures with precise shapes and sizes, due in part, the availability of diverse ligands and limited metal ions.[13-21] In particular, [2,2':6',2"]-terpyridine (tpy) based ligands have been shown to generate interesting complex motifs predicted on their ability to coordinate diverse metal ions through <tpy-M^{2+}-tpy> connectivity.[16, 22, 23] Using designer poly(terpyridine) monomers with incorporated programmed structural features, several novel nanomolecular constructs have been synthesized[16, 22, 24-30] utilizing both homo- and heteroleptic connectivity. While homoleptic complexes involving symmetric monomers are quite facile, heteroleptic assemblies involving multiple building blocks still remain challenging owing to their inherent tendency to produce competitive products resulting from self-sorting.[31-34] These constructs mainly rely on specific stoichiometry, geometrical size and shape of the components; however, the selective formation of a heteroleptic complex from a mixture of different multivalent ligands is even more attractive as they allow access to additional complex molecular architectures. Recently, we have reported a variety of heteroleptic structures, such as the isomeric molecular bowtie and butterfly,[35] hexagonal spoked-wheel,[36] Sierpiński triangle,[37] and a molecular rhombus,[38] which were obtained using multicomponent stepwise or one-step synthetic protocols.

Herein, we report the heteroleptic assembly of a novel terpyridine-based trimetallic molecular trapezoid using three different *bis*-terpyridine ligands with three different modes of <tpy-M^{2+}-tpy> connectivity (M = Ru, Fe, and Zn). The vast majority of currently reported constructs have been limited to those possessing two different metal centers and only a handful of Metal−Organic complex arrays containing three or more metal centers have been reported by Tashiro and Yaghi.[39-41] Since 52 different metals have been reported to be incorporated into the [tpy-M-tpy] bonding motif, there would appear to be new interesting structural and chemical possibilities, if multiple different metals could be specifically located during assembly process.

Our molecular trapezoid was obtained by the stepwise combination of one linear 180°-*bis*terpyridine with two 60°-*bis*tpy, followed by self-assembly with a 120° based <*bis*tpy-Fe^{2+}-*bis*tpy> capping component. Initially, the preparation of the macrocycle began with the synthesis of **1**, which was accessed (70%) by treatment of 1,4-dibromo-2,5-*bis*(hexadecyl-oxy)benzene (**S2**) with 4-[([2,2′:6′,2′′]terpyridin-4-yl)phenyl]-boronic acid[42] through a Suzuki–Miyaura coupling. The ^{1}H NMR spectrum of **1** exhibited a triplet at δ = 3.98 ppm due to -OCH_2 linkage, a distinctive singlet at 7.09 ppm for the central phenylene connector and an overall simplicity for the terpyridine peaks, confirming its rigid, symmetric motif. Monomer **1** was utilized to prepare corresponding *bis*Ru^{III} adduct **2** (by treatment with 3 equiv. of RuCl$_3$·xH$_2$O in EtOH under reflux). Subsequent treatment of **2** with 60°-*bis*tpy **3**[43] in a 1:3 ratio in presence of *N*-ethylmorpholine gives the desired

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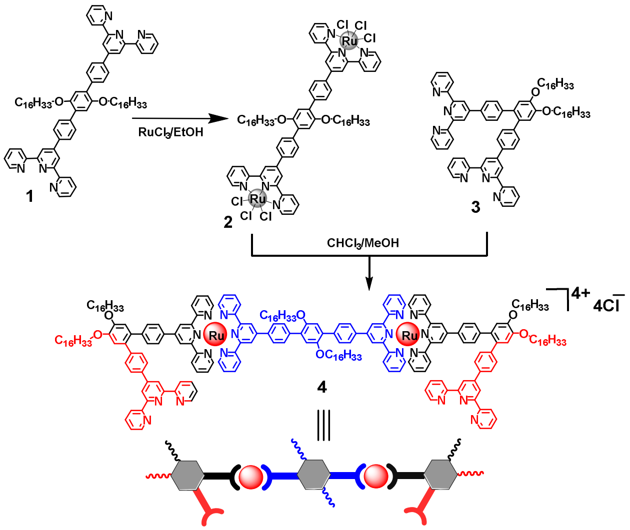
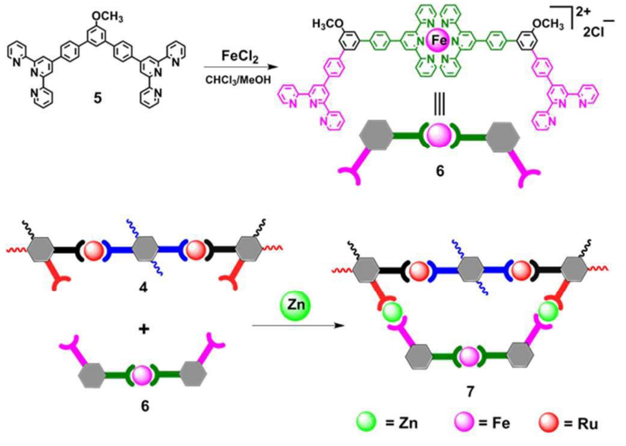


Scheme 1. Synthesis of *bis*Ru^{II}-complex **4**.

*bis*Ru^{2+}-complex **4**, which after column chromatography (Al_2O_3) was obtained in 45% yield with four Cl^- counterions (Scheme 1).

This capping complex **4** was characterized by ^1H NMR spectroscopy, which revealed two sharp singlets at 9.10 and 9.04 ppm assigned to the 3′,5′-protons from the coordinated tpy-units of 60°- and 180°-*bis*ligands. Another singlet at 8.80 ppm corresponds to the non-coordinated terpyridine moieties. The remaining NMR peaks are assigned with the help of 2D-COSY and NOESY NMR data. The MALDI-MS data further confirm the formation of **4** (supporting information).

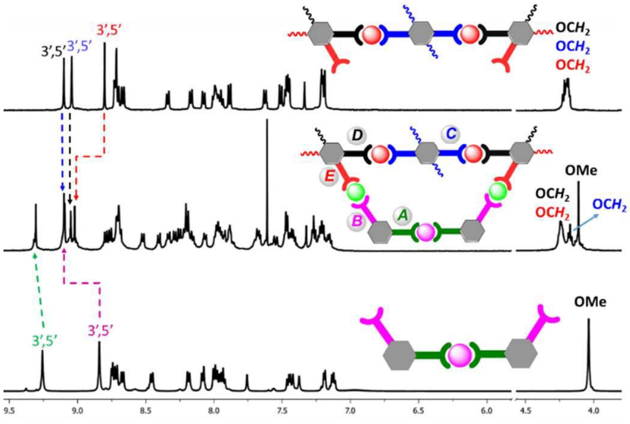
Each Fe^{2+}-dimeric capping component possesses a central benzene unit, which instilled the desired directed 120° angle between two terpyridine termini, required for half of the trapezoid. The 120°-*bis*terpyridine precursor **5**, prepared by a two-fold Suzuki cross coupling of 4-[([2,2′:6′,2′]′-terpyridin-4-yl)phenyl]boronic acid and 1,3-dibromo-5-methoxybenzene (**S3**), was utilized to prepare the corresponding monoFe^{II}-dimer **6** (Scheme 2). Proof for the formation of Fe^{II}-dimer was obtained from the ^1H NMR spectrum, which revealed two singlets at 9.25 and 8.84 ppm assigned to the 3′,5′-protons of coordinated and uncoordinated terpyridine moieties, respectively. The ^1H NMR spectrum also showed the characteristic singlet at 4.03 ppm for the installed -OC*H*$_3$ marker. A consistent MALDI-MS signal at m/z = 1500.47 for [**6**-2Cl]$^+$ further confirms the formation of desired dimer **6**.



Scheme 2. Synthesis of Fe^{II}- dimer **6** and molecular trapezoid **7**.

The facile one-step, self-assembly of *bis*Ru^{2+}-complex **4** and Fe^{2+}-dimer **6** with $Zn(NO_3)_2{\cdot}6H_2O$ in precise 1:1:2 ratio in $CHCl_3$/MeOH (1:1) at 25 °C gave the desired trimetallic molecular trapezoid **7** (Scheme 2). After being stirred for 1hr, the counterions were exchanged with PF_6^- by treatment with an aqueous NH_4PF_6 solution. The desired pure complex **7** was obtained as red solid in near quantitative yield. The structure of **7** was subsequently characterized by 1D, 2D, and DOSY NMR spectroscopy, ESI- and ESI-TWIM mass spectrometry along with UV-Vis spectroscopy.

The ^1H NMR spectrum of **7** (in CD_3CN, Figure 1) exhibited a set of sharp signals with a simple pattern consistent with the formation of a discrete, symmetrical product. The molecular trapezoid **7** exhibits five nonequivalent terpyridine moieties and the expected aromatic region in the ^1H NMR spectrum, which was complicated due to substantial overlap of closely similar terpyridine peaks; assignment of the peaks was readily achieved based on 2D COSY and NOESY NMR data. Characteristic aspects of this spectrum include the observation of five singlets at 9.31, 9.10, 9.09, 9.05, and 9.02 ppm corresponding to the 3',5'-protons of five different terpyridine moieties. The expected and notable upfield shift of 6',6"-tpy*H* of arm B and E, compared to their uncoordinated analog strongly supports the <tpy-Zn^{2+}-tpy> complexation, which is typical due to the electron shielding effect of inherent pseudo-octahedral geometry. In the nonaromatic region, the critical OC*H*$_2$ marker of **2** appears as triplet at 4.17 ppm, along with a broad multiplet attributed to the overlapping peaks of remaining OC*H*$_2$ protons from 60°-corner **3**. The singlet assigned to the OC*H*$_3$ marker shifted downfield to 4.11 ppm when compared to Fe^{II}-dimer **6**.



The chemical composition of the molecular trapezoid **7** was confirmed by its ESI mass spectrum, which exhibits a series of

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Figure 1. Stacked ^{1}H NMR spectra of *bis*Ru^{2+}-complex **4** (above), trapezoid **7** (middle), and Fe^{2+}-dimer **6** (below). Arrows depict assigned resonance shifts that occur upon complex formation. Alkyl chains are omitted for clarity.

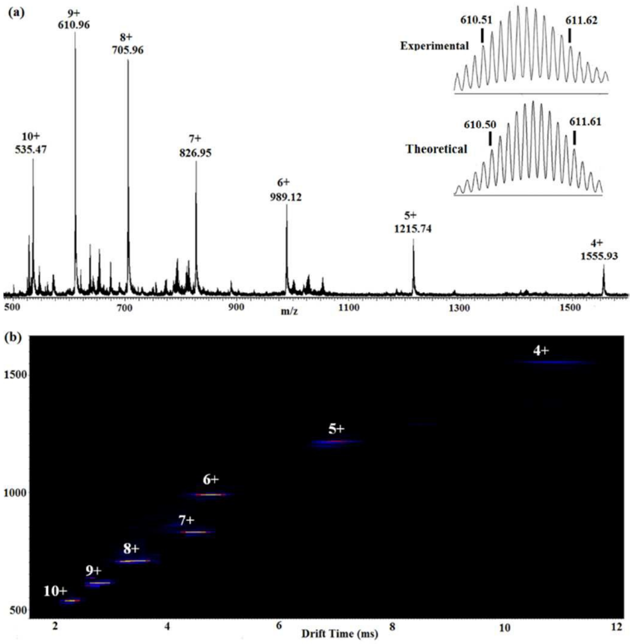

Figure 2. (a) ESI-MS and (b) 2D ESI-TWIM-MS plot (m/z vs drift time) for **7**. The charge states of the intact assemblies are marked.

sharp peaks at m/z = 1555.93, 1215.74, 989.12, 826.95, 705.96, 610.96, and 535.47 amu due to consecutive loss of counter PF$_6^-$ ions; this corresponds to trapezoid cations with charge states 4+ to 10+, respectively (Figure 2a). These MS results provide strong support for the assembly of complex **4**, dimer **6**, and Zn^{2+} ions in a precisely 1:1:2 ratio with 10 PF$_6^-$ counterions. All charge states were isotopically resolved and found to be in agreement with the theoretical distribution. ESI-MS coupled with traveling wave ion mobility (TWIM),[44, 45] a variant of mass spectroscopy further validates the structure of molecular trapezoid. The TWIM spectrum reveals a single band with narrow drift time distribution for charge states 4+ to 10+ with the expected step pattern (Figure 2b), clearly indicating the presence of a single species and ruling out the possibility of other structures. The self-assembly of this trapezoidal complex was further proven by ^{1}H DOSY NMR spectroscopy. The appearance of a single, narrow diffusion trace (Figure S15) demonstrates the presence of a single species in solution and excluded the possibility of any other macrocyclic or oligomeric products.

The structure of trapezoid **7** was further confirmed by collision cross section (CCS) analysis of the ions with charge states +6 to +10 deduced from their drift times measured by TWIM-MS experiment (Table S1). CCS is the rotationally averaged, forward-moving surface area of the ion. The theoretically predicted CCS value (1207.4 Å^2) for the counterion-free complex, based on 100 energy minimized structures using the trajectory model (TM),[46, 47] agrees well with the average experimental CCS (1130 Å^2) for charge states +6 to +10. The differences between the experimental and theoretical CCS values are most likely due to the counterions.

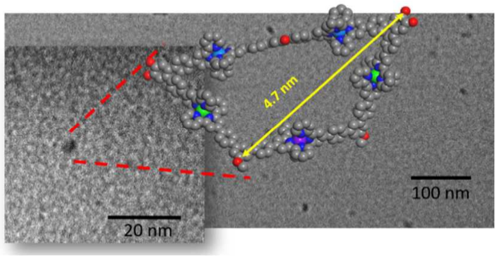

Figure 3. TEM images of complex **7** and a representative, computer-generated, energy-minimized structure of molecular trapezoid **7** (aliphatic chains are omitted for clarity).

Transmission electron microscopy (TEM) images were acquired to obtain an insight into the shape and size of the individual molecules. At higher magnification, the images of single molecules exhibit a shape and size correlating well with optimized geometry of **7** (Figure 3). The average distance between the furthest edges (4.7 nm) correlates well with the size obtained from optimized molecular models.

The UV-Vis spectra of trapezoid **7** revealed a set of characteristic metal-ligand charge transfer (MLCT) bands in MeCN at 25 °C, as shown in Figure 4. Terpyridine-based ligands exhibits typical ligand to ligand (LL) π–π* charge transfer (CT) bands at 283 and 312 nm localized on the terpyridine-phenyl subunit. Complexation with Ru^{2+} results in a MLCT band at 494 nm due to the CT active Ru^{2+} center, this absorption lies in the visible region and is responsible for the intense red color of the complex; whereas in case of Fe^{2+}, the complexation results in a MLCT band at 570 nm is responsible for the intense purple color of the complexes. However, no MLCT band is observed for the tpy-Zn^{2+}-tpy complexes, as a result, the complex shows the dark red color.

In summary, a novel heteroleptic, trimetallic, molecular trapezoid has been synthesized *via* a three-component self-assembly protocol. The structural units were pre-designed using three different *bis*terpyridine ligands with 60°, 120°, and 180° angles. The multicomponent assembly of the trapezoid was achieved incorporating three different <tpy-M^{2+}-tpy> sides using Ru, Fe, and Zn metal ions. To the best of our knowledge, this is a novel example of a trimetallic macrocycle where three

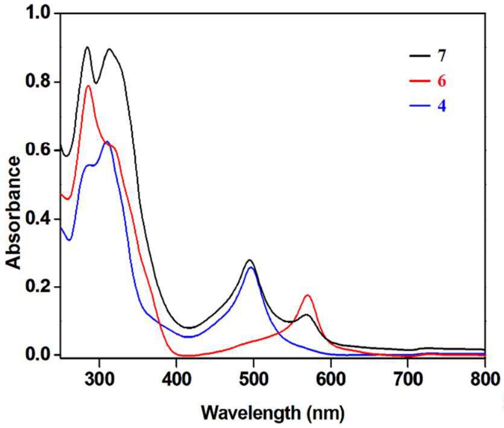

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Figure 4. UV–Visible absorption spectra of complex **4**, **6**, and **7** in MeCN at 298 K.

different metal atoms are involved in the coordination assembly process. The successful preparation of this heteroleptic, multi-metallic, discrete molecular architecture, in nearly quantitative yield, demonstrates the ease of access to novel and diverse complex supramolecular materials possessing differing, logically positioned, <tpy-M^{2+}-tpy> linkages within the structural framework.

Notes and references

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