DESIGN AND CONSTRUCTION OF NANOARCHITECTURES USING
SMART BUILDING BLOCKS

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DESIGN AND CONSTRUCTION OF NANOARCHITECTURES USING SMART BUILDING BLOCKS

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Dissertation

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ABSTRACT

A series of metallomacrocycles employing functionalized \textit{bis}(terpyridine) building blocks were designed and constructed by both self-assembly and step-wise procedures. Based on terpyrine-metal(II)-terpyridine connectivity, application oriented metallomacrocycles possessing controlled ligand juxtapositioning (\textit{i.e.}, 60°, 109°, 120° angles) led to the ability to form trigonal, pentagonal, and hexagonal shape-persistance macrocycles, respectively. Angular control units consisted of benzene, triphenylamine and carbazole moieties. Transition metals [Ru(II), Fe(II), and Zn(II)] were used as the glue to bind together the terpyridine ligands. All the intermediates and final products were characterized by means of $^1$H NMR, $^{13}$C NMR, UV/Vis, and mass techniques.

Using a simple cation exchange reaction, I have built a multi-walled carbon nanotube (MWNT) nanocomposite that was confirmed by Transmission Electron Microscope (TEM) and Energy Dispersive X-ray Spectroscopy (EDXS) analysis to extend our modular chemistry. Studies of photoelectrochemical and luminescence properties have shown these metallomacrocycles to be useful for fabricating molecular devices such as dye-sensitized solar cells and organic light-emitting diodes.
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CHAPTER I

RECENT APPLICATION PROGRESS FOR METALLODENDRIMERS

1.1 Introduction

Since the mid-1980s, two of the most intriguing and rapidly expanding research areas in chemistry are branched macromolecular architectures\textsuperscript{1,2} and self-assembly processes, both of which have become key fundamental research factors for scientists world-wide. These seemingly disparate fields have, in fact, merged beautifully in recent years to create one of the pillars of nano-scale science with diverse potentially utilitarian applications. Numerous reasons for the rapid emergence of these molecular curiosities can be cited, for instance: unprecedented control over structural unit positioning, a general ease-of-construction, well-behaved and tunable solubility features that facilitate characterization and further modification, and the overwhelming abundance of documented proof that such species can, in fact, be constructed for practical as well as aesthetic purposes. However, it is important to note that with the advent of more recent mass spectroscopy techniques, absolute purity and perfect branching are, in many cases, difficult to obtain. But perhaps one of the most important attributes with dendrimer
chemistry, which tends to propagate this new polymeric regime, is its vast potential to be easily integrated into, and meld with, more mature chemistries.

The merger of supramolecular chemistry, defined as "chemistry beyond the molecule" by Lehn,\textsuperscript{3} and the chemistry of dendrimers led directly to "supramacromolecular" chemistry\textsuperscript{4} and the creation of the metallodendritic regime. Incorporation of metal ions into the dendritic infrastructure was initiated by the Balzani\textsuperscript{5-7} and Newkome\textsuperscript{8,9} research groups in the early 1990s, either by the use of metal branching centers or by internal metal complexation and encapsulation at specific binding site(s), respectively. From a structural viewpoint, metallodendrimers can be classified into

\begin{figure}
\centering
\includegraphics[width=\textwidth]{metallodendrimers.png}
\caption{Metals serving in different roles in metallodendrimers.}
\end{figure}
categories based on structural positioning (Figure 1.1), for example metal centers are located at the core, branching points, connectors between branching centers, terminal groups, and incorporated as structural auxiliaries, in which metals are introduced to the framework after dendritic construction. In general, the metal loci possess positional homogeneity within the structure but metals at different framework positions have also been created. Although metalodendrimers have been discussed to some degree in recent literature,

10-15 this Chapter will attempt to address recent developments in the chemistry and potential applications; as well, selected multi-branched, metal-based constructs, that are not strictly within the dendritic arena (i.e. construction with only 2 - 3 repetitive reaction sequences) are also considered.

1.2 General Structures and Their Potential Applications

1.2.1 Catalysts

Among the potential applications of metalodendrimers, catalysis appears to be one of the most promising areas,10,16-25 since the dendritic infrastructure can be controlled to ensure the appropriate size, shape, and constitution. The ability to preprogram an appropriate surface, so necessary to instill the desired solubility characteristics, is readily possible based on one's synthetic ability to tailor the specific (macro)molecular infrastructures; advantages of homogeneous and heterogeneous catalysis can also be probed without the loss of well-defined molecular features.26 In 1994, the first publication appeared in which organometallic and inorganic catalysts were prepared using either organic macromolecules, such as lightly cross-linked polystyrene or inorganic polymers,
such as silica.\textsuperscript{27-31} Since dendritic materials can be created with controlled shape as well as internal and external catalytic sites, their diverse microenvironments afford new opportunities to explore specific utilitarian applications.

1.2.1.1 Ni-based Dendritic Catalysts

One of the first reported examples of a metallodendrimer catalyst\textsuperscript{32} resulted from the attachment of monoanionic chelating "N-C-N"-type pincer moieties to the periphery of a carbosilane dendrimer, followed by the complexation of nickel(II) ions.\textsuperscript{22,23,33,34} These pincer-based carbosilane metalloendrimers (Figure 1.2) have been used as a Kharasch addition\textsuperscript{35} catalyst, whereby an atom-transfer radical-addition reaction between

Figure 1.2 van Koten’s Ni-containing metallodendrimer and urea-linked metalloendron catalysts for the Kharasch addition reaction.
an olefin and a polyhalogenated alkane was effected. These dendritic catalysts are based on the unique feature of the [(N-C-N)NiX] moiety possessing a low Ni(II)/Ni(III) redox potential \(E_{1/2} = 0.14\) V vs. SCE;\(^{36}\) however, the catalytic activity of these metalloendrimers was shown to decrease with increasing generation during the Kharasch-type addition of CCl\(_4\) to methyl methacrylate (MMA) under standard reaction conditions. It was suggested that the Ni(II) sites were partly, irreversibly oxidized to Ni(III) indicative of a back-reaction of the Ni(III) sites with intermediate radical (Cl\(_3\)C-MMA·) or initial radical (·CCl\(_3\)) that become less efficient with time. Based on molecular modeling,\(^{37}\) the Ni-Ni inter-site distance in these metalloendrimers was relatively small, causing Cl-bridging in mixed-valance intermediates affording a rationale for the observed inhibition in these congested metalloendrimers. Preliminary investigation of these dendritic systems within a membrane reactor has shown another possible application for these metalloendrimers.\(^{36}\) van Koten’s group also described the use of amino acid-based dendrons, as molecular scaffolds, for the urea-mediated attachment of catalytically active organometallic Ni "pincer" complexes.\(^{38}\)

Although nickel complexes, derived from \(o\)-diphenylphosphinophenols,\(^{39}\) have been used to catalyze the oligomerization of ethylene monomers by the Shell Higher Olefins Process,\(^{40}\) recently, van Leeuwen’s group has constructed a nickel catalyst embedded at the core of a carbosilane dendrimer.\(^{41}\) Since these dendron-based diphenylphosphinophenol ligands can form more stable \(bis(P,O)\)-Ni complexes than those of the corresponding parent ligand in toluene, the former out-performed the later for the oligomerization of ethylene. This metalloendrimer (Figure 1.3) is one of the rare
examples in which the core-functionalized dendritic catalyst is far more active than its parent complex due in-part to site-isolation of the catalytic nucleus.

1.2.1.2 Cu-based Dendritic Catalysts

Chow et al. designed a Cu(II)-bis(oxazoline) dendritic catalyst (Figure 1.4) to accelerate the Diels-Alder reaction between cyclopentadiene and crotonyl imide. A kinetic study supporting a two-step mechanism for this Diels-Alder reaction was demonstrated, in which a reversible binding of the dienophile to the copper complex was followed by the rate-determining step between the resulting dienophile-catalysts and the
diene. In addition, the initial complexation constant for this dienophile-catalyst complex gradually decreased with increasing dendrimer generation, while the Diels-Alder reaction rate constant remained similar for the 0 - 2\textsuperscript{nd} generation catalysts; it notably decreased at the 3\textsuperscript{rd} generation.\textsuperscript{42} These observations were rationalized as a consequence of back-folding of the dendritic arms at the 3\textsuperscript{rd} generation thereby inhibiting access to the catalytic center. Thus, the increased steric size impeded both the reactivity and binding profile of the catalyst. These results were described as an exo- to endo-active site transition that hindered the approach of the diene toward the dienophile-catalyst complex.\textsuperscript{43,44}

Figure 1.4 Chow’s dendritic copper(II)-bis(oxazoline) metalloendrimer developed for the Diels-Alder reaction.
Buckminsterfullerene [C_{60}] can be used as a compressed spherical core in the facile construction of globular dendrimers\textsuperscript{45-47} and lipofullerenes with an octahedral pattern.\textsuperscript{48-50} The use of C_{60}, as the core, allowed not only the synthesis of adducts with $T_h$ symmetry,\textsuperscript{51} but also those with $C_{2v}$, $C_s$, and $C_3$ symmetries. Hirsch \textit{et al.}\textsuperscript{52} synthesized enantiomerically pure $C_3$-symmetrical fullerene dendrimers, such as $all-R\text{-}^{f}A$, $all-S\text{-}^{f}C$, $all-R\text{-}^{f}C$, and $all-S\text{-}^{f}A$, as well as $all-S\text{-}^{f}A$ and $all-S\text{-}^{f}C$ lipofullerenes involving an octahedral [3:3] addition pattern (Figure 1.5). The novel near-core incorporation of the

![Figure 1.5 A fullerene dendritic ligand for Cu(OTf) complexation](image-url)
bis(oxazoline) moieties that subsequently form internal Cu(II) complexes was capable of serving as catalytic sites for the cyclopropanation of styrene with ethyl diazoacetate. The stereoselectivity caused by these prototypes (termed dendrizymes) was shown to be very low when compared to those obtained with other bis(oxazoline) catalysts. The ee-trans values for the cyclopropanation of styrene using the all-S-A and all-S-C in the presence of Cu(OTf), as co-catalyst, were determined to be 2 and 1, respectively; whereas, the ee-cis values were found to be 9 and 7, respectively.

1.2.1.3 Rh-based Dendritic Catalysts

Hydroformylation has been widely used for homogeneous catalytic processes to produce aldehydes and alcohols. Reek et al. have reported the synthesis of dendrimers possessing both mono- and bi-dentate end-groups through the hydrosilylation of different generations of carbosilane dendrimers with HSiMe2Cl or HSiMeCl2, followed by reaction with LiCH2PPh2-(N,N,N',N'-tetramethylethylenediamine (TMEDA). These Ph3P-functionalized carbosilane dendrimers were used, as ligands, for the Rh-catalyzed hydroformylation of 1-octene. The rhodium metalloendrimers were shown to possess the same selectivity when compared to the related monomeric analogues; the catalytic activity was shown to be dependent on the generation and flexibility of the metalloendrimers. These results are in agreement with Alper et al.'s observations employing rhodium-complexes coordinated to the bidentate phosphine-functionalized polyamidoamine dendrimers on silica.

Reetz et al. have introduced polypropylenimine (PPI) dendrimers as the core for building phosphine-coated constructs that can complex with Rh(COD)-BF4, where COD
= 1,5-cyclooctadiene, to instill the desired catalytic character. Hydroformylation of 1-octene with these metalloendrimers was shown to have turn-over numbers that were comparable to that of monomeric analogues. It was pointed out that these catalysts could be easily recovered by means of membrane separation technology.\(^6^0\) Whereas, Gong et al.\(^6^1\) have used water-soluble, phosphonated dendritic ligands based on the PAMAM frame for a similar transformation. These metalloendrimers were tested as the catalyst in a two-phase hydroformylation using either styrene or 1-octene under mild (40 °C, 20 atm) reaction conditions. In case of styrene, Rh(I) complexes exhibited a higher selectivity to form 2-phenylpropionaldehyde (branched type) over hydrocinnamaldehyde (linear-type) products. In contrast to styrene, the hydroformylation of 1-octene was shown to favor 1-nonanal (linear-type) over 2-methylpentanal.

Jeffrès and Morris\(^6^2\) have developed dendrimers that utilized a polyhedral oligosilsesquioxane (POSS) core with up to 72 termini. Using a similar strategy, Cole-Hamilton et al.\(^6^3^-^6^5\) introduced the polyhedral oligosilsesquioxane core to construct alkylphosphine-coated dendrimers capable of reacting with either [Rh(acac)(CO)\(_2\)] or [Rh\(_2\)(OAc)\(_4\)]. The hydrocarbonylation of propen-1-ol using the 1\(^{st}\) generation dendritic ligand shown in Figure 1.6 led to the formation of identical products (butane-1,4-diol and 2-methylpropan-1-ol) to those reported elsewhere;\(^6^6\) however, the formation of the linear alcohol (butane-1,4-diol) clearly occurred via a two-step reaction, i.e. hydroformylation to form 4-hydroxybutan-1-al and subsequent reduction. The construction of 2-methylpropane-1-ol probably occurred via a hydroxycarbene intermediate with intermolecular protonation of the acyl moiety.\(^6^3\)
Another dendrimer possessing 16 Ph$_2$P-termini was shown to exhibit much higher linear selectivity (14 : 1) than those of the monomeric analogues (3 - 4 : 1) in the hydroformylation of oct-1-ene catalyzed by the Rh(I) complex. In this metallodendrimer, the phosphorus atoms were separated by 4 - 7 Å within one arm, while its distance is in the 5 - 10 Å range between arms (from molecular modeling). Indeed, analogous metallodendrimers containing two CH$_2$ units between the Si and P atoms showed no special selectivity enhancement over that of the monometallic catalysts. This positive dendritic effect was explained by steric crowding coupled with diminished arm length inducing an eight-membered bidentate coordination that enhanced the linear selectivity.

Figure 1.6 Cole-Hamilton’s dendrimer based on a polyhedral oligomeric silsesquioxane core.

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Kakkar et al.\textsuperscript{67,68} reported the divergent synthesis of a novel series of organophosphine dendrimers possessing both a phosphorus core and branching centers with [-OSiMe\textsubscript{2}O-] connectivity as well as terminal hydroxy groups. The treatment of these multi-tiered phosphorus centers with [Rh(µ-Cl)(η\textsuperscript{4}-1,5-COD)]\textsubscript{2} generated metallodendrimers containing both internal and external [RhCl(η\textsuperscript{4}-COD)PR\textsubscript{3}] organometallic centers; such complexes were shown to catalyze the hydrogenation (25 °C, 20 bar H\textsubscript{2}, 30 min, THF) of 1-decene in a 1:200 metal-to-substrate ratio. There was a slight decrease in turnover frequencies with the larger Rh(1)\textsubscript{46} metallodendrimer. After one hydrogenation cycle using this Rh(1)\textsubscript{46} metallodendrimer, the organic products were extracted into pentane and the dendritic catalyst was isolated, recrystallized from THF/hexane, and reused with only a 5 % decrease in catalyst's activity [resulting in a turnover number of \textit{ca.} 200 mol\textsubscript{prod}(mol\textsubscript{cat})\textsuperscript{-1} and turnover frequency of \textit{ca.} 400 mol\textsubscript{prod}(mol\textsubscript{cat})\textsuperscript{-1}h\textsuperscript{-1}], which was found to be similar to that of the corresponding monometallic complex. Indeed, other metallodendrimers\textsuperscript{68} were derived from these organophosphine dendrimers by treatment with [Rh(COD)Cl]\textsubscript{2} by means of a bridge-splitting procedure. Catalytic hydrogenation of 1-decene with these 3,5-dihydroxybenzyl alcohol-based organometallic dendritic materials\textsuperscript{69} under standard conditions (25 °C, 20 bar H\textsubscript{2}) was found to be dependent upon two distinct factors: reaction time and generation number; the maximum conversion was accomplished in a 5 hour timeframe.

Also, the use of dendrimers, as templates to prepare network carriers containing cavities of predetermined size and disposition, has been reported.\textsuperscript{70} Recently, Rossell \textit{et al.}\textsuperscript{71} have constructed cationic Rh-containing carbosilane metallodendrimers, whose catalytic activity was tested for the hydrogenation of 1-hexene under mild conditions (25
°C, 10 bar H₂, 1h, Me₂CO) in a 1:500 metal-to-substrate ratio. There was a slight decrease in turnover frequency with the larger Rh(I) metalloendrimers, but they obtained comparable results with Kakka’s group. Similar ruthenodendrimers were also evaluated as catalysts in the hydrogen transfer of cyclohexanone with 2-propanol. Similar ruthenodendrimers were also evaluated as catalysts in the hydrogen transfer of cyclohexanone with 2-propanol.

Reek et al. developed a new bicarbazolediol (BICOL)-based, chiral monodentate phosphoramidite ligand, in which the N-sites in the bicarbazole skeleton permitted the easy introduction of metal centers. As a model reaction, the Rh-catalyzed asymmetric hydrogenation of methyl 2-acetamidocinnamate was evaluated. Using a ligand to rhodium ratio of 2.2, the enantioselectivity induced by the rhodium complex (Figure 1.7) was 93% at full conversion, which is comparable to the results obtained by Feringa et al. using 1,1'-binaphthol- (BINOL)-derived monodentate phosphoramidite ligands.

Figure 1.7 A dendritic phosphoramidite ligand for Rh catalysis.
monophos. These results demonstrated the ability of the bicarbazole bidentate to induce a high degree-of-enantioselectivity.

Arya and Alper et al. initiated a new strategy to explore the application of immobilized dendritic ligands anchored onto silica gel and polystyrene-based beads for use in hydroformylation reactions in order to minimize the recycling cost of the Rh catalyst. To examine the recycling behavior of the polystyrene-supported Rh catalyst in a hydroformylation reaction, $p$-methoxystyrene was selected as a model compound. The 1$^{\text{st}}$ generation catalyst was found to be very reactive up to the 4$^{\text{th}}$ cycle (99 %) but the conversion to the product decreased to 56 % for the 5$^{\text{th}}$ cycle. While, the 2$^{\text{nd}}$ generation catalyst was found to be equally reactive (> 99 % for the 4$^{\text{th}}$ cycle), there also was a continued reactive behavior observed for the 5$^{\text{th}}$ cycle (> 85 %). It was generally believed that the polymer-supported catalysts are less reactive compared to homogeneous catalysts; however, these results emphasize the enhanced recycling potential since this approach facilitated the recovery of the catalyst using various size exclusion techniques.

Busetto et al. have reported the synthesis and catalytic properties for various rhodium complexes of the type $[\text{Rh}\{\text{C}_5\text{H}_4\text{CO}_2\text{(CHR)}_2\text{OH}\}(\text{L,L})]$, $[\text{R} = \text{H, Me, Ph}; \text{L,L} = \text{2CO, 2,5-norbornadiene (NBD)}]$ prepared from the readily available sodium β-hydroxyalkoxycarbonyl-cyclopentadienides, Na[\text{C}_5\text{H}_4\text{CO}_2\text{(CHR)}_2\text{OH}]$, and $[\text{Rh}($\text{L,L}$)$Cl$]_2$. The rhodium complexes, $[\text{Rh}\{1R,2S\text{-CpCO}_2\text{(CHMe)}_2\text{OH}\}(\text{NBD})]$ and $[\text{Rh}\{1S,2S\text{-CpCO}_2\text{(CHMe)}_2\text{OH}\}(\text{NBD})]$, where $\text{Cp} = \eta^5$-$\text{C}_5\text{H}_5$, are active catalysts for the hydroformylation of hex-1-ene. They synthesized a new family of DAB-$\text{dendr-}$-$[\text{NH(O)}\text{COCH}_2\text{CH}_2\text{OC(O)C}_5\text{H}_4\text{Rh(\text{NBD})}_n] (n = 4, 8, 16, 32, 64)$ metalloendrimers by
treatment of the PPI dendrimers with alkoxy carbonylcyclopentadienyl complexes of Rh(I).

Chiral diphosphines are the most widely used ligands in the asymmetric, catalytic hydrogenation of C=\( \equiv \)C and C=O bonds\(^{85} \). \( 3,4\)-Bis(diphenylphosphino)pyrrolidine (pyrphos), which was easily synthesized from natural tartaric acid, contains an amino group to which organic or inorganic supports may be directly attached. Rh-pyrphos complexes and its derivatives have been studied for the asymmetric hydrogenation of dehydroamino acid and found to exhibit 99% ee\(^{86,87} \). Chan et al.\(^{88} \) synthesized the novel chiral dendritic diphosphine ligand for Rh(I)-catalyzed asymmetric hydrogenation of \( \alpha \)-acetamidocinnamic acid, as a model reaction. In the case of dendritic pyrphos-Rh catalysts (from 1\(^{st} \) - 4\(^{th} \) generation), a dramatic change in catalytic activity was observed in the transition from the 3\(^{rd} \) to 4\(^{th} \) generation, which might correlate with a change in shape of the metallodendrimer from a flattened or pancake-like motif to a more globular structure.

\( N \)-Heterocyclic carbene (NHC) ligands have attracted considerable attention in both homogeneous catalysts and organometallic chemistry because their strong coordination to metals compared to conventional ligands, such as phosphines, prevented their dissociation from metal center\(^{89,90} \). Tsuji et al.\(^{91} \) synthesized imidazolium salts bearing Fréchet-type polybenzyl ether dendrons and investigated their catalytic performance as well as the dendritic effect on the hydrosilylation of ketones (Figure 1.8). A positive dendritic effect was found in solvents, such as benzene and CH\(_2\)Cl\(_2\); the rationale was that the dendron's aromatic character interacted with the rhodium metal. Indeed, the dendritic effect was also influenced by the concentration of the reaction.
When the hydrosilylation of acetophenone was conducted under dilute conditions, the yield of 1-phenylethanol decreased considerably to 44% after 46 h with the 1\textsuperscript{st} generation catalyst, while with the higher generations (2\textsuperscript{nd} - 4\textsuperscript{th}) catalysts, the yields were unchanged.

1.2.1.4 Pd-based Dendritic Catalysts

There has been great interest in olefin oxidation since the successful application of the Wacker process\textsuperscript{92} for the industrial production of acetaldehyde. This catalytic system consisted of an aqueous acidic solution of a palladium salt with a copper(I) salt and oxygen or air, as an oxidant; however, application of the Wacker process to longer chain...
alkenes has been a challenge due to their low solubility in aqueous media. This has led to research in biphasic systems using tetraalkylammonium salts, polyethylene glycols, as well as cyclodextrins.

Alper et al. immobilized palladium-modified PAMAM-like dendron complexes onto silica for carbonylation of iodobenzene in MeOH to generate methyl benzoate under low pressures of CO at 100 °C. Product yields were high overall and the catalyst could be recycled 4 - 5 times without significant loss of activity. This type of PAMAM-type dendron-Pd complex was also used for the oxidation of terminal alkenes to generate methyl ketones under mild conditions; oxidative selectivity towards the terminal vs. internal double bonds was also determined.

Kragl et al. described the retention of diaminopropyl-type metalloendrimers bearing palladium phosphine complexes on ultra- or nanofiltration membranes and their use as catalysts for allylic substitution in a continuously operating chemical membrane reactor. Their results demonstrated a viable procedure for catalyst recovery because these metalloendrimers acting as catalyst supports offered an advantage that the intrinsic viscosity of the solution is smaller facilitating filtration.

Screttas et al. synthesized a PPI dendrimer with an iminophosphine surface functionality, DAB-dendr-[1,2-(N=CHC₆H₄PPh₂)]₃₂ ("DAB-32-imiphos"), and the corresponding reduced aminophosphine-based constructs, DAB-dendr-[1,2-(NHCH₂C₆H₄PPh₂)]₃₂ ("DAB-32-amiphos") as well as evaluated these P,N-dendritic ligands, as catalyst for the Heck reaction by coordination with Pd. Palladium acetate (1 %) in the presence of 3 equivalents of DAB-32-imiphos, lithium acetate, and a solvent mixture of tri-n-butylamine and acetic acid at 130 °C for 15.5 h converted bromobenzene
completely to a mixture of ca. 90 % trans-stilbene and ca. 10 % isomers. The reaction seemed to proceed better in a novel equimolar solvent mixture of a tertiary amine and acetic acid. A marked dependence of the conversion on the [equiv. of dendritic ligand]/[Pd] ratio has been observed; the higher this ratio, the lower the conversion, which became zero for ratios greater than 15. This result implied that there is a rather strong inter-arm interaction within the dendrimer to which the metal is coordinated, preventing the substrate from competing for a coordination site on the metal. However, due to the diminished thermal stability of the ligands, it probably underwent degradation under the reaction conditions and the extensive formation of Pd-black. Thus, these catalytic systems were not recoverable.

Reek and van Leeuwen et al. functionalized carbosilane dendrimers with diphenylphosphane-termini, then transformed these moieties into the corresponding palladium complexes. Similar to the above work, these Pd-functionalized dendrimers were used to explore their catalytic behavior in continuously operated membrane reactors. The 2nd generation carbosilane dendrimer, serving as the starting point, was a white solid whose X-ray crystal structure was determined and whose molecular volume of 2,414 Å³ was anticipated to be large enough for catalyst separation from the reaction mixture by nanofiltration. These phosphine-functionalized dendrimers were synthesized by repeated hydrosilylation of double bonds with HSiMe₂Cl or HSiMeCl₂, followed by termination with Ph₂PCH₂Li/TMEDA. The phosphine-terminated dendrimers were metalated with [PdCl(η³-C₃H₇)]₂ to yield either bidentate palladium phosphine metallodendrimers or mixtures, when monodentate dendritic phosphines were used. All these metallodendrimers were used as catalysts in allylic alkylation of allyl
trifluoroacetate and diethyl methylsodiomalonate yielding diethyl allyl(methyl)malonate. The reaction was first conducted in a batch process; all metallodendrimers showed a very high catalytic activity. Using 0.2 % of catalyst, the yield was greater than 80 % after 30 min and only small differences of reaction rates were observed for the different catalysts. The metallodendrimer containing 12 chelated palladium atoms with a calculated volume of $ca. 7600 \, \text{Å}^3$ was used as a catalyst in a continuous process. Retention of this catalyst in the membrane reactor was determined to be 98.1 %, which corresponds to a calculated value of only 25 % decreased activity after flushing the reactor (15 times). Samples taken from the flow stream were not catalytically active, which confirmed that the observed decrease of activity was due to decomposition of the palladium complex and not due to the loss of dendritic catalyst.

The Sonogashira reaction$^{105,106}$ couples aryl or vinyl halides to terminal alkynes and has wide-spread synthetic appeal due to an efficient conversion without requiring the preparation of an organometallic intermediate. Astruc et al.$^{107,108}$ synthesized a series of $\text{bis(tert-butylphosphine)}$- and $\text{bis(cyclohexylphosphine)}$-functionalized Pd(II) monomers and PPI-coated catalysts and investigated the Sonogashira carbon-carbon coupling reaction under efficient copper-free procedures. The $\text{tert-butyl}$ metallodendrimer series was shown to catalyze the Sonogashira reaction of iodoarenes with phenylacetylene at 25 °C, although longer reaction times than with monomeric catalysts were required; whereas, the cyclohexyl-counterparts were active at 80 °C and maintained the same catalytic efficiency after five recycling operation as well as proved to be easier to recover than the former $\text{tert-butyl}$ series due to solubility considerations.
van Koten’s group\textsuperscript{109} investigated the aldol condensation of benzaldehyde and methylisocyanate to afford oxazoline that was catalyzed by cationic cyclopalladated carbosilane dendrimers serving as Lewis acids. Their catalytic performance was compared to that of the parent mononuclear derivative [Pd(C\textsubscript{6}H\textsubscript{3}\{CH\textsubscript{2}NMe\textsubscript{2}\}-2-(SiMe\textsubscript{3})-5)(pyr)(H\textsubscript{2}O)][BF\textsubscript{4}]. Results indicated that up to the 2\textsuperscript{nd} generation, the selectivity of the reaction was not affected; however, the rate-of-reaction decreased with increasing steric congestion at the dendrimer's periphery.

Using divergent procedures, Moberg \textit{et al.}\textsuperscript{110} prepared the 1\textsuperscript{st} - 4\textsuperscript{th} generation dendritic substituents based on 2,2-\textit{bis}(hydroxymethyl)propionic acid and (1\textit{R},2\textit{S},5\textit{R})-methoxyacetic acid. The resultant dendrons were attached to 2-(hydroxymethyl)pyridinooxazoline and \textit{bis}[4-(hydroxymethyl)oxazoline]; the resulting ligands were assessed in Pd-catalyzed allylic alkylation. Introduction of a chiral dendritic substituent on the pyridinooxazoline ligand has less effect on the enantioselectivity, two diastereomers (\textit{R})- and (\textit{S})-chiral dendron ligands each resulted in 79 \% ee. In contrast, substitution of the \textit{bis}(oxazoline) ligand with the same chiral dendron gave the (\textit{S},\textit{S})-chiral dendron ligand, which exhibited higher stereoselectivity (94 \% ee) than the \textit{bis}(oxazoline) ligand with achiral dendrons. The lesser enantioselectivity in the reactions using the pyridinooxazoline ligands was explained by the ring-distance between the dendritic substituent and the catalytic center and/or the high flexibility of the system. In the case of the \textit{bis}(oxazoline) series, the dendritic wedges seemed to be situated close enough to the catalytic center to have an effect on both stereoselectivity and reactivity, thereby leading to increased stereoselectivity but decreased catalytic activity.
Recently, van Koten et al.\textsuperscript{111} designed a specific metallodendrimer possessing encapsulated (within a tailored macrocycle) catalytic sites to influence regio- as well as stereo-control (Figure 1.9). The $N,C,N$-pincer moiety was linked to the core and the other was used to coordinate the active metal atom as well as to provide the next branching point at a remote -Si(Ph$_2$)- site within a macrocycle for further extension of the dendritic structure. Following this approach, they synthesized a new macrocyclic carbodiazasilane ligand and a para-OH functionalized ligand, as cages, then their attachment to a central core and the subsequently transformed to the corresponding palladium(II) complexes by

![Figure 1.9 A tricyclopalladated metallodendrimer.](image-url)
oxidative addition. The aldol condensation of benzaldehyde and methyl isocyanoacetate was higher using the tricyclopalladated catalyst than with other mononuclear models tested; however, the steric chiral environment around the Pd center did not have an influence on the diastereoselectivity of the resultant reaction.

The Pd(II) allyl and Pd(0) fumaronitrile complexes bearing pyridyl-dithioether-based metallodendrimers, as ancillary ligands, have been constructed by Canovese and Chessa et al.\textsuperscript{112} The reactivity (based on the second-order rate constant and equilibrium constant) of these complexes was tested with respect to allyl amination using piperidine. No macroscopic effects were observed when going from a nondendritic model to the 2\textsuperscript{nd} generation dendritic substrates; although the 3\textsuperscript{rd} generation complex exhibited notable variations in the observed rate and equilibrium constant. This phenomenon was rationalized as a rearrangement that was induced by an increase in steric hindrance at the allyl fragment and a concomitant distortion of the ligand environment at the metal core. This suggested a justification for the decreased rate constant and increased equilibrium constant values.

Heck olefin arylation,\textsuperscript{113} one of the most widely used reactions in synthetic organic chemistry, has been successfully conducted in solution with a variety of aryl iodides, bromides, and chlorides, using numerous dendritic catalytic systems. Recently, Portnoy et al.\textsuperscript{114} constructed the first poly(aryl benzyl ether) dendronized polystyrene resin and then decorated it with Pd(dba)\textsubscript{2} in THF at 25 °C. Treatment of bromobenzene with methyl acrylate under typical Heck conditions was conducted from which the 2\textsuperscript{nd} and 3\textsuperscript{rd} generation catalysts proved superior in all parameters to the monodendron analogue. Thus, the selectivity of the catalysis was significantly improved with higher
dendron generation. To examine whether these observed dendritic effects were limited only to electron-deficient olefinic substrates, the performance of the metallo-dendrimers with butyl vinyl ether, as a substrate, was tested. According to the regio- and stereo-selectivity results, the proportion of the α-arylated product increased as the generation number of the polymer template was increased. The decrease in β-/α-arylation ratio for butyl vinyl ether was attributed to a higher portion of the olefin insertion occurring through cationic intermediates (enforcing α-arylation) vs. neutral intermediates (yielding mixtures of α- and β-arylated enol ether).\textsuperscript{115} This change in the distribution between the two alternative catalytic pathways may result from the more polar environment of the catalytic units in the case of the higher generation catalysts. Alternatively, or additionally, the reason for this change may be associated with the increased local loading of phosphines in higher generation of dendrons.

Kaneda \textit{et al.}\textsuperscript{116} constructed a dendrimer-bound Pd(II) complex, which was prepared by complexation of the diphenylphosphinomethyl-capped PPI dendrimer, DAB-dendr-[N(CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2}]\textsubscript{16}, with PdCl\textsubscript{2}(PhCN)\textsubscript{2}. This catalyst showed selective activity in the hydrogenation of conjugated dienes to monoenes under an atmospheric pressure of H\textsubscript{2}. The dendritic catalyst was easily recovered from reaction mixtures and could be reused without any loss in catalytic activity. Allylic amination using dendrimer-bound Pd(0) and Pd(II) complexes was also investigated\textsuperscript{117-119} in which these catalysts showed high stereoselectivity ascribed to surface congestion. Employing a thermomorphic system made it possible to efficiently recycle the dendritic catalysts.

Gade \textit{et al.}\textsuperscript{120} reported a strong positive dendritic effect in the asymmetric catalysis in the allylic amination of 1,3-diphenyl-1-acetoxypropene with morpholine.
when using pyrophos-palladium-functionalized PPI and PAMAM dendrimers. A remarkable and unprecedented increase in catalyst selectivity was observed as a function of the dendrimer's generation. This steady increase of $ee$-values for these allylic aminations was less pronounced for the PPI-derived Pd-catalysts than for the corresponding PAMAM-catalysts for which an increase in selectivity from 9% $ee$ for a mononuclear reference system to 69% $ee$ for the $Pd_{64}$-dendrimer was realized.

The synthesis of artificial active sites\textsuperscript{121-125} for hosting transition metal catalysts with unique reactivity profiles is an important issue, but it can be technically difficult. Gagné \textit{et al.}\textsuperscript{126} first synthesized a polymerizable amino-acid containing a diphosphine ligand possessing eight styrenyl units; this ligand was utilized in the synthesis of a series of $P_2$Pd$X_2$ complexes ($X_2 = (R)$-BINOL, (S)-BINOL, Cl$_2$, and 1,3-Ph$_2$-allyl$^+$). Their metallomonomers were used as co-monomers in the synthesis of permanently porous ethylene dimethacrylate (EDMA)-base polymers which in turn served as catalysts for the alkylation of allylic acetates. Removal of the large ligands from the metalloendrimer post-polymerization ensured that the catalyst had sufficient room at the active site to accommodate the reactants necessary to accomplish catalysis.

1.2.1.5 Ru-based Dendritic Catalysts

Hoveyda’s group\textsuperscript{127} synthesized two efficient and recyclable dendritic Ru-based metathesis catalysts (Figure 1.10). The structure of the monomeric catalyst differs from the Grubbs’ catalyst, [Ru(PPh$_3$)$_2$Cl$_2$(=CHPh)],\textsuperscript{128,129} in that a chelating carbene (2-\textit{isopropoxystyrene}) takes the place of the benzylidene and one phosphine. In the 4-directional Si-centered dendrimer, the [-($CH_2$)$_3$SiMe$_2$(CH$_2$)$_3$OC(O)(CH$_2$)$_2$] branches are
units connected to the styrenyl ether ligand. The yield of ring-closing metathesis of TsN(CH$_2$CH=CH)$_2$ using only 5 mol % of ruthenium-based dendritic catalyst was shown to proceed at 99 % conversion. The catalyst was recovered with 13 % vacant styrenyl ligand sites (i.e., 13 % Ru loss). Repetitive use of the dendritic catalyst led to complete conversion of TsN(CH$_2$CH=CH)$_2$ in 91 % yield. The dendritic catalyst remained active after 6 cycles (although 59 % of the Ru content was lost) affording yields of 87 % in the ring-closing metathesis process. The high level of activity was suggested to arise, at least partially, to the release of a highly active monophosphine Ru complex into the solution. It suggested that the catalytically active Ru species was released from the dendrimer into the reaction mixture and could be trapped again by a styrenyl ether ligand arm of the dendrimer. Another analogous 4-directional metallo dendritic catalyst (Figure 1.10) was prepared in which the last phosphine ligand was replaced by a diamino-carbene ligand used in the Grubbs catalyst for the design of an extremely efficient next generation metathesis catalyst. This dendritic catalyst exhibited greater activity than the former in that it promoted formation of trisubstituted allylic alcohol and was recovered with only an 8 % Ru loss. It also catalyzed tandem ring-opening or ring-closing metathesis and was easily separable from reaction mixtures because of its polarity and high molecular weight. Ring-closing metatheses of diethyl diallylmalonate to the favored five-membered cyclopentene ring using chelating dendritic ligands coordinated to Ru have also been achieved by the van Koten group.

Using an efficient electron-transfer chain reaction with [Ru$_3$(CO)$_{12}$] catalyzed by [FeCp($\eta^6$-C$_6$Me$_6$)], Astruc et al. introduced 32 or 64 [Ru$_3$(CO)$_{11}$] clusters into a 32-branched dendritic phosphine synthesized by Reetz et al. using the double phosphine-
methylation of a 3rd generation PPI dendrimer\textsuperscript{133} with PPh\textsubscript{2}CHOH.\textsuperscript{134} The bis(phosphine)s end units possessing two cyclohexyl groups on each phosphorus were reacted with monoruthenium carbone complexes, which were made by replacement of PCy\textsubscript{3} to PPh\textsubscript{3} in the Hoveyda's metathesis catalyst.\textsuperscript{127,135} These constructs provided four generations of new, stable metallo dendrimers containing ruthenium-benzylidene units at the periphery.\textsuperscript{136} The 4th generation metallo dendrimer containing 32 ruthenium-benzylidene units, however, was found to have rather low solubility in common organic solvents, unlike the 1st - 3rd generation complexes that contained 4-, 8-, and 16-ruthenium-benzylidene moieties, respectively. The poor solubility of the 32-Ru metallo dendrimer was presumably due to peripheral steric congestion. The X-ray crystal structure of the model mononuclear complex in which the dendritic branch was replaced

Figure 1.10 Hoveyda’s dendritic Ru-based metathesis catalysts.
by a benzyl group revealed distorted square pyramidal geometry and the classic geometric features of a Ru=C double bond. These 1st - 3rd generations of metallodendrimers and the model complex were efficient catalysts for the ring-opening metathesis polymerization of norbornene under ambient conditions giving dendrimer-cored star-shape polymers. Analyses of the molecular weights by size-exclusion chromatography (SEC) gave data that were close to theoretical, which indicated that all the branches were efficiently polymerized. It was determined that dendrimer-cored star-shape polymers with ca. 100 norbornene units on each dendritic branch were synthesized with these ruthenium carbene-based dendrimers.

Moss, et al.\textsuperscript{137} investigated the Fischer-Tropsch synthesis\textsuperscript{138} using the hexa-branched ruthenium metallodendrimer supported on silica. The dendritic branches each possessed 18-electron [RuCp(CO)]\textsubscript{2}alkyl termini. Under Fischer-Tropsch conditions, this metallodendrimer was metastable. The "time-on-stream" behavior of this catalyst in the CO hydrogenation was compared to an impregnated Ru/SiO\textsubscript{2} catalyst and showed no Fischer-Tropsch specific product pattern, which was substantiated by the rate-of-formation of some specific hydrocarbons. This study showed that a single ruthenium site was not sufficient for this particular reaction.

Majoral’s group\textsuperscript{139} used a 3rd generation metallodendrimer containing 24 terminal ruthenium diphosphine complexes to catalyze the Knoevenagel condensation\textsuperscript{140} between malononitrile and cyclohexanone leading to the corresponding unsaturated nitrile and Michael addition between ethyl cyanoacetate and diethyl ethylidene malonate. The activity was compared with that of the simple monomeric complexes but was often higher; recycling was also possible without significant loss of catalytic activity.
Catalytic hydrogenation of organic substrates is a widely studied chemical transformation. An alternative method, which avoids the use of gaseous hydrogen and uses standard reflux techniques, is provided by hydrogen-transfer processes where the hydrogen is supplied by a hydride donor (such as: cyclohexadiene or formic acid), which itself undergoes oxidation (dehydrogenation) during the course of the reaction. These catalytic systems are relatively stable, easy to handle, and environmentally friendly. Rossell et al. synthesized a series of metallodendrimers by treatment of phosphanyl-terminated carbosilane dendrimers displaying only one phosphorus ligand per arm with [RuCl₂(p-cymene)]₂ (Figure 1.11). Activity of the multi-(η⁶-arene)-ruthenium(II) species was compared with the corresponding ruthenium(II) mononuclear complexes in the reduction of cyclohexanone by a hydrogen transfer reaction. Dendritic systems showed lower activities than that found for related mononuclear complexes. Among 1st generation metallodendrimers, the neutral species was more active than the corresponding cationic analog, following the same trend found for mononuclear species. Under standard conditions, the cationic species resulted in only 62 % conversion, showing possible catalyst decomposition. The 3rd generation metallodendrimer was less active than that of the 1st generation; nevertheless, these systems showed higher activities than those reported in the literature for other dendritic systems.

1.2.1.6 Ti-based Dendritic Catalysts

Tilley et al. synthesized a series of dendritic Ti-containing catalysts for the epoxidation of cyclohexene; these catalysts were shown to be very selective and more active in terms of yields and initial rates than the Shell catalyst prepared by the
treatment of silica with [Ti(OiPr)₄]. The 2nd and 3rd generation alkoxyaryl-terminated carbosilane dendrimers have been used as building blocks for the synthesis of high surface area xerogels. The acid-catalyzed hydrolysis of Si[CH₂CH₂CH₂Si-(CH₂CH₂Si(OEt)₃)₃]₄ and Si{CH₂CH₂CH₂Si[CH₂CH₂CH₂Si(CH₂CH₂Si(OEt)₃)₃]₃}₄ in benzene generated monolithic gels; the resulting xerogels possessed surface areas of 600 and 800 m²/g, respectively, in which the surface area of these xerogels increased with increasing dendritic radii. These xerogel-like gels were treated with Ti(OiPr)₄ to yield the desired catalyst system. All three gels were subsequently used as catalysts in the epoxidation of cyclohexene and shown to be very selective and significantly more active (in terms of yield and initial rate) than the traditional Shell catalyst.

Figure 1.11 Single and double metallic layer-containing ruthenium metalloconstructs.

Figure 1.11 Single and double metallic layer-containing ruthenium metalloconstructs.
Seebach et al.\textsuperscript{150,151} synthesized a hexa-armed dendrimer attached the $C_2$ symmetry ligand, TADDOL (α,α,α',α'-tetraaryl-1,3-dioxolane-4,5-dimethanol), complexing with Ti(OCHMe\textsubscript{2})\textsubscript{4} at the periphery. Using this chiral metallodendrimer, the enantiomeric addition\textsuperscript{152} of diethylzinc to benzaldehyde proceeded with the same enantioselectivity ($ee$, 97\%) as that of the monomeric chiral catalyst. Since this metallodendrimer had a molecular weight of only 3833 Da, its recovery had to be conducted by column chromatography rather then by an ultrafiltration technique. To simplify the recover process, Fréchet-type dendrons with styrenyl end groups to cross-link the catalyst into a polystyrene support were used whereby the TADDOL core was subsequently coordinated with Ti(IV).\textsuperscript{150,153-156} This polymeric catalyst showed: (1) an enantioselectivity above 9:1 for all polymers of low loading (\textit{i.e.}, 0.1 mmol TADDOL per g polymer), only the dendritic polymer gave rise to a constant selectivity of 98:2 in 20 sequential applications; (2) the catalytic performance dropped with increasing the chain length of the spacers between the TADDOL core and polymer backbone; (3) the low-loaded dendritic catalyst beads with the shortest spacer kept their swelling properties high even after 20 runs, while all others did not swell even after multiple reuse; and (4) the rate-of-reaction was the same with or without stirring using the beads of dendritic catalyst that had the shortest spacer filling the whole reaction volume under standard conditions. Thus, free diffusion of reactants and products to and from the active center was obtained.

Also, Seebach \textit{et al}.\textsuperscript{157} used dendritic Ti-TADDOLates with the 1\textsuperscript{st} - 4\textsuperscript{th} generation Fréchet-type dendrons in the enantioselective addition of Et\textsubscript{2}Zn to benzaldehyde. There was no detectable decrease of selectivity (98:2) up to the 2\textsuperscript{nd} generation and the rates marginally decreased up to the 3\textsuperscript{rd} generation. Enantiomeric branches caused no change
for stereoselectivity within experimental error. It was denoted that there might be applications for special properties such as high molecular weight, good solubility, and spacing of central sites from cross-linked polymer matrices.

Pu et al.\textsuperscript{158,159} have used 4,4',6,6'-tetrabromo-1,1'-bi-2-naphthol to construct a novel series of rigid and cross-conjugated optically active dendrimers. Following complexation with Ti(\(\text{O}^\text{\text{\text{T}}\text{r}}\))\textsubscript{4}, the chiral dendrimer exhibited high enantioselectivity in the catalysis of the reaction of 1-naphthaldehyde with diethylzinc; notably, the system catalyzed this reaction with 100 % conversion and 90 % \textit{ee} in 5 h without by-products. The advantage of this metallo-dendrimer over BINOL was that it could be easily removed from the reaction mixture by simple precipitation with MeOH.

Using (\(\text{R}\))-6,6'-dibromo-1,1'-binaphthol, Yoshida et al.\textsuperscript{160} synthesized optically active Ti-1,1'-binaphthol metallo-dendrimers containing poly(benzyl ether) wedges at the 6,6'-positions. The Ti-binaphthol-catalyzed allylation of the aldehyde and allyl stanane, as the model reaction,\textsuperscript{161} was demonstrated. Enantioselectivity remained constant with increased generation 0 - 3 (90 ± 2 % \textit{ee}; nondendritic parent, 87 % \textit{ee}).

Renewed interest in \(\beta\)-diketiminato transition metal complexes is partially due to this ligand's ability to stabilize coordinatively unsaturated complexes,\textsuperscript{162} which can function as catalysts for non-metallocene olefin polymerizations.\textsuperscript{163} Gómes et al.\textsuperscript{164,165} reported the synthesis and ethylene polymerization using mixed cyclopentadieny(\(\beta\)-diketimino) complexes possessing either titanium or zirconium catalytic sites engulfed with the 1\textsuperscript{st} generation carbosilane dendritic wedges linked to the \(\beta\)-diketiminato ligand (Figure 1.12). Mixed cyclopentadieny(\(\beta\)-diketiminato) complexes of titanium were obtained by direct reaction of (\(\eta^5\)-C\(_5\)H\(_5\))TiCl\(_3\) with dendritic \(\beta\)-diketimine in the presence
of triethylamine acting as a Lewis base promoting protonolysis of the metal-chloride bond. The catalysts' efficacy was better than the performance of the metalloocene complexes (η⁵-C₅H₅)MCl₃ (M = Ti, Zr); however, they displayed slightly higher activities than their non-dendritic counterparts.

1.2.1.7 Fe-based Dendritic Catalysts

Catalytic reduction of nitrate has been known for some time, but use of the iron-based redox catalyst [Fe(II)(η⁵-C₅H₄CO₂⁻)(η⁶-C₆Me₆)][PF₆] was the first example of an organometallic catalyst to effect this reaction.¹⁶⁶,¹⁶⁷ Astruc et al.¹⁶⁸ synthesized an
analogous water-soluble hexametallic redox catalyst employing the CpFe$^+$ group to induce hexa-allylation of hexamethylbenzene. The kinetics of an [FeCp(arene)]$^+$-centered star and dendritic-based star bearing the [FeCp(arene)]$^+$ group at the periphery were compared. Remarkably, the kinetics of catalysts bearing the [FeCp(arene)]$^+$ moiety attached to the dendritic core at the center of a star was determined to be one order-of-magnitude lower than that of such a star bearing the catalyst at the periphery.

Togni et al.$^{169}$ synthesized dendrimers using a cyclophosphazene core and 16 peripheral chiral ferrocenyl ligands (Figure 1.13). The periphery of these ferrocenyldiphosphine metallo dendrimers was decorated with [Rh(COD)$_2$][BF$_4$] to instill the desired catalytic properties necessary to reduce dimethyl itaconate. These metalloconstructs showed 98% ee, which compared well with the 99 % ee obtained with monomeric Rh-based josiphos catalyst.

1.2.1.8 Co-based Dendritic Catalysts

Jacobsen et al.$^{170}$ reported the synthesis of dendrimer-bound [Co(III)-(salen)] complexes, which demonstrated significantly enhanced catalytic activity in the hydrolytic kinetic resolution of terminal epoxides (Figure 1.14). This metal-salen [$H_2$ salen = \textit{bis}(salicylidenedi)ethylenediamine] catalyst has led to a proposed mechanism for asymmetric ring-opening (ARO) reactions involving the simultaneous activation of both epoxide and nucleophile by different metal-salen units.$^{171}$ These metallo dendrimers generated from the G0 ~ G2 PAMAM cores were compared and it was found that the best results were obtained with a simple core (4-branched) construct over that derived from either G1 or G2 cores. This catalytic system was shown to possess a positive
dendritic effect because of cooperativity in the key mechanistic step whereby a coordinated nucleophile attacks an epoxide coordinated to adjacent cobalt atom. Thus, it was the proximity of the two different cobalt complexes that favored the reaction.

Phthalocyanines and their metal complexes have interesting catalytic, electronic, and optical properties.\textsuperscript{172} Kimura \textit{et al.}\textsuperscript{173} synthesized a phthalocyanine-centered
dendrimer possessing Newkome-type dendrons$^{174}$ and subsequently used the 2$^{nd}$ generation cobalt-metallated phthalocyanine dendrimer, as the catalyst for the oxidation of mercaptoethanol by dioxygen (Figure 1.15). Catalytic stability was enhanced by the encapsulation within the dendritic structure due to the catalytic activity of metallophthalocyanines being influenced by phthalocyanine aggregation resulting from strong intermolecular stacking.

Figure 1.14 Breinbauer and Jacobsen’s dendritic PAMAM-Co(salen) complex.
For the Pauson-Khand [2+2+1] cycloaddition\textsuperscript{175} of alkyne, alkene, and carbon monoxide as well as promoted by Co\textsubscript{2}(CO)\textsubscript{8}, Portnoy \textit{et al.}\textsuperscript{176} synthesized a dendronized support modified with 2- and 4-(diphenylphosphino)benzoic acid groups; Co\textsubscript{2}(CO)\textsubscript{8} was then incorporated into the support. A notable increase in catalytic activity and selectivity for the intramolecular Pauson-Khand reaction was found for the Co complexes immobilized on the 2\textsuperscript{nd} and 3\textsuperscript{rd} generation dendron-functionalized polystyrene, when compared with the analogous non-dendronized support.
1.2.1.9 Mn-based Dendritic Catalysts

Suslick et al.\textsuperscript{177-179} designed dendritic chloromanganese(III) porphyrins for the catalysis of alkene epoxidation with iodosylbenzene, as an oxygen donor (Figure 1.16). The dendritic wedges were derived from the 1\textsuperscript{st} and 2\textsuperscript{nd} generation aromatic polyesters that provided a confined environment thus instilling better intra- and intermolecular regioselectivities than those obtained with the unsubstituted 5,10,15,20-

![Figure 1.16 Suslick’s dendritic chloromanganese(III) porphyrin.](image)

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tetraphenylporphyrinatotetramanganese(III) cation. The least hindered double bond of unconjugated dienes, such as found in 1,4-heptadiene and limonene, was epoxidized preferentially. Similarly epoxidation of a terminal monoalkene and cyclooctene mixture using a 2nd generation dendritic metalloporphyrins showed a 2- to 3-fold higher selectivity towards the 1-alkenes relative to a nondendritic catalyst. This regioselectivity was significantly reduced when compared to that of the classical picket-fence porphyrin, 5,10,15,20-tetrakis(2′,4′,6′-triphenylphenylporphyrin).180,181

Kawi et al.182 reported the anchoring of different PAMAMs to ultra-fine silica, then a Mn(II) salen complex was immobilization onto this functionalized silica surface to afford a bound dendritic catalyst for subsequent olefin epoxidation. Activity was determined to increase with increasing generation indicating the importance of amino group concentration on the periphery as well as the Mn loading of the Mn-selen complex. However, the length of the dendritic backbone chain also played an important role in improving the accessibility between the active sites and the reactant species to enhance the catalytic activity.

1.2.2 Luminescence

Luminescence can be defined as the emission of light (as in the broad sense of ultraviolet, visible, or near infrared radiation) by electronic excited states of atoms or molecules. Luminescence is an important phenomenon that is useful for monitoring excited state behavior183 as well as for utilitarian applications (e.g., laser, display, sensors, etc.).184 Since dendrimers are complex multifunctional constructs possessing well-defined
chemical tree-like structures as well as a high degree-of-order and they are capable of containing selected chemical units within predetermined sites in their structure, their incorporation into luminescence science can lead to systems capable of performing very interesting functions. In this section, we will review recent advances in the field of luminescent metallodendrimers.

1.2.2.1 Ru-based Metallodendrimers

Since the discovery of the photophysical properties of $[\text{Ru(bpy)}_3]^{2+}$ (bpy =2,2′-bipyridine), the light absorbing properties of this and related chromophores have been a research topic of great interest.$^{185,186}$ Recent attention has focused on the development of metallic supramolecular systems designed to absorb light and carry out a specific task such as the conversion of light energy to electrical or chemical energy.$^{187}$

Six dendrons built around a $[\text{Ru(bpy)}_3]^{2+}$-type core and bearing up to 24 4′-tert-butyphenyloxy or 48 benzyl units in the periphery have also been prepared by complexation of $\text{RuCl}_3$ or $[\text{Ru(bpy)}_2(\text{Cl})_3]$ with bipyridine ligands carrying dendritic wedges in the 4,4′-positions.$^{188}$ All the examined compounds show the characteristic luminescent excited state is again protected by the dendritic branches towards quenching by dioxygen. For three compounds containing the 4′-tert-butyphenyloxy peripheral units, the electrochemical behavior and the excited state quenching via electron transfer were studied in MeCN solution. The core of metallodendrimer showed an electrochemical behavior typical of encapsulated electroactive units. The reaction of the luminescent excited state of the $[\text{Ru(bpy)}_3]^{2+}$-type core with three electron transfer quenchers (namely, methylviologen dication, tetrathiafulvalene, and anthraquinone-2,6-disulfonate anion)
took place by a dynamic mechanism in all cases. The value of the quenching rate constant decreased with increasing number and size of the dendritic branches.

Campagna et al. studied the racemic species [(phen)$_2$Ru(phen-5,6-dione)(PF$_6$)$_2$] (phen = 1,10-phenanthroline), [(phen)$_2$Ru(phen-5,6-diamine)(PF$_6$)$_2$], [Ru(phen-5,6-dione)$_3$(PF$_6$)$_2$], [(phen)$_2$Ru(tpphz)(PF$_6$)$_2$] (tpphz = tetrapyrido[3,2-$a$:2',3':c:3"-,$h$:2",3"-]phenazine), [(phen)$_2$Ru($\mu$-tpphz)Ru(phen)$_2$(PF$_6$)$_4$], and [{(phen)$_2$Ru($\mu$-tpphz)}$_3$Ru(PF$_6$)$_8$], the stereochemically pure dinuclear species $\Delta\Delta$-[(phen)$_2$Ru($\mu$-tpphz)Ru(phen)$_2$(PF$_6$)$_4$], $\Lambda\Lambda$-[(phen)$_2$Ru($\mu$-tpphz)Ru(phen)$_2$(PF$_6$)$_4$], and $\Delta\Lambda$-
[(phen)₂Ru(µ-tpphz)Ru(phen)₂(PF₆)₄], and the stereochemically pure dendritic tetranuclear complexes [(Δ-(phen)₂Ru(µ-tpphz))₃-Δ-Ru(PF₆)₈] [(Δ-(phen)₂Ru(µ-tpphz))₃-Λ-Ru(PF₆)₈], and [(Δ-(phen)₂Ru(µ-tpphz))₃-Λ-Ru(PF₆)₈] (Figure 1.17). In all cases, luminescence decay was shown to be non-exponential with lifetimes in the range from 10⁻⁵ to 10⁻⁸ s. Also, energy transfer occurred in the dendritic tetranuclear complexes from the central chromophore to those on the periphery.

Vögtle et al. reported that the luminescent cyclam-based hosts, 1,4,8,11-tetraakis(naphthylmethyl)cyclam (A) and 1,4,8,11-tetra-3,5-bis[3′,5′-bis(2″-oxymethyl-naphthyl)benzyloxy]benzyl-1,4,8,11-tetraazacyclotetradecane (B), can be assembled with the luminescent metal complex [Ru(bpy)(CN)₄]²⁻ by a proton-driven process that causes strong changes in the luminescence properties. (Figure 1.18) In the {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·A} and {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·B} adducts formed in this way, very efficient energy transfer took place from the naphthyl units of (A) and (B) to the metal-ligand complex. Also, {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·A} and {[Ru(bpy)(CN)₄]²⁻·(2H⁺)·B} adducts can be disrupted by distinct chemical inputs, namely, addition of DABCO (1,4-diazabicyclo[2.2.2]octane), yielding the starting species [Ru(bpy)(CN)₄]²⁻ and A or B, or addition of triflic acid, with formation of (A·2H)²⁺ or (B·2H)²⁺ and protonated forms of [Ru(bpy)(CN)₄]²⁺. Such processes caused strong changes in the luminescent properties.

The metalloendrimer that is surface-coated with electrochemiluminescent (ECL) polypyridyl Ru(II) complexes, dendr-4-[Ru(L)₂(L')] (L=bpy-CO-, mbpy-(CH₂)₃CO-), were reported by Kim et al. The electrochemical properties of Ru(II) metalloendrimer containing the 4-carboxypropyl-4′-methyl-2,2′-bipyridine ligand were quite similar with those of the [Ru(bpy)₃(PF₆)₂] complex; however, the ECL intensity of
Figure 1.18 The [Ru(bpy)(CN)₄][Ru(bpy)_2(mbpy-(CH₂)₃CO-)(PF₆)₈] was significantly greater than that of the corresponding Ru(II) compounds containing the o-phenyl ligand and [Ru(bpy)_3(PF₆)₂] complex. The length of spacer connecting metal complex to dendrimer affected ECL intensity; as the length of spacer increased, ECL intensity increased. The dendr-4-[Ru(bpy)_2(mbpy-(CH₂)₃CO-)] was observed as the most efficient ECL materials.
1.2.2.2 Ir-based Metallodendrimers

*Bis*- and *tricyclometalated* iridium(III) complexes have been of increased interest recently owing to the possibility of their use as phosphorescent materials in organic light emitting devices (OLEDs).\textsuperscript{192-194} In these devices, singlet and triplet excited states arising from charge recombination are “trapped” with a chromophore in which fast intercombination conversion resulted in ambient temperature electrophosphorescence. One of the factors governing the performance of phosphorescence OLEDs is the spin-orbital coupling causing the singlet-triplet mixing of the excited states of the chromophore.

The Burn’s group\textsuperscript{195} synthesized a metallodendrimer consisting of a *fac-tris*(2-phenylpyridine) iridium core, phenylene dendrons, and 2-ethylhexyloxy surface groups. This device was prepared using a neat solution-processed method consisting of a iridiodendrimer emissive layer with an evaporated 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-based (BCP) electron-transport/hole-blocking layer. This unique metallodendrimer device exhibited bright green luminescence with a turn-on voltage of 4.5 V and peak brightness of 1,680 cd/m\textsuperscript{2} at 12 V but the maximum efficiency of the device was low, only reaching 0.14 lm/W (0.47 cd/A) at 9.5 V. Blend devices such as ITO/IrppyD:CBP:BCP:LiF/Al, ITO/IrppyD/TCTA/BCP/LiF/Al, and ITO/IrppyD:TCTA/TPBI/LiF/Al have also been examined; where, IrppyD is the metallodendrimer, CBP is 4,4′-*bis*(N-carbazolyl)biphenyl, TCTA is 4,4′,4″-*tris*(N-carbazolyl)triphenylamine, and TPBI is 1,3,5-*tris*(2-N-phenylbenzimidazolyl)benzene. It was observed that the efficiency of these dendritic devices remained relatively constant.
over a range of brightness. This resulted from a balanced charge injection and uniform distribution of iridiodendrimer in the host layer.

A simple convergent procedure has been applied to the preparation of the solution-processable phosphorescent metallodendrimers with biphenyl-based dendrons and \textit{fac-tris}(2-phenylpyridyl)iridium(III) cores.\textsuperscript{196} The attachment point and branching of the dendrons were important for controlling the color of the light emission. The photoluminescent quantum yield of neat metallodendrimer film increased with increasing the generation; thus, suggesting the ability of the metallodendrimer architecture to control intermolecular interaction. Recently, the modified \textit{fac-tris}(2-phenylpyridine)iridium(III)-cored metallodendrimer containing phenylene- and carbazole-based dendrons with 2-ethylhexyloxy surface groups were reported.\textsuperscript{197} By studying the triplet-triplet annihilation in neat film state, the triplet exciton diffusion length varied in the range of 2 - 10 nm depending on the dendron size. Also, the estimated current densities for triplet-triplet annihilation to half the efficiency of a metallodendrimer LED was less than 1 A/cm\textsuperscript{2}. The nearest-neighbor hopping rate decreased exponentially with intermolecular spacing indicating that energy migration was dominated by the exchange mechanism.

Tokito \textit{et al.} synthesized the 1\textsuperscript{st} and 2\textsuperscript{nd}-generation metallodendrimer consisting of a \textit{fac-tris}(2-phenylpyridine)iridium(III) core and hole-transporting phenylcarbazole-based dendrons.\textsuperscript{(Figure 1.19)} The OLEDs using a film containing a mixture of the iridium(III) metallodendrimer and 1,3-\textit{bis}[5-(4-tert-butylphenyl)-1,3,4-oxadiazole-2-yl]benzene as an electron-transporting material exhibited higher efficiency than those using the neat metallodendrimer film. The current for a given voltage is higher in the OLED using neat G1 than those in the OLEDs using the dendrimer consisting of the \textit{Ir}(ppy)\textsubscript{3} core and
phenylene-based dendrons\textsuperscript{198} indicating that the hole drift mobility of the dendrimer was improved by using hole-transporting dendrons. However, OLED using the neat G2 showed less current and higher turn-on voltage than that of neat G1.

Complexes $[\text{Ir}(\text{C}^\text{N})_2(\text{G1-bpy})(\text{PF}_6)]$, where $\text{C}^\text{N}$ is a cyclometalating ligand derived from 2-(2′-thienyl)pyridine and 2-phenylpyridine, and G1-bpy is a dendritic bipyridine ligand of the 1\textsuperscript{st} generation, $4,4^\prime$-$\text{bis}[3^\prime,5^\prime$-$\text{bis}$($\text{benzyloxy}$)$\text{phenylethyl}$]-$2,2^\prime$-bipyridine, were synthesized by Balashev \textit{et al.}\textsuperscript{199} The luminescence behavior of mixed-ligand cyclometalated Ir(III) complexes with a dendritic bipyridine ligand strongly depends on the structure of the cyclometalating ligand (effect through the singlet-triplet splitting energy), temperature, and matrix (effect of the hardness and polarity).
Introduction of dendritic substituents can be considered as one more influencing factor; polyether-dendritic substituents in the 4 and 4′ positions of the bipyridine ligand exerted a “soft” effect on the spectral and luminescence properties of the complexes \([\text{Ir}(C^\text{N})_2(G1-bpy)(\text{PF}_6)]\), manifested in slight destabilization of the electronically excited charge-transfer state involving the bipyridine ligand, compared to the model complexes \([\text{Ir}(C^\text{N})_2(bpy)(\text{PF}_6)]\).

1.2.2.3 Lanthanide-based Metalloendrimers

Lanthanide ions are known to display a very long-lived luminescence, which is a useful property for several applications, such as in sensors\(^{200-202}\) and fluoroimmunoassays.\(^{203}\) Because of the forbidden nature of their electronic transitions, lanthanide ions exhibit very weak absorption bands, which can be a severe drawback for applications based on luminescence. Thus, there have been several efforts to circumvent this difficulty, such as the attachment of a dendrimer or dendron possessing strong chromophores.

These examples\(^{204-207}\) in solution have shown that: (1) the absorption spectrum of the dendrimer was unchanged; (2) the fluorescence of the dansyl units was quenched; (3) the quenching effect was very large for \(\text{Nd}^{3+}\) and \(\text{Eu}^{3+}\), moderate for \(\text{Er}^{3+}\) and \(\text{Yb}^{3+}\), small for \(\text{Tb}^{3+}\), and very small for \(\text{Gd}^{3+}\); and (4) in the case of \(\text{Nd}^{3+}\), \(\text{Er}^{3+}\), and \(\text{Yb}^{3+}\), the quenching of the dansyl fluorescence was accompanied by a sensitized, near-infrared emission of the lanthanide ion. These observations were explained using the energy levels and redox potentials of both the dendrimer (Figure 1.20) and metal ions.
Fréchet-type dendrons bearing carboxylate-focal moieties were self-assembled around Er$^{3+}$, Tb$^{3+}$ or Eu$^{3+}$ ions, as the resultant core, leading to the formation of dendrimers, as shown in Figure 1.21. Experiments were conducted in toluene revealing that the UV excitation of the chromophoric groups, contained in the branches,
caused the sensitized emission of the lanthanide ion presumably by energy-transfer based on the Förster mechanism.\textsuperscript{213} The lower sensitization effect found for the coordinated Eu\textsuperscript{3+}, when compared to that of the Tb\textsuperscript{3+}, was ascribed to a weaker spectral overlap, but it could also be related to the fact that Eu\textsuperscript{3+} can quench the donor excited state by electron-

![Figure 1.21 Kawa and Fréchet’s Tb-cored metalloendrimer.](image-url)
transfer. These metallodendrimers exhibited enhanced luminescence activity both in solution and the bulk, as the shell size increased. This enhancement was attributed to both an "antenna effect", the energy transfer from the ligand to the core, and a "shell effect"; the site isolation of steric exclusion phenomenon that keeps the Ln$^{3+}$ cores apart from one another leads to a decrease in their rate of self-quenching.

Tian et al. synthesized dendritic europium complexes containing grafted carbazole units, as their functional peripheries. (Figure 1.22) Under the indirect excitation of carbazole units, a characteristic red emission peak at 615 nm due to the Eu(III) ion transition of $^5D_0 \rightarrow ^7F_2$ was observed for the complexes in solution or solid films. As a result of the light-harvesting and site-isolation of carbazole dendrons, compared with the reference compound [Eu(BPPD)$_3$(Phen)], photoluminescence efficiencies of [Eu(MCPD)$_3$(Phen)], [Eu(BCPD)$_3$(Phen)], and [Eu(TCPD)$_3$(Phen)] in the film state are 3.3, 7.9, and 4.5 fold increased, respectively; where, BPPD is 1-[3,5-bis(phenylmethoxy)phenyl]-3-phenylpropan-1,3-dione, MCPD is 1-{4-[4-(9H-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3-dione, BCPD is 1-{3,5-bis[4-(9H-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3-dione, TCPD is 1-{3,4,5-tris[4-(9H-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3-dione, Phen is 1,10-phenanthroline. EL device, ITO/NPB/CBP:Eu(TCPD)$_3$(Phen)/BCP/Mg:Ag, showed white light emission with the CIE coordinates of (0.333, 0.348); where, NPB is $N,N'$-bis(1-naphthyl)-$N,N'$-diphenyl-1,1'-diphenyl-4,4'-diamine. Its maximum external quantum efficiency was more than 1.1 % and maximum brightness reached 229 cd/m$^2$. The origin of the blue and green emission was attributed to the dendron-grafted carbazole units forming an exciplex and an electroplex with CBP and ligand $\beta$-diketone, respectively. The results suggested that
modifying ligand can not only tune the carrier-transporting properties of complexes, but also provided a useful clue to the use of electroplexes or exciplex to realize broad or even white electroluminescence.

Er$^{3+}$-, Tb$^{3+}$-, and Er$^{3+}$-cored metallodendrimers were prepared by the self-assembly of three fluorinated dendrons, each with a carboxyl anion focal point, around the lanthanide ion.$^{216}$ Energy transfer from the peripheral fluorinated phenyl moieties of
the dendrons to the lanthanide cation was evidenced spectroscopically for the Eu$^{3+}$- and Tb$^{3+}$-cored metallodendrimers in solution. The excitation of perfluorinated aromatic groups was found to decay with ca. 0.7 ns and a longer decay with lifetime in the range 1 - 1.5 ms over a wide concentration range ($\mu$M - mM), similar to that of the lanthanide emission appears to be due to vibrations among surrounding C-H bonds of the intermediate shell of the flexible dendrimer scaffold. Antenna effects and energy harvesting from the surface of the dendrimer and transfer to the core were the main mechanisms for luminescence in the metallodendrimer with lanthanide cations.

1.2.2.4 Mixed Metals-Based Metallodendrimers and Others

Considerable attention has been devoted to the synthesis of mono- or polynuclear transition metal complexes and the study of their photophysical, photochemical, and electrophysical properties, especially by the Balzani’s group.\textsuperscript{17,217-223} Balzani et al.\textsuperscript{224} designed a polynuclear metal complex of nanometric size and dendritic shape, constructed on an Os(II)-based core and containing 21 Ru(II)-based units in the branches. Divergent and convergent synthetic approaches were demonstrated.\textsuperscript{219} The light harvesting capability increased with increasing nuclearity and these metallodendrimers were shown to exhibit luminescence in solution at room temperature. Campagna et al.\textsuperscript{225} reported analogous new trinuclear dendrons: [Cl$_2$Os{($\mu$-2,3-dpp)Ru(bpy)$_2$}$_2$]$^{4+}$, [Cl$_2$Os{($\mu$-2,3-dpp)Os(bpy)$_2$}$_2$]$^{4+}$, and [(bpy)Ru{($\mu$-2,3-dpp)Os(bpy)$_2$}$_2$]$^{6+}$, where bpy = 2,2’-bipyridine and 2,3-dpp = 2,3-\textit{bis}(2-pyridinyl)pyrazine. The redox behavior, absorption, and luminescence properties have been measured. The luminescence properties were dominated by the photophysical properties of the subunit(s) in which the
lowest-lying excited state of their structure was localized, suggesting the fast intercomponent energy transfer in their new trinuclear dendrons. However, the properties of these metallo dendrimers were not fully satisfactory, because the lowest-lying excited state involving the intermediate chromophore(s) was at higher energy than the lowest-lying excited states of both the central and peripheral chromophores. As a consequence, these intermediate chromophore(s) constitute a barrier to the periphery-to-center energy transfer. To overcome these problems, suitable alternative metals that facilitate efficient periphery-to-center energy transfer in larger species were introduced.\textsuperscript{226} They prepared [Os{[(μ-2,3-dpp)Ru-[(μ-2,3-dpp)PtCl\textsubscript{2}]}\textsubscript{2}](PF\textsubscript{6})\textsubscript{8}] or OsRu\textsubscript{3}Pt\textsubscript{6}, in which the external layer of metal-subunits was coated with PtCl\textsubscript{2} units.

Turro’s group\textsuperscript{227} has investigated and conducted a statistical analysis of luminescence quenching of the photoexcited sensitizer, [Ru(phen)]\textsubscript{2}\textsuperscript{2+}, using [Co(phen)]\textsubscript{3}\textsuperscript{3+} on the surface of a PAMAM polyanion. An extension of the random-deposition model,\textsuperscript{228} previously developed for the "one-dimensional" case of DNA to analyze the luminescence quenching, showed that the electron-donor and acceptor metal complexes do not bind randomly on the dendrimer surfaces.

1,4,8,11-Tetraazacyclotetradecane (cyclam) is one of the more extensively investigated ligands in coordination chemistry.\textsuperscript{229,230} Both cyclam and its 1,4,8,11-tetramethyl derivative in aqueous solution can be mono- and di-protonated and can coordinate numerous metal ions such as, Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) that display large stability constants. Numerous extensive investigations have been performed on metal ion interactions of dendrimers, which have a cyclam, as a core unit, and Fréchet-type dendrons, as peripheral units.\textsuperscript{231-234} Complexation with Zn\textsuperscript{2+} engaged
the N-lone pairs and thereby prevented exciplex formation with a resulting intense naphthyl fluorescence.\textsuperscript{233} This strong fluorescent signal was quite suitable for monitoring the formation of complexes in dendrimer-metal titration experiments. Another complexation study of dendritic ligands with lanthanide ions (M = Nd\textsuperscript{3+}, Eu\textsuperscript{3+}, Gd\textsuperscript{3+}, Tb\textsuperscript{3+}, Dy\textsuperscript{3+}) has led qualitatively to similar results; an increase of the naphthyl units emission band at 337 nm and a complete disappearance of the exciplex band at 480 nm have been observed.\textsuperscript{235}

Sha \textit{et al.} synthesized the dendritic 8-hydroxyquinoline ligand based on PAMAM dendron to coordinate with Zn(II). (Figure 1.23)\textsuperscript{236} It was found that the luminescence intensity of G2 dendron was higher than that of the G1 dendron. When dendrons were coordinated with Zn(II), a red-shift was observed and the intensity of the Zn(II) complexes was higher than that of the corresponding ligands.

Kim \textit{et al.} designed the erbium(III)-cored complexes based on metalloporphyrins or dendritic porphyrins for optical amplification.\textsuperscript{237} The Er(II)-cored complex with Pt(II)-porphyrin showed a higher intensity for near-infrared emission of Er\textsuperscript{3+} ion than that of Er(III)-cored complex with Zn(II)-porphyrin. The Er(III)-cored complex with Pt(II)-porphyrin bearing the Fréchet-type dendrons (G2) showed a seven times increase in intensity compared with the Er(III)-cored complex with only Pt(II)-porphyrin. The lifetimes of the emission band of Pt(II)-porphyrin ligand in the visible region were found to be 30 and 40 µs for the Er(III)-cored complex and the Er(III)-cored dendritic complex based on Pt(II)-porphyrin in deoxygenated THF solution, respectively. This result means that the energy transfer from the metalloporphyrins to Er\textsuperscript{3+} ions takes place through the triplet state.
In another effort to obtain strong fluorescence, Halet et al. designed heterometallic dendritic molecules using branched Pd(II) and Pt(II) alkynyl complexes. A series of Re(I) alkynyl precursors, $[1,3-(\text{HC}≡\text{C})_2-5-\{(\text{N}^\text{N})(\text{CO})_3\text{ReC}≡\text{C}\}C_6\text{H}_3]$ ($\text{N}^\text{N} = \text{tBu}_2\text{bpy}, \text{Me}_2\text{bpy}$ or bpy), and their trinuclear branched Re(I)-Pd(II) mixed-metal alkynyl complexes, $[1,3-\{\text{Cl}$(\text{PET}_3)_2\text{PdC}≡\text{C}\}2-5-\{(\text{N}^\text{N})(\text{CO})_3\text{ReC}≡\text{C}\}C_6\text{H}_3$] have been prepared. All complexes exhibited an intense low-energy absorption at ca. 410 - 430 nm, this was tentatively assigned to the $[d\pi(\text{Re})→\pi^*(\text{diimine})]$ MLCT transition, probably with some mixing of alkynyl-to-diimine $[\pi(\text{C}≡\text{C})→\pi^*(\text{diimine})]$ LLCT character.
1.2.3 Sensors

Metalloendrimers have attracted wide-spread interest for various sensing applications, such as: ion detection, gas sensing, and redox-active switches because of their polyvalent characteristics. Several recent examples of successful sensors using the metalloendrimers have appeared.

Castellano et al. reported the formation of a luminescence lifetime-based sensor for cyanide and other counterions using Ru(II) diimines possessing metal-to-ligand charge transfer (MLCT) excited states with the anion recognition capabilities of 2,3-di(1H-2-pyrolyl)quinoxaline (DPQ). Using time-resolved photoluminescence decay, its viability as a lifetime-based sensor for anions has been tested. There were significant changes to the UV-vis and steady-state emission properties after addition of several ions (e.g., fluoride, cyanide, and phosphate).

Ferrocene can be used to detect carbon monoxide (CO) by coordination, which increases the electron acceptability by the formation of a stable Fe-CO bond. Kim et al. have synthesized and investigated a ferrocenyl-based dendrimer, as a CO gas sensor. The metalloendrimer sensor showed a linear increase by 10 times up to 40 % volume concentration, above which, it was saturated. The transient responses exhibited a delay time of 50 s, the rising time of 150 s, and the falling time of 420 s, which was fair for a gas sensor when considering the diffusion time of gas into the chamber and the continued reaction with the remaining gas in the chamber after the introduction of the gas has been terminated.
Since phosphorescence quenching is very sensitive to and selective for oxygen, quantification of dissolved molecular oxygen (O$_2$) using phosphorescence quenching is a well-known method.$^{239,242-244}$ Vinogradov et al.$^{245-247}$ have designed a new metallodendrimer consisting of an encapsulated Pd or Pt porphyrins that are widely used as basic phosphors. The mass of the dendrimer’s outer shell surrounding luminescent chromophores has been used to increase diffusion barriers for oxygen and other quenchers in solution. Recently, a phosphorescent oxygen nanosensor using the dendritic structure and two-photon absorbing antenna (Figure 1.24) has been reported.$^{248}$ Two-photon light-harvesting and intramolecular energy transfer were accompanied by intersystem crossing within the acceptor chromophore thereby inducing its phosphorescence.

van Koten et al.$^{249-252}$ designed a series of square-planer platinum(II) complexes using $N,C,N'$-tridentate-coordination monoanionic "pincer" ligand, [PtX(4-E-2,6-\{CH$_2$NRR$'$\}_2-C$_6$H$_2$)] (X=Cl, Br, I, toyl; R, R$'$=Et, Me; E=H, OH, OSiMe$_2$-tBu). These complexes spontaneously adsorb SO$_2$ gas to form pentacoordinated adducts. Adduct formation in the solid-state or in solution was fast as well as reversible and was shown by a characteristic color change of the material from colorless to bright orange. Since facile methods have been developed to remove SO$_2$ from adducts and to regenerate the square-planer starting complexes, these complexes fulfill several essential prerequisites of sensor materials for repeated diagnostic SO$_2$ detection. A platinum sensor has been found to be highly selective for SO$_2$ and particularly sensitive for submillimolar to molar amounts. Their response capacity was tunable by electronic and steric modifications of the ligand by introduction of, for example, different $N$-substituents. The periphery of these metallo-
dendrimers was shown to be an appropriate macromolecular support for anchoring the detection-active sites, thus allowing full recovery of the sensor materials for repetitive use. Recently, a technique for signal detection using quartz crystal microbalance (QMB) has been reported. In such a sensor device, substrate binding is accomplished by a change of the net mass of the surface (host-guest complex vs. host only). QMBs are
highly sensitive balances, which translate small mass changes (typically in the order of nanograms) of the QMB disc into an inverse modification of its resonance frequency that can readily be recorded.\textsuperscript{253,254}

Nanoparticle-cored dendrimers can also be useful for sensing. A new mode of construction involved the assembly of dendrons onto gold nanoparticles giving rise to stable nanoparticle-cored dendrimers (Figure 1.25).\textsuperscript{255-258} These metallodendrimers can selectively recognize oxo-anions and ATP\textsuperscript{2-} using cyclic voltammetry (redox recognition by variation of the redox potential of the ferrocenyl group). The selective recognition and titration of these oxo-anions can be conducted in the presence of other less interacting anions, such as: hydrogenosulfate, chloride or the anion of the supporting electrolyte (BF\textsubscript{4}\textsuperscript{-} or PF\textsubscript{6}\textsuperscript{-} in large quantity) by the following: (1) supramolecular interaction between the oxygen atom of the anion and the amido or silyl group conjugated with the ferrocenyl group; (2) electrostatic interaction between the oxo-anion and cationic ferrocenium generated upon anodic oxidation; and (3) topological effects at the dendrimer periphery whereby the small microcavities offer a narrow, selective channel for the supramolecular interaction. In the absence of this topology effect, the change in potential was very weak.\textsuperscript{259} A platinum electrode can be modified with the dendrimer by scanning the ferrocenyl region to give a very stable modified electrode that can be efficiently used as the sensor. Upon washing this electrode with CH\textsubscript{2}Cl\textsubscript{2}, the ATP\textsuperscript{2-} was removed and the original cyclic voltammetry wave of the dendrimer was recovered for repeated use. This operation can be conducted many times, because the supramolecular forces involved in the recognition are weak.
Figure 1.25 Dendronized gold colloids.
Recently, Beer et al. have developed a surface-enhanced optical anion sensor based on gold nanoparticles. Dodecanethiol-stabilized gold nanoparticles were modified by ligand substitution with a disulfide-substituted zinc porphyrin to provide 30 and 80 receptors per gold nanoparticle. Titration of both the free receptor and modified gold nanoparticles with various anions in CH$_2$Cl$_2$ or DMSO solution revealed a significant change in the intense porphyrin absorption bands. From calculated stability constant results, it revealed highly enhanced anion binding affinities (up to two orders of magnitude with chloride and dihydrogenphosphate in DMSO) for the surface-bound porphyrin receptor with respect to the free metalloporphyrin.

1.2.4 Molecular Switches

Switching systems based on photochromic behavior, optical control of chirality, fluorescence, intersystem crossing, electrochemically and photochemically induced changes in liquid crystals, thin films, and membrane, and photoinduced electron and energy transfer have been synthesized and studied. Among the above various techniques, the fastest of these processes is intramolecular and intermolecular electron and energy transfer. So far, theoretical work strongly supports the idea that an electron transfer reaction can form the basis for a molecular switch. However, the field has been slow to develop, because the optimal use of electron transfer processes requires careful control of molecular structure, electronic coupling, and thermodynamics in a complex array of donors and acceptors.
Generally, a porphyrin has been often used as molecular switching system because of their tunable electrochemical and spectral properties by substitution of appropriate metals. Also, it should provide the creation of arrays with four-fold symmetry. Lindsey et al. synthesized the pentamer, consisting of four Zn(II)-porphyrins (Zn-Por)s surrounding a central free-based-porphyrin (FBPor).\textsuperscript{279} (Figure 1.26) This system underwent energy transfer from the Zn-Por to FBPor with a quantum yield of \textit{ca.} 90\% based on the quenching of the Zn-Por emission. This system was designed for the absorption of energy by one chromophore, transfer of this excitation, and final dissipation of this energy by emission in some other chromophore. However, it is possible to apply the molecular switch based on competing routes of energy transfer, one of which is non-radiation processes. An example of such a switch employing energy transfer in porphyrin arrays is an optoelectronic gate synthesized by Lindsey’s group.\textsuperscript{281} This consisted of three porphyrins and a light-absorbing dye in a linear or branched arrangement; their operation was identical. The branched type consisted of a trisubstituted Zn-Por with a borondipyrromethane dye (BDPY) and magnesium-porphyrin (Mg-Por) and FBPor on its periphery. The FBPor \textit{para} to the BDPY has the lowest-energy excited state, and is highly fluorescent. Excitation of the BDPY with 485 nm light initiated the stepwise energy transfer. The energy becomes localized on the FBPor and is dissipated radiatively as fluorescence at 650 nm. The quantum yield for the total process was \textit{ca.} 0.8 for both the linear and the branched architectures. Activation of a non-radiative decay pathway within the system can modulate this emission. The Mg-Por has the lowest oxidation potential (\textsuperscript{1}E_{1/2} = 0.34 V vs. SCE) and vacancy in its highest-occupied-molecular-obital (HOMO) can be easily created by electrochemical or chemical oxidation. For this
experiment, iron perchlorate \([\text{Fe(ClO}_4\text{)}_3]\) was used as the chemical oxidant. Once oxidized, the energy was transferred to the Mg-Por\(^+\), which has low-lying absorption indicative of a variety of low energy singlet-singlet transitions. These are non-radiative and thus no emission was observed from the monocationic species. Furthermore, the fluorescence signal was fully restored by returning to the neutral species by addition of triethylamine or electrochemical reduction. This system demonstrated the ability to modulate energy transfer in large arrays; however, the “ON/OFF” switching of fluorescence was limited by diffusional processes, which are relatively slow compared to the energy transfer events.

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\begin{align*}
&\text{Figure 1.26 Lindsey’s pentameric porphyrin-Zn(II) complex.}
\end{align*}
\]
The trigonal and tetrahedral metallomacromolecules synthesized by Vauthey et al. are systems in which these ideas might be applied.\textsuperscript{282} Interestingly, these systems showed significant contributions from both through-space Förster (TB) and through-bond (TS) energy transfer mechanisms. In Figure 1.27(A), the Zn-Por to FBPor distance is 35.5 Å along the shortest line, and 67.5 Å \textit{via} the bonded pathway. The rate of Zn-Por $\rightarrow$ FBPor energy transfer is $\tau = 62$ ps, and occurs primarily \textit{via} a TS mechanism. Only when the bonded pathway became smaller ($< 45$ Å) did the authors observe a shift to the TB mechanism. However, in components in which the interchromophore distance is 27 Å through space and 32 Å through the bonded pathway, [Figure 1.27(B)] the TS mechanism was still dominant. The TB mechanism was disrupted by the $sp^3$-hybridized center carbon. This again demonstrated the essential need to give significant communication. The conjugation of the linker is especially important when energy and electron transfer events occur across large distances.

Gust et al. designed a synthetic antenna capable of understanding energy transfer induced by electron transfer.$^{280}$ Four Zn-Por chromophores were covalently linked to a FBPor electron donor, forming a cross, and the FBPor was in turn attached to a C$_{60}$ electron acceptor. (Figure 1.28) Excitation of a Zn-Por resulted in energy transfer, $\tau = 240$ ps, to the FBPor, with a quantum yield of 0.69. The excited state of the FBPor decayed exclusively by electron transfer, $\tau = 3$ ps, giving rise to the charge-separated Zn-Por$_{4}$-FBPor$^{+}$-C$_{60}^{-}$ state, which has a lifetime of $\tau = 1$ ns. There are several parameters that determine the efficiency of energy transfer in light-harvesting antennas. The choice of metal for substitution in the porphyrin is the key point in determining the rate and yield of energy transfer, because the metal exercises control both over the electrochemical
Figure 1.27 Vauthey’s trigonal and tetrahedral shape porphyrin-Zn(II) complex.
properties and over the excited state lifetime. A TB energy transfer mechanism is dominant for most antenna complexes, and the choice of linkage is thus critical in determining electronic coupling between sites. This includes factors such as substitution site and steric hindrance, in addition to site-to-site distance and bond type. Several small, fast, and highly efficient energy transfer steps are likely to be much more efficient than a single, one-step energy transfer.
1.2.5 Others

Dendritic magnetic resonance imaging (MRI) contrast agents,\textsuperscript{283} consisting of Gd(III) complexes of the chelator 2-(4-isothiocyanatobenzyl)-6-methyldiethyl-enetriaminepentaacetic acid anchored to amino-terminated PAMAMs have been developed.\textsuperscript{284} These complexes enhanced magnetic resonance images and were found to be more effective contrast agents than other commercially available macromolecule-chelated complexes, such as those formed using albumin, polylysine, and dextrin. Recently, Tóth \textit{et al.}\textsuperscript{285-287} synthesized a series of multivalent lanthanide(III)-glycoconjugates, based on 1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane- (DOTA) monoamide functionalized chelators (Figure 1.29). These DOTA-like chelators are well-know to form Ln(III) complexes possessing high thermodynamic and kinetic stability, which is of crucial importance for \textit{in vivo} applications.\textsuperscript{288} The \textit{in vitro} relaxivity of Gd(III)-glycoconjugates using the lectin-mediated molecular imaging agents has been measured; the feasibility of \textit{in vivo} MRI applications based on receptor binding, in general, depends on the receptor concentration as well as the relaxivity of the receptor-bound species. However, the flexibility of the glycodendrimer moiety in solution limited the relaxivity of their Gd(III) complexes to values lower than expected from their molecular weight. In spite of the limits, the lectin-glycoconjugated interaction can slow down considerably the tumbling rate and therefore increase the relaxivity of the Gd(III) chelates.

Metalloendrimers containing numerous metal elements that can provide robust redox systems are electron-reservoirs that can be used as molecular batteries\textsuperscript{289-291} or in
nano-devices for molecular electronics. Astruc et al. have synthesized metalloendrimers containing 54 ferrocenyl units using a precise convergent method as well as other metalloendrimers resulting from divergent construction and containing theoretically 81 and 243 ferrocenyl groups at the dendrimer periphery. The ferrocene-ferrocenium redox couple for these ferrocenyl metalloendrimers was, however, not suitable as an electron-reservoir due to a low redox potential of the silylferrocenyl group. Later, an excellent electron-reservoir system \([\text{FeCp}(\eta^6\text{C}_6\text{Me}_6)])^{+/-}\) has been grafted onto the commercial 5\(^{th}\) generation PPI dendrimer (theoretically 64 amine termini) using the chlorocarbonyl complex \([\text{Fe}(\eta^5\text{C}_5\text{H}_4\text{COCl})(\eta^6\text{C}_6\text{Me}_6)(\text{PF}_6)])\) to give the corresponding amido-based dendrimer \(\text{dendr-}{}^{-1}[\text{NHCOC}_5\text{H}_4\text{Fe}(\eta^6\text{C}_6\text{Me}_6)(\text{PF}_6)]_{64}\). This metalloendrimer has been reduced to its deep-purple 19-electron Fe(I) form using the prototype...
19-electron, electron-reservoir complex [Fe(I)Cp(η⁶-C₆Me₆)]. The latter reacted with 64 equivalents of C₆₀ by single exergonic electron transfer from each Fe(I) site to C₆₀ to give the *dendr-*{[(NHCOC₆H₄)Fe(II)(η⁶-C₆Me₆)(C₆₀⁻)]₆₄} hybrid that was characterized *inter alia* by its Mössbauer and EPR spectra.²⁹¹

Photodynamic therapy (PDT) is a promising technique for the localized treatment of tumors; numerous photosensitizers have been recently explored in preclinical and clinical study.³⁰⁰-³⁰⁵ Dendritic porphyrins can transport absorbed energy over relatively large distances using dendritic architectures, thereby mimicking the antenna complex and bacteriochlorophyl photosystem.³⁰⁶,³⁰⁷ On the other hand, numerous porphyrins have been known to effectively produce highly toxic singlet oxygen through excitation by light at a characteristic wavelength; some are being used as photosensitizers for PDT (Figure 1.30). Consequently, dendritic porphyrins may have the potential to act as novel photosensitizers used in PDT. Kataoka *et al.*³⁰⁸ synthesized the 3rd generation aryl ether dendritic porphyrin with either 32 quaternary ammonium groups (32[+]DPZn) or 32 carboxylic groups (32[-]DPZn) and evaluated them as a novel, metallodendrimer class of photosensitizers for PDT. Notably, 32[+]DPZn achieved remarkably higher singlet oxygen-induced cytotoxicity against LLC cells than protoporphyrin IX, demonstrating their highly selective photosensitizing effect in combination with a reduced systemic toxicity.

Since Grätzel introduced the dye-sensitized solar cells (DSSCs),³⁰⁹,³¹⁰ which realized the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of nanocrystalline morphology, DSSCs are an attractive, low-cost type of solar cell offering
Figure 1.30 Schematic depiction of ‘photodynamic therapy’ (PDT) using a dendrimer with a protoporphyrin photosensitizer core, which upon irradiation with light and subsequent reaction with oxygen creates tissue damaging singlet oxygen.
Yamamoto et al. have developed the DSSC using the metallodendrimer consisting of a charge-separable and hole-transporting phenylazomethine with a triphenylamine (TPA) core and complexation with SnCl$_2$.

Electrochemical oxidation of the TPA core revealed that the dendron units in the dendrimer have 0.35 of the attenuation factor ($\beta$) in the electron transfer. Spectroscopic analysis indicated that the complexation between triphenylamine with dendritic phenylazomethine (TPA-DPA) and SnCl$_2$ occurred stepwise in an outward radial direction following the basicity gradient of imines in each dendritic shell. DSSCs prepared using larger TPA-DPAs exhibited higher open-circuit voltage. The increase in radius and association with I$_3^-$ contributes exponentially to the inhibition of back-electron-transfer based on the difference in $\beta$ values. This contribution is advantageous for improving the open-circuit voltage, since back-electron-transfer increases exponentially with voltage. Complexation with SnCl$_2$ reduces the resistance of TPA-DPA for hole-transfer through the dendritic shells, thereby improving the fill-factor.

1.3 Conclusion Remark

The unique features of the dendritic architecture and the rich chemistry of organo-transition metal complexes have been combined in metallodendrimers to create the potential for a wide range of utilitarian applications. The ability of dendrimers to probe the twilight zone between homogeneous and heterogeneous catalysis as well as applying the techniques associated with combinatorial-type chemistry starts to probe the diverse areas of the developing nanoworld of technology. Since organometallic complexes have
opened many new avenues in supramolecular chemistry, metallodendrimers will continue to play an important role in not only organometallic chemistry and polymer science but also material science. These new interfaces will be rich areas for future science to pursue.
CHAPTER II

CONSTRUCTION OF TRIANGULAR METALLOMACROCYCLES: \[M_3(1,2-BIS(2,2':6',2''-TERPYRIDIN-4'-YLETHNYL)BENZENE)_3\] \(M_3 = 3\text{Ru(II)}, 3\text{Fe(II)},\) AND 2Ru(II)-Fe(II)]

2.1 Introduction

It has been well documented that the self-assembly of supramolecular species is based on a combination of the inherent structural information, such as the ligand juxtaposition, incorporated within the polytopic building blocks. Stang, Fujita, Atwood, and many others have elegantly demonstrated the structural beauty arising from the application of such positioning. The often high yields of thermodynamically favored, self-assembled constructs confirm the methodology but the ligand-metal bonds must possess some degree-of-lability in order to incorporate a self-repairing mechanism so necessary to eliminate mistakes generated from the initially formed kinetic products; some degree-of-reversibility is critical in the early assembly stages. We were thus surprised to isolate, in many cases, > 90 % of metallo-macrohexamers based on the formation of six \(<\text{tpy-Ru(II)-tpy}>\) (where, tpy = terpyridine) bonds, especially since this mode of connectivity is irreversible under normal reaction conditions; in general, intramolecular reactions (\textit{i.e.,} macrocyclization processes)
were found to be favored over intermolecular connectivity (oligomeric polymerization). The design of simple molecular triangles might be accomplished in two different ways: (1) by using 180° connecting linear linking units in combination with 60° angular building blocks or (2) by using distorted angular components with angles greater than 60° in combination with distorted linear linking units with valent angles less than 180°. As an example, rigid cyclic trimetallic complexes with metal-metal bonds or bridging ligands are known\textsuperscript{325} and their formation has been shown to be influenced by several factors, including concentration,\textsuperscript{326,327} stoichiometry\textsuperscript{328} or the presence of a template.\textsuperscript{326} Up to now, metallo-triangles utilizing \textless tpy-metal(II)-tpy\textgreater  connectivity are unknown.

In this Chapter, a logical extension of this metallomacrocycle formation procedure would start from the preparation of \textit{bis}(terpyridine) monomer 4, in which the two ligating moieties are rigidly held at a 60° angle with respect to each other, and the use of this monomer for the construction of triangular metallomacrocycles employing Fe(II) and Ru(II), as connecting centers.

2.2 Results and Discussion

Substituted and heterocyclic aromatic compounds have proven useful as rigid building blocks in self-assembly processes.\textsuperscript{322,323,329-332} The combination of proper carbon framework with various substitution patterns can result in a plethora of directed angles, including the elusive 60° angle necessary for pre-designed triangles.\textsuperscript{332} Our strategy involved the preparation of a \textit{bis}(terpyridinyl) monomer possessing the critical 60° bond angle with respect to the two ligating moieties. This would facilitate the assembly of
three building blocks with three connecting transition metals in the desired triangle-shaped nanoarchitecture. According to our strategy, 1,2-dibromobenzene has been chosen as the skeleton for a 60° monomeric bis-ligand, as it presents an ideal substrate for the subsequent <tpy-metal(II)-tpy> connectivity leading to the desired macrocyclization or assembly process.

Construction (Scheme 2.1) of the desired angular building block, 1,2-bis(2,2':6',2"-terpyridin-4'-ylethynyl)benzene (4) started with ethynylation of 1,2-dibromobenzene to give 1,2-bis(3-hydroxy-1-butynyl)benzene (1) followed by deprotection to afford 1,2-diethynylbenzene (2), which was subsequently reacted with 2.5 equivalents of 4'-trifluoromethanesulfonyl-2,2':6',2"-terpyridine (4-tpyOTf; 3) via a palladium-catalyzed cross-coupling using {[(C₆H₅)₄P]Pd(0)} in base solvent to yield (41

![Scheme 2.1 Synthesis of building block for triangular metallomacrocycle: (a) 2-methyl-3-butyn-2-ol, Pd(dba)₂, Ph₃P, Cul, Et₃N; (b) KOH, MeOH/toluene; (c) {[((C₆H₅)₄P]Pd(0)}, 'Pr₂NH/toluene.](image-url)
% 4, as an air-stable, white-off solid. The structure of building block 4 was confirmed (1H NMR) by the definitive downfield shift (Δδ = 0.24) for the singlet for the 3',5'-tpyH upon the acetylenic linkage formation. In 13C NMR, the peak shift for the −C≡C− from 81.36 and 82.03 to 92.14 and 92.52 ppm, respectively. Also, a mass peak (ESI-MS) at \( m/z = 611.4 \ [M + Na]^+ \) was recorded.

For further support of this transformation, a single crystal for X-ray analysis was grown by vapor diffusion of hexane into a CHCl₃ solution of 4. The ORTEP representation of 4 (Figure 2.1) confirms the desired angle-of-directionality (ca. 62°) between the ligands. One terpyridine lies approximately in the same plane as the benzene moiety; whereas, the other terpyridine is tilted ca. 30° out-of-this-plane and the alkyne connections are linear.

Figure 2.1 ORTEP drawing of bis(terpyridine) ligand 4.
In order to confirm the specificity and stability of [Ru(tpy)_2] motif, the simple monoligand 7, which possesses the acetylenic group and their complex 9 as a model were prepared (Scheme 2.2). The simple monoligand was initiated from the readily available 4-iodotoluene, followed by ethynylation with trimethylsilylacetylene, then deprotected with KF in MeOH/THF at 25 °C to afford the desired 4-ethynyltoluene 6, which was then treated with one equivalent of 4-tpyOTf using a palladium-catalyzed cross-coupling procedure. The structure of the mono(terpyridine) was analyzed by ¹H and ¹³C NMR and mass spectrometer. Reaction of 4-(2,2':6',2''-terpyridin-4'-ylethynyl)toluene 7 with RuCl₃·8H₂O (generating the [Ru(7)Cl₃] intermediate; Scheme 2.2) following by the addition of unmetallated ligand 7 afforded the desired ruthiocomplex 9. This complex exhibited (¹H NMR) a downfield shift for the 3',5'-tpyH (s; δ = 8.86, Δδ = 0.32) and an upfield shift of the 6,6''-tpyH (d; δ = 7.39, Δδ = −1.36) relative to that of the starting ligand. The desired the structure of complex 9 was easily confirmed by the mass peak at m/z = 941.3 [M − PF₆⁻]⁺.

Reaction of a 1:1 mixture of ligand 4 and FeCl₂ in MeOH for 24 hours at 25 °C (Scheme 2.3) gave the self-assembled triangular Fe(II) metallomacrocycle 10, which revealed (¹H NMR) two doublets for the benzene moieties identical to that of the starting ligand at δ = 8.04 and 7.78 supporting the symmetric structure, in contrast to linear oligomers. Also observed was an expected upfield shift for the doublet (δ = 7.10, Δδ = −1.48) arising from the 6,6''-tpyHs and downfield shift for the 3',5'-tpyH signals (δ = 9.19, Δδ = 0.54) relative to the corresponding signals in the uncomplexed ligand [Figure 2.2 (A)]. Other diagnostic spectral attributes (¹³C NMR) included the two distinct peaks at δ = 91.5 and 96.3 for the acetylene carbons. COSY and HETCOR spectra of the
Scheme 2.2 Synthesis of model 9: (a) trimethylsilylacetylene, Pd(dba)$_2$, CuI, Ph$_3$P, Et$_3$N; (b) KF, MeOH/THF; (c) Pd(dba)$_2$, CuI, Ph$_3$P, Et$_3$N; (d) RuCl$_2$·3H$_2$O, MeOH, reflux; (e) 1 equiv. 7, N-ethylmorpholine, MeOH, reflux.

*bisterpyridine* 4 and the self-assembled macrocycle 10 further verified the peak assignments and delegated coupling patterns. This triangular structure was further established by mass peaks at $m/z = 2659.7$ [M + 2H – PF$_6$]$^+$ (Calcd. $m/z = 2659.27$) resulting from the loss of PF$_6$$^-$, which is a known phenomena.$^{334}$ While metallomacrocycle 10, initially isolated as the 6 Cl$^-$ salt, exhibited solubility in MeOH and hot H$_2$O; its conversion to the 6 PF$_6$$^-$ salt facilitated solubility in MeCN, acetone, DMF, and DMSO.
Figure 2.2 $^1$H NMR spectra of the bis(terpyridine) ligand (A) and the self-assembled Fe(II) metallomacrocycle 10 (B).

The self-assembled Ru(II) counterpart 11 was prepared by treatment of MeOH solution of monomer 4 with one equiv. of [Ru(Cl)$_2$(DMSO)$_4$] over 36 h at 50 °C. Although the initial desired trimer was obtained (ca. 70 %), after column chromatography followed by counterion exchange (Cl$^-$ to PF$_6^-$), the pure macrocycle 11 was isolated (ca. 30 %). The complete absence ($^1$H NMR) of extraneous peaks excluded the presence of starting materials, intermediates, and oligomeric materials, the diagnostic shifts for the doublets ($\delta = 7.35, \Delta\delta = -1.23$) of 6,6"-tpyHs, and the 3',5'-tpyHs ($\delta = 9.01, \Delta\delta = 0.36$) along with definitive ESI-MS data ($m/z = 2796.4 [M + H - PF_6^-]^+$), all of the spectral data support the structural assignment.
Scheme 2.3 Synthesis of homonuclear triangular metallomacrocycles using a self-assembly method: (a) i) FeCl$_2$·8H$_2$O, MeOH, ii) NH$_4$PF$_6$/MeOH; (b) i) [RuCl$_2$·(DMSO)$_4$], MeOH, reflux, ii) NH$_4$PF$_6$/MeOH.

A step-wise approach (Scheme 2.4) was also undertaken, in which the diamagnetic [Ru$_2$(4)$_3$(Cl)$_4$] 13 was prepared by treatment of bis[Ru(III)] adduct 12 with two equiv. of unmetalated bis(terpyridine) 4 and 4-ethylmorpholine (0.2 mL) at 50 °C. Finally, reaction of resultant oligomer with one equiv. of [Ru(Cl)$_2$·(DMSO)$_4$] with refluxing afforded the corresponding metallomacrocycle 11. Structural support ($^1$H NMR, $^{13}$C NMR, MS data) for the metallomacrocycle was identical to the results derived for 11 from the above self-assembly method. This procedure might also permit the specific introduction of different metal centers (i.e., Os, Fe, and Zn) in the connectivity sites. In order to show another example, reaction with one equiv. of FeCl$_2$·4H$_2$O with the diamagnetic bis-complex 13 was conducted to obtain the desired heteronuclear metallomacrocycle 15, which exhibited ($^1$H NMR) signals for the 3',5'-tpyHs protons that were split into three types of peaks at $\delta = 9.18$ (Fe), 9.05 (Fe/Ru), and 9.01 (Ru) ppm in a
Scheme 2.4 Synthesis of heteronuclear triangular metallomacrocycles using a stepwise method: (a) RuCl$_3$·3H$_2$O, MeOH, reflux; (b) 2 equiv. 4, N-ethylmorpholine, MeOH, reflux; (c) i) RuCl$_3$·3H$_2$O, N-ethylmorpholine or FeCl$_2$·8H$_2$O, MeOH, reflux, ii) NH$_4$PF$_6$/MeOH.
1:1:1 ratio. Also, two doublets at $\delta = 6.93$ (Ru) and 6.87 (Fe) ppm in a 2:1 ratio for the 5,5"-tpyHs position as additional supporting spectral evidence. Its mass spectrum displayed the signals of multiple-charged entities ranging from $m/z = 1302.1 \ [M - 2\text{PF}_6^-]^{2+}$ to 337.3 $[M - 6\text{PF}_6^-]^{6+}$ charge states. Absorption spectra (Figure 2.3) recorded for ethynyl-substituted complexes in dilute MeCN solution exhibit the expected absorption transitions. In the case of 10, an intense ligand-centered $\pi-\pi^*$ transition of terpyridine moieties is clearly apparent at $\lambda_{\text{max}} = 283 \text{ nm} (\varepsilon = 1.27 \times 10^5)$ and 326 nm ($\varepsilon = 1.26 \times 10^5$), while the metal-ligand charge-transfer (MLCT) transition, which is described

Figure 2.3 UV spectra of homo- and heteronuclear triangular metallomacrocycles: (A) triangle 15; (B) triangle 11; (C) triangle 10.
as the promotion of an electron from the metal-centered $d$-orbitals to an unfilled ligand-centered $\pi^*$ orbitals,\textsuperscript{335} has a maximum ($\lambda_{\text{max}}$) around 578 nm with molar absorption coefficients at the peak of $ca. 6.43 \times 10^4 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ per Fe(II)-triangle. Similarly, triangle 11 exhibited two ligand-centered $\pi-\pi^*$ transition of terpyridine moieties and a MLCT at $\lambda_{\text{max}} = 275$ nm ($\varepsilon = 7.28 \times 10^4$), 316 nm ($\varepsilon = 8.01 \times 10^4$), and 496 nm ($\varepsilon = 4.23 \times 10^4$), respectively. The triangle 15 exhibited two metal-ligand charge transfer (MLCT) bands attributed to the Ru(II)- and Fe(II)-complex at $\lambda_{\text{max}} = 499$ nm ($\varepsilon = 5.86 \times 10^4$) and 582 nm ($\varepsilon = 2.38 \times 10^4$), respectively. This observation from its UV absorption spectrum

Figure 2.4 Cyclic voltammetric responses of 1 mM solutions of (a) Ru(II)-terpyridine monocomplex 9; (b) triangular Ru(II) metallomacrocycle 11.
further supports the proposed structure of heteronuclear metallomacrocycle 15.

The cyclic voltammogram (CV) of a 1 mM solution of Ru(II) triangle 11 in MeCN is shown in Figure 2.4(b). Two terpyridine ligand-centered reductions and one oxidation of the ruthenium center were observed and the corresponding potentials are listed in Table 1. The first redox couple at –1.43 V with a peak-to-peak separation (ΔE_p) of 70 mV is reversible; whereas, the second redox couple, exhibiting a very sharp oxidative peak at –1.61 V, is not. This oxidative peak indicates that there is an adsorption of the reduction product on the electrode surface. The oxidative couple at 0.95 V is reversible with ΔE_p of 40 mV and its current intensity is comparable to the first reduction.

Table 2.1. Redox potentials (V vs. Fc/Fc^+) of ruthiomacrocycle 11 and model 9 in 0.1 M TBAPF_6 MeCN at glassy carbon electrode; scan rate = 100 mV/sec.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E_{pc}</th>
<th>E_{pa}</th>
<th>E_{1/2}</th>
<th>E_{ox} (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>-1.46</td>
<td>-1.39</td>
<td>-1.43</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>-1.72</td>
<td>-1.61</td>
<td>-</td>
<td>0.92</td>
</tr>
<tr>
<td>9</td>
<td>-1.55</td>
<td>-1.49</td>
<td>-1.52</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1.80</td>
<td>-</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.48</td>
<td>0.95</td>
</tr>
</tbody>
</table>

For comparison, the CV of model [Ru(tpy)_2(PF_6)_2] 9 exhibits a similar behavior to that of 6; however, CV can be useful for quantitative purposes, based on measurements of
the peak current. The peak current for a reversible couple (at 25 °C) is given by the Randles-Sevcik equation:

\[ I_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \upsilon^{1/2} \]

where \( n \) is the number of electrons, \( A \) is the electrode area (in cm\(^2\)), \( C \) is the concentration (in mol·cm\(^{-3}\)), \( D \) is the diffusion coefficient (in cm\(^2\)·s\(^{-1}\)), and \( \upsilon \) is the scan rate (in V·s\(^{-1}\)).

From an analysis of the CV of the first reduction peaks intensities of 9 \((I_p^{\text{mono}})\) and triangle 11 \((I_p^{\text{tri}})\), the peak current ratio \((I_p^{\text{mono}} : I_p^{\text{tri}} = 1:1.4)\) was observed, taking into consideration the expected difference in diffusion coefficients. This result closely agrees with the expected theoretical ratio of 1:1.5, which suggests that in each compound, all metal centers undergo reduction simultaneously and the macromolecule contains the desired three ruthenium metal centers. The presence of a single oxidation potential for the Ru(II/III) couple within the solvent window at all scan rates suggests further that the three ruthenium centers in this macrocycle are oxidized at the same potential, as expected for non-interacting centers in identical environments.

These metallomacrocycles possess internal steric interactions that can be observed in the computer-generated CPK representations (Figure 2.5). As shown in the modeling studies, there is higher packing inside of the triangular metallomacrocycle compared to the outside. In solution, a dynamic process should affect the chemical shifts of the \(^1\)H NMR signal of terpyridinyl protons due specifically to steric effect. Variable temperature \(^1\)H NMR spectra of \([\text{Fe}_3(4)_3(\text{PF}_6)_6]\) (Figure 2.6) show that with decreasing temperature, the rotation about the acetylene axis between benzene moiety and terpyridine group is
Figure 2.5 Computer generated CPK presentation of triangular metallomacrocyle 10.

Figure 2.6 $^1$H NMR spectra depending on temperature of Fe(II) triangular metallomacrocyle 10.
restricted due to the steric interactions of 4,4''-tpyH. This should give a downfield shift at low temperature because of coupling of the 4,4''-tpyH which are constrained “inside” and “outside” of the cyclic structure. This means that the bis(terpyridine) complex rotation is slowed with decreasing temperature.

2.3 Conclusions

In conclusion, it has demonstrated the formation and characterization of a unique, self-assembled, triangular metallomacrocycle by using <tpy-metal(II)-tpy> connectivity, which is stable and irreversible under the reaction conditions. This coordination-directed triangle gave entry into a shape-persistent, dense-packed architecture. Also, the step-wised construction permits specific introduction of different metal centers, coupled with the ability to tailor the periphery of the triangular metallomacrocycles. Therefore, based on the reversible redox characteristics and the heterogeneous metal core structure, these types of molecular constructs are ideal candidates for energy storage devices and nanomachinery.

2.4 Experimental Section

**General procedure.** Chemicals were purchased from Aldrich and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets pre-coated with Al₂O₃ IB-F or SiO₂ IB2-F (Baker-flex) and visualized by UV light. Column chromatography was conducted using neutral/basic Al₂O₃, Brockman Activity I
(60 - 325 mesh) or SiO\textsubscript{2} (60 - 200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl\textsubscript{3}, as solvent, unless otherwise indicated, with Me\textsubscript{4}Si, as the internal standard (0 ppm). Infrared (IR) spectra were recorded on an ATI Matheson Genesis FTIR spectrophotometer. UV/Vis absorption spectra were measured in MeCN at 25 °C with a Hewlett-Packard 8452A diode array spectrophotometer. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap mass spectrometer (ESI-MS). All the electrochemical experiments were performed with CHI 440 Electrochemical Workstation (CH Instruments Inc, Austin, Texas). 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}, from Fluka) in MeCN (redistilled) was used as the supporting electrolyte (degassed with argon). A platinum wire was employed as the counter electrode. An aqueous Ag/AgCl electrode, separated by a 0.1 M TBAPF\textsubscript{6} salt-bridge, was used as the reference. Ferrocene (Fc) was added as an internal reference and all the potentials were referenced relative to the Fc/Fc\textsuperscript{+} couple. A glassy carbon electrode (CHI, 3 mm in diameter), polished with 1.0 and 0.3 μm aluminum paste and ultrasonicated in deionized water and CH\textsubscript{2}Cl\textsubscript{2} bath, was used as the working electrode. The scan rate for cyclic voltammetry (CV) was 100 mV/sec. All experiments were performed at 20 ± 2 °C.

**1,2-Bis(3-hydroxy-1-butynyl)benzene (1).** A Schlenk flask was charged with 1,2-dibromobenzene (2.56 mL, 17.49 mmol), 2-methyl-3-butyn-2-ol (5.08 mL, 52.46 mmol), \textit{bis}(dibenzylideneacetone) palladium(0) (1.01 g, 1.75 mmol), triphenylphosphine (920 mg, 3.0 mmol), and copper(I) iodide (670 mg, 3.0 mmol), and triethylamine (100 mL). The mixture was degassed and back-filled with argon three times, then stirred at 80 °C.
for 3 days. The reaction mixture was filtered and the solvent evaporated *in vacuo* to give the crude product, which was column chromatographed (SiO$_2$) eluting with hexane:EtOAc (6:4; v/v) to afford (63%) 1, as a light yellow oil: $^1$H NMR: $\delta$ 7.39 (dd, $J = 3.3$, 3.3 Hz, 4,5-Ar$H$, 2H), 7.24 (dd, $J = 3.3$, 3.3 Hz, 3,6-Ar$H$, 2H), 1.64 [s, C(CH$_3$)$_2$, 12H]; $^{13}$C NMR: $\delta$ 31.66, 65.90, 81.08, 98.34, 125.72, 128.05, 131.43.

1,2-Diethynylbenzene (2). 1,2-Bis(3-hydroxy-1-butynyl)benzene (2.5 g, 10.32 mmol) was dissolved in toluene (100 mL) containing potassium hydroxide (1.42 g, 25.42 mmol) and MeOH (50 mL) in a round-bottom flask equipped with a Dean-Stark trap fitted with reflux condenser. The mixture was heated at 110 °C for 4h. The reaction mixture was cooled to 25 °C, washed with water, dried (MgSO$_4$), and filtered. The solvent was evaporated *in vacuo* to give a residue, which was column chromatographed (SiO$_2$) eluting with hexane to give (42%) 2, as a colorless oil: $^1$H NMR: $\delta$ 7.53 (dd, $J = 3.3$, 3.3 Hz, 4,5-Ar$H$, 2H), 7.32 (dd, $J = 3.6$, 3.6 Hz, 3,6-Ar$H$, 2H), 3.35 (s, C≡CH, 2H); $^{13}$C NMR: $\delta$ 81.36, 82.03, 125.25, 128.74, 132.85.

1,2-Bis(2,2':6',2"'-terpyridin-4'-ylethynyl)benzene (4). A Schlenk flask was charged with 1,2-diethynylbenzene (400 mg, 3.17 mmol), 4'-([(trifluoromethyl)-sulfonyl]oxy)-2,2':6',6"'-terpyridine (2.78 g, 7.29 mmol), tetrakis(triphenylphosphine) palladium(0) (370 mg, 320 µmol), diisopropylamine (40 mL), and toluene (80 mL). The mixture was degassed and back-filled (3X) with argon then stirred at 80 °C for 3 days. The reaction mixture was filtered, and the solvent evaporated *in vacuo* to give a crude product, which was column chromatographed (Al$_2$O$_3$) eluting with CHCl$_3$ to afford (41%) the pure 4, as a off white solid: m.p. 274 - 275 °C; $^1$H NMR: $\delta$ 8.65 (s, 3',5'-tpy$H$, 4H), 8.58 (d, $J = 7.8$ Hz, 6,6"-tpy$H$, 4H), 8.49 (d, $J = 4.2$ Hz, 3,3"-tpy$H$, 4H), 7.80 (dd, $J$
= 7.8, 7.5 Hz, 4,4"-tpyH, 4H), 7.66 (dd, J = 3.3, 3.3 Hz, 4,5-ArH, 2H), 7.43 (dd, J = 3.3, 3.3 Hz, 3,6-ArH, 2H), 7.24 (dd, J = 6.9, 5.7 Hz, 5,5"-tpyH, 2H); $^{13}$C NMR: δ 92.14, 92.52, 121.46, 123.42, 124.10, 125.71, 129.14, 132.46, 133.55, 137.21, 149.06, 155.44, 155.56; IR (KBr): ν 3052, 2219, 1600, 1581, 1565, 1465, 1390, 1263, 885, 790, 755, 619, 576 cm$^{-1}$; ESI-MS: m/z 611.4 [M + Na]$^+$ (Calcd m/z 611.20); Crystal data: C$_{40}$H$_{34}$N$_6$, M = 588.65, triclinic, space group $P_{1}$, $a = 10.8137(10)$, $b = 12.4510(10)$, $c = 13.061(5)$ Å, $\alpha = 68.247(5), \beta = 75.799(5), \gamma = 66.262(7), V = 1485.6(3)$ Å$^3$, $T = 102$ K, $Z = 2$, $\mu$(Mo-K$\alpha$) = 0.080 mm$^{-1}$, 10773 independent reflections, $R_{\text{int}} = 0.038$, $R_1 = 0.054$, $wR_2 = 0.141$ (all data).

**Trimethyl-$p$-tolyethynylsilane (5).** A round bottom flask was charged with 4-iodotoluene (5 g, 22.93 mmol), trimethylsilylacetylene (3.38 g, 34.39 mmol), bis(dibenzylideneacetone)Pd(0) (660 mg, 1.15 mmol), triphenylphosphine (600 mg, 2.30 mmol), copper iodide (440 mg, 2.30 mmol), and triethylamine (100 mL). The mixture was degassed and back-filled ($3\times$) with argon, then stirred under nitrogen for 12 h at 60 °C. Solvent was removed in vacuo to give a residue, which was column chromatographed (SiO$_2$) eluting with hexane:EtOAc(15:1; v/v) to afford (92 %) pure 5, as a colorless oil: $^1$H NMR: δ 7.38 (d, J = 7.8 Hz, 3,5-ArH, 2H), 7.12 (d, J = 7.8 Hz, 2,6-ArH, 2H), 2.35 (s, ArCH$_3$, 3H), 0.26 (s, TMS, 9H); $^{13}$C NMR: δ 0.25, 21.72, 93.43, 105.57, 120.26, 129.16, 132.08, 138.82.

**4-Ethynyltoluene (6).** A solution of the trimethyl-$p$-tolyethynylsilane (2.2 g, 11.71 mmol) in MeOH (50 mL) and THF (50 mL) was treated with KF (820 mg, 14.05 mmol) at 25 °C. After 12 h, the solvent was evaporated in vacuo to give a solid that was column chromatographed (SiO$_2$) eluting with hexane to afford (89%) pure 6, as colorless
oil: \(^1\)H NMR: \(\delta\) 7.41 (d, \(J = 7.8\) Hz, 3,5-Ar\(H\), 2H), 7.15 (d, \(J = 8.1\) Hz, 2,6-Ar\(H\), 2H), 3.05 (s, C\(CH\), 1H), 2.37 (s, Ar\(CH_3\), 3H); \(^{13}\)C NMR: \(\delta\) 21.69, 76.65, 119.22, 129.26, 132.22, 139.15.

4-(2,2':6',2"-terpyridin-4'-ylethynyl)toluene (7). A mixture of 4-ethynyltoluene (1.80 g, 15.51 mmol), 4'-[(trifluoromethyl)sulfonyl]oxy]-2,2':6',6"-terpyridine (5.91 g, 15.51 mmol), and tetrakis(triphenylphosphine)palladium(0) (890 mg, 780 \(\mu\)mol) was charged into diisopropylamine (30 mL) and toluene (100 mL). The mixture was degassed and back-filled (3×) with argon and stirred at 80 °C for 3 days. The solvent was removed \(\textit{in vacuo}\) to afford a solid that was column chromatograph (Al\(_2\)O\(_3\)) eluting with EtOAc to afford (41%) pure 7, as a off white solid: m.p. 165 - 166 °C; \(^1\)H NMR: \(\delta\) 8.75 (d, \(J = 4.2\) Hz, 6,6"-tpy\(H\), 2H), 8.65 (d, \(J = 7.8\) Hz, 3,3"-tpy\(H\), 2H), 8.58 (s, 3',5'-tpy\(H\), 2H), 7.90 (dd, \(J = 7.5\), 7.8 Hz, 4,4"-tpy\(H\), 2H), 7.48 (d, \(J = 7.8\) Hz, 3,5-Ar\(H\), 2H), 7.38 (dd, \(J = 6.3\), 5.7 Hz, 5,5"-tpy\(H\), 2H), 7.21 (d, \(J = 7.8\) Hz, 2,6-Ar\(H\), 2H), 2.40 (s, Ar\(CH_3\), 3H); \(^{13}\)C NMR: \(\delta\) 21.83, 87.10, 94.50, 119.57, 121.59, 123.15, 124.28, 129.48, 132.12, 133.99, 137.41, 139.60, 149.21, 155.47, 155.71; ESI-MS: \(m/z\) 348.2 [M + H]\(^+\) (Calcd. \(m/z\) 348.14).

\(\left[\text{RuCl}_3\right](7)\) (8). 4-(2,2':6',2"-Terpyridin-4'-ylethynyl)toluene (192 mg, 330 \(\mu\)mol) was added to a solution to a solution of RuCl\(_3\) \(3\)H\(_2\)O (171 mg, 660 \(\mu\)mol) in MeOH (70 mL), then the suspension was refluxed for 24 h. After cooling, the resultant dark red solid was filtered, washed with MeOH and CHCl\(_3\), and dried \(\textit{in vacuo}\) to yield (> 80 %) the mono[Ru(III)] adduct 8, as a dark brown solid: m.p. > 400 °C; IR (KBr): \(\nu\) 3058, 2215, 1596, 1540, 1469, 1417, 1245, 885, 794, 615, 530 cm\(^{-1}\). This material was used in next step without further purification.
**[Ru(7)2(PF6)2]** (9). Mono(terpyridine) ligand 7 (157 mg, 450 µmol) was added to a suspension of mono[Ru(III)] adduct 8 (250 mg, 450 µmol) in MeOH (50 mL), then N-ethylmorpholine (50 µL) was added; the mixture was refluxed for 24 h. After cooling, the resulting deep red solution was filtered through celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate 9, which was filtered, sequentially washed with MeOH, Et₂O, and acetone, then dried *in vacuo* to afford (> 80 %) a dark red solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 8.86 (s, 3',5'-tpyH, 2H), 8.51 (d, J = 8.1 Hz, 3,3''-tpyH, 2H), 7.95 (dd, J = 7.5, 7.5 Hz, 4,4''-tpyH, 2H), 7.68 (d, J = 8.1 Hz, 3,5-ArH, 2H), 7.41 (d, J = 4.8 Hz, 2,5-ArH, 2H), 7.39 (d, J = 7.5 Hz, 6,6''-tpyH, 2H), 7.19 (dd, J = 6.6, 6.0 Hz, 5,5''-tpyH, 2H), 2.46 (s, ArC₃H₃, 3H); ¹³C NMR (CD₃CN): δ 21.79, 86.80, 98.38, 119.28, 125.65, 128.74, 130.81, 131.65, 133.13, 139.34, 142.15, 153.69, 156.28, 158.60; IR (KBr): v 3058, 2917, 2215, 1598, 1540, 1511, 1469, 1417, 1245, 885, 794, 613, 532 cm⁻¹; UV/vis (CH₃CN): λₘₐₓ 279 (ε = 2.86 × 10⁴), 319 (3.79 × 10⁴), 333 (3.91 × 10⁴), 498 nm (2.02 × 10⁴ dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 941.3 [M − PF₆⁻]⁺ (Calcd m/z 941.16).

**[Fe₃(4)₃(PF₆)₆]** (10). A MeOH solution of one equivalent of FeCl₂·4H₂O (52 mg, 260 µmol) was added to a solution of 1,2-*bis*(2,2':6',2''-terpyridin-4'-ylethynyl)benzene (4; 154 mg, 260 µmol) in MeOH (100 mL). The stirred solution was maintained at 25 °C for 24 h. The resultant deep purple solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed (SiO₂) eluting with sat. *aq.* KNO₃·H₂O·MeCN (1:1:7; v/v/v) to afford (> 70 %) 10, as a dark purple solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 9.19 (s, 3',5'-tpyH, 4H), 8.42 (d, J = 8.1 Hz, 3,3''-tpyH, 4H),
8.04 (dd, J = 3.3, 3.3 Hz, 4,5-ArH, 2H), 7.78 (dd, J = 3.3, 3.3 Hz, 3,6-ArH, 2H), 7.56 (dd, J = 7.8, 7.8 Hz, 4,4"-tpyH, 4H), 7.10 (d, J = 5.4 Hz, 6,6"-tpyH 4H), 6.86 (dd, J = 6.9, 6.3 Hz, 5,5"-tpyH, 4H); 13C NMR (CDCl3): δ 91.50, 96.29, 124.83, 125.27, 126.38, 128.44, 131.70, 133.27, 133.92, 139.66, 154.06, 158.23, 161.13; IR (KBr): ν 3070, 2217, 1608, 1484, 1425, 1240, 1010, 840, 788, 728, 557, 480 cm⁻¹; UV/Vis (CH3CN): λmax 283 (ε = 1.27 × 10⁵), 326 (1.26 × 10⁵), 578 nm (6.43 × 10⁴ dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 2659.7 [M + 2H – PF6]⁺ (Calcd m/z 2659.27); Elem. Anal. (% (+6H2O): Calcd. C, 49.51; H, 2.91; N, 8.66. Found. C 49.98; H, 2.99; N, 8.29.

[(RuCl3)2(4)] (12). 1,2-Bis(2,2':6',2"-terpyridin-4'-ylethynyl)benzene (192 mg, 330 µmol) was added to a solution of RuCl3⋅3H2O (171 mg, 660 µmol) in MeOH (70 mL), then the suspension was refluxed for 24 h. After cooling, the resultant dark red solid was filtered, washed with MeOH and CHCl3, and dried in vacuo to yield (> 80 %) the bis[Ru(III)] adduct 12, as a dark brown solid: m.p. > 400 °C; IR (KBr): ν 3058, 2204, 1602, 1540, 1469, 1417, 1243, 873, 786, 613, 470 cm⁻¹. This material was used in next step without further purification.

[Ru2(4)3(Cl)4] (13). The bisligand 4 (235 mg, 400 µmol) was added to a suspension of bis[Ru(III)] adduct 12 (200 mg, 200 µmol) in MeOH (100 mL); the mixture was refluxed for 12 h. After cooling, the resulting deep red solution was filtered through celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed (Al2O3) eluting with sat. aq. KNO3:H2O:MeCN (1:1:10; v/v/v) to give (> 47 %) 13, as a dark red solid: m.p. > 400 °C.
[Ru₃(4)₃(PF₆)₆] (14). A mixture of RuCl₃·3H₂O (12 mg, 47 µmol) and N-ethylmorpholine (300 µL), was added to a suspension of precursor 13 (100 mg, 47 µmol) in MeOH, then the mixture was refluxed for 36 h. After cooling, the resultant deep red solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed (SiO₂) eluting with sat. aq. KNO₃:H₂O:MeCN (1:1:7; v/v/v) to afford (> 35 %) 14, as a dark red solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 9.01 (s, 3',5'-tpyH, 4H), 8.44 (d, J = 8.1 Hz, 3,3"-tpyH, 4H), 7.97 (dd, J = 3.3, 3.3 Hz, 4,5-ArH, 2H), 7.74 (dd, J = 3.3, 3.3 Hz, 3,6-ArH, 2H), 7.59 (dd, J = 7.8, 7.8 Hz, 4,4"-tpyH, 4H), 7.35 (d, J = 5.7 Hz, 6,6"-tpyH, 4H), 6.95 (dd, J = 6.9, 6.3 Hz, 5,5"-tpyH, 4H); ¹³C NMR (CDCl₃): δ 91.50, 95. 53, 125.40, 125.56, 126.60, 128.68, 131.19, 131.58, 133.89, 139.04, 153.60, 156.30, 158.46; IR (KBr): ν 3083, 2219, 1608, 1475, 1421, 1245, 1031, 836, 786, 613, 557, 512 cm⁻¹; UV/Vis (CH₃CN): λₘₐₓ 275 (ε = 7.28 × 10⁴), 316 (8.01 × 10⁴), 496 nm (4.23 × 10⁴ dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 2796.4 [M + H − PF₆⁻]⁺ (Calcd m/z 2796.17), 2649.8 [M − 2PF₆⁻]⁺ (Calcd m/z 2650.20), 2504.6 [M − H − 3PF₆⁻]⁺ (Calcd m/z 2504.23), 2357.7 [M − 3H − 4PF₆⁻]⁺ (Calcd m/z 2357.26), 2214.4 [M − H − 5PF₆⁻]⁺ (Calcd m/z 2214.31).

[Ru₂Fe(4)₃(PF₆)₆] (15). FeCl₂·8H₂O (9.3 mg, 47 µmol) was added to a suspension of the precursor 13 (100 mg, 47 µmol) in MeOH, then the mixture was refluxed for 36 h. After cooling, the resultant deep purple-red solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed (SiO₂) eluting with sat. aq. KNO₃:H₂O:MeCN (1:1:7; v/v/v) to afford (> 35%) 15, as a dark purple-red solid: m.p. >
400 °C; $^1$H NMR (CD$_3$CN): $\delta$ 9.18 (s, 3',5'-tpy$H$, Fe, 4H), 9.06 (s, 3',5'-tpy$H$, Ru/Fe, 4H), 9.01 (s, 3',5'-tpy$H$, Ru, 4H), 8.47 - 8.42 (m, 3,3''-tpy$H$, 12H), 8.02 - 7.95 (m, 4,5-Ar$H$, 6H), 7.77 - 7.72 (m, 3,6-Ar$H$, 6H), 7.60 - 7.53 (m, 4,4''-tpy$H$, Ru and 5,5''-tpy$H$, Fe, 12H), 7.35 (dd, $J$ = 4.8, 5.1 Hz, 4,4''-tpy$H$, Ru, 8H), 7.12 (d, $J$ = 5.1 Hz, 6,6''-tpy$H$, Fe, 4H), 6.93 (dd, $J$ = 6.3, 6.6 Hz, 5,5''-tpy$H$, Ru, 8H), 6.87 (dd, $J$ = 6.6, 6.0 Hz, 5,5''-tpy$H$, Fe, 4H); $^{13}$C NMR (CDCl$_3$): $\delta$ 91.62, 91.66, 95.56, 125.02, 125.36, 125.49, 125.59, 126.50, 126.64, 126.69, 128.59, 128.70, 131.21, 131.60, 132.37, 133.38, 133.83, 133.95, 139.06, 139.45, 153.64, 154.21, 156.35, 158.38, 158.51, 158.53, 161.23; UV/Vis (CH$_3$CN): $\lambda_{\text{max}}$ 276 ($\varepsilon$ = $1.34 \times 10^5$), 319 (1.25 $\times 10^5$), 499 (5.86 $\times 10^4$), 582 (2.38 $\times 10^4$ dm$^3$·mol$^{-1}$·cm$^{-1}$); ESI-MS: m/z 1302.1 [M − 2PF$_6^{-}$]$^+$ (Calcd m/z 1301.9), 819.8 [M − 3PF$_6^{-}$]$_2^+$ (Calcd m/z 819.6), 579.0 [M − 4PF$_6^{-}$]$_3^+$ (Calcd m/z 578.5), 433.9 [M − 5PF$_6^{-}$]$_4^+$ (Calcd m/z 433.8), 337.3 [M − 6PF$_6^{-}$]$_5^+$ (Calcd m/z 337.3).

**Directed Route to [Ru$_3$(4)]$_3$(PF$_6$)$_6$ (11).** Bis(terpyridine) ligand 4 (100 mg, 16.9 µmol) was added to a MeOH solution with an equivalent [Ru(Cl)$_2$(DMSO)$_4$] (82 mg, 16.9 µmol), then the suspension was refluxed for 24 h, to give (30 %) a dark red solid, which was filtered, then column chromatographed (SiO$_2$). The sample was identical in all respects to the above.
CHAPTER III

DESIGN, SELF-ASSEMBLY, AND PHOTOPHYSICAL PROPERTIES OF PENTAMERIC METALLOMACROCYCLES: \([M_5(N\text{-HEXYL}\{3,6\text{-BIS}(2,2',6',2''\text{-TERPYRIDIN-4'-YL})\text{CARBAZOLE})_5]\ [M = \text{Fe(II)}, \text{Ru(II)}, \text{AND Zn(II)}] \)

3.1 Introduction

The design of highly ordered supramolecular structures has attracted considerable interest in that the self-assembly of specifically tailored building blocks, possessing appropriate directivity of binding loci underpin the generation of novel, utilitarian supramolecular complexes with two- and three-dimensional nano- and macrostructures.\(^\text{316,319,336}\) Owing to their electronic and steric versatility, aromatic \(N\)-heterocycles continue to play a prominent role as classical ligands in coordination compounds,\(^\text{337,338}\) bridging ligands in binuclear derivatives,\(^\text{339-341}\) and as building blocks for supramacromolecular assemblies. In addition to the ability of these polyheteroaromatics to be connected by metal centers, they provide the opportunity of \(\pi\)-back bonding and thereby may affect delocalization and transport of electrons as well as capture photons for light-energy conversion.\(^\text{342,343}\)

So far, many successful strategies have been developed for the construction of metallomacro cyclic structures with trigonal,\(^\text{320,344}\) square,\(^\text{345-351}\) hexagonal,\(^\text{322,323,352}\)
heptagonal, and octagonal shapes; the pentagonal shape has been reported albeit to a limited extent relative to its homologous counterparts.

Since the invention of the solar cell fabricated by silicon, many researchers have been interested in the potential utilitarian applications for solar energy capture; however, the desired silicon materials are very expensive due to the need for highly clean procedures in their processing - thus an alternative, low-cost, solar cell material is required for commercialization. Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO$_2$ photoelectrode have been actively studied, since Grätzel et al. reported their low-cost and high efficiencies, $\eta$, of up to 10% with a DSSC, based on a Ru-complex photosensitizer. Several ruthenium complexes, e.g., cis-dithiocyanato-bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) and trithiocyanato-4,4',4''-tricarboxy-2,2:'6,2''-terpyridine ruthenium(II) have been used in DSSCs, as efficient photosensitizers.

In this Chapter, the assembly and photophysical properties (photoluminescence and photovoltaics) of a related family of metallomacrocycles based on a carbazole unit connecting two, rigidly held, and appropriately directed (ca. 109.5°) terpyridine ligands are described. This predesigned bis(terpyridine) ligand was then self-assembled to give metallopentacycles utilizing terpyridine-metal(II)-terpyridine, $\langle$(tpy)-metal(II)-(tpy)\rangle connectivity. The initial results on the photoelectrochemical properties of nanocrystalline TiO$_2$ thin films, successfully sensitized by these metallopentacycles are also presented.
3.2 Results and Discussion

Chemically, carbazole has been shown to be easily functionalized at its 3-, 6- or 9-positions.\(^{370}\) Therefore, the synthesis of the key building block 3 began with commercially available 9H-carbazole, which was \(N\)-alkylated with 1-bromohexane using KOH to give (71\%) 1 that was subsequently treated with 3 equiv. of DMF and POCl\(_3\) (Vilsmeier reagent) to form (52 \%) the desired dialdehyde 2. (Scheme 3.1) This transformation was supported (\(^1\)H and \(^13\)C NMR) by the appearance of absorptions at 10.15 (–CHO) and 191.72 (–CHO) ppm, respectively, and the specific 3,6-substitution pattern was confirmed by the aromatic coupling constants. Dialdehyde 2 was treated with 3 equivalents of 2-acetylpyridine under basic conditions for 24 h at 25 °C, followed by the addition of excess NH\(_4\)OAc in AcOH. After refluxing for 12 h, the desired angular building block 3 was isolated (34 \%) and structurally confirmed (\(^1\)H NMR) by the peaks at 4.38 (t) for NCH\(_2\), 8.11 (d) for 3-ArH, and 7.90 ppm (dd) for 4,4''-tpyH (these signals integrated in the expected 1:1:2 ratio), as well, a mass peak (ESI-MS) at \(m/z\) 715.2 [M + H]\(^+\) was recorded.

![Scheme 3.1 Synthesis of building block for metallopentacycles](image)

\[\text{Scheme 3.1 Synthesis of building block for metallopentacycles: (a) 1-bromohexane, KOH, DMF, reflux; (b) DMF, POCl}_3; (c) } i) 4.4\text{ equiv. 2-acetylpyridine, NaOH, ii) NH}_4\text{OAc, AcOH, reflux.}\]
Treatment of 3 with one equiv. of FeCl$_2$·4H$_2$O in MeOH for 12 h at 25 °C (Scheme 2) gave the self-assembled pentameric complex [Fe$_5$(3)$_5$(PF$_6$)$_{10}$] 4. The $^1$H NMR spectrum of 4 revealed two sharp doublets at 8.56 (3-ArH) and 8.08 ppm (2-ArH). These sharp peaks imply the presence of a single homogenous environment for all such groups; this is in stark contrast to the broadened or multiple signals expected for linear oligomers. The observed upfield shift for the doublet at 7.31 ppm (6,6''-tpyHs; $\Delta\delta = -1.49$) and downfield shift for the singlet at 9.39 ppm (3',5'-tpyHs; $\Delta\delta = 0.46$) when compared to the

Scheme 3.2 Synthesis of homonuclear metallopentacycles using self-assembly method: (a) i) $M^{2+}$, reflux, ii) NH$_4$PF$_6$/MeOH.
absorptions for the uncomplexed starting material, confirm the symmetry associated with
macrocyclization. Lastly, the pentagonal motif was established (ESI-MS) by the
definitive signals for multiple-charged entities ranging from the +5 to +10 charge states
derived from the loss $^{334}$ of both PF$_5$ and PF$_6^-$.

The self-assembled Ru(II) counterpart, [Ru$_5$(3)$_5$(PF$_6$)$_{10}$] 5, was prepared by the
treatment of a MeOH solution of monomer 3 with one equiv. of [Ru(Cl)$_2$(DMSO)$_4$] over
36 h at 50 °C. This method gave the desired pentameric complex possessing chloride
counterions, which, after chromatography and counterion exchange (Cl$^-$ to PF$_6^-$), afforded (overall ca. 35 %) the pure macrocycle 5. The $^1$H NMR of 5 exhibited a similar
pattern (to that of 4) including the diagnostic shifts for the doublet at 7.54 ppm (6,6''-tpy$H$s; $\Delta \delta = -1.26$), and the singlet at 9.24 ppm (3',5'-tpy$H$s; $\Delta \delta = 0.31$) in accord with
ring-formation. The ESI-MS of 5 gave signals for the multiple-charged entities ranging
from the +5 to +8 charge states.

The [Zn$_5$(3)$_5$(PF$_6$)$_{10}$] 6 was generated by the reaction of a 1:1 mixture of ligand 3
with Zn(BF$_4$)$_2$·8H$_2$O in MeCN for 24 h at 80 °C affording (35 %) a light yellow solid.
The absence ($^1$H NMR) of extraneous peaks excluded the presence of starting materials,
intermediates, and oligomeric materials. The diagnostic shifts of the doublets at 7.93 ppm
(6,6''-tpy$H$s; $\Delta \delta = -0.87$) and the singlet at 9.17 ppm (3',5'-tpy$H$s; $\Delta \delta = 0.24$) along with
definitive ESI-MS data all support the structural assignment. COSY and HETCOR
spectra of the bis(terpyridine)s and the corresponding self-assembled metallomacrocycles
verified the peak assignments as well as the coupling patterns.

To elucidate and support the composition of these metallopentacycles, their
UV/Vis absorbencies were measured (MeCN). From the absorption spectra of 4 and 5 in
Figure 3.1, each showed the lowest energy ligand-centered $\pi-\pi^*$ transitions of the terpyridine moieties at $\sim$310 and $\sim$390 (shoulder) nm. While the metal-ligand charge-transfer (MLCT) transitions, which are derived from the promotion of an electron from the metal [Fe(II) or Ru(II)]-centered $d$-orbitals to unfilled ligand-centered $\pi^*$ orbitals appeared at 573 and 504 nm, respectively. In the case of the pentagonal Zn(II) metallomacrocycle 6, the absorption bands at $\lambda_{\text{max}} = 240, 285, 316, 398$ nm originating from intra-ligand charge transfer ($^1\text{ILCT}$) are observed without MLCT peaks; the MLCT
of Zn(II) to terpyridine can be excluded.\textsuperscript{371}

Although the Ru(II) complexes of bipyridinyl ligands exhibit characteristic red luminescence from the $^3$MLCT state, in the case of the Ru(II) complex with terpyridinyl ligands, this state is quenched by a low-lying $^3$MC state and the room temperature emission is not observed.\textsuperscript{372} Whereas the ruthiopentacycle employing the carbazole moiety, which is a well-known material for fluorescence, does not show fluorescence at 25 °C; however, the pentagonal Zn(II) metallomacrocycle shows a strong yellow emission when excited with UV light (400 nm). The fluorescence of the pentagonal Zn(II) metallomacrocycle in MeCN solution is shown in Figure 3.1(C).

The electrochemical responses of the metallopentacycles were characterized by cyclic voltammetry (CV) experiments using 0.2 mM solutions of the relevant compound dissolved in DMF with 0.1 M Bu$_4$NBF$_4$ at 25 °C. Whereas metallopentacycles 4 and 5 showed metal related redox waves for Fe(III)/Fe(II) and Ru(III)/Ru(II) pentamers at 0.49 and 0.57 V vs. Fc$^+$/Fc, respectively, the electrochemical response of the Zn(III)/Zn(II) couple in pentamer 6 was not observed due to the completely filled $d$-shell of the Zn(II)-complex.\textsuperscript{373}

Cathodic scans of pentamers 4 - 6 however, exhibited a set of reversible reduction waves that were followed by large current reduction peaks at more negative potentials, reflecting complex processes probably associated with decomposition. The first two reduction processes for 4 (Table 3.1) are related to metal reduction events,\textsuperscript{352} and the only distinguishable peak in 5 is related to the monoelectronic reduction of one of the coordinated terpyridine ligands.\textsuperscript{352} In the case of 6, two closely positioned reversible waves are observed before current induced irreversible events take place. Based on the
half-wave potential difference associated with these signals, terpyridine and metal-related processes are suggested as an explanation of the CV response,\textsuperscript{323,352} instead of sequential terpyridine associated events.

From the CV responses at different scan rates (20~100 mV/s\textsuperscript{-1}), values of the diffusion coefficients of 4 - 6 were obtained (D; Table 3.1) using the Randles-Sevick equation.\textsuperscript{374} These values are nearly equal, further supporting the proposed structure of the three metallopentacycles.

Table 3.1. Electrochemical data of metallopentacycles, 4 - 6, (0.2 mM) obtained in 0.1 M TBABF\textsubscript{4} in DMF at 25 °C using a glassy carbon working electrode; scan rate = 100 mV/sec.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{1/2}) (vs. Fe\textsuperscript{3+}/Fe)/V</th>
<th>D ((10^{-8} \text{ cm}^2/\text{s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L/L\textsuperscript{-}</td>
<td>M(I)/M(0)</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-1.837</td>
</tr>
<tr>
<td>5</td>
<td>-1.843</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>-1.791</td>
<td>-</td>
</tr>
</tbody>
</table>

A photoelectrochemical solar cell is closely related to a battery, fuel cell or other type of electrochemical system, in that it is composed of two electrodes and an electrolyte. Unlike batteries or fuel cells where the energy is stored in the reactants and is then released through the electrical discharge during the formation of chemical reaction products, photoelectrochemical cells utilize the input optical energy to drive
electrochemical reactions. A dye-sensitized solar cell can be considered as a hybrid version of photogalvanic cells and solar cells, based on semiconductor electrodes. The cell consists of a dye-coated semiconductor electrode and a counter electrode arranged in a sandwich configuration and the inter-electrode space is filled with an electrolyte containing a redox mediator (A/A\(^-\)). In these studies, a bisterpyridine-metal(II) complex, as dye, TiO\(_2\), as the semiconductor, and (I\(_2\)/I\(_3\)^-\)), as the redox mediator were utilized. The key reactions taking place in a dye-sensitized photoelectrochemical solar cell are shown schematically in Figure 3.2. Optical excitation of the metallopentacycles as dye with visible light leads to excitation of the metallopentacycles to an electronically excited state that undergoes electron-transfer quenching, injection electrons into the conduction band of the nanocrystalline TiO\(_2\) semiconductor:

\[
S^* \rightarrow S^+ + e^- \text{ (conducting band)}
\]

The oxidized metallopentacycles are subsequently reduced back to the ground state (S) by the electron donor (I\(_3^-\)) present in the electrolyte filling the pores:

\[
S^+ + I_3^- \rightarrow S + I_2
\]

The electrons in the conduction band collect at the back collector electrode and subsequently pass through the external circuit to arrive at the counter electrode, where they effect the reverse reaction of the redox mediator:
\[ \text{I}_2 + e^- \rightarrow \text{I}_3^- \] (at the counter electrode)

The net effect of visible light irradiation is the regeneration of the dye, the redox mediator, and the driving of electron through the external circuit. The process thus leads to direct conversion of sunlight to electricity. If the above cited reactions alone take place, the solar cell will be stable, delivering photocurrents indefinitely. The maximum photovoltage obtainable will be the difference between the Fermi level (conduction band)

![Figure 3.2 Schematic energy diagram or ruthiopentacycle, 7, based on a nanocrystalline TiO\textsubscript{2} electrode and I\textsubscript{2}/I\textsubscript{3} redox electrolyte.](image-url)
of the semiconductor under illumination and the redox potential of the mediating redox couple. The photocurrent obtainable is a complex entity depending on the spectral, redox properties of the dye, efficiency of charge injection, and structural properties of the semiconductor electrode to collect and channel the electrons through the external circuit.

Because of the light absorption properties of constructed metallopetacycles, these materials were also studied as sensitizer materials for DSSCs. Photovoltaic performance experiments using dye-covered nanocrystalline TiO$_2$ electrodes (prepared by dipping the semiconductor substrate in a 0.2 mM MeCN solution of each one of the metallopetacycles) properly fitted in a solar cell device,$^{375}$ were conducted using a

![Figure 3.3 I-V plot obtained from DSSC assembled with modified TiO$_2$ electrode with metallomacrocycles 4 (□), 5 (○), and 6 (△).](image-url)

105
polychromatic (1.5 mW·cm$^{-2}$) incident light source and an electrolyte containing 0.3M KI + 0.015M I$_2$ dissolved in a 4 to 1 ratio of propylene and ethylene carbonate. The surface coverage ($\Gamma$) of each metallopentacycle on the TiO$_2$ electrode was calculated using UV/Vis spectroscopy experiments, as reported by Grätzel.\textsuperscript{376} Notably, the values obtained (Table 3.2) are fairly close to each other, thus supporting the similar structure and dimensions of compounds 4 - 6. Discharge experiments (Figure 3.3) conducted with these devices also allowed the calculation of some of the values in Table 3.2. Whereas the fill-factor ($ff$) of the three electrodes studied here remains similar, the short circuit photocurrent ($j_{sc}$) as well as the open circuit photopotential ($V_{oc}$) for the ruthiopentacycle showed the best results. Also, total photoconversion efficiency of the cell ($\eta$) using electromagnetic radiation spanning the visible region of the spectrum exhibited the highest value in the case of the ruthiopentacycle 5.

Table 3.2 Photovoltaic performances and surface coverage values of ITO/TiO$_2$/metallopentacycle/KI-I$_2$ electrolyte/graphite dye-sensitized solar cells measured using a polychromatic 1.5 mW/cm$^2$ light source.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_{sc}$\textsuperscript{a} ($\mu$A/cm$^2$)</th>
<th>$V_{oc}$\textsuperscript{b} (mV)</th>
<th>$ff$\textsuperscript{c} (%)</th>
<th>$\eta$\textsuperscript{d} (%)</th>
<th>$\Gamma$\textsuperscript{e} ($10^{11}$ mol/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>90.4</td>
<td>250</td>
<td>32.6</td>
<td>0.49</td>
<td>3.03</td>
</tr>
<tr>
<td>5</td>
<td>300.4</td>
<td>290</td>
<td>26.3</td>
<td>1.53</td>
<td>5.49</td>
</tr>
<tr>
<td>6</td>
<td>137.6</td>
<td>269</td>
<td>29.5</td>
<td>0.73</td>
<td>6.22</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Short-circuit photocurrent; \textsuperscript{b} Open-circuit photovoltage; \textsuperscript{c} Fill-factor; \textsuperscript{d} Photoconversion efficiency of the cell; \textsuperscript{e} Surface coverage.
3.3 Conclusions

The formation and characterization of a series of unique, self-assembled, pentagonal metallomacrocycles have been demonstrated. Employing terpyridine-metal(II)-terpyridine connectivity, these complexes were shown to be stable and irreversible under the reaction conditions. The structures of these pentagonal architectures were characterized by means of $^1$H and $^{13}$C NMR, UV/Vis spectroscopy, and mass spectroscopy. Preliminary studies of photoelectrochemical performance for the metallopentacycles demonstrated their potential for solar cell development.

3.4 Experimental Section

**General procedure.** Chemicals were purchased from Aldrich 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 used neutral/basic Al$_2$O$_3$, Brockman Activity I (60-325 mesh), or SiO$_2$ (60-200 mesh) from Fisher Scientific and used the stipulated solvent combination for elution. The melting points were determined on Electrothermal 9100 heater. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl$_3$, except where noted. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap Mass Spectrometer (ESI-MS). UV/Vis absorption spectra were obtained on Hewlett-Packard UV/Vis spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer. All the
electrochemical experiments were performed with CHI 440 Electrochemical Workstation (CH Instruments Inc, Austin, Texas). A 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, from Fluka) in DMF was used as the supporting electrolyte (degassed with argon). A platinum wire was employed as the counter electrode. A silver wire electrode was used as the reference. Ferrocene (Fc) was conducted as an internal reference and all the potentials were referenced relative to the Fc/Fc⁺ couple. A graphite electrode (CHI, 2 mm in diameter), polished with 1.0 and 0.3 µm aluminum paste and ultrasonicated in deionized water and DMF bath, was used as the working electrode. The scan rate for cyclic voltammetry (CV) was 100 mV/sec. All experiments were performed at 20 ± 2 ºC.

**N-Hexylcarbazole (1).** A stirred mixture of KOH (2.08 g, 35.88 mmol), 1-bromohexane (5.92 g, 35.88 mmol) and 9H-carbazole (5 g, 29.90 mmol) dissolved in DMF (40 mL) was refluxed for 12h. The mixture was poured into distilled water and extracted with CH₂Cl₂. The combined extract was dried (MgSO₄), filtered, and concentrated in vacuo to give a crude product, which was column chromatographed on SiO₂ eluting with a hexane/EtOAc (15:1; v/v) mixture to afford (71 %) 1, as white solid: 5.34 g; m.p. 62 - 63 ºC; ^1H NMR: δ 8.09 (d, J = 7.5 Hz, 5-ArH, 2H), 7.42 (m, 3,4-ArH, 4H), 7.21 (dd, J = 7.5, 6.6 Hz, 2-ArH, 2H), 4.26 (t, J = 7.2 Hz, NCH₂, 2H), 1.84 (m, NCH₂CH₂, 2H), 1.37 - 1.26 [m, CH₂(CH₂)₃CH₃, 6H], 0.85 (t, J = 6.9 Hz, CH₃, 3H); ^13C NMR: δ 14.22, 22.75, 27.18, 29.13, 31.79, 43.27, 108.84, 118.87, 120.53, 123.02, 125.75, 140.63; ESI-MS: m/z 274.1 [M + Na]⁺ (Calcd. m/z 274.2).

**N-Hexyl-3,6-diformylcarbazole (2).** To a stirred mixture of DMF (85 mL) and 1,2-dichloroethane (25 mL) cooled to 0 ºC, phosphoryl chloride (79.29 g, 520 mmol) was added, then 1 (5.2 g, 20.69 mmol) was added. After stirring for 48 h at 90 ºC, the mixture
was poured into distilled water, extracted with CHCl₃, and dried (MgSO₄). The crude product was column chromatographed on SiO₂ eluting with a hexane/EtOAc (4:1; v/v) mixture to afford (52%) 2, as white solid: 3.31 g; m.p. 137 - 138 °C; ¹H NMR: δ 10.15 (s, CHO, 2H), 8.68 (s, 5-ArH, 2H), 8.10 (d, J = 8.4 Hz, 3-ArH, 2H), 7.56 (d, J = 8.4 Hz, 2-ArH, 2H), 4.40 (t, J = 6.9 Hz, NC₃H₂, 2H), 1.92 (m, NCH₂C₂H₂, 2H), 1.40 - 1.29 [m, CH₂(CH₂)₃CH₂, 6H], 0.87 (t, J = 6.6 Hz, CH₃, 3H); ¹³C NMR: δ 14.15, 22.69, 27.08, 29.12, 31.66, 44.05, 109.99, 123.40, 124.51, 128.06, 129.89, 145.01, 191.72; ESI-MS: m/z 330.2 [M + Na]⁺ (Calcd. m/z 330.1).

N-Hexyl-[3,6-bis(2,2'';6',2''-terpyridin-4-yl)carbazole (3). To a stirred mixture of dialdehyde 2 (2.3 g, 7.48 mmol) and EtOH (100 mL), 2-acetylpyridine (3.99 g, 32.92 mmol) was added, followed after 2 min. by NaOH powder (1.3 g, 32.5 mmol). After the dark pink solution had been stirred at 25 °C for 24 h, the solvent was evaporated in vacuo to yield the intermediate, as a dark brown solid. Ammonium acetate (23 g, excess) and glacial AcOH (100 mL) were added to this solid, then this mixture was refluxed for 12 h. After cooling, the dark brown solution was neutralized with aqueous Na₂CO₃. The crude product was extracted with CH₂Cl₂. The combined extract was dried (MgSO₄), then concentrated in vacuo to give a resultant residue that was column chromatography on Al₂O₃ eluting with a hexane/CH₂Cl₂ (1:1; v/v) mixture to afford (34 %) 3, as off-white solid: 1.82 g; m.p. 204 - 205 °C; ¹H NMR: δ 8.93 (s, 3',5'-tpyH, 4H), 8.81-8.79 (m, 6,6''-tpyH, 5-ArH, 6H), 8.72 (d, J = 7.8 Hz, 3,3''-tpyH, 4H), 8.11 (d, J = 8.4 Hz, 3-ArH, 2H), 7.90 (dd, J = 7.8, 7.5 Hz, 4,4''-tpyH, 4H), 7.54 (d, J = 8.4 Hz, 2-ArH, 2H), 7.37 (dd, J = 5.1, 6.9 Hz, 5,5''-tpyH, 4H), 4.38 (t, J = 6.9 Hz, NCH₂, 2H), 1.96 (m, NCH₂CH₂, 2H), 1.46-1.34 [m, CH₂(CH₂)₃CH₂, 6H], 0.89 (t, J = 6.9 Hz, CH₃, 3H); ¹³C NMR: δ 14.24,
[Fe₅(3)₅(PF₆)₁₀] (4). A solution of one equiv. of FeCl₂·4H₂O (54 mg, 270 µmol) in MeOH, was added to a stirred solution of ligand 3 (195 mg, 270 µmol) in MeOH (100 mL), and then maintained at 25 °C for 24 h. After the resultant deep purple solution was filtered through Celite, a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on SiO₂ eluting with a H₂O/MeCN/sat. aq. KNO₃ (1:10:1; v/v/v) mixture to afford (> 50 %) 4, as a purple solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 9.39 (s, 3',5'-tpyH, 5-ArH, 6H), 8.75 (d, J = 8.1 Hz, 3,3''-tpyH, 4H), 8.56 (d, J = 8.7 Hz, 3-ArH, 2H), 8.08 (d, J = 8.4 Hz, 2-ArH, 2H), 7.92 (dd, J = 7.8, 7.5 Hz, 4,4''-tpyH, 4H), 7.31 (d, J = 5.1 Hz, 6,6''-tpyH, 4H), 7.12 (dd, J = 6.6, 6.0 Hz, 5,5''-tpyH, 4H), 4.71 (t, J = 6.6 Hz, NCH₂CH₂, 2H), 2.09 (m, NCH₂CH₂, 2H), 1.49-1.38 [m, CH₂(CH₂)₃CH₃, 6H], 0.95 (t, J = 6.9 Hz, CH₃, 3H); ¹³C NMR (CD₃CN): δ 14.42, 23.45, 27.68, 29.93, 32.44, 44.59, 112.14, 121.99, 122.59, 124.89, 125.03, 127.43, 128.35, 129.46, 139.74, 143.77, 152.57, 154.16, 159.35, 161.27; UV/vis (MeCN): λ_max (ε) 239(9.65 × 10⁴), 285(1.25 × 10⁵), 319(1.08 × 10⁵), 573 nm(5.80 × 10⁴ dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 914.7 [M – 5PF₆]⁵⁺ (Calcd. m/z 914.7), 702.8 [M – 4PF₆⁻ – 4PF₅ + 2H]⁶⁺ (Calcd. m/z 702.8), 622.7 [M – 3PF₆⁻ – 4PF₅]⁷⁺ (Calcd. m/z 622.8), 519.2 [M – 7PF₆⁻ – PF₅]⁸⁺ (Calcd. m/z 519.7), 460.6 [M – PF₆⁻ – 8PF₅]⁹⁺ (Calcd. m/z 460.6), 384.8 [M – 10PF₆]¹⁰⁺ (Calcd. m/z 384.9).

[Ru₅(3)₅(PF₆)₁₀] (5). To a stirred solution of 3 (131 mg, 180 µmol) in MeOH, [Ru(Cl)₂(DMSO)₄]³⁷⁷ (89 mg, 180 µmol) was added; the mixture was refluxed for 48 h.
After cooling, the resultant deep red solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on SiO₂ eluting with a combination of a H₂O/MeCN/sat. aq. KNO₃ (1:7:1; v/v/v) to afford (> 35 %) 10, as a dark red solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 9.30 (s, 5-ArH, 2H), 9.24 (s, 3',5'-tpyH, 4H), 8.79 (d, J = 8.1 Hz, 3,3″-tpyH, 4H), 8.48 (d, J = 8.4 Hz, 3-ArH, 2H), 8.03-7.95 (m, 4,4″-tpyH, 2-ArH, 6H), 7.54 (d, J = 5.0 Hz, 6,6″-tpyH, 4H), 7.22 (dd, J = 5.8, 5.7 Hz, 5,5″-tpyH, 4H), 4.66 (t, J = 6.1 Hz, NCH₂, 2H), 2.07 (m, NCH₂C₂H₂, 2H), 1.49-1.26 (m, CH₂(C₂H₅)₃CH₃, 6H), 0.91 (t, J = 6.9 Hz, CH₃, 3H); ¹³C NMR (CD₃CN): δ 14.41, 23.45, 27.67, 29.92, 32.44, 44.35, 112.05, 121.62, 122.42, 124.99, 125.63, 127.37, 128.55, 129.39, 139.08, 143.61, 150.22, 153.55, 156.58, 159.57; UV/Vis (MeCN) λₘₚₙₐₓ (ε) 237 (1.56 × 10⁵), 285 (1.94 × 10⁵), 308 (2.49 × 10⁵), 504 nm (1.21 × 10⁴ dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 545.7 [M – 8PF₆⁻]⁸⁺ (Calcd. m/z 545.6), 644.4 [M – 7PF₆⁻]⁷⁺ (Calcd m/z 644.3), 775.3 [M – 6PF₆⁻]⁶⁺ (Calcd. m/z 775.8), 960.7 [M – 5PF₆⁻]⁵⁺ (Calcd. m/z 960.0).

[Zn₅(3)₅(PF₆)₁₀] (6). To a stirred solution of 3 (95 mg, 130 µmol) in MeCN, Zn(BF₄)₂·8H₂O (51 mg, 130 µmol) was added, then the mixture was refluxed for 48 h. After cooling, the resultant solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on Al₂O₃ eluting with a H₂O/MeCN/sat. aq. KNO₃ (1:7:1; v/v/v) mixture to afford (> 35 %) 10, as a light-yellow solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 9.24 (s, 5-ArH, 2H), 9.17 (s, 3',5'-tpyH, 4H), 8.84 (d, J = 8.1 Hz, 3,3″-tpyH, 4H), 8.45 (d, J = 8.4 Hz, 3-ArH, 2H), 8.20 (dd, J = 7.8, 7.8 Hz, 4,4″-tpyH, 4H), 8.02 (d, J = 8.7 Hz, 2-ArH, 2H), 7.93 (d, J = 4.2 Hz, 6,6″-tpyH, 4H), 7.43 (dd, J = 5.4, 5.4 Hz, 5,5″-tpyH, 4H), 7.22 (dd, J = 5.8, 5.7 Hz, 5,5″-tpyH, 4H).
tpyH, 4H), 4.66 (t, J = 6.1 Hz, NCH₂, 2H), 2.07 (m, NCH₂CH₂, 2H), 1.52-1.31 [m, CH₂(CH₂)₂CH₃, 6H], 0.92 (t, J = 7.2 Hz, CH₃, 3H); ¹³C NMR (CD₃CN): δ 14.39, 23.43, 27.63, 29.89, 32.41, 42.07, 112.18, 122.23, 122.24, 124.24, 124.90, 127.65, 128.54, 128.82, 142.03, 144.07, 149.10, 149.22, 150.83, 158.23; UV/Vis (MeCN) λ_{max} (ε) 240 (2.64 × 10⁵), 285 (2.50 × 10⁵), 316 (1.79 × 10⁵), 398 nm (1.29 × 10⁵ dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 924.3 [M – 5PF₆⁻]⁵⁺ (Calcd m/z 924.2), 745.2 [M – 6PF₆⁻]⁶⁺ (Calcd m/z 746.0), 466.0 [M – 8PF₆⁻ – PF₅⁻]⁹⁺ (Calcd m/z 465.9), 389.8 [M – 10PF₆⁻]¹⁰⁺ (Calcd m/z 389.6).

**Fabrication of Photovoltaic Cell Device.** Nanocrystalline TiO₂ electrodes were prepared by applying a 4 V potential difference³⁷⁸ between a steel sheet and an ITO conducting glass substrate immersed in a 10 mL [0.5 g TiO₂ (P25, Degussar AG, Germany, a mixture of ca. 30 % rutile and 70 % anatase, BET surface area 55 m²/g) in 5% 2-propanol in water (v/v)] colloidal suspension for 40 s. Following previous reports in the literature,³⁷⁹ the electrodes were then taken out from the electrophoretic apparatus, sintered at 450 ºC in air for 30 min, and characterized by general tools (AFM, XRD, Raman spectroscopy, cyclic voltammetry and profilometry). From the characterization results, it was found that the electrode thus prepared consisted of nanoparticulated TiO₂ in anatase phase, with roughness factors of 540, an average thickness of ~2 µm and a flat band potential, E_{FB}, of −0.2 V vs. NHE which is a value that agrees well with previous reports.³⁸⁰,³⁸¹ This flat band potential value of −0.2 V vs. NHE that was measured for the electrophoretically prepared nanocrystalline TiO₂ electrodes, is substantially more positive than that reported for nanocrystalline electrode prepared using the typical spin coating protocol (− 0.5 V vs. NHE). This effect, which has been reported³⁸¹ recently, is
associated with an increase of Ti$^{+3}$ dopant surface sites that result from hydrogen adsorption during the electrophoretic deposition process. Pentamers, as dye, were coated onto the TiO$_2$ layer by dipping the electrode for 12 h in a MeCN solution (ca. 0.2 mmol/L). The assembled devices for photovoltaic measurements were consisted of a dye-coated TiO$_2$ electrode, Ti substrate covered with a film of colloidal graphite as a counter electrode, the electrolyte containing a deoxygenated 0.3 M of KI + 0.015 M of I$_2$ aqueous solution, and a Teflon tape that was used to maintain a 0.5 mm gap between the two electrodes.
CHAPTER IV

HEXAMERIC METALLOMACROCYCLES: DESIGN, CONSTRUCTION, AND NANOHYBRID COMPLEX WITH FUNCTIONALIZED MULTI-WALLED CARBON NANOTUBES

4.1 Introduction

In recent years, there has been an increasing interest in the coordination of relatively simple ligands to afford di- and polynuclear complexes that exhibit high order, structural complexity,\textsuperscript{3,316} both in solution and the solid state. Although contemporary supramolecular chemistry has its roots in classical covalent macrocycles,\textsuperscript{383} metal-mediated and architecturally-directed self-assembly has now been widely used to construct novel, ordered nanoscale arrays, such as grids,\textsuperscript{384,385} helicates,\textsuperscript{356} cubes,\textsuperscript{386} cylinders,\textsuperscript{387} and cages.\textsuperscript{388}

In general, the majority of metallocycles that have been created so far are based on structures possessing hetero-organic sides with metal corners; this mode of construction has been elegantly exploited by Stang,\textsuperscript{316,389,390} and Atwood,\textsuperscript{318} and has been the topic of numerous reviews.\textsuperscript{391-395} Recently, a different series of metallomacrocycles has been reported based on \textit{bis}(terpyridinyl)aryl monomers possessing a critical, preset coordination angle of 120 ° with respect to the two metal-ligating moieties. This
facilitates the assembly of six building blocks with six connecting metals in the ubiquitous benzenoid architecture.\textsuperscript{322-324}

In recent years, the integration of organic and inorganic nanohybrid structures has drawn broad interdisciplinary attention,\textsuperscript{396-398} as this approach to innovative materials bears interesting opportunities for the control over fine-tuning desirable functionalities.\textsuperscript{399,400} In the continuous search for suitable systems useful in photovoltaics, electron donor-acceptor arrays are particularly promising. Relevant aspects include (i) solubility, (ii) optimizing the frontier orbital energy levels and offsets of donors and acceptors, (iii) improving the absorption cross section/solar light harvesting, (iv) stabilizing radical ion pair states, (v) optimizing the layer and interface morphologies, and (vi) fine-tuning the charge carrier mobility. Carbon nanotubes should as well be included in this picture.

Herein, the design and preparation of new extended members of a "modular building block set"\textsuperscript{401} that are capable of forming either stable or irreversible "higher order" architectures are reported. Incorporation of linear triple bonds in these building blocks between the central connective aromatic ring and the (two) terpyridine ligand(s) generates relatively rigid yet simple scaffolding that can be employed for preparation of novel carbon-rich nanoarchitectures possessing tunable chemical, physical, electronic, and optical properties. Subsequent treatment of a carboxylate-modified, multi-walled carbon nanotubes (MWNTs) with these metallohexamers afforded ionically hybridized carbon nanotubes that can be envisioned as components in devices such as single-electron transistors,\textsuperscript{402,403} molecular diodes,\textsuperscript{404-406} memory elements,\textsuperscript{407} logic gates,\textsuperscript{408,409} and nanoscale low ohmic metallic contacts.\textsuperscript{410}
4.2 Results and Discussion

Construction of the desired 120°-based bisligand (Scheme 4.1) began with initial reduction (BH$_3$·THF) of 5-tert-butylisophthalic acid to give (95 %) the corresponding diol 1, which was subsequently oxidized (PCC/CH$_2$Cl$_2$) to afford (92 %) dialdehyde 2. Each transformation was evidenced by the appearance of pivotal absorptions ($^{13}$C NMR) at 65.62 (CH$_2$OH) and 191.69 (CHO) ppm, respectively. Wittig-type olefination of aldehyde 2 with a mixture of CBr$_4$, Ph$_3$P, and zinc in CH$_2$Cl$_2$ gave (90 %) the tetrabromide 3 that was supported ($^{13}$C NMR) by the new resonance at 90.24 ppm (C=CB$_r$$_2$). Two-stage dehydrobromination of bromide 3 using t-BuOK in THF afforded

\[ \text{HOOC} \text{COOH} \rightarrow \text{(a)} \rightarrow \text{(b)} \rightarrow \text{(c)} \rightarrow \text{(d)} \rightarrow \text{(e)} \]

Scheme 4.1 Synthesis of building block for metallohexamer: (a) BH$_3$·THF, THF; (b) PCC, CH$_2$Cl$_2$, 25 °C; (c) Zn, Ph$_3$P, CBr$_4$, CH$_2$Cl$_2$, 25 °C; (d) i) t-BuOK, THF, -76 °C, ii) n-BuLi, Et$_2$O, 0 °C, H$_2$O; (e) Pd(Ph$_3$P)$_4$, $^{1}$Pr$_2$NH/toluene.
the dibromo intermediate (not shown), which was subsequently treated, without further purification, with \(n\)-BuLi in Et\(_2\)O to give (80\%) 1,3-\(\text{bis}(\text{diethynyl})\)-5-\(\text{tert}\)-butylbenzene (4), as a white solid. Support for this transformation was the appearance of two new peaks (\(^{13}\text{C NMR}\)) at 83.37 (C≡CH) and 77.54 (C≡CH) ppm. Reacting this \(\text{bisalkyne} 4\) with 2.5 equivalents of 4'-trifluoromethanesulfonyl-2,2':6',2''-terpyridine\(^{333}\) (tpy-OTf) by means of a Pd-catalyzed cross-coupling procedure mediated by [(PPh\(_3\))\(_4\)Pd(0)] in diisopropylamine, then afforded (35\%) the desired angular monomer 6, as an off-white solid. The successful coupling was evidenced by appearance of the expected new signals (\(^1\text{H and}^{13}\text{C NMR}\)) attributed to the terpyridinyl moieties and the presence of two similar alkyne peaks (\(^{13}\text{C NMR}\)) at 93.60 and 87.80 ppm.

Figure 4.1 ORTEP drawing of \(\text{bis}(\text{terpyridine})\) ligand 6.
For further support of this conversion, a single crystal was grown by vapor diffusion of hexane into a CHCl₃ solution of 6 for X-ray analysis. The ORTEP representation of 6 (Figure 4.1) confirms the desired angle-of-directionality (ca. 120°) between the ligands. Two terpyridines lie approximately in the same plane as the benzene moiety and the alkyne connections are linear.

Self-assembly of bis-terpyridine 6, upon treatment with one equivalent of FeCl₂·4H₂O in MeOH (Scheme 2) gave, after chromatography and counterion exchange, (70 %) the diamagnetic, hexameric Fe(II) metallomacrocycle 7, which was characterized (¹H NMR) by a resonance at 1.56 ppm [C(CH₃)₃] indicating the presence of a single homogeneous environment for all such groups; this is in contrast to the broadened or multiple signals realized for either linear or polymeric oligomers. Also obtained were the notable upfield and downfield shifts (¹H NMR) of the doublet at 7.22 ppm (Δδ = −1.54) for the 6,6'-tpyHs and the singlet at 9.13 ppm (Δδ = 0.51) for the 3',5'-tpyHs, respectively, when compared to the absorptions for the parent 6. Other diagnostic signals (¹³C NMR) included two signals at 97.82 and 87.98 ppm attributed to the dissymmetric acetylenic carbons. COSY and HETCOR spectra of both the starting ligand 6 and self-assembled macrocycle 7 verified the peak assignments, as well as coupling patterns. This hexagonal structure was further established (ESI MS) by the observation of signals (m/z = 1345.34, 1046.20, and 852.66) assigned to multiple-charged entities ranging from +4 to +6 charge states, derived from the loss of PF₅ and PF₆⁻, either separately or together. Hexameric metallomacrocycle 7, initially isolated as the 12 Cl⁻ salt, was soluble in MeOH and hot H₂O; subsequent conversion to the corresponding 12 PF₆⁻ salt facilitated solubility in MeCN, acetone, DMF, and DMSO.
Scheme 4.2 Synthesis of homonuclear hexagonal metallomacrocycles using self-assembly method: (a) i) FeCl$_2$·4H$_2$O, reflux, ii) NH$_4$PF$_6$/MeOH.

The related diamagnetic, hexameric ruthiomacrocycle, [Ru$_6$(6)$_6$(PF$_6$)$_{12}$], (10, Scheme 4.3) was prepared by both a single step as well as step-wise procedures. The diamagnetic *bis*-complex 9 was readily prepared by treatment of the paramagnetic precursor 8 with two equivalents of unmetallated *bis*-terpyridine 6. The $^1$H NMR of trimer 9 showed equivalent 3',5'-tpy$H$ peaks (8.94, 8.92, 8.77 ppm; 1:1:1 ratio) as well as two anticipated singlets arising from nonequivalent tert-butyl groups (1.52, 1.47 ppm; 1:2 ratio). Treatment of trimer 9 with one equivalent of [Ru(Cl)$_2$(DMSO)$_4$]$^{377}$ insert in refluxing MeOH for 36 h gave the desired hexameric complex possessing chloride counterions, which, after chromatography and counterion exchange (Cl$^-$ to PF$_6^-$), afforded (overall 30 %) the pure hexamer 10. This metallocycle was spectrally identical
to the product formed through the self-assembly protocol. The $^1$H NMR of the hexa-Ru(II) complex 10 revealed a similar pattern to that of the Fe(II) based metallomacrocycle 7, except for slight chemical shift difference of the diagnostic doublet (7.47 ppm, $\Delta\delta = -1.29$) of the 6,6'-tpyHs, and the singlet for the 3',5'-tpyHs (8.95 ppm, $\Delta\delta = 0.33$). The ESI MS of macrocycle 10 exhibited signals for the multiple-charged entities ranging from +2 to +4 charge states ($m/z = 2776.58$, 2030.75, and 1386.68).

Scheme 4.3 Synthesis of homonuclear hexagonal ruthiomacrocycle using step-wise and self-assembly method: a) RuCl$_3$·3H$_2$O, MeOH, reflux; (b) 2 equiv. 6, $N$-ethylmorpholine, MeOH, reflux; (c) i) [Ru(Cl)$_2$(DMSO)$_4$], MeOH, reflux; ii) NH$_4$PF$_6$/MeOH; (d) i) [Ru(Cl)$_2$(DMSO)$_4$], MeOH, reflux; ii) NH$_4$PF$_6$/MeOH.
To elucidate and support the composition of these metallohexamers, their UV/Vis spectra were measured. (Figure 4.2) The absorption data of 7 and 10 each showed two ligand-centered $\pi-\pi^*$ transitions at ~284 and ~335 nm. The metal-ligand charge-transfer (MLCT) transitions, which were derived from the promotion of an electron from the metal [Fe(II) or Ru(II)]-centered $d$-orbitals to an unfilled ligand-centered $\pi^*$ orbital, appeared at 584 and 502 nm, respectively.

![UV absorption spectra for metallohexamers: (A) 7; (B) 10.](image)

Following the reported acid treatment ($\text{H}_2\text{SO}_4/\text{HNO}_3$) of MWNTs, the partially oxidized carbon nanotubes were generated. Ion coordination of hexamer 10 to these nanotube carboxylate binding sites was conducted by simple cation exchange to afford
(Scheme 4.4) a new surface-bound nano-hybrid complex. Binding sites on the modified surface of the MWNTs were readily detected (TEM) by the presence of the electron-dense Ru(II)-hexamer 10 (Figure 4.3). The irregular MWNT coating by hexamer 10 is caused by the randomness of the surface carboxylate moieties. Computer-aided structure simulation revealed a macrocyclic external diameter of 49.7 Å for hexamer 10; this calculated size agrees well with the observed ca. 5 nm electron dense spots visible on the MWNT’s surface caused by the monomeric hexamer, as shown in the TEM microphotograph; the presence of large aggregates of hexamers is also noted. Energy Dispersive X-ray Spectroscopy (EDXS) spectra revealed a distinct peak a 2.6 keV corresponding to ruthenium-based surface absorption thereby further confirming the construction of the hexamer-MWNT composite (Figure 4.4).

Scheme 4.4 Idealized structure of hexamer/MWNT nanohybrids.
Figure 4.3 Computer generated space-filling representation [upper-right (inset)] and TEM photographs of Ru(II)-based hexamer 10 immobilized on a carboxylate-modified MWNT’s surface: [upper-right] = red arrows represent single hexamer and yellow arrows show the agglomerates of several hexamers.
Raman spectra for pure hexamer 10, the acid-treated MWNT, and the hexamer/MWNT hybrid are shown in Figure 4.4. A $D$-mode at $\sim$1348 cm$^{-1}$, which has been attributed to the breakdown of translational symmetry produced by its microcrystalline structure$^{412}$ as well as a $G$-mode located at the 1580 cm$^{-1}$ related to the tangential shear mode ($E_{2g}$)$^{413}$ additionally confirm the structures. Figure 4.5(c) also shows the $D^*$-mode, as a shoulder, at $\sim$1615 cm$^{-1}$ (calculated by using Lorentzian multi-peak analysis method), which has a counterpart in the disordered $sp^2$ carbons. The frequency of the $D^*$-mode in graphite corresponds to the mid-zone maximum in the phonon density of states in the optical branch$^{414,415}$ and as structural disorder tends to
introduce structure in the Raman spectrum near positions of maxima in the one-phonon density of states of the ordered (parent) material, the $D^*$-mode is therefore another anticipated signature for surface-wall-disorder, functionalization, or wall-defects, after processing. Introducing defects along the MWNT’s surface in a controlled manner, using the initial acid treatment followed by Raman spectroscopy to examine the vibrational response facilitated an understanding of changes along the MWNT surface. Consequently, peak changes, when the hexamer is introduced to the MWNT’s surface, were observed as a decrease in the $D^*$-mode peak. Upon introduction of the hexamer, a substantial shift (ca. 3 cm$^{-1}$) in the $E_{2g}$ mode as well as a shift of hexamer’s peaks, which appeared near the $G$-mode and $D$-mode of the oxidized MWNT, were realized.

![Figure 4.5 Raman spectra of (A) hexamer 10, (B) the hexamer/MWNT nanohybrid, and (C) the oxidized MWNT.](image-url)
4.3 Conclusions

A pair of hexameric metallomacrocycles have been readily assembled on the basis of terpyridine-metal(II)-terpyridine connectivity. These hexameric metallomacrocycles were characterized by means of \(^1\)H and \(^{13}\)C NMR, UV/Vis spectroscopy, mass spectrometry, and, in the case of Ru(II) metallomacrocycle, by TEM. The complexation of the Ru(II)-hexamer to MWNTs was successfully achieved through of a simple cation exchange process. Use of these rigid metallomacrocycles that can be readily attached to a functionalized carbon nanotube affords access to useful nanohybrid structures.

4.4 Experimental Section

**General procedure.** Chemicals were commercially purchased 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 neutral/basic Al\(_2\)O\(_3\), Brockman Activity I (60-325 mesh) or SiO\(_2\) (60-200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater and are uncorrected. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl\(_3\), as the solvent, except where noted. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap mass spectrometer (ESI-MS). UV/Vis absorption spectra were obtained on Hewlett-Packard UV/Vis spectrophotometer. Raman spectra were measured in backscattering geometry with Jobin Yvon T64000 triple monochrometer; an argon laser with a
wavelength of 514.7 nm and power of 20 mW as excitation source. TEM images were obtained by using scanning transmission electron microscopy (TEM; FEI; Tacnai 12) at an acceleration voltage of 120 kV. EDXS analyses were conducted on an EDAX, EDAMIII apparatus. Samples for TEM were prepared by drop-casting the solution of acid-treatment MWNT, which is treated aqueous NaOH, dispersed in MeCN onto a carbon film-coated grid, then air dried and washed several times with MeCN to remove any residual unreacted hexamers.

1,3-Bis(hydroxymethyl)-5-tert-butylbenzene (1). To a solution of 5-tert-butylisophthalic acid (10 g, 45 mmol) in dry THF (60 mL) at 0 °C, was added dropwise a BH₃·THF solution (270 mL, 270 mmol) over 30 min. After 1 h, the stirred solution was warmed to 25 °C for 24 h. Excess of a satd. aq. NaHCO₃ solution was carefully added; the mixture was extracted with CHCl₃ and then dried (MgSO₄). The combined extract was concentrated in vacuo to give a residue, which was column chromatographed (SiO₂) eluting with a mixture of hexane : EtOAc (1:4; v/v) to afford (95 %) 1, as a white solid: m.p. 74 - 75 °C; ¹H NMR: δ 7.29 (s, 4,6-ArH, 2H), 7.16 (s, 2-ArH, 1H), 4.64 (s, CH₂OH, 4H), 2.40 (s, CH₂O, 2H), 1.32 [s, C(CH₃)₃, 9H]; ¹³C NMR: δ 31.56, 34.94, 65.62, 123.12, 123.57, 141.09, 152.10.

1,3-Bis(formyl)-5-tert-butylbenzene (2). 1,3-Bis(hydroxymethyl)-5-tert-butylbenzene (3 g, 15.5 mmol) was added to a stirred mixture of pyridinium chlorochromate (10 g, 46.3 mmol) in anh. CH₂Cl₂ (200 mL) at 0 °C; the solution was then warmed to 25 °C for 24 h. The mixture was filtered through a Celite pad, then concentrated in vacuo to give a crude product, which was column chromatographed (SiO₂) eluting with a mixture of hexane : EtOAc (1:1; v/v) to give (92 %) 2, as a white solid: m.p. 62 - 63 °C; ¹H
NMR: δ 10.12 (s, CHO, 2H), 8.19 (s, 2,4,6-ArH, 3H), 1.42 [s, C(CH₃)₃, 9H]; ¹³C NMR: δ 31.32, 35.36, 129.26, 131.86, 137.22, 153.93, 191.69.

1,3-Bis(2,2-dibromoethenyl)-5-tert-butylbenzene (3). Initially, a stirred suspension of zinc (2.78 g, 42.6 mmol), (C₆H₅)₃P (11.17 g, 42.6 mmol), and CBr₄ (14.12 g, 42.6 mmol) in anh. CH₂Cl₂ (100 mL) was created at –20 °C, then maintained with stirring at 25 °C for 30 h. 1,3-Bis(formyl)-5-tert-butylbenzene (2.7 g, 14.2 mmol) was added to this suspension; then stirring was continued for 2 h. The reaction mixture was poured into pentane (150 mL) and the insoluble material was filtered. The filtrate was poured into excess hexane and filtered (Celite) to afford a filtrate, which was evaporated in vacuo to give (52 %) 3, as a colorless oil: ¹H NMR: δ 7.59 (s, 2-ArH, 1H), 7.50 (s, 4,6-ArH, 2H), 1.34 [s, C(CH₃)₃, 9H]; ¹³C NMR: δ 31.42, 35.06, 90.24, 125.27, 126.14, 135.37, 136.96, 151.77.

1,3-Bis(diethynyl)-5-tert-butylbenzene (4). To a stirred solution of 3 (6.5 g, 12.9 mmol) in anh. THF (200 mL), was added in KOT-Bu (5.0 g, 51.8 mmol) at –76 °C over 1 h. The mixture was stirred for an additional 5 h at –76 °C and then quenched with excess H₂O. The mixture was extracted with CHCl₃, dried (MgSO₄), and concentrated in vacuo to give a residue, which was flash column chromatographed (SiO₂) eluting with a hexane : EtOAc (1:1; v/v) mixture to afford (89 %) a yellow oil.

An n-BuLi (5.05 mL; 2.5M in hexane, 12.62 mmol) solution was added dropwise to this crude oil (3.9 g, 11.5 mmol) in anh. Et₂O (100 mL) at 0 °C over 30 min. After further stirring for 30 min at 0 °C, the solution was cooled to –10 °C and carefully quenched with H₂O (5 mL). The mixture was poured into ice-cold water (200 mL) and extracted with Et₂O. The combined organic extract was washed with brine, dried
(MgSO₄), and concentrated in vacuo to give a residue that was column chromatographed (SiO₂) eluting with hexane to afford (91 %) 4, as a colorless oil: ^1^H NMR: δ 7.54 (s, 2,6-ArH, 2H), 7.50 (s, 4-ArH, 1H), 3.10 (s, CH, 2H), 1.33 [s, C(CH₃)₃, 9H]; ^1^3^C NMR: δ 31.17, 34.75, 77.54, 83.37, 122.27, 129.88, 132.95, 151.72.

**1,3-Bis(2,2':6',2''-terpyridin-4'-ylethynyl)-5-tert-butylbenzene (6).** 1,3-Bis-(diethynyl)-5-tert-butylbenzene (800 mg, 4.4 mmol) and 4'-[(trifluoromethyl)-sulfonyloxy]-2,2':6',6''-terpyridine (3.85 g, 10.9 mmol) were coupled by a Pd-catalyzed coupling procedure using tetrakis(triphenylphosphine)palladium(0) (500 mg, 440 µmol), diisopropylamine (40 mL), and toluene (50 mL) at 80 °C. After 3 days, the solvent was removed in vacuo to give a residue, which was column chromatographed (Al₂O₃) eluting with CHCl₃ to afford (35 %) pure 6, as a off-white solid: m.p. 269 - 270 °C; ^1^H NMR: δ 8.76 (d, J = 5.7 Hz, 6,6''-tpyH, 4H), 8.65 (d, J = 7.8 Hz, 3,3''-tpyH, 4H), 8.62 (s, 3',5'-tpyH, 4H), 7.92 (dd, J = 7.8, 6.6 Hz, 4,4''-tpyH, 4H), 7.65 (s, 2,6-ArH, 2H), 7.61 (s, 4-ArH, 1H), 7.38 (dd, J = 6.6, 5.7 Hz, 5,5''-tpyH, 4H), 1.41 [s, C(CH₃)₃, 9H]; ^1^3^C NMR: δ 31.43, 35.06, 87.80, 93.60, 121.57, 122.81, 123.24, 124.30, 130.25, 132.30, 133.52, 137.35, 149.28, 152.21, 155.61, 155.68; ESI-MS: m/z 667.4 [M + Na⁺] (Calcd. m/z= 667.3).

[^Fe₆(6)₆(PF₆)₁₂](7). A MeOH solution of one equiv. of FeCl₂·4H₂O (62 mg, 310 µmol) was added to a stirred solution of 1,3-bis(2,2':6',2''-terpyridin-4'-ylethynyl)-5-tert-butylbenzene (199 mg, 310 µmol) in MeOH (150 mL). After 24 h at 25 °C, the resultant deep purple solution was filtered through Celite; a slight excess of methanolic ammonium hexafluorophosphate was added in order to precipitate the complex, which was column chromatographed (SiO₂) eluting with a H₂O : CH₃CN : sat. aq. KNO₃ (1:10:1; v/v/v)
mixture to afford (>70 %) 7, as a purple solid: m.p. > 400 °C; $^1$H NMR (CD$_3$CN): $\delta$ 9.13 (s, 3',5'-tpyH, 4H), 8.56 (d, $J$ = 7.8 Hz, 3,3''-tpyH, 4H), 8.11 (s, 4,6-ArH, 2H), 7.97 (m, 2-ArH, 4,4''-tpyH, 4H), 7.22 (d, $J$ = 5.4 Hz, 6,6''-tpyH, 4H), 7.15 (dd, $J$ = 6.6, 6.0 Hz, 5,5''-tpyH, 4H), 1.56 [s, C(CH$_3$)$_3$, 9H]; $^{13}$C NMR (CD$_3$CN): $\delta$ 31.37, 35.90, 87.98, 97.82, 123,26, 125.17, 125.66, 126.29, 128.75, 132.30, 133.32, 138.44, 140.13, 154.32, 158.42, 161.34; UV/vis (MeCN): $\lambda_{\text{max}}$ ($\varepsilon$) = 285 (2.75 x 10$^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$), 338 (3.55 x 10$^5$), 584 nm (1.74 x 10$^5$); ESI MS: m/z = 1345.34 [M − 3PF$_6$ − PF$_5$]$^{4+}$ (Calcd. m/z = 1344.99), 1046.20 [M − 4PF$_6$ − PF$_5$]$^{5+}$ (Calcd. m/z = 1046.99), 852.66 [M − 4PF$_6$ − 2PF$_5$]$^{6+}$ (Calcd. m/z = 851.50).

$[(\text{RuCl}_3)_2(6)]$ (8). The bisligand 6 (40.6 mg, 63 µmol) was added to a solution of RuCl$_3$·3H$_2$O (32.9 mg, 126 µmol) in MeOH (40 mL), then the suspension was refluxed for 12 h. After cooling, the resultant dark red solid was filtered, washed with MeOH and CHCl$_3$, and dried in vacuo to give (> 80 %) the bis[Ru(III)] adduct 8, as a dark brown solid. This material was used in next step without further purification.

$[\text{Ru}_2(6)_3(\text{Cl})_4]$ (9). The bisligand 6 (77.4 mg, 120 µmol) was added to a suspension of bis[Ru(III)] adduct 8 (63.6 mg, 60 µmol) in MeOH (50 mL), then N-ethylmorpholine (5 drops) was added; the mixture was refluxed for 24 h. After cooling, the resulting deep red solution was filtered through Celite, followed by the addition of a slight excess of methanolic ammonium hexafluorophosphate to precipitate the complex, which was subsequently column chromatographed (Al$_2$O$_3$) eluting with a H$_2$O : CH$_3$CN : sat. aq. KNO$_3$ (1:10:1; v/v/v) mixture to give (> 47 %) trimer 9, as a dark red solid: m.p. > 400 °C; $^1$H NMR (CD$_3$CN; PF$_6$$^-$ counterion): $\delta$ 8.94 (s, 3',5'-tpyH
coordinated of center ligand, 4H), 8.92 (s, 3',5'-tpyH coordinated of side ligand, 4H), 8.86 (d, \( J = 4.5 \) Hz, 6,6''-tpyH free ligand, 4H), 8.77 (d, \( J = 8.1 \) Hz, 3,3''-tpyH free ligand, 4H), 8.68 (s, 3',5'-tpyH free ligand, 4H), 8.86 (d, \( J = 3.3 \) Hz, 3,3''-tpyH coordinated of center and side ligand, 8H), 8.38 (dd, \( J = 7.2 \), 6.3 Hz, 3,3''-tpyH free ligand, 4H), 8.01-7.92 (m, 4,4''-tpyH coordinated center and side ligand, 2-ArH, 4,6-ArH coordinated and free ligand, 17H), 7.81 (dd, \( J = 6.6 \), 5.7 Hz, 5,5''-tpyH free ligand, 4H), 7.45 (d, \( J = 3.9 \) Hz, 6,6''-tpyH coordinated of center and side ligand, 8H), 7.23 (dd, \( J = 6.6 \), 5.7 Hz, 5,5''-tpyH coordinated of center and side ligand, 8H), 1.52 [s, C(CH₃)₃ center ligand, 9H], 1.47 [s, C(CH₃)₃ side ligand, 18H].

\[\text{[Ru₆(6)₆(PF₆)₁₂]} \] (10). To a solution of the above precursor \( 9 \) (136 mg, 60 \( \mu \text{mol} \)) in MeOH, \([\text{Ru(Cl)}₂(DMSO)₄]\)\(^{377} \) (29 mg, 60 \( \mu \text{mol} \)) was added; the mixture was refluxed for 36 h. After cooling to 25 °C, the resultant deep red solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was purified column chromatographed (SiO\(_2\)) eluting with a \( \text{H}_2\text{O} : \text{CH}_3\text{CN} : \text{sat. aq KNO}_3 \) (1:10:1; v/v/v) mixture to afford (> 35 %) hexamer 10, as a dark red solid: m.p. > 400 °C; \(^1\text{H NMR (CD}_3\text{CN)}: \delta 8.95 \) (s, 3',5'-tpyH, 4H), 8.57 (d, \( J = 7.8 \) Hz, 3,3''-tpyH, 4H), 8.00 (m, 4-ArH, 2-ArH, 4,4''-tpyH, 7H), 7.47 (d, \( J = 5.1 \) Hz, 6,6''-tpyH, 4H), 7.24 (dd, \( J = 6.3 \), 6.0 Hz, 5,5''-tpyH, 4H), 1.52 [s, C(CH₃)₃, 9H]; \(^{13}\text{C NMR: } \delta 31.81, 35.89, 87.88, 97.01, 123.31, 125.79, 126.45, 128.90, 131.21, 132.03, 133.55, 139.49, 153.80, 154.37, 156.44, 158.60; UV/vis (CH₃CN): \( \lambda_{\text{max}} 283 \) (\( \varepsilon = 1.66 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \)), 333 (2.70 \times 10^5), 502 nm (1.46 \times 10^5); ESI MS: \( m/z = 2776.58 \) [M + 3H - 2PF₆⁻ - 3PF₃]\(^{2+} \) (Calcd. \( m/z = 2775.91 \)), 2030.75 [M - 2H - PF₃]\(^{3+} \) (Calcd. \( m/z = 2029.21 \)), 1386.68 [M + H - 2PF₆⁻ - 3PF₃]\(^{4+} \) (Calcd. \( m/z = 1387.45 \)).
Hexamer-MWNT Nanohybrid Complexation. A 250 mL flask charged with 5.0 g of crude MWNT and 100 mL of 60 % HNO₃ aqueous solution was sonicated in a bath for 30 min. The mixture was then stirred for 24 h under reflux. After cooling to 20 °C, it was diluted with 200 mL of deionized water and then filtrated. The filtrate was washed with deionized water until the pH of the filtrate reached 7. The filtered solid was then dried in vacuo for 12 h at 60 °C to give 3.05 g of carboxylic acid-functionalized MWNT (MWNT-COOH). Dried MWNT-COOH (160 mg) and NaOH (excess) was suspended in 30 mL of deionized water and stirred at 25 °C for 12 h. The mixture was then separated by filtration and washed with deionized water. Subsequently, it was dried in vacuo at 25 °C for 6 h to give 150 mg of carboxylate-functionalized MWNT sodium salt (MWNT-CO₂Na). The MWNT-CO₂Na (ca. 100 mg) was charged in 30 mL of MeCN and sonicated for 30 min. Then 50 mg of ruthiomeracrocyle 10 dissolved in 5 mL of anhydrous MeCN was added dropwise at 25 °C and kept with stirring for 48 h. The solid was then separated from the mixture by filtration and washed several times with excess MeCN. The raw product was suspended in excess MeCN followed by dialysis using MWC = 10,000 membrane. The black solid was collected and dried overnight in vacuo at 25 °C, affording ca. 100 mg of hexamer-MWNT nanohybrid.
CHAPTER V

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES FOR LUMINESCENT HEXAMERIC METALLOMACROCYCLES: Zn(II)-ION DIRECTED SELF-ASSEMBLY OF BIS(TERPYRIDINE) LIGANDS

5.1 Introduction

Supramolecular chemistry and molecular self-assembly, the underlying cornerstones of nanotechnology, have been the subject of intense research interests as evidenced by the exponential growth of publications in these areas over the last decade.\textsuperscript{316} Although contemporary supramolecular chemistry has its roots in classical covalent macrocycles, metal-mediated and architecturally-directed self-assembly has been widely used to construct novel, ordered macromolecular arrays.\textsuperscript{417} Many interesting constructs can thus be accessed with high efficiency by the incorporation of these synthetic parameters.\textsuperscript{418}

Substituted polypyridines possessing directed N-loci, have been shown to form stable coordination and hydrogen-bonded complexes with various metal ions and molecules, respectively. This family of heterocycles has been widely used as ligands for transition metal cations and as the fundamental building blocks in supramolecular chemistry.\textsuperscript{419,420} Especially, 2,2':6',2''-terpyridine complexes with Ru(II) and Os(II) have
attracted increasing interest due to the structural advantage in designing photofunctional supramolecular assemblies. Newkome’s group has developed novel type metallomacrocycles, which has been constructed by the preparation of a bis(terpyridinyl) monomer possessing a 120° angle with respect to the two metal-ligating moieties thereby facilitating the facile assembly of six building blocks with six connecting metals in the ubiquitous benzenoid architecture.322,323

Up to now, through attachment of different transition metal complexes onto organic ligands421-426 or polymer chains,427-430 many research groups have achieved the fine tuning of light-emitting properties. Among them, using the Zn(II) ion as a template to assemble organic building blocks into polymer chains through the construction of photoluminescent metal-containing polymers has the potential to lead to the formation of high-performance emissive or host materials in electroluminescent devices. Herein, the synthesis of a family of self-assembled zinc(II) hexagonal metallomacrocycles is reported and their photophysical properties, such as absorption and fluorescence characteristics, depending on the incorporation of ethynyl connectivity in the metallomacrocycles are investigated to evaluate their different electronic differences.431

5.2 Results and Discussion

Substituted and heterocyclic aromatic compounds have proven useful as rigid building blocks in self-assembly chemistry.322,323,329-332 The combination of the proper carbon framework with various substitution patterns can result in a plethora of angles, including the elusive 120° angle necessary for pre-designed hexagonal structures.332 Two
ligands, 1 and 2, were chosen as the skeleton for a building blocks possessing the desired directed ligands for complexation but different length between benzene and terpyridine moieties, affording an ideal substrate for subsequent (tpy)-Zn(II)-(tpy), where tpy = 2,2':6',2''-terpyridine.

Synthesis of the key building block, bis(terpyridine) ligand 1, began by treatment of known dialdehyde with 4.4 equivalent of 2-acetylpyridine under basic condition at 25 °C for 12 h, followed by addition of excess NH$_4$OAc in AcOH then refluxed for 24 h to afford the desired angular 1,3-bis(2,2':6',2''-terpyridinyl)-5-tert-butylbenzene (1) in 32% overall yield. The structure of 1 was confirmed by singlets ($^1$H NMR) at 1.52 for the C(CH$_3$)$_3$, 8.10 for 4-ArH, and 7.91 ppm for 4,4''-tpyH (integration in the expected 9:1:4 ratio) and a mass peak (ESI-MS) at $m/z$ = 619.3 [M + Na$^+$]. Another key building block 2 was prepared starting from 1,2-diethynyl-5-tert-butylbenzene (DETB) and 2.4 equivalents of the known 4'-trifluoromethanesulfonyl-2,2':6',2''-terpyridine (TfO-tpy). Palladium-catalyzed cross-coupling of DETB and TOf-tpy with tetrakis(triphenyl-

![Figure 5.1 Chemical structures of ligand 1 and 2.](image-url)
phosphine)palladium(0) in base solvent afforded (41%) the second building block, 1,3-
bis(2,2':6',2''-terpyridinylethynyl)-5-tert-butylbenzene (2), as an off-white solid, that is
stable in air at room temperature. The structure of 2 was confirmed by $^1$H NMR at the
singlets at 1.41 (s) for C(CH$_3$)$_3$ and 7.61 for 4-Ar$H$ as well as the doublet of doublet at
7.92 ppm for 4,4''-tpy$H$ (these signals integration in the expected 9:1:4 ratio), and the
expected mass peak (ESI-MS) at $m/z$ 667.4 [M + Na]$^+$. 

The relative diamagnetic, hexagonal Zn(II) metallomacrocycles (3 or 4) were
prepared, through self-assembly, by reacting one equivalent of the $\textit{bis}$-terpyridine)
ligands (1 or 2, respectively) with one equivalent of Zn(BF$_4$)$_2$·8H$_2$O in MeCN for 24 h
under 75 ºC. The spectra ($^1$H NMR) of metallomacrocycles (3 or 4) revealed sharp
singlets for [C(CH$_3$)$_3$] at 1.72 and 1.51 ppm, respectively, similar in peak shape with that
of starting ligand. This suggests the presence of a single homogenous environment for all
such groups; this would be in contrast to that expected for either linear or polymeric
oligomers, in which more complex patterns would be envisioned.$^{322,323,352}$ There are
notable upfield and downfield shifts for the doublet (7.96 ppm, $\Delta\delta = -0.79$ for 3; 7.88
ppm, $\Delta\delta = -0.88$ for 4) for the 6,6''-tpy$H$ and for the 3',5'-tpy$H$ signals (9.21 ppm, $\Delta\delta =
0.43$ for 3; 8.93 ppm, $\Delta\delta = 0.31$ for 4), when compared to the absorptions of the
uncomplexed starting material. Especially in case of 4, other diagnostic spectral attributes
($^{13}$C NMR) included the two distinct and different peaks at 98.94 and 87.32 ppm for
acetylene carbons, respectively. COSY and HETCOR spectra of the $\textit{bis}$-terpyridines (1
and 2) and the self-assembled metallomacrocycles (3 and 4) verified the peak
assignments as well as coupling patterns. These hexagonal structures were established
Figure 5.2 Chemical structures of hexagonal metallamacrocycles 3 and 4.
(ESI-MS) by the signals of multiple-charged entities ranging from +2 to +8 (for 3) and from +2 to +9 (for 4) charge state derived from the loss of PF₆⁻ generated from the cyclic hexamer.

The spectroscopic properties of the metallomacrocycles were conducted in solution (MeCN) state. As shown in Figure 1 at short wavelength ca. \( \lambda_{\text{abs}} = 280 \) nm, the two complexes display similar absorption intensity and molar extinction coefficients (\( \varepsilon = 3.31 \times 10^5 \) for 3, \( \varepsilon = 3.49 \times 10^5 \) for 4) in MeCN; however, the metallomacrocycle 4 shows a higher molar extinction coefficients (\( \varepsilon = 3.14 \times 10^5 \)), comparing that (\( \varepsilon = 1.32 \times 10^5 \)) for 3 at ca. \( \lambda_{\text{abs}} = 330 \) nm, which may be attributed to the incorporated acetylene.

![Figure 5.3 UV/vis absorption (solid line) and emission (dashed line) of hexagonal metallomacrocycles 3 and 4.](image)

Figure 5.3 UV/vis absorption (solid line) and emission (dashed line) of hexagonal metallomacrocycles 3 and 4.
moieties. In other word, such absorption intensity differences may come from the mixing of metal’s orbitals into the acetylenic $\pi-\pi^*$ band, which is similar to that shown for the Pt-acetylene complex system.$^{425,433}$ The photoluminescence (PL) spectra of the complexes (3 and 4) were measured in MeCN solution at an excitation wavelength of 310 and 330 nm, respectively. The effect of incorporating an acetylene unit on the spectroscopic property in fluorescence studies is more dramatic. These results should be explained by efficient exciton migration to trapping sites in acetylene unit.

Figure 5.4 shows the incident photon-to-current efficiency (IPCE) normalized by

![Figure 5.4 Photocurrent action spectra for ITO/TiO\textsubscript{2}/Zn(II)-hexamer/KI-I\textsubscript{2} electrolyte/Graphite system: 3 (dot line) and 4 (solid line).](image-url)
surface coverage \((\Gamma)\) for ITO/TiO\(_2\)/Zn(II)-hexamer/KI-I\(_2\) electrolyte/Graphite system. When irradiated with visible light \((\lambda > 380\, \text{nm})\), photocurrent generation at low wavelength range \((400 - 480\, \text{nm})\) is observed. The surface coverage of the hexamer 3 is \(2.19 \times 10^{-11}\, \text{mol/cm}^2\) and for 4 is \(1.14 \times 10^{-11}\, \text{mol/cm}^2\). The system consisting of the hexamer 4 revealed enhanced photocurrent as compared to that of hexamer 3. Although no firm explanation for the enhanced photocurrents is available, the photocurrent observed for the hexamer 4 system as compared to that derived from 3 should be attributed to the ethynyl group inside the metallomacrocycle as an electron trap that facilitates charge separation.

The thermal stability of the metallomacrocycles was evaluated by thermogravimetric analysis (TGA). The initial decomposition temperatures were 410 ºC (for 3) and 485 ºC (for 4) under a nitrogen atmosphere and 95 % of their mass was retained. From these results, the formed metallomacrocycles show an excellent thermal stability indicating the suitable materials to apply the electronic devices.

5.3 Conclusions

Two kinds of Zn(II)-terpyridinyl-based hexagonal metallomacrocycles, which showed a blue fluorescence, can be readily synthesized by Zn(II)-ion directed self-assembly. The TiO\(_2\) electrode modified by ethynyl-group incorporated Zn(II)-metallomacrocycles revealed enhanced photoelectrochemical properties. Although the results may have a limited impact for energy conversion owing to the low photocurrent values, the study highlights fundamental effects of Zn(II) metal-terpyridine complexes on
charge transport at organometallics/electrode interface. From absorption and emission results, the incorporation of ethynyl group in the metallomacrocycle is useful for tuning their photophysical and thermal properties. These materials offer promise in the field of organic light-emitting diodes or optoelectronic devices.

Figure 5.5 TGA curve for hexagonal metallomacrocycles 3 (dot line) and 4 (solid line).
5.4 Experimental Section

**General procedure.** Chemicals were purchased from Aldrich 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. Column chromatography was conducted using basic Al₂O₃, Brockman Activity I (60-325 mesh) or SiO₂ (60-200 mesh) from Fisher Scientific. The melting points were determined on Electrothermal 9100 heater. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl₃, except where noted. UV/VIS absorption spectra were measured in MeCN at 25 °C with a Hewlett-Packard 8452A diode array spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap mass spectrometer (ESI-MS). Thermogravimetric analysis (TGA) was conducted with a DuPont model 2950 at a heating rate of 20 °C/min under a nitrogen atmosphere.

**1,3-Bis(2,2′:6′,2″-terpyridin-4-yl)-5-tert-butylbenzene (1).** The commercially available 5-tert-butyl-1,3-diformylbenzene (2.8 g, 14.72 mmol) was dissolved in EtOH (100 mL), then 2-acetylpyridine (7.26 mL, 64.76 mmol) was added, followed after 2 min by NaOH pellets (3.11 g, 77.71 mmol). After stirring the dark pink solution at 25 °C for 12 h, the solvent was evaporated in vacuo to yield dark red intermediate. Ammonium acetate (20 g, excess) and glacial AcOH (100 mL) were added; the mixture was then refluxed for 24 h. The dark brown solution was cooled, and neutralized with an aq. Na₂CO₃ to afford a dark brown precipitate, which was extracted by CHCl₃ and column
chromatographed (Al₂O₃) eluting with a mixture of DCM/EtOAc (2:1; v/v) to afford (32 %) 1, as off-white solid: m.p. 163 - 165 °C; ¹H NMR: δ 8.78 (s, 3',5'-tpyH, 4H), 8.75 (d, J = 5.4 Hz, 6,6''-tpyH, 4H), 8.70 (d, J = 7.8 Hz, 3,3''-tpyH, 4H), 8.10 (s, 4-ArH, 1H), 7.93 (s, 2,6-ArH, 2H), 7.91 (dd, J = 6.6, 7.8 Hz, 4,4''-tpyH, 4H), 7.37 (dd, J = 5.4, 6.6 Hz, 5,5''-tpyH, 4H), 1.52 [s, C(CH₃)₃, 9H]; ¹³C NMR: δ 31.79, 35.43, 119.70, 121.66, 124.03, 124.12, 125.35, 137.09, 139.72, 149.35, 151.22, 152.86, 156.15, 156.50; ESI-MS: m/z 619.3 [M + Na⁺] (Calcd. m/z = 619.7).

1,3-Bis(2,2':6',2''-terpyridin-4-ylethynyl)-5-tert-butylbenzene (2). 1,3-Bis(diethynyl)-5-tert-butylbenzene (Chapter 4, compound 4; 800 mg, 4.4 mmol) and 4'-(trifluoromethyl)sulfonyloxy]-2,2':6',6''-terpyridine³³³ (3.85 g, 10.9 mmol) were coupled by Pd-catalyzed coupling procedure using tetrakis(triphenylphosphine)palladium(0) (500 mg, 440 µmol), diisopropylamine (40 mL), and toluene (50 mL) at 80 °C. After 3 days, the solvent was removed in vacuo to give a residue, which was column chromatographed (Al₂O₃) eluting with CHCl₃ to afford (35 %) pure 2, as a off-white solid: m.p. 269 - 270 °C; ¹H NMR: δ 8.76 (d, J = 5.7 Hz, 6,6''-tpyH, 4H), 8.65 (d, J = 7.8 Hz, 3,3''-tpyH, 4H), 8.62 (s, 3',5'-tpyH, 4H), 7.92 (dd, J = 7.8, 6.6 Hz, 4,4''-tpyH, 4H), 7.65 (s, 2,6-ArH, 2H), 7.61 (s, 4-ArH, 1H), 7.38 (dd, J = 6.6, 5.7 Hz, 5,5''-tpyH, 4H), 1.41 [s, C(CH₃)₃, 9H]; ¹³C NMR: δ 31.43, 35.06, 87.80, 93.60, 121.57, 122.81, 123.24, 124.30, 130.25, 132.30, 133.52, 137.35, 149.28, 152.21, 155.61, 155.68; ESI-MS: m/z 667.4 [M + Na⁺] (Calcd. m/z = 667.27).

[Zn₆(1)₆(PF₆)₁₂] (3). To a solution of the above precursor 1 (118 mg, 190 µmol) in MeCN, Zn(BF₄)₂·8H₂O (76 mg, 190 µmol) was added then the mixture was refluxed for 24 h. After cooling, the resultant solution was filtered through Celite, then a slight excess
of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed (SiO$_2$) eluting with a satd. aq. KNO$_3$: H$_2$O: CH$_3$CN (1:1:10; v/v/v) solvent mixture to afford (> 25 %) 3, as a off-white solid: m.p. > 410 °C (dec.); $^1$H NMR (CD$_3$CN): $\delta$ 9.21 (s, 3',5'-tpy$H$, 4H), 8.90 (d, $J$ = 7.5 Hz, 3,3''-tpy$H$, 4H), 8.75 (s, 4-Ar$H$, 1H), 8.49 (s, 2,6-Ar$H$, 2H), 8.25 (dd, $J$ = 7.5, 6.9 Hz, 4,4''-tpy$H$, 4H), 7.96 (d, $J$ = 5.4 Hz, 6,6''-tpy$H$, 4H), 7.50 (dd, $J$ = 6.9, 5.4 Hz, 5,5''-tpy$H$, 4H), 1.72 [s, C(CH$_3$)$_3$, 9H]; $^{13}$C NMR (CD$_3$CN): $\delta$ 31.72, 36.55, 119.28, 123.33, 124.54, 126.43, 128.80, 138.89, 142.42, 149.03, 149.20, 151.07, 155.68, 157.18; UV/Vis (CH$_3$CN) $\lambda$$_{max}$ (ε) 288 (3.31 $\times$ 10$^5$), 323 (1.76 $\times$ 10$^5$), 338 nm (1.32 $\times$ 10$^5$ dm$^3$.mol$^{-1}$.cm$^{-1}$); ESI-MS: m/z 569.1 [M – 8PF$_6^{-}$]$^{8+}$ (Calcd m/z = 569.0), 671.1 [M – 7PF$_6^{-}$]$^{7+}$ (Calcd m/z = 671.0), 807.3 [M – 6PF$_6^{-}$]$^{6+}$ (Calcd m/z = 807.0), 997.6 [M – 5PF$_6^{-}$]$^{5+}$ (Calcd m/z = 997.4), 1283.3 [M – 4PF$_6^{-}$]$^{4+}$ (Calcd m/z = 1283.0), 1759.1 [M – 3PF$_6^{-}$]$^{3+}$ (Calcd m/z = 1759.1), 2709.8 [M – 2PF$_6^{-}$]$^{2+}$ (Calcd m/z = 2710.9).

$[\text{Zn}_6(2)_{6}(\text{PF}_6)_{12}]$ (4) was prepared in an analogous manner except by starting with precursor 2 (146 mg, 230 μmol) in MeCN to afford after purification (> 30 %) 4, as a gray-white solid: m.p. > 485 °C (dec.); $^1$H NMR (CD$_3$CN): $\delta$ 8.93 (s, 3',5'-tpy$H$, 4H), 8.62 (d, $J$ = 7.8 Hz, 3,3''-tpy$H$, 4H), 8.21 (dd, $J$ = 7.8, 6.6 Hz, 4,4''-tpy$H$, 4H), 8.05 (s, 2,6-Ar$H$, 2H), 8.03 (s, 4-Ar$H$, 1H), 7.88 (d, $J$ = 5.4 Hz, 6,6''-tpy$H$, 4H), 7.45 (dd, $J$ = 6.6, 5.4 Hz, 5,5''-tpy$H$, 4H), 1.51 [s, C(CH$_3$)$_3$, 9H]; $^{13}$C NMR (CD$_3$CN): $\delta$ 31.34, 35.90, 87.32, 98.94, 122.95, 124.36, 126.55, 128.93, 132.62, 133.82, 140.06, 142.58, 148.38, 149.41, 150.88, 154.50; UV/Vis (CH$_3$CN) $\lambda$$_{max}$ (ε) 237 (2.73 $\times$ 10$^5$), 286 (3.49 $\times$ 10$^5$), 331 nm (3.14 $\times$ 10$^5$ dm$^3$.mol$^{-1}$.cm$^{-1}$); ESI-MS: m/z 521.8 [M – 9PF$_6^{-}$]$^{9+}$ (Calcd m/z = 521.7), 605.3 [M – 8PF$_6^{-}$]$^{8+}$ (Calcd m/z = 605.0), 712.0 [M – 7PF$_6^{-}$]$^{7+}$ (Calcd m/z = 712.1), 855.1
Fabrication of Photocurrent Cell Device. Nanocrystalline TiO$_2$ electrodes were prepared by applying a 4 V potential difference$^{378}$ between a steel sheet and an ITO conducting glass substrate immersed in a 10 mL [0.5 g TiO$_2$ (P25, Degussar AG, Germany, a mixture of ca. 30 % rutile and 70 % anatase, BET surface area 55 m$^2$/g) in 5% 2-propanol in water (v/v)] colloidal suspension for 40 s. Following the literature,$^{379}$ the electrodes were taken out of the electrophoretic apparatus, sintered at 450 ºC in air for 30 min, and characterized by general tools (AFM, XRD, Raman spectroscopy, cyclic voltammetry, and profilometry). From the characterization results, it was found that the electrode consisted of nanoparticulated TiO$_2$ in the anatase phase, with roughness factors of 540, an average thickness of ~2 µm and a flat band potential, $E_{FB}$, of −0.2 V vs. NHE. This value agrees well with previous reports,$^{381,434}$ and is substantially more positive than that reported for nanocrystalline electrode prepared by the typical spin coating protocol (−0.5 V vs. NHE). This effect, which has been reported$^{381}$ recently, is associated with an increase of Ti$^{+3}$ dopant surface sites that result from hydrogen adsorption during the electrophoretic deposition process. Hexamers, as the dye, were coated onto the TiO$_2$ layer by dipping the electrode for 12 h in a MeCN solution (ca. 0.2 mmol/L). The assembled devices for photovoltaic measurements consisted of a dye-coated TiO$_2$ electrode, Ti substrate covered with a film of colloidal graphite as a counter electrode, the electrolyte containing a deoxygenated 0.3 M of KI + 0.015 M of I$_2$ aqueous solution,$^{382}$ and Teflon tape that was used to maintain a 0.5 mm gap between the two electrodes.
CHAPTER VI

DESIGN, SYNTHESIS, AND PHOTOELECTROCHEMICAL PROPERTIES OF HEXAGONAL METALLOMACROCYCLES BASED ON TRIPHENYLAMINE:

\[ M_6(4,4'-BIS(2,2':6',2''-TERPYRIDINYL)TRIPHENYLAMINE)_{6}(X)_{12}; \]  
\[ M, X = \text{Fe(II), PF}_6 \text{ AND Zn(II), BF}_4 \]

6.1 Introduction

The design and construction of supramolecular macrocyclic architectures have been the subject of considerable attention by many research groups over the past decade.\(^{435,436}\) Elegant work in the area of self-assembly by Stang et al.,\(^{327,437,438}\) Lehn et al.,\(^{385,439,440}\) Constable et al.,\(^{441-446}\) and many others\(^{447-451}\) has offered a better understanding of (macro)molecular systems. This has led to many successful strategies aimed at the construction of metallomacrocyclic structures with specific structural motifs such as, triangles,\(^{344}\) squares,\(^{345-349,452}\) pentagons,\(^{453}\) and hexagons.\(^{322,323,352}\)

The combination of various substitution patterns can result in a plethora of predetermined internal bond angles within molecular superstructures. So far, our strategy has been based on \(m\)-\(bis\)(terpyridinyl)arenes possessing the specific 120° angle with respect to the two ligating moieties for the construction of hexagonal metallomacrocycles. This angle facilitates the assembly of six programmed building
blocks with six connecting transition metals in the ubiquitous benzenoid shape, which is envisioned to be the basis of a ‘modular building block set’ capable of being used to access ‘high order’ (fractal) architectures.

Owing to the relatively simple synthetic accessibility and stability of oxidized triarylamines, they have been widely used as hole-transport components in optoelectronics in both photoreceptor devices and organic light-emitting diodes. In this Chapter, a new type of bis(terpyridine) ligand that can form the desired hexagonal metallomacrocycle incorporating the disubstituted triphenylamine subunit, as an angle-control element as well as potentially offering an opportunity to improve selected photophysical properties is described. The incorporation of this triphenylamine moiety into a structurally rigid metallomacrocyclic assembly will start to expand the understanding of the optoelectronic characteristics in specific supramolecular macroconstructs.

6.2 Results and Discussion

Treatment of triphenylamine with excess of DMF and POCl₃, the well-known Vilsmeier reagent, gave (52 %) the desired dialdehyde, which was supported by the appearance of the characteristic absorption (¹³C NMR) at 191.72 ppm assigned to the ArCHO and mass peak (ESI-MS) at m/z 323.8 [M + Na]⁺. Reaction of 1 with 4.4 equiv. of 2-acetylpyridine under basic conditions at 25 ºC for 24 h, followed by addition of excess NH₄OAc in AcOH and then refluxing for 12 h gave the angular building block 2 in 34 % yield. (Scheme 6.1) The successful creation of 2 was evidenced by the appearance of the
expected new signals (\(^1\)H NMR) at 8.73 (m, 6,6\(^{‴}\)-tpy\(H\), 3\(^{‴}\),5\(^{‴}\)-tpy\(H\)), 8.67 (d, 3,3\(^{‴}\)-tpy\(H\)), and 7.35 ppm (dd, 5,5\(^{‴}\)-tpy\(H\)) attributed to the terpyridinyl moieties and the presence of the definitive number and position of the peaks in the \(^{13}\)C NMR; a mass peak (ESI-MS) at \(m/z\) 816.3 [M + Ag]\(^+\) further confirmed the structure.

Vapor diffusion of hexane into a CHCl\(_3\) solution of 2 afforded the desired single crystals necessary for X-ray analysis (Figure 6.1). The crystal structure data revealed the terpyridines to be approximately coplanar and possessed the desired angle (119.69°) juxtaposition necessary for hexamer formation. The pyridine rings of the terpyridinyl moieties adopted the anti-conformation with N-C-C-N torsion angles in the range of 159.63° (15) to 176.25° (17), typical of all such structures. The crystal packing architecture of ligand 2 revealed channels created by solvent encapsulation (Figure 6.2A) while side view (Figure 6.2B) of the crystal packing exhibits a layered stacking with an average separation of \(ca.\ 4.4\ \text{Å}\). Inspection of the unit cell reveals two antiparallel terpyridine ligands.

Scheme 6.1 Synthesis of building block for hexagonal metallomacrocycle: (a) POCl\(_3\), DMF, dichloroethane; (b) i) 4.4 equiv. 2-acetylpyridine, NaOH, ii) NH\(_4\)OAc, AcOH, reflux.

Vapor diffusion of hexane into a CHCl\(_3\) solution of 2 afforded the desired single crystals necessary for X-ray analysis (Figure 6.1). The crystal structure data revealed the terpyridines to be approximately coplanar and possessed the desired angle (119.69°) juxtaposition necessary for hexamer formation. The pyridine rings of the terpyridinyl moieties adopted the anti-conformation with N-C-C-N torsion angles in the range of 159.63° (15) to 176.25° (17), typical of all such structures. The crystal packing architecture of ligand 2 revealed channels created by solvent encapsulation (Figure 6.2A) while side view (Figure 6.2B) of the crystal packing exhibits a layered stacking with an average separation of \(ca.\ 4.4\ \text{Å}\). Inspection of the unit cell reveals two antiparallel terpyridine ligands.
Figure 6.1 ORTEP drawing of bis(terpyridine) ligand 2.

Figure 6.2 Crystal packing of ligand 2: (A) top view of packing morphology indicating solvent (CHCl₃) encapsulation channels, (B) side view of the asymmetric units packing.
The diamagnetic, hexameric Fe(II) complex 3, [Fe₆(2)₆(PF₆)₁₂], was readily prepared by self-assembly of ligand 2 by treatment with one equivalent of FeCl₂·4H₂O in MeOH for 12 h (Scheme 6.2). The ¹H NMR spectrum of 3 revealed a sharp triplet at 9.20 ppm (3',5'-tpyH), indicating the presence of a single homogenous environment; this is in contrast to the broadened or multiple signals realized for either linear or polymeric oligomers, as demonstrated in related systems.³²³ The Fe(II) metallomacrocycle was confirmed by the observed upfield shift for the doublet at 7.24 ppm (6,6″-tpyHs; ∆δ = −1.49) and a downfield shift for the singlet at 9.20 ppm (3',5'-tpyHs; ∆δ = 0.47) when compared to the absorptions for the uncomplexed starting material. The hexagonal cyclic motif was further established (ESI-MS) by definitive signals for multiple-charged entities ranging from a +8 to +11 charge state derived from the loss of PF₅ and PF₆⁻, either separately or together.

The related yellow semicrystalline [Zn₆(2)(BF₄)₁₂] was generated (55 %) by the treatment of a 1:1 mixture of ligand 2 with Zn(BF₄)₂·8H₂O in MeCN for 24 h at 80 °C. The absence (¹H NMR) of extraneous peaks excluded the presence of starting materials, intermediates, and linear oligomers. The diagnostic shifts of the doublets at 7.87 ppm (6,6″-tpyHs; ∆δ = −0.86) and the singlet at 8.99 ppm (3',5'-tpyHs; ∆δ = 0.26) along with definitive ESI-MS data (m/z 544.4 [M − 9BF₄⁻]⁹⁺, 624.5 [M − 8BF₄⁻]⁸⁺, 725.1 [M − 7BF₄⁻]⁷⁺, 860.3 [M − 6BF₄⁻]⁶⁺, 1049.6 [M − 5BF₄⁻]⁵⁺, 1333.6 [M − 4BF₄⁻]⁴⁺, 1807.8 [M − 3BF₄⁻]³⁺), all support the structural assignment.

The UV/Vis spectra of 3 and 4 were measured (MeCN) and are shown in Figure 6.3. The Fe(II) hexamer showed the lowest energy ligand-centered π-π* transitions of the terpyridine moieties at 423 nm. While the metal-to-ligand charge-transfer (MLCT)
transitions derived from the promotion of an electron from the Fe(II) $d$-orbitals to unfilled ligand $\pi^*$ orbitals\(^{335}\) appeared at 582 nm. In the case of the Zn(II) hexamer 4, absorption bands at $\lambda_{\text{max}} = 285, 319, 330, 433$ nm originating from intra-ligand charge transfer ($^1\text{ILCT}$) were observed without MLCT peaks; the MLCT of the Zn(II) terpyridine complex can be excluded.$^{371}$ The Zn(II) hexamer shows a strong yellow emission at 575 nm when excited with UV light (400 nm). The fluorescence of the Zn(II) hexamer in
MeCN solution is shown in Figure 6.3(B); whereas, the Fe(II) hexamer does not show the emission peak.

![UV/Vis absorption and emission spectra](image)

Figure 6.3 UV/Vis absorption (solid line) and emission (dashed line) spectra for metallomacrocycles 3 [A], 4 [B].

Due to their light absorption properties, constructs 3 and 4 were also studied as sensitizer materials for solar cell devices. Photovoltaic experiments using dye-covered nanocrystalline TiO₂ electrodes (prepared by dipping the semiconductor substrate into a 0.2 mM MeCN solution of each hexamer) properly fitted in a solar cell device, were conducted using an 1.5 mW·cm⁻²) incident light source and an electrolyte containing 0.3M KI + 0.015M I₂ dissolved in a 4 to 1 ratio of propylene and ethylene carbonate.
Because the photocurrent action spectra (Figure 6.4) showed a significant photo-response, which is associated to excitation of the metallomacrocycles, discharge experiments (Figure 6.5) conducted with these devices allows the calculation of the values shown in Table 6.1. The fill-factor ($ff$), the short circuit photocurrent ($I_{sc}$), as well as the open circuit photopotential ($V_{oc}$) for the Zn(II) metallomacrocycle showed superior results over the Fe(II) metallomacrocycle. Further, the total photoconversion efficiency of the cell ($\eta$) using electromagnetic radiation spanning the visible region of the spectrum exhibited better values than in the case of the Zn(II) metallomacrocycle 4.

Figure 6.4 Photocurrent action spectra for metallomacrocycles 3 (solid line); 4 (dashed line).
Figure 6.5 I-V plot obtained from DSSC assembled with modified TiO<sub>2</sub> electrode with metallomacrocycles 3 (□) and 4 (○).

Table 6.1 Photovoltaic performances and surface coverage values of ITO/TiO<sub>2</sub>/metallohexacycle/KI-I<sub>2</sub> electrolyte/graphite dye-sensitized solar cells measured using a polychromatic 1.5 mW/cm<sup>2</sup> light source.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( J_{sc} \text{a} (\mu A/cm^2) )</th>
<th>( V_{oc} \text{b} (mV) )</th>
<th>( \text{ff} \text{c} (%) )</th>
<th>( \eta \text{d} (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>160</td>
<td>255</td>
<td>26.9</td>
<td>0.032</td>
</tr>
<tr>
<td>4</td>
<td>230</td>
<td>391</td>
<td>68.1</td>
<td>0.180</td>
</tr>
</tbody>
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\( \text{a} \) Short-circuit photocurrent; \( \text{b} \) Open-circuit photovoltage; \( \text{c} \) Fill-factor; \( \text{d} \) Photoconversion efficiency of the cell.
6.3 Conclusions

A new ditopic triphenylamine-based bis(terpyridine) ligand possessing a critical 119.69° angle relative to each coordination site has been crafted and demonstrated to form of a series of unique, self-assembled, hexagonal metallomacrocycles. The structures of the ligand and the corresponding metallomacrocycles were confirmed by means of $^1$H and $^{13}$C NMR, UV/vis spectroscopy, and mass spectroscopy. Preliminary results of photoelectrochemical performances for these materials show their potential for application in dye-sensitized solar cells.

6.4 Experimental Section

**General procedure.** Chemicals were purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets 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 Fisher Scientific. The melting points were determined on an Electrothermal 9100 heater. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl$_3$, except where noted. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap Mass Spectrometer (ESI-MS). UV/Vis absorption spectra were obtained on Hewlett-Packard UV/Vis spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer.
4,4’-Diformyltriphenylamine (1). Phosphorus oxychloride (37.3 mL, 400 mmol) was added dropwise to a stirred DMF (62 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and then at 25 °C for another 1 h. Triphenylamine (8.0 g, 32.6 mmol) dissolved in dichloroethane was added, then stirred at 80 °C for 48 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH 7 with aq. NaOH solution and extracted with CH₂Cl₂. The extract was washed with sat. brine solution, dried (MgSO₄), filtered, and concentrated in vacuo to give a residue that was purified by column chromatography (SiO₂) eluting with a hexane : EtOAc (3:1; v/v) mixture to afford (52 %) 1, as a light-yellow solid: m.p. 143 °C; ¹H NMR: δ 9.90 (s, CΗΟ, 2H), 7.78 (d, J = 8.4 Hz, 3,5-ArH, 3,5-Ar’H, 4H), 7.41 (t, J = 7.5 Hz, 3,5-Ar’’H, 2H), 7.27 (t, J = 7.2 Hz, 4-Ar’’H, 1H), 7.21-7.17 (m, 2,6-ArH, 2,6-Ar’H, 3,5-Ar’’H, 6H); ¹³C NMR: δ 122.98, 124.75, 126.47, 127.28, 130.36, 131.52, 145.72, 152.23, 190.71; ESI-MS: m/z 323.8 [M + Na]+ (Calcd. m/z 324.1).

4,4’-Bis(2,2’:6’,2”-terpyridinyl)triphenylamine (2). The dialdehyde 1 (4.8 g, 15.9 mmol) was dissolved in EtOH (100 mL) then 2-acetylpyridine (8.49 g, 70.1 mmol) was added, followed after 2 min by NaOH powder (2.8 g, 70.0 mmol). After the dark pink solution had been stirred at 25 °C for 24 h, the solvent was evaporated in vacuo to yield a dark brown solid intermediate. Ammonium acetate (26 g, excess) and glacial AcOH (100 mL) were added and the mixture was refluxed for 12 h. The dark brown solution was cooled, and neutralized with aqueous Na₂CO₃. The crude product was extracted with CH₂Cl₂ and column chromatographed (Al₂O₃) eluting with a hexane : EtOAc (1:2; v/v) mixture to afford (34 %) 2, as yellow solid: m.p. 290-291 °C (dec.); ¹H NMR: δ 8.73 (m, 6,6”-tpyH, 3’,5’-tpyH, 8H), 8.67 (d, J = 7.8 Hz, 3,3”-tpyH, 4H), 7.90-7.83 (m, 4,4”-tpyH,
2,6-ArH, 6H), 7.35 (dd, J = 4.8, 7.2 Hz, 5,5'-tpyH, 4H), 7.27-7.21 (m, 3,5-ArH, 2,5-Ar'H, 3,5-Ar'H, 7H), 7.14 (t, J = 4.8 Hz, 4-Ar'H, 1H); 13C NMR: δ 118.60, 121.55, 123.97, 124.12, 124.16, 125.47, 128.52, 129.77, 132.86, 137.04, 147.27, 148.52, 149.53, 149.89, 156.12, 156.58; ESI-MS: m/z 816.3 [M + Ag]^+ (Calcd. m/z 816.2).

[Fe₆(2)₆(PF₆)₁₂] (3). A MeOH solution of one equivalent of FeCl₂·4H₂O (54 mg, 270 μmol) was added to a stirred solution of monomer 2 (190 mg, 270 μmol) in MeOH (40 mL) at 25 °C. After 24 h, the resultant deep purple solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was purified by column chromatography (SiO₂) eluting with a H₂O : CH₃CN : satd. aq. KNO₃ (1:7:1; v/v/v) mixture to afford (> 50 %) 3, as a purple solid: m.p. > 400 °C (dec.); ¹H NMR (CD₃CN): δ 9.20 (s, 3',5'-tpyH, 4H), 8.64 (d, J = 7.8 Hz, 3,3''-tpyH, 4H), 8.37 (d, J = 8.4 Hz, 3,5-ArH, 4H), 7.93 (dd, J = 7.2, 7.2 Hz, 4,4''-tpyH, 4H), 7.58 (d, J = 6.9 Hz, 2,6-ArH, 2,6-Ar'H, 4H), 7.45-7.37 (m, 3,4,5-Ar'H, 3H), 7.24 (d, J = 5.4 Hz, 6,6''-tpyH, 4H), 7.11 (dd, J = 6.6, 6.0 Hz, 5,5''-tpyH, 4H); 13C NMR (CD₃CN): δ 119.19, 121.86, 124.91, 126.90, 127.95, 128.36, 130.19, 131.35, 131.61, 139.79, 147.60, 150.60, 150.68, 154.20, 159.26, 161.36; UV/vis (MeCN): λ_max (ε) 224 (3.06 × 10⁵), 283 (4.37 × 10⁵), 321 (3.43 × 10⁵), 423 (1.77 × 10⁵), 582 nm (2.88 × 10⁵); ESI-MS: m/z 428.9 [M – 11PF₆]¹¹⁺ (Calcd. m/z = 429.8), 494.2 [M – 6PF₆⁻ – 4PF₅]¹⁰⁺ (Calcd. m/z 494.8), 558.1 [M – 9PF₆]⁹⁺ (Calcd. m/z 557.5), 657.2 [M – 3PF₆⁻ – 5PF₅]⁸⁺ (Calcd. m/z 657.1).

[Zn₆(2)₆(BF₄)₁₂] (4). A stirred mixture of Zn(BF₄)₂·8H₂O (77 mg, 200 μmol) and 2 (143 mg, 200 μmol) in MeCN was refluxed for 48 h. After cooling to 25 °C, the resultant
solution was filtered through Celite, then Et₂O (150 mL) was added to precipitate the complex, which was filtrated to afford (> 75 %) 4, as an orange solid: m.p. > 400 °C (dec.); ¹H NMR (CD₃CN): δ 8.99 (s, 3’,5’-tpyH, 4H), 8.76 (d, J = 8.1 Hz, 3,3”-tpyH, 4H), 8.25 (d, J = 8.4 Hz, 3,5-ArH, 4H), 8.19 (dd, J = 8.1, 6.9 Hz, 4,4”-tpyH, 4H), 7.87 (d, J = 4.5 Hz, 6,6”-tpyH, 4H), 7.56 (dd, J = 8.4, 6.9 Hz, 3,5-Ar’H, 2H), 7.49 (d, J = 8.4 Hz, 2,6-ArH, 4H), 7.45-7.39 (m, 4-Ar’H, 5,5”-tpyH, 5H); ¹³C NMR (CD₃CN): δ 119.23, 121.59, 124.26, 124.65, 128.12, 128.55, 130.45, 130.89, 131.36, 142.31, 147.28, 149.07, 149.13, 150.89, 151.00, 156.36; UV/vis (MeCN): λ max (ε) 285 (5.97 × 10⁵), 319 (3.72 × 10⁵), 330 (3.62 × 10⁵), 433 nm (4.29 × 10⁵); ESI-MS: m/z 544.4 [M – 9BF₄]⁺ (Calcd. m/z = 544.4), 624.5 [M – 8BF₄]⁺ (Calcd. m/z 623.3), 725.1 [M – 7BF₄]⁺ (Calcd. m/z 724.8), 860.3 [M – 6BF₄]⁺ (Calcd. m/z 860.1), 1049.6 [M – 5BF₄]⁺ (Calcd. m/z 1049.4), 1333.6 [M – 4BF₄]⁺ (Calcd. m/z 1333.5), 1807.8 [M – 3BF₄]⁺ (Calcd. m/z 1806.9).

**Fabrication of photovoltaic cell device:** Nanocrystalline TiO₂ electrodes were prepared by applying a 4 V potential difference between a steel sheet and an ITO conducting glass substrate immersed in a 10 mL [0.5 g TiO₂ (P25, Degussar AG, Germany, a mixture of ca. 30 % rutile and 70 % anatase, BET surface area 55 m²/g) in 5% 2-propanol in water (v/v)] colloidal suspension for 40 s. Following previous reports in the literature, the electrodes were then taken out of the electrophoretic apparatus, sintered at 450 °C in air for 30 min, and characterized by general tools (AFM, XRD, Raman spectroscopy, cyclic voltammetry, and profilometry). From the characterization results, it was found that the electrode thus prepared consisted of nanoparticulated TiO₂ in the anatase phase, with roughness factors of 540, an average thickness of ~2 µm and a
flat band potential, $E_{FB}$, of $-0.2$ V vs. NHE. This value agrees well with previous reports,\textsuperscript{381,434} and is substantially more positive than that reported for nanocrystalline electrode prepared using the typical spin coating protocol ($-0.5$ V vs. NHE). This effect, which has been reported\textsuperscript{381} recently, is associated with an increase of Ti$^{+3}$ dopant surface sites that result from hydrogen adsorption during the electrophoretic deposition process. Hexamers, as the dye, were coated onto the TiO$_2$ layer by dipping the electrode for 12 h in a MeCN solution (ca. 0.2 mmol/L). The assembled devices for photovoltaic measurements consisted of a dye-coated TiO$_2$ electrode, Ti substrate covered with a film of colloidal graphite as a counter electrode, the electrolyte containing a deoxygenated 0.3 M of KI + 0.015 M of I$_2$ aqueous solution,\textsuperscript{382} and Teflon tape that was used to maintain a 0.5 mm gap between the two electrodes.
CHAPTER VII

SYNTHESIS OF 5-SUBSTITUTED 1,3-[BIS(2,2':6',2''-TERPYRIDIN-4'-YLETHYNYL)]BENZENE LIGANDS AND COORDINATION-DRIVEN SELF-ASSEMBLY

7.1 Introduction

The first synthesis of 2,2':6,2''-terpyridine was reported by Morgan and Burstall in the early 1930s, and subsequently shown to form stable complexes by chelating a broad variety of transition metal ions. The different approaches to the new design of terpyridine-metal complexes have stimulated numerous pursuits to the goal of creating novel, tailor-made materials for use as supramolecular photonic materials and nanosciences.

In this Chapter, the goal involved the design and preparation of terpyridine ligands that would form the basis of 'modular building block set' capable of forming stable, irreversible, and non-\( H \)-bonding 'higher order' architectures, as exemplified by the smaller hexameric metallomacrocycles. The novel logical extension based on the preparation of a \( bis(\text{terpyridine}) \) monomer possessing an acetylenic spacer and different aryl functionalities to probe the intermolecular assembly properties as well as the photophysical properties is shown. The use of the carbon-carbon triple bond as a linking...
unit between aromatic ring and terpyridine ligand allows access to relatively rigid and yet simple scaffolding to novel molecular and carbon-rich nanoarchitecture with unusual structure, electronic, and optical properties.464-467

7.2 Results and Discussion

To obtain the desired functionalized bis(terpyridine) building blocks possessing the 120° directed bonding motif, the creation of a family of 1,3-diethynyl-5-(substituted)benzenes was undertaken based on different 1,3-dibromobenzenes 1. Metal-halogen exchange with 1,3,5-tribromobenzene (2) using 1.0 equiv. of n-BuLi in Et2O gave the thermally unstable monolithio intermediate, which was transformed to either iodide 1a468 (92 %) or aldehyde469 1b (76 %) upon treatment with I2 or DMF, respectively. The coupling of 1a with 3,5-di-tert-butylphenylacetylene470 was realized by using the Pd(0)-catalyzed cross-coupling procedure to afford (94 %) 1c, which possessed (NMR) the appropriate signals for the tert-butyl moieties as well as the presence of two similar but yet different, alkyne peaks (13C NMR) at 93.46 and 85.45 ppm. The debromination of pentabromophenol (3) using AlCl3 in benzene gave (75 %) 3,5-dibromophenol471 (1d), which is a useful starting monomer, since it can be easily alkylated using a series of 4'-haloterpyridines in the presence of K2CO3 using DMF, as solvent. 4-Cyanoaniline (4a) and p-nitroaniline (4b) were each dibrominated to afford 5a472 and 5b, respectively, which were converted to the diazonium salt and subsequently reduced to afford 1e472 and 1f, respectively. Their structures were supported (1H NMR)
Scheme 7.1 Synthesis of different functionalized dibromobenzenes: (a) n-BuLi, I₂, -78 °C; (b) 3,5-di-tert-butylphenylacetylene, Pd(dba)₂, Ph₃P, CuI, Et₃N; (c) n-BuLi, DMF, -78 °C; (d) AlCl₃, C₆H₆, reflux; (e) AcOH, Br₂; (f) H₂SO₄, NaNO₂, reflux; (g) Behara’s amine, DCC, 1-HOBT, DMF; (h) L-phenylalanine methyl ester’ HCl, DCC, 1-HOBT, Et₃N, DMF.
by the appearance of a spike (ca. 7.92 - 8.01 ppm) for the new aryl 4-proton. Treatment of 3,5-dibromobenzoic acid 1g with the Behera’s amine\textsuperscript{174,473} under peptide coupling conditions\textsuperscript{474,475} gave (75 \%) the triester dendron 1h, which was characterized (\textsuperscript{13}C NMR) by the two new signals at 173.59 and 163.84 ppm, corresponding to the ester and amide carbonyl moieties, respectively. Lastly, amidation of acid 1g with L-phenylalanine methyl ester hydrochloride was similarly accomplished to give (74 \%) 1i; successful conversion was indicated (\textsuperscript{13}C NMR) by signals at 37.99 (\textsuperscript{49}C), 53.91 (CONHCH), and 171.97 (CONH) ppm.

The intermediate bis-alkyne 6 was prepared (Scheme 7.2) from dibromoarene 1 with HC≡CSiMe\textsubscript{3} under Pd-catalyzed cross-coupling conditions in a base solvent. After completion, deprotection of the trimethylsilyl group using KF in MeOH/THF afforded (> 65 \%) the corresponding terminal bis-alkynes 6, which was confirmed (\textsuperscript{1}H NMR) by the

\[ R = H (a); CH_3 (b); CH_2OH (c); = (d); CHO (e); OH (f); CN (g); \]
\[ NO_2 (h); \]
\[ (i); \]
\[ (j) \]

Scheme 7.2 Synthesis of bis(terpyridine) building blocks: (a) \textit{i}) TMS-acetylene, Pd(db\textsubscript{a})\textsubscript{2}, Ph\textsubscript{3}P, Cu\textsubscript{I}, Et\textsubscript{3}N; \textit{ii}) KF, THF/MeOH; (b) (Ph\textsubscript{3})\textsubscript{4}Pd, C\textsubscript{6}H\textsubscript{5}Me/Pr\textsubscript{2}NH.
presence of a singlet at 3.07 - 3.13 ppm for the unique terminal alkyne proton. Synthesis of key bis-terpyridine building blocks 7 was accomplished by treatment of 6 with 2.5 equivalents of 4'-trifluoromethanesulfonyl-2,2':6',2''-terpyridine (tpy-OTf) by a Pd-catalyzed cross-coupling procedure using [(Ph3P)4Pd] in base solvent to afford the corresponding desired air-stable, angular building blocks 7. Structural confirmation of these ligands utilized 1H NMR, 13C NMR, and mass spectrometry. Unfortunately, in case of 7g and 7h, it was difficult to obtain the 13C NMR due to material recrystallization while conducting the NMR study.

Previously, we had investigated the synthetic pathway to hexameric metallomacrocycles possessing a 17 Å hole; thus, in order to increase the inner-diameter of this cavity and to test the rigidity of the cavity, the inclusion of two alkynes within each monomer permits this cavity to be expanded to 24 Å. The bis(terpyridine) ligand 7b was treated with one equivalent of Zn(BF4)2·8H2O in MeCN at 80 °C for 12 h to give after chromatography and counterion exchange (BF4− to PF6−) the diamagnetic, hexameric Zn(II) metallomacrocycle 8, which revealed (1H NMR) a spike at 2.57 ppm [Ar(CH3)], indicating the presence of a single homogenous environment for all such groups; this is in contrast to the broadened or multiple signals realized for either linear or polymeric oligomers. There are the notable upfield and downfield shifts (1H NMR) for the doublet at 7.87 ppm (Δδ = – 0.87) for the 6,6''-tpyH and singlet at 8.92 ppm (Δδ = 0.32) for the 3',5'-tpyH, respectively, when compared to the absorptions the parent ligand 7b. Other diagnostic spectral attributes (13C NMR) included the two distinct peaks at 98.56 and 87.40 ppm attributed to the dissymmetric acetylenic carbons. That hexagonal structure was established (ESI-MS) by the signals of multiple-charged entities ranging
from +3 to +12 charge states which calculated as the loss of both PF$_5$ and PF$_{6}^{-}$ together.$^{334}$ Hexameric metallomacrocycle 8 with either BF$_4^{-}$ or PF$_{6}^{-}$ exhibited similar

\[ \text{Scheme 7.3 CPK representation (below) and synthesis of hexagonal metallomacrocycle (upper): (i) M}^{2+}, \text{ reflux; (ii) NH}_4\text{PF}_6/\text{MeOH.} \]
solubility in MeCN, acetone, DMF, and DMSO.

The self-assembly of 7b under similar conditions except using FeCl$_2$·4H$_2$O in MeOH gave (70 %) the diamagnetic, hexameric Fe(II) metallomacrocycle 9, which revealed ($^1$H NMR) a spike at 2.62 ppm (ArCH$_3$) indicative of a macrocyclic infrastructure. There are the notable upfield and downfield shifts ($^1$H NMR) for the doublet at 7.22 ppm ($\Delta\delta = -1.52$) for the 6,6''-tpyH and singlet at 9.13 ppm ($\Delta\delta = 0.53$) for the 3',5'-tpyH, when compared to ligand 7b. Other diagnostic spectral attributes ($^{13}$C NMR) included the two distinct peaks at 97.49 and 88.10 ppm attribution to the dissymmetric acetylenic carbons. This hexagonal structure was established (ESI-MS) by the observation of signals assigned to multiple-charged entities ranging from the +3 to +10 charge states, derived from the loss of both PF$_5$ and PF$_6^-$ together.$^{334}$

Third, the self-assembled Ru(II) counterpart, [Ru$_6$(7b)$_6$(PF$_6$)$_{12}$] 10 was prepared (70 %) in an analogous manner from 7b with one equiv. of [Ru(Cl)$_2$(DMSO)$_4$]$^{377,476}$ over 24 h at 50 ºC and after column chromatography followed by counterion exchange (Cl$^-$ to PF$_6^-$) the pure metallomacrocycle 10 was isolated (– 30 %). The diagnostic shifts for the doublets for 6,6''-tpyH (7.47 ppm, $\Delta\delta = -1.27$) and 3',5'-tpyH (8.95 ppm, $\Delta\delta = 0.35$) along with definitive ESI-MS data as the signals of multiple-charged entities ranging from the +5 to +10 charge states. The COSY and HETCOR spectra of both the starting ligand 7b and self-assembled macrocycles 9 - 10 verified the peak assignments, as well as coupling patterns. The solubility of both 9 and 10, isolated initially as the 12 Cl$^-$ salt, exhibited solubility in MeOH and hot H$_2$O; whereas conversion to the corresponding 12 PF$_6^-$ salt, facilitated solubility in MeCN, acetone, DMF, and DMSO.
To elucidate and support the composition of the hexameric metallomacrocycles, their UV/vis absorbencies were measured under MeCN solution. The absorption spectrum of ligand 7b shows three major $\pi-\pi^*$ transition at $\sim 230$, $\sim 255$, and $292$ nm [Figure 7.1 (A)]. From the absorption spectra of 8 and 10 in Figure 7.1 (C) and (D) respectively, each showed the lowest energy at $\sim 330$ nm and $\sim 310$ nm as shoulder, which was red-shifted by more than 18 nm comparing to that of ligand 7b. Such bathochromic shifts may come from the mixing of [Fe(II) or Ru(II)]’s orbitals into the acetylenic $\pi-\pi^*$ band, which looks like a Pt-acetylene complex system. While the metal-ligand charge-transfer (MLCT) transitions, which are derived from the promotion of an electron

![Figure 7.1 UV/vis absorption (solid line) and emission (dashed line) spectra for (A) ligand 7b; metallomacrocycles (B) 8; (C) 9; (D) 10.](image)
from the metal [Fe(II) or Ru(II)]-centered \(d\)-orbitals to an unfilled ligand-centered \(\pi^*\) orbitals,\(^{335}\) clearly appeared at 581 and 501 nm, respectively. In case of related Zn(II) pentameric metallomacrocycle,\(^{453}\) the absorption bands at \(\lambda_{\text{max}} = 236, 284,\) and 332 nm, which originate from intraligand charge transfer (\(^1\)ILCT) are observed without MLCT peaks, because the MLCT of Zn(II) to terpyridine can be excluded.\(^{371}\) A fluorescence study on the metallomacrocycle was performed using MeCN. Figure 7.2 (B) shows typical absorption and emission spectra of complex 9. The emission band centered on \(\lambda_{\text{max}}\) value 467 nm with shoulder peaks around 417 nm. While the photoluminescence of other metal-terpyridine complexes (\(i.e.\) Pt-complexes) originate from MLCT, zinc(II)-terpyridine complex synthesized in this paper shows the fluorescence came from intra-ligand charge transfer (ILCT).\(^{477}\)

The TGA data for metallomacrocycles and its ligand are shown in Figure 7.2 to afford insight into their thermal stability. In case of ligand 7b, small weight losses (\(ca. 5\%\)) occur below 150 °C because of associated water-of-hydration. All the metallomacrocycles (8 - 10) as well as ligand 7b have shown similar initial decomposition temperature in the 348 - 356 °C range under an inert atmosphere. Upon the formation of metallomacrocycles, they show enhanced weight loss after the initial decomposition temperature, which are probably due to presence of metal ions. From these results, these metallomacrocycle shows good thermal stability.
7.3 Conclusions

The synthetic route described here has been demonstrated for construction of the utilitarian derivatives for self-assembly to hexameric metallomacrocycles using the transition metals. The structures of these ligands were characterized by means of $^1$H and $^{13}$C NMR, as well as mass spectrometry. The conversion of these extended $bis$-ligands to a stable hexameric structure using metal(II)-ions [Fe(II), Ru(II), and Zn(II)], as connecting center, successfully and to be especially shown the fluorescence property for
the Zn(II)-hexameric metallomacrocycles have been demonstrated. This result imply that the constructed ligands should provide a tool for self-assembly and a potential application in electro- and photo-luminescence devices.

7.4 Experimental Section

**General procedure.** Chemicals were commercially purchased 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. Column chromatography was conducted using basic Al₂O₃, Brockman Activity I (60 - 325 mesh) or SiO₂ (60 - 200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl₃, except where noted. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap Mass Spectrometer (ESI-MS). UV/Vis absorption spectra were measured in MeCN at 25 °C with a Hewlett-Packard 8452A diode array spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer. Thermogravimetric analysis (TGA) was conducted with a DuPont model 2950 at a heating rate of 10 °C/min under a nitrogen atmosphere.

**1-Iodo-3,5-dibromobenzene (1a).** To a solution of 1,3,5-tribromobenzene (2; 13.4 g, 42.7 mmol) in Et₂O (300 mL) at -78 °C, was added n-BuLi (27.0 mL of a 1.6 M solution in hexane, 43.2 mmol) within 30 min. After an additional hour, solid I₂ (10.96 g, 43.2 mmol) was added all at once; the mixture was warmed to 25 °C, then H₂O (100 mL)
was added, followed by usual extractive workup with CH₂Cl₂. The extract was concentrated in vacuo to give a residue, which was recrystallized (Et₂O) to afford (92%) 1a, as brown crystal: m.p. 119 - 121 °C (lit. 123 °C); ¹H NMR: δ 7.62 (t, J = 1.7 Hz, 4-ArH, 1H), 7.77 (d, J = 1.7 Hz, 2,6-ArH, 2H); ¹³C NMR: δ 94.43, 123.34, 133.60, 138.46.

3,5-Di-tert-butylphenylacetylene. The stirred mixture of 3,5-di-tert-butylphenol (11 g, 53.32 mmol) and pyridine (30 mL) was degassed and back-filled (3×) with argon, then cooled to 0 °C. Trifluoromethanesulfonic anhydride (16.5 g, 58.44 mmol) was added slowly, then the mixture was warmed to 25 °C. After 2 h, water was added, the product was extracted with hexane to give an organic layer, which was washed with 10% aq. HCl, followed by an aq. satd. NaCl solution, dried (MgSO₄), filtered, and concentrated in vacuo to give (94%) 3,5-di-tert-butylphenol trifluoromethanesulfonate, as a colorless oil.

To a Schlenk flask, this triflate (17 g, 50.12 mmol), 2-methyl-3-butyn-2-ol (12.6 g, 150 mmol), [(dba)₂Pd] (1.7 g, 3.0 mmol), Ph₃P (2.62 g, 10.0 mmol), CuI (1.90 g, 10.0 mmol), LiCl (6.37 g, 150 mmol), and Et₃N (150 mL) were added. The flask was degassed and back-filled (3×) with nitrogen, sealed, and stirred at 80 °C for 4 days. The reaction mixture was then filtered and the solvent was removed in vacuo to give the crude product, which was recrystallized (hexane) to give (81%) 1-(3-hydroxy-3-methyl-1-butyl)-3,5-di-tert-butylbenzene, as a white solid (11.1 g). This crystalline product was placed in a flask equipped with a Dean-Stark apparatus, then toluene (200 mL) containing KOH (1.8 g) and MeOH (50 mL) were added. The mixture was heated to 110 °C and maintained at that temperature for 4 h. The reaction mixture was cooled to 25 °C, washed with water, dried (MgSO₄), filtered and concentrated in vacuo to give a residue, which
was passed through a short silica column eluting with hexane to give (86%) 3,5-di-tert-butylphenylacetylene, as a light-yellow solid: m.p. 84 - 85 °C (lit.\(^{470}\) m.p. 86-87 °C); \(^1\)H NMR: \(\delta 7.45 (t, J = 1.8 \text{ Hz}, 4-\text{ArH}, 1\text{H}), 7.38 (d, J = 1.8 \text{ Hz}, 2,6-\text{ArH}, 2\text{H}), 3.05 (s, C≡CH, 1\text{H}), 1.34 [s, C(CH\(_3\))\(_3\), 18\text{H}]; \(^{13}\)C NMR: \(\delta 31.51, 35.00, 76.00, 85.06, 121.25, 123.46, 126.59, 151.08.

3,5-Dibromobenzaldehyde (1b). A stirred solution of 1,3,5-tribromobenzene (2; 10 g, 31.76 mmol) dissolved in Et\(_2\)O (150 mL) was cooled to -78 °C in a dry ice/acetone bath under N\(_2\) atmosphere. \(n\)-BuLi (12.96 mL, 2.5 M solution in hexane, 32.40 mmol) was added over a 10 min period by syringe; the exchange reaction was allowed to proceed for an additional 30 min. Then DMF (4.92 mL, 63.52 mmol) was slowly added, then the reaction mixture was warmed to 25 °C for 1 h. The solvent was removed \textit{in vacuo} to give (76%) \(1\)b, which was recrystallized in Et\(_2\)O and hexane: m.p. 89 - 90 °C (lit.\(^{469}\) m. p. 86 - 90 °C); \(^1\)H NMR: \(\delta 9.91 (s, \text{CHO}, 1\text{H}), 7.95 (d, J = 1.8 \text{ Hz}, 2,6-\text{ArH}, 2\text{H}), 7.93 (t, J = 1.6 \text{ Hz}, 4-\text{ArH}, 1\text{H}); \(^{13}\)C NMR: \(\delta 124.16, 131.42, 139.11, 139.80, 189.38.

5-(3',5'-Di-tert-butylphenylethynyl)-1,3-dibromobenzene (1c). A Schlenk flask was charged with 3,5-di-tert-butylphenylacetylene (880 mg, 4.11 mmol), 1-iodo-3,5-dibromobenzene (1a; 1.78 g, 4.93 mmol), [(dba)\(_2\)Pd] (170 mg, 300 \(\mu\)mol), Ph\(_3\)P (128 mg, 490 \(\mu\)mol), CuI (93 mg, 490 \(\mu\)mol), and Et\(_3\)N (20 mL). The flask was degassed and back-filled with argon several times, sealed, and stirred at 80 °C for 24 h. After 3 h, the mixture was filtered and the solvent was evaporated \textit{in vacuo} to give a solid, which was flash chromatographed eluting with hexane to give (94%) \(1\)c, as white solid: m.p. 95 - 96 °C; \(^1\)H NMR: \(\delta 7.65-7.63 (m, 2,4,6-\text{ArH}, 3\text{H}), 7.46 (t, J = 1.8 \text{ Hz}, 4-\text{Ar'H}, 1\text{H}), 7.38 (d, J = 172
3.5-Dibromophenol (1d). A mixture of pentabromophenol (3; 10 g, 20.47 mmol) and AlCl₃ (26 g, 190 mmol) in benzene (100 mL) was refluxed under N₂ atmosphere for 12 h. The reaction was cooled to 25 °C and then slowly poured into aq. HCl diluted iced water. The mixture was extracted (3×) with EtOAc. The combined organic phase was dried (MgSO₄) and concentrated in vacuo to give the crude product, which was flash column chromatographed on SiO₂ eluting with hexane then CH₂Cl₂ to give (75%) the desired crystalline dibromophenol 1d: m. p. 78 - 79 ºC (lit.⁴⁷¹ m. p. 82 ºC); ¹H NMR: δ 7.26 (t, J = 1.6 Hz, 4-ArH, 1H), 6.97 (d, J = 1.5 Hz, 2,6-ArH, 2H), 5.03 (br, ArO, 1H); ¹³C NMR: δ 118.10, 123.39, 126.97, 156.95.

3,5-Dibromobenzonitrile (1e). 4-Cyanoaniline (4a; 3 g, 25.39 mmol) was dissolved in glacial AcOH (20 mL) and cooled to 0 °C, then Br₂ (2.62 mL, 50.79 mmol) was added followed by slow warming to 25 ºC. Precipitation of the crude product occurred upon the addition of H₂O (300 mL). After filtration, the solid was washed with water and air-dried; it was used without any further purification.

4-Amino-3,5-dibromobenzonitrile (5a; ca. 25.39 mmol) was dissolved in hot EtOH (30 mL) and H₂SO₄ (95%; 2.61 mL, 50.78 mmol) was added. After heating for 10 min, sodium nitrite (2.63 g, 38.08 mmol) was added. The stirred solution was refluxed for 30 min or until gas evolution stopped. The suspension was then cooled to 0 ºC; after filtration, the solid was collected and rinsed with a minimum amount of EtOH and then H₂O. The crude product was flash column chromatographed on SiO₂ eluting with a CH₂Cl₂ : Et₂O (1:1) solvent mixture to give (91%) the desired 1e: m. p. 97 - 98 ºC (lit.⁴⁷²
m. p. 100 °C); \(^1\)H NMR: \(\delta\) 7.92 (t, \(J = 1.6\) Hz, 4-Ar\(H\), 1H), 7.75 (d, \(J = 1.8\) Hz, 2,6-Ar\(H\); 2H); \(^{13}\)C NMR: \(\delta\) 115.68, 116.12, 123.81, 133.66, 139.05.

3,5-Dibromonitrobenzene (1f). Using the above deamination procedure, 4-nitroaniline (4b) was converted to 3,5-dibromonitrobenzene (5b), which was flash column chromatographed on SiO\(_2\) eluting with Et\(_2\)O followed by recrystallization (EtOH): m. p. 103 - 104 °C (lit.\(^472\) m. p. 104 °C); 52 %; \(^1\)H NMR: \(\delta\) 8.33 (d, \(J = 1.5\) Hz, 2,6-Ar\(H\), 2H), 8.01 (t, \(J = 1.7\) Hz, 4-Ar\(H\); 1H); \(^{13}\)C NMR: \(\delta\) 123.73, 125.84, 128.25, 140.31.

Di-\textit{tert}-butyl 4-[2-(\textit{tert}-Butoxycarbonyl)ethyl]-4-(3,5-dibromobenzamido)-heptanedioate (1h). To the stirred DMF (40 mL) solution of 3,5-dibromobenzoic acid (1g; 1.0 g, 3.57 mmol), DCC (740 mg, 3.57 mmol), and 1-HOBT (480 mg, 3.57 mmol), Behara’s amine (1.48 g, 3.57 mmol) was added; the mixture was stirred at 25 °C for 24 h. After filtration, the solvent was evaporated \textit{in vacuo} to give a residue, which was column chromatographed on SiO\(_2\) eluting with a mixture of CH\(_2\)Cl\(_2\) : EtOAc (80:20; v/v) affording (75%) 1h, as white solid: m. p. 135 - 136 °C; \(^1\)H NMR: \(\delta\) 7.94 (d, \(J = 1.5\) Hz, 2,6-Ar\(H\), 2H), 7.76 (t, \(J = 1.8\) Hz, 4-Ar\(H\), 1H), 7.66 (s, NH\(CO\), 1H), 2.32 (t, \(J = 7.5\) Hz, CH\(_2\)CH\(_2\)CO, 6H), 2.12 (t, \(J = 7.5\) Hz, CH\(_2\)CH\(_2\)CO, 6H), 1.45 [s, C(CH\(_3\))\(_3\), 27H]; \(^{13}\)C NMR: \(\delta\) 28.30, 30.18, 30.49, 58.29, 81.30, 123.27, 129.31, 136.70, 138.49, 163.84, 173.59.

\(\text{\textit{(L)}}\)-Methyl 2-(3',5'-Dibromobenzamido)-3-phenylpropanoate (1i). A mixture of 3,5-dibromobenzoic acid (1g; 2.37 g, 8.47 mmol), 1-HOBT (1.26 g, 9.31 mmol), and DCC (1.92 g, 9.31 mmol) in DMF (50 mL) was stirred at 0 °C for 1 h. A slurry of \(\text{\textit{L}}\)-phenylalanine methyl ester hydrochloride (2.01 g, 9.31 mmol) and Et\(_3\)N (2.6 mL, 18.63
mmol) in DMF (20 mL) was added then stirred at 25 °C for an additional 24 h. After filtration, H₂O was added, and then extraction with Et₂O, then the extract was washed successively with satd. aq. NaHCO₃ and brine. The solution was dried (MgSO₄) and the residue was column chromatographed eluting with a mixture of CH₂Cl₂ : EtOAc (90:10; v/v) to give (74%) 1i, as white solid: m. p. 110 - 112 °C; ¹H NMR: δ 7.80 (s, 4-ArH, 1H), 7.76 (s, 2,6-ArH, 2H), 7.35-7.26 (m, Ar'H, 3H), 7.13 (d, J = 7.8 Hz, 2,6-Ar'H, 2H), 6.53 (d, J = 7.5 Hz, NH, 1H), 5.05 (q, J = 7.7Hz, NHCH, 1H), 3.80 (s, OCH₃, 3H), 3.25 (m, Ar'CH₂, 2H); ¹³C NMR: δ 37.99, 52.82, 53.91, 123.54, 127.62, 128.95, 129.20, 129.48, 135.72, 137.36, 137.40, 164.28, 171.97.

**General Procedure for Diethynyl Arenes (6).** A Schlenk flask was charged with Me₃SiC≡CH (2.4 equiv.), aryl dibromide (1 equiv.), [(dba)₂Pd] (0.05 equiv.), Ph₃P (0.2 equiv.), CuI (0.2 equiv.), and dry Et₃N. The flask was then evacuated and back-filled with argon several times, sealed, and stirred at 80 °C. After 48 h, the solvent was removed *in vacuo* to give the crude product, which was flash column chromatographed on SiO₂ to afford the purified protected dialkyne to which KF (3 equiv.) dissolved in MeOH/THF was added. The mixture was stirred at 25 °C for 12 h, then filtrated and concentrated *in vacuo* to give the resultant residue, which was column chromatographed on SiO₂ eluting with hexane giving the desired free dialkyne.

6a (from *m*-dibromobenzene): a colorless oil (67 %); ¹H NMR: δ 7.66 (s, 2-ArH, 1H), 7.50 (d, J = 7.8 Hz, 4,6-ArH, 2H), 7.31 (t, J = 7.5 Hz, 5-ArH, 1H), 3.13 (s, C≡CH, 2H); ¹³C NMR: δ 78.17, 82.79, 122.68, 128.62, 132.56, 135.82.
6b (from 3,5-dibromotoluene): a colorless oil (71 %): $^1$H NMR: $\delta$ 7.44 (s, 4-ArH, 1H), 7.23 (s, 2,6-ArH, 2H), 3.07 (s, C≡CH, 2H), 2.32 (s, CH$_3$, 3H); $^{13}$C NMR: $\delta$ 21.14, 77.71, 82.98, 122.46, 132.98, 133.32, 138.50.

6c (from 3,5-dibromobenzyl alcohol): a light brown solid (65 %): m. p. 77 - 78 °C; $^1$H NMR: $\delta$ 7.54 (s, 4-ArH, 1H), 7.48 (s, 2,6-ArH, 2H), 4.67 (s, CH$_2$OH, 2H), 3.55 (br, CH$_2$OH, 1H), 3.10 (s, C≡CH, 2H); $^{13}$C NMR: $\delta$ 64.44, 78.22, 82.66, 122.92, 130.88, 134.91, 141.64.

6d (from 1b): a white solid (78 %): m. p. 112 - 114 °C; $^1$H NMR: $\delta$ 7.65 (d, $J$ = 1.5 Hz, 2,6-ArH, 2H), 7.55 (s, 4-ArH, 1H), 7.44 (t, $J$ = 1.5 Hz, 4-Ar'H, 1H), 7.38 (d, $J$ = 1.8 Hz, 2,6-Ar'H, 2H), 3.11 (s, C≡CH, 2H), 1.35 [s, C(CH$_3$)$_3$, 18H]; $^{13}$C NMR: $\delta$ 31.53, 35.06, 78.60, 82.11, 86.38, 92.25, 121.77, 123.05, 123.47, 124.60, 126.17, 135.02, 135.37, 151.20.

6e (from 1c): an off-white solid (78 %): m. p. 111 - 113 °C; $^1$H NMR: $\delta$ 9.98 (s, CHO, 1H), 7.95 (d, $J$ = 1.5 Hz, 2,6-ArH, 2H), 7.83 (6, $J$ = 1.5 Hz, 4-ArH, 1H), 3.20 (s, C≡CH, 2H); $^{13}$C NMR: $\delta$ 79.81, 81.41, 123.99, 133.23, 136.79, 140.78, 190.60.

6f (from 1d): an off-white solid (71 %): m. p. 121 - 122 °C; $^1$H NMR: $\delta$ 7.22 (t, $J$ = 1.5 Hz, 4-ArH, 1H), 6.96 (d, $J$ = 1.2 Hz, 2,6-ArH, 2H), 4.58 (br, ArOH, 1H), 3.08 (s, C≡CH, 2H); $^{13}$C NMR: $\delta$ 78.20, 82.46, 119.81, 123.85, 128.79, 155.28.

6g (from 1e): an off-white solid (66 %): m. p. 144 - 146 °C; $^1$H NMR: $\delta$ 7.79 (t, $J$ = 1.5 Hz, 4-ArH, 1H), 7.72 (d, $J$ = 1.5 Hz, 2,6-ArH, 2H), 3.23 (s, C≡CH, 2H); $^{13}$C NMR: $\delta$ 80.49, 80.80, 113.63, 124.42, 135.35, 139.51.
6h (from 1f): an off-white solid (69 %) m. p. 110 - 111 °C; \(^1\)H NMR: \(\delta 8.29\ (d, J = 1.2\ Hz, 2,6-ArH, 2H), 7.33\ (t, J = 1.2\ Hz, 4-ArH, 1H), 3.26\ (s, C≡CH, 2H); ^{13}\)C NMR: \(\delta 80.50, 80.93, 127.10, 128.62, 141.01.\)

6i (from 1h): an off-white solid (69 %): m. p. 123 - 124 °C; \(^1\)H NMR: \(\delta 7.91\ (d, J = 1.5\ Hz, 2,6-ArH, 2H), 7.67\ (t, J = 1.5\ Hz, 4-ArH, 1H), 7.38\ (s, NHCO, 1H), 3.11\ (s, C≡CH, 2H), 2.31\ (t, J = 7.5\ Hz, CH₂CH₂CO, 6H), 2.12\ (t, J = 7.5\ Hz, CH₂CH₂CO, 6H), 1.43\ [s, C(CH₃)₃, 27H]; ^{13}\)C NMR: \(\delta 28.27, 30.11, 30.40, 58.17, 78.83, 81.15, 82.04, 123.06, 131.09, 135.86, 137.86, 164.99, 173.45.\)

6j (from 1i): a light yellow solid (67%): m. p. 119 - 121 °C; \(^1\)H NMR: \(\delta 7.79\ (s, 2,6-ArH, 2H), 7.72\ (s, 4-ArH, 1H), 7.33-7.29\ (m, 3,4,5-Ar'H, 3H), 7.12\ (d, J= 3.6\ Hz, 2,6-Ar'H, 2H), 6.55\ (d, J=7.5\ Hz, NH, 1H), 5.08\ (q, J=7.6\ Hz, NHCH, 1H), 3.79\ (s, OCH₃, 3H), 3.26\ (m, Ar'CH₂, 2H), 3.15\ (s, C≡CH, 2H); ^{13}\)C NMR: \(\delta 38.07, 52.76, 53.88, 79.32, 81.80, 91.05, 123.44, 127.56, 128.61, 129.19, 129.51, 130.72, 130.98, 138.50, 172.02.\)

**General Procedure for Coupling Terminal Acetylene and TfOtpy (7).** A Schlenk flask was charged with *bis*-alkyne (1 equiv.), tpy-OTf (2.4 equiv.), [(PPh₃)₄Pd] (0.05 equiv.), dried (iso-Pr)₂NH, and toluene. The flask was evacuated and back-filled with argon several times, sealed with a cap, and stirred at 80 °C for 48 h. The solvent was removed in vacuo to give the crude product, which was flash column chromatographed on Al₂O₃ eluting with CHCl₃ to afford the desired *bis*-terpyridine ligand 7.

7a (from 6a) as an off-white solid (34 %): m. p. 287 - 289 °C; \(^1\)H NMR: \(\delta 8.75\ (d, J = 6.0\ Hz, 6,6''-tpyH, 4H), 8.65\ (d, J = 8.1\ Hz, 3,3''-tpyH, 4H), 8.62\ (s, 3',5'-tpyH, 4H), 7.90\ (dd, J = 6.0, 9.0\ Hz, 4,4''-tpyH, 4H), 7.80\ (s, 2-ArH, 1H), 7.61\ (d, J = 7.4\ Hz, 4,6-
ArH, 2H), 7.45 (t, J = 7.5 Hz, 5-ArH, 1H), 7.38 (dd, J = 5.7, 6.3 Hz, 5,5''-tpyH, 4H); $^{13}$C NMR: δ 88.45, 92.79, 121.46, 123.15, 123.26, 124.25, 128.99, 132.62, 133.31, 135.29, 137.14, 149.44, 155.82, 155.87; ESI-MS: m/z 595.4 [M + Li$^+$] (Calcd. m/z = 595.2).

7b (from 6b) as an off-white solid (39 %): m. p. 254 - 255 °C; $^1$H NMR: δ 8.74 (d, J = 4.2 Hz, 6,6''-tpyH, 4H), 8.63 (d, J = 7.8 Hz, 3,3''-tpyH, 4H), 8.60 (s, 3',5'-tpyH, 4H), 7.88 (dd, J = 7.5, 7.3 Hz, 4,4''-tpyH, 4H), 7.60 (s, 4-ArH, 1H), 7.42 (s, 2,6-ArH, 2H), 7.38 (dd, J = 5.1, 6.9 Hz, 5,5''-tpyH, 4H), 2.62 (s, CH$_3$, 3H); $^{13}$C NMR: δ 21.31, 88.08, 93.07, 121.44, 123.02, 123.14, 124.21, 132.45, 133.41, 137.12, 138.83, 149.38, 155.73, 155.82; ESI-MS: m/z 625.3 [M + Na$^+$] (Calcd. m/z = 625.2).

7c (from 6c) as an off-white solid (33 %): m. p. 280 - 281 °C; $^1$H NMR (DMSO-$d_6$): δ 8.77 (d, J = 3.9 Hz, 6,6''-tpyH, 4H), 8.66 (d, J = 8.1 Hz, 3,3''-tpyH, 4H), 8.56 (s, 3',5'-tpyH, 4H), 8.05 (dd, J = 7.8, 7.8 Hz, 4,4''-tpyH, 4H), 7.97 (s, 4-ArH, 1H), 7.77 (s, 2,6-ArH, 2H), 7.56 (dd, J = 4.8, 6.6 Hz, 5,5''-tpyH, 4H), 5.49 (br, CH$_2$OH, 1H) 4.61 (s, CH$_2$OH, 2H); $^{13}$C NMR (DMSO-$d_6$): δ 61.86, 87.58, 92.81, 120.91, 121.81, 121.97, 124.84, 130.79, 132.21, 133.42, 137.59, 144.37, 149.45, 154.23, 155.47; ESI-MS: m/z 619.4 [M + H$^+$] (Calcd. m/z = 619.2).

7d (from 6d) as an off-white solid (27 %): m. p. 254 - 255 °C; $^1$H NMR: δ 8.77 (d, J = 4.2 Hz, 6,6''-tpyH, 4H), 8.66 (d, J = 8.1 Hz, 3,3''-tpyH, 4H), 8.63 (s, 3',5'-tpyH, 4H), 7.91 (dd, J = 7.5, 7.8 Hz, 4,4''-tpyH, 4H), 7.77 (s, 2,6-ArH, 2H), 7.71 (t, J = 1.5 Hz, 4-ArH, 1H), 7.46 (s, 2,4,6-ArH, 3H), 7.38 (dd, J = 4.8, 4.8 Hz, 5,5''-tpyH, 4H), 1.38 [s, C(CH$_3$)$_3$, 18H]; $^{13}$C NMR: δ 31.57, 35.10, 86.48, 88.78, 92.23, 92.59, 121.64, 121.85, 123.35, 123.48, 123.53, 124.37, 124.97, 126.30, 133.19, 134.40, 135.39, 137.48, 149.22, 151.21, 155.50, 155.58; ESI-MS: m/z 823.6 [M + Na$^+$] (Calcd. m/z = 823.9).
7e (from 6e) as an off-white solid (31%); m. p. 250 - 251 °C; \(^1\)H NMR: \(\delta 10.01\) (s, CHO, 1H), 8.73 (d, \(J = 4.5\) Hz, 6,6''-tpyH, 4H), 8.62 (d, \(J = 8.1\) Hz, 3,3''-tpyH, 4H), 8.60 (s, 3',5'-tpyH, 4H), 8.01 (s, 2,6-ArH, 2H), 7.94 (s, 4-ArH, 1H), 7.87 (dd, \(J = 7.5, 7.8\) Hz, 4,4''-tpyH, 4H), 7.36 (dd, \(J = 5.1, 6.0\) Hz, 5,5''-tpyH, 4H); \(^1^3\)C NMR: \(\delta 89.87, 91.13, 121.42, 123.12, 124.23, 124.31, 124.46, 132.02, 132.63, 133.06, 137.12, 149.46, 155.70, 155.90, 190.56; ESI-MS: \(m/z\) 639.5 [M + Na\(^+\)] (Calcd. \(m/z = 639.7\)).

7f (from 6f) as an off-white solid (31%): m. p. 271 - 273 °C; \(^1\)H NMR (DMSO-\(d_6\)): \(\delta 10.29\) (s, ArOCH, 1H), 8.76 (d, \(J = 3.9\) Hz, 6,6''-tpyH, 4H), 8.04 (d, \(J = 7.8\) Hz, 3,3''-tpyH, 4H), 7.36 (dd, \(J = 5.1, 6.0\) Hz, 5,5''-tpyH, 4H); \(^1^3\)C NMR (DMSO-\(d_6\)): \(\delta 87.23, 92.77, 119.81, 120.89, 121.97, 122.95, 124.82, 126.46, 132.19, 137.56, 149.43, 154.22, 155.42, 157.69; ESI-MS: \(m/z\) 627.3 [M + Na\(^+\)] (Calcd. \(m/z = 627.2\)).

7g (from 6g) as an off-white solid (38%): m. p. 276 - 278 °C; \(^1\)H NMR: \(\delta 8.76\) (d, \(J = 3.9\) Hz, 6,6''-tpyH, 4H), 8.65 (d, \(J = 7.8\) Hz, 3,3''-tpyH, 4H), 8.63 (s, 3',5'-tpyH, 4H), 7.96 (s, 4-ArH, 1H), 7.91 (dd, \(J = 7.8, 7.8\) Hz, 4,4''-tpyH, 4H), 7.83 (s, 2,6-ArH, 2H), 7.40 (dd, \(J = 4.8, 4.8\) Hz, 5,5''-tpyH, 4H); ESI-MS: \(m/z\) 636.2 [M + Na\(^+\)] (Calcd. \(m/z = 636.2\)).

7h (from 6h) as an off-white solid (34%): m. p. 269 - 271 °C; \(^1\)H NMR: \(\delta 8.76\) (d, \(J = 3.9\) Hz, 6,6''-tpyH, 4H), 8.65 (d, \(J = 7.8\) Hz, 3,3''-tpyH, 4H), 8.65 (s, 3',5'-tpyH, 4H), 8.42 (s, 2,6-ArH, 2H), 8.05 (s, 4-ArH, 1H), 7.90 (dd, \(J = 7.8, 7.8\) Hz, 4,4''-tpyH, 4H), 7.39 (dd, \(J = 4.8, 4.8\) Hz, 5,5''-tpyH, 4H); ESI-MS: \(m/z\) 653.3 [M + Na\(^+\)] (Calcd. \(m/z = 653.2\)).
7i (from 6i) as a yellow solid (36 %): m. p. 113 - 114 °C; $^1$H NMR: $\delta$ 8.74 (d, $J = 3.9$ Hz, 6,6'-tpyH, 4H), 8.64 (d, $J = 7.2$ Hz, 3,3''-tpyH, 4H), 8.63 (s, 3',5'-tpyH, 4H), 8.11 (s, 2,6-ArH, 2H), 7.92-7.87 (m, 4-ArH, 4,4''-tpyH, 5H), 7.65 (s, CONH, 1H), 7.38 (dd, $J = 5.4$, 6.6 Hz, 5,5''-tpyH, 4H), 2.38 (t, CH$_2$CH$_2$CO, $J = 6.9$ Hz, 6H), 2.19 (t, CH$_2$CH$_2$CO, $J = 6.9$ Hz, 6H), 1.48 [s, C(CH$_3$)$_3$, 27H]; $^{13}$C NMR: $\delta$ 28.33, 30.25, 30.55, 58.24, 81.26, 88,94, 92.00, 121.39, 123.18, 123.63, 124.25, 131.12, 133.00, 136.23, 137.08, 137.34, 149.45, 155.82, 155.90, 164.94, 173.62; ESI-MS: $m/z$ 1030.7 [M + H$^+$] (Calcd. $m/z = 1030.5$).

7j (from 6j) as an off-white solid (31 %): m. p. 250 - 252 °C; $^1$H NMR: $\delta$ 8.75 (d, $J = 3.9$ Hz, 6,6'-tpyH, 4H), 8.64 (d, $J = 7.5$ Hz, 3,3''-tpyH, 4H), 8.63 (s, 3',5'-tpyH, 4H), 8.03 (s, 4-ArH, 1H), 7.92-7.87 (m, 2,6-ArH, 4,4''-tpyH, 6H), 7.40-7.33 (m, 3,4,5-Ar'H, 5,5''-tpyH, 7H), 7.20 (d, $J=6.6$ Hz, 2,6-Ar'H, 2H), 6.64 (d, $J=7.5$ Hz, NH, 1H), 5.15 (q, $J=7.5$ Hz, NHCH, 1H), 3.82 (s, OCH$_3$, 3H), 3.33 (m, Ar'CH$_2$, 2H); $^{13}$C NMR: $\delta$ 38.20, 52.82, 54.02, 89.49, 91.64, 121.47, 123.21, 124.02, 124.32, 127.69, 129.06, 129.60, 130.97, 132.86, 135.20, 135.92, 137.15, 137.83, 149.53, 155.85, 155.99, 165.33, 172.03; ESI-MS: $m/z$ 800.3 [M+Li]$^+$ (Calcd. $m/z = 800.3$).

$[\text{Zn}_6(7b)_6(12\text{PF}_6)_{12}]$ (8). To a solution of 7b (171 mg, 280 µmol) in MeCN (20 mL) was added Zn(BF$_4$)$_2$ · 8H$_2$O (109 mg, 280 µmol) then mixture was refluxed for 12 h. After cooling, the resultant solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added. The resultant precipitate was column chromatographed on SiO$_2$ eluting with a sat. aq. KNO$_3$ : H$_2$O : CH$_3$CN (1:1:7) solution to afford (>35 %) 8, as an off-white solid: m. p. 351 °C (dec); $^1$H NMR (CD$_3$CN): $\delta$ 8.92 (s, 3',5'-tpyH, 4H), 8.61 (d, $J = 7.8$ Hz, 3,3''-tpyH, 4H), 8.20 (dd, $J =$
[Fe₆(7b)₆(PF₆)₁₂] (9). A MeOH solution of one equiv. of FeCl₂·4H₂O (59.7 mg, 0.30 µmol) was added to a stirred solution of 7b (187 mg, 0.30 µmol) in MeOH (150 mL). After 24 h at 25 °C, the resultant deep purple solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on SiO₂ eluting with a H₂O : CH₃CN : satd. aq. KNO₃ (1:10:1; v/v/v) mixture to afford (>70 %) 9, as a purple solid: m. p. 348 °C (dec.); ¹H NMR (CD₃CN): δ 9.13 (s, 3',5'-tpyH, 4H), 8.57 (d, J = 7.5 Hz, 3,3''-tpyH, 4H), 8.13 (s, 4-ArH, 1H), 7.96 (dd, J = 6.9, 7.5 Hz, 4,4''-tpyH, 4H), 7.87 (d, J = 6.0 Hz, 6,6''-tpyH, 4H), 7.15 (dd, J = 6.9, 6.0 Hz, 5,5''-tpyH, 4H), 2.62 (s, ArCH₃, 3H); ¹³C NMR (CD₃CN): δ 21.37, 88.10, 97.49, 123.33, 125.19, 126.33, 128.75, 133.27, 133.77, 135.49, 140.12, 141.49, 154.32, 158.43, 161.35; UV/Vis (MeCN) λ max (ε) = 225 (2.07 x 10⁵), 285 (2.35 x 10⁵), 336 (2.77 x 10⁵), 581 nm (1.29 x 10⁵ dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 429.7 [M – 7PF₆⁻ – 3PF₅⁻]⁺⁺⁺ (Calcd. m/z = 429.8), 420.7 [M – 7PF₆⁻ – 4PF₅⁻]⁺⁺⁺ (Calcd. m/z = 420.8), 411.7 [M – 7PF₆⁻ – 5PF₅⁻]⁺⁺⁺ (Calcd. m/z = 411.8), 402.7 [M – 7PF₆⁻ – 6PF₅⁻]⁺⁺⁺ (Calcd. m/z = 402.8), 393.7 [M – 7PF₆⁻ – 7PF₅⁻]⁺⁺⁺ (Calcd. m/z = 393.8), 384.7 [M – 7PF₆⁻ – 8PF₅⁻]⁺⁺⁺ (Calcd. m/z = 384.8), 375.7 [M – 7PF₆⁻ – 9PF₅⁻]⁺⁺⁺ (Calcd. m/z = 375.8), 366.7 [M – 7PF₆⁻ – 10PF₅⁻]⁺⁺⁺ (Calcd. m/z = 366.8), 357.7 [M – 7PF₆⁻ – 11PF₅⁻]⁺⁺⁺ (Calcd. m/z = 357.8), 348.7 [M – 7PF₆⁻ – 12PF₅⁻]⁺⁺⁺ (Calcd. m/z = 348.8), 339.7 [M – 7PF₆⁻ – 13PF₅⁻]⁺⁺⁺ (Calcd. m/z = 339.8), 330.7 [M – 7PF₆⁻ – 14PF₅⁻]⁺⁺⁺ (Calcd. m/z = 330.8), 321.7 [M – 7PF₆⁻ – 15PF₅⁻]⁺⁺⁺ (Calcd. m/z = 321.8), 312.7 [M – 7PF₆⁻ – 16PF₅⁻]⁺⁺⁺ (Calcd. m/z = 312.8), 303.7 [M – 7PF₆⁻ – 17PF₅⁻]⁺⁺⁺ (Calcd. m/z = 303.8), 294.7 [M – 7PF₆⁻ – 18PF₅⁻]⁺⁺⁺ (Calcd. m/z = 294.8), 285.7 [M – 7PF₆⁻ – 19PF₅⁻]⁺⁺⁺ (Calcd. m/z = 285.8), 276.7 [M – 7PF₆⁻ – 20PF₅⁻]⁺⁺⁺ (Calcd. m/z = 276.8), 267.7 [M – 7PF₆⁻ – 21PF₅⁻]⁺⁺⁺ (Calcd. m/z = 267.8), 258.7 [M – 7PF₆⁻ – 22PF₅⁻]⁺⁺⁺ (Calcd. m/z = 258.8), 249.7 [M – 7PF₆⁻ – 23PF₅⁻]⁺⁺⁺ (Calcd. m/z = 249.8), 240.7 [M – 7PF₆⁻ – 24PF₅⁻]⁺⁺⁺ (Calcd. m/z = 240.8), 231.7 [M – 7PF₆⁻ – 25PF₅⁻]⁺⁺⁺ (Calcd. m/z = 231.8), 222.7 [M – 7PF₆⁻ – 26PF₅⁻]⁺⁺⁺ (Calcd. m/z = 222.8), 213.7 [M – 7PF₆⁻ – 27PF₅⁻]⁺⁺⁺ (Calcd. m/z = 213.8), 204.7 [M – 7PF₆⁻ – 28PF₅⁻]⁺⁺⁺ (Calcd. m/z = 204.8), 195.7 [M – 7PF₆⁻ – 29PF₅⁻]⁺⁺⁺ (Calcd. m/z = 195.8), 186.7 [M – 7PF₆⁻ – 30PF₅⁻]⁺⁺⁺ (Calcd. m/z = 186.8), 177.7 [M – 7PF₆⁻ – 31PF₅⁻]⁺⁺⁺ (Calcd. m/z = 177.8), 168.7 [M – 7PF₆⁻ – 32PF₅⁻]⁺⁺⁺ (Calcd. m/z = 168.8), 159.7 [M – 7PF₆⁻ – 33PF₅⁻]⁺⁺⁺ (Calcd. m/z = 159.8), 150.7 [M – 7PF₆⁻ – 34PF₅⁻]⁺⁺⁺ (Calcd. m/z = 150.8), 141.7 [M – 7PF₆⁻ – 35PF₅⁻]⁺⁺⁺ (Calcd. m/z = 141.8), 132.7 [M – 7PF₆⁻ – 36PF₅⁻]⁺⁺⁺ (Calcd. m/z = 132.8), 123.7 [M – 7PF₆⁻ – 37PF₅⁻]⁺⁺⁺ (Calcd. m/z = 123.8), 114.7 [M – 7PF₆⁻ – 38PF₅⁻]⁺⁺⁺ (Calcd. m/z = 114.8), 105.7 [M – 7PF₆⁻ – 39PF₅⁻]⁺⁺⁺ (Calcd. m/z = 105.8), 96.7 [M – 7PF₆⁻ – 40PF₅⁻]⁺⁺⁺ (Calcd. m/z = 96.8), 87.7 [M – 7PF₆⁻ – 41PF₅⁻]⁺⁺⁺ (Calcd. m/z = 87.8), 78.7 [M – 7PF₆⁻ – 42PF₅⁻]⁺⁺⁺ (Calcd. m/z = 78.8), 69.7 [M – 7PF₆⁻ – 43PF₅⁻]⁺⁺⁺ (Calcd. m/z = 69.8), 60.7 [M – 7PF₆⁻ – 44PF₅⁻]⁺⁺⁺ (Calcd. m/z = 60.8), 51.7 [M – 7PF₆⁻ – 45PF₅⁻]⁺⁺⁺ (Calcd. m/z = 51.8), 42.7 [M – 7PF₆⁻ – 46PF₅⁻]⁺⁺⁺ (Calcd. m/z = 42.8), 33.7 [M – 7PF₆⁻ – 47PF₅⁻]⁺⁺⁺ (Calcd. m/z = 33.8), 24.7 [M – 7PF₆⁻ – 48PF₅⁻]⁺⁺⁺ (Calcd. m/z = 24.8), 15.7 [M – 7PF₆⁻ – 49PF₅⁻]⁺⁺⁺ (Calcd. m/z = 15.8), 6.7 [M – 7PF₆⁻ – 50PF₅⁻]⁺⁺⁺ (Calcd. m/z = 6.8), 1.7 [M – 7PF₆⁻ – 51PF₅⁻]⁺⁺⁺ (Calcd. m/z = 1.8).
487.1 [M – 9PF$_6$]$^9$ (Calcd. m/z = 487.3), 566.4 [M – 8PF$_6$]$^8$ (Calcd. m/z = 566.4), 678.4 [M – 3PF$_6^-$ – 4PF$_5$]$^7^+$ (Calcd. m/z = 678.9), 803.5 [M – 6PF$_6^-$]$^6^+$ (Calcd. m/z = 803.5), 993.4 [M – 5PF$_6^-$]$^5^+$ (Calcd. m/z = 993.1), 1277.4 [M – 4PF$_6^-$]$^4^+$ (Calcd. m/z = 1277.7), 1752.2 [M – 3PF$_6^-$]$^3^+$ (Calcd. m/z = 1751.9).

[Ru$_6$(7b)$_6$(PF$_6$)$_{12}$] (10). To a solution of 7b (244 mg, 110 µmol) in MeOH (100 mL), [Ru(Cl)$_2$(DMSO)$_4$] (55 mg, 110 µmol) was added; the mixture was refluxed for 36 h. After cooling to 25 °C, the resultant deep red solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on SiO$_2$ eluting with a satd. aq. KNO$_3$: H$_2$O: MeCN (1:1:10; v/v/v) mixture to afford (> 35 %) hexamer 10, as a dark red solid: m. p. 349 °C (dec.); $^1$H NMR (CD$_3$CN): δ 8.95 (s, 3',5'-tpy$_H$, 4H), 8.58 (d, $J$ = 8.1 Hz, 3,3''-tpy$_H$, 4H), 8.03 – 7.97 (m, 4-ArH, 4,4''-tpy$_H$, 5H), 7.80 (s, 2,6-ArH, 2H), 7.47 (d, $J$ = 5.7 Hz, 6,6''-tpy$_H$, 4H), 7.24 (dd, $J$ = 6.3, 5.7 Hz, 5,5''-tpy$_H$, 4H), 2.58 (s, ArC$_H$$_3$, 3H); $^{13}$C NMR (CD$_3$CN): δ 21.36, 87.97, 96.67, 123.37, 125.79, 126.47, 128.88, 131.12, 133.63, 135.25, 139.47, 141.38, 153.79, 156.43, 158.58; UV/Vis (CH$_3$CN) $\lambda_{\text{max}}$ ($\epsilon$) = 215 (3.04 $\times$ 10$^5$), 283 (3.61 $\times$ 10$^5$), 332 (4.86 $\times$ 10$^5$), 501 nm (2.53 $\times$ 10$^5$ dm$^{-3}$·mol$^{-1}$·cm$^{-1}$); ESI-MS: m/z 471.5 [M – 5PF$_6^-$ – 5PF$_5$]$^{10^+}$ (Calcd. m/z = 678.9), 541.8 [M – 3PF$_6^-$ – 6PF$_5$]$^{9^+}$ (Calcd. m/z = 678.9), 618.1 [M – 6PF$_6^-$ – 2PF$_5$]$^{8^+}$ (Calcd. m/z = 618.5), 731.0 [M – 4PF$_6^-$ – 3PF$_5$]$^{7^+}$ (Calcd. m/z = 730.3), 876.8 [M – 3PF$_6^-$ – 3PF$_5$]$^{6^+}$ (Calcd. m/z = 876.2), 1069.7 [M – 5PF$_6^-$]$^{5^+}$ (Calcd. m/z = 1069.0).
CHAPTER VIII

SUMMARY

The challenges of supramolecular chemistry have opened a new field of molecular nanotechnology predicted on molecular architecture that utilize programmed self-assembly combined with sequential covalent chemical synthesis to achieve ordered structure. This research was dedicated to the design, synthesis, characterization, and application of a series of metallomacrocycles via terpyridine-metal(II)-terpyridine connectivity. Various pre-designed building blocks consisting of controlled functional juxtaposed terpyridine moieties were constructed. These materials proved to be valuable for the construction of rigid and shape-persistence metallomacrocycles because of the powerful metal-binding ability with terpyridine ligands.

During the construction of homo- and heteronuclear trigonal metallomacrocycles using 1,2-bis(2,2′:6′,2″-terpyridin-4′-ylethynyl)benzene, a combination of self-assembly and step-wise synthetic strategies was utilized. Especially, the step-wise method permits specific introduction of different metal ion combinations giving access to induce dipole moment. The resultant constructs also showed densely packed architecture causing steric hindrance for terpyridine-metal(II)-terpyridine complex rotation inside of the triangle, which may be ideal candidate for nanomachines. Other important characteristics of these
metallomacrocycles were their photophysical and redox properties, which may provide useful in diverse photophysical applications. Since the carbazole unit can introduce the desirable directivity angle (ca. 105°) to build a pentagon shape and is easily modified, a building block for pentagonal metallomacrocycle was used to demonstrate the viability of this process. While Fe(II)- and Ru(II)-pentamers were constructed by self-assembly procedure, they showed typical metal-ligand charge transfer (MLCT) transition; whereas the Zn(II)-pentamer showed intra-ligand charge transfer (ILCT) providing to strong emission at 560 nm. Using their light absorption characteristics, these preliminary studies of their photoelectrochemical performance implied their potential use in solar cell development.

To construct the hexagon-shape metallomacrocycles, the bis(terpyridine) ligands using benzene and triphenylamine units were designed since the meta-position of benzene and 4,4′-position of triphenylamine provide the desired 120° angle to construct hexagonal architecture. Two different Zn(II)-hexamers showed different absorption and emission behavior depending on whether ethynyl group is or is not in the hexameric structure. Using 1,3-bis(2,2',6',2''-terpyridin-4'-ylethynyl)-5-tert-butylbenzene, Ru(II)- and Fe(II)-hexameric macrocycles were constructed by both self-assembly and step-wise procedures. In order to expend the concept of modular chemistry to high level, the nanohybrid with carboxylate-functionalized, multi-walled carbon nanotubes (MWNTs) by simple cation exchange reaction was constructed. Its structural and morphological characteristics were demonstrated by both TEM imaging with Energy Dispersive X-ray Spectroscopy (EDAX) and Raman spectroscopy. Another hexameric metallomacrocycle series was designed and constructed by bis(terpyridine)triphenyl-amine ligand. The
crystal structure of the ligand showed the possibility to form the hexagon as $119.69^\circ$ angle between the directed ligands. Also, it would be interesting to test if they could be used as dye-sensitizers for solar cells, according to the preliminary results this is a viable scenario.

Several functionalized building blocks, especially having $120^\circ$ juxtaposition angle, were synthesized by Pd-catalyzed cross-coupling procedure. These monomers may provide easy access to the use of transition metal connectivity in future developments in the transformation of molecular chemistry to supramolecular chemistry, organometallic chemistry as well as polymer chemistry.

The design of the supramolecules is unlimited on a human scale. Tailored approaches to such molecules – metallomacrocycles in this dissertation – are only at early stage of the utilization of transition metal connectivity in supramacromolecular chemistry. The practical application of these materials shall play an increasing role in macromolecular constructs. The goal of this basic research is finally to apply these novel materials as future energy storage modules, photovoltaic devices, and other molecular electronic devices.
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