Hexagonal Terpyridine–Ruthenium and –Iron Macrocyclic Complexes by Stepwise and Self-Assembly Procedures

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Abstract: Methods for the self-assembly, as well as directed construction, of hexaruthenium metallomacrocycles employing bisterpyridine building blocks are described. Self-assembly is effected by a combination of equimolar mixtures of bismetalated and nonmetalated bis(terpyridinyl) monomers each possessing the requisite planar, 60°, terpyridine–metal–terpyridine connectivity. Stepwise synthesis of the identical hexamer is also discussed and used to aid in verification of the self-assembled product. Preparation and analysis of the related Fe^{II} metallomacrocycle are detailed and its TEM image confirms the hexameric structure. Characterization of the metalated products includes cyclic voltammetry along with the routine analytical techniques.

Keywords: iron · metallomacrocycles · metallocycle · N ligands · self-assembly · ruthenium

Introduction

Contemporary, eloquent work in the area of self-assembly by Stang et al.,[1] Lehn et al.,[2] and many others,[3–7] prompted our investigation of the self-assembly of (macro)molecules through formation of stable transition metal complexes. More specifically, our goal involved the design and preparation of polyterpyridinyl ligands that would form the basis of "modular building block sets"[8] capable of forming stable, irreversible, and non-*H*-bonding "higher order" (fractal) architectures. We herein report the construction of a series of bis(terpyridine) monomers that facilitate the preparation of hexametallomacrocycles.

Linear bis(terpyridyl) monomers have been used in the formation of numerous ordered assemblies, such as layered polyelectrolyte films,[9] grids,[10] racks,[11] Ru^{II}-based dendrimers,[12] helicating ligands,[13] and photoactive molecular-scale wires.[14] Progress in directed synthesis of cyclic rigid structures[15] can be found in "shape-persistent" phenylacetylenes,[16–18] diethynylbenzene macrocycles,[19] and a 24-phenylene hexagon.[20] Whereas advances through self-assembly have yielded, for example, chiral[21] and achiral[22] circular helicates, cylindrical cage structures,[23] Pt-coordinated bipyridyl squares,[24] metal-templated catenanes,[25–28] [2]catenanes with metals in their backbones,[29, 30] and cyclic porphyrin trimers.[31]

Our strategy for macrocycle formation involved the preparation of a bis(terpyridine) monomer possessing a 60° angle with respect to the two ligating moieties. This would facilitate the assembly of six building blocks with six connecting metals in the ubiquitous benzenoid architecture. The potential to synthesize such constructs, with little equilibration (metal–ligand exchange) under mild physicochemical conditions, is predicated on the unique strength of the terpyridine(tpy)–Ru coordination.[32] It was also envisioned that these rigid structures, which possess an overall +12 charge, would be an ideal counterion to dendritic macromolecular series composed of 12, 36, or 108 carboxylate surface groups; preliminary gel-like materials support a complementary interaction. A timely, comprehensive review of 2,2′:6′,2″-terpyridine ligands has also appeared.[33]

Results and Discussion

Synthesis of the key bis(terpyridine) monomer **3** (Scheme 1) began by treatment of the known dialdehyde **1**[34] (prepared

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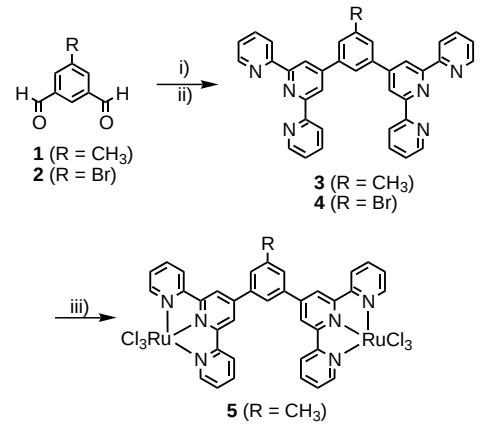


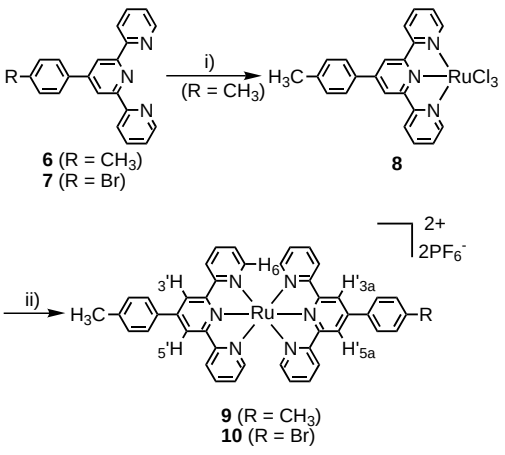
Scheme 1. Synthesis of the key monomers **3, 4**, and bis(Ru^{III}) adduct **5**: i) 2-acetylpyridine, NaOH, EtOH, 20 h, room temperature; ii) $AcO^-NH_4^+$, AcOH, 4 h, reflux; iii) $RuCl_3 \cdot 3H_2O$, EtOH, 12 h, reflux.

from 1,3-bis(bromomethyl)-5-methylbenzene)[35] with at least three molar equivalents of 2-acetylpyridine[36] under basic conditions at 25 °C for 20 h, followed by addition of excess NH_4OAc in AcOH and reflux for 4 h to afford the desired angular 1,3-bis(2,2′:6′,2″-terpyridin-4′-yl)-5-methylbenzene (**3**) in 22% overall yield. The structure of **3** was confirmed by singlets (^{1}H NMR) at $\delta = 2.59$ ppm for the arylCH_3, at $\delta =$ 7.82 pm for the 4,6-Ar*H*, and at $\delta = 8.83$ ppm for the 3′,5′-pyr*H* (these signals integrate in the expected 3:2:4 ratio), and a mass peak (ESI-MS) at *m*/*z* 555 [M + H^+]. The related 3,5-bis(2,2′:6′,2″-terpyridin-4′-yl)-1-bromobenzene (**4**) was similarly prepared (35%) from bromodialdehyde **2**,[34] whose structure was verified by the observation of singlets (^{1}H NMR) at $\delta = 8.15$ ppm (2,6-Ar*H*) and $\delta = 8.81$ ppm (3′,5′-pyr*H*) that integrated in a 1:2 ratio as well as a mass peak (ESI-MS) at *m*/*z* 620 [M + H^+].

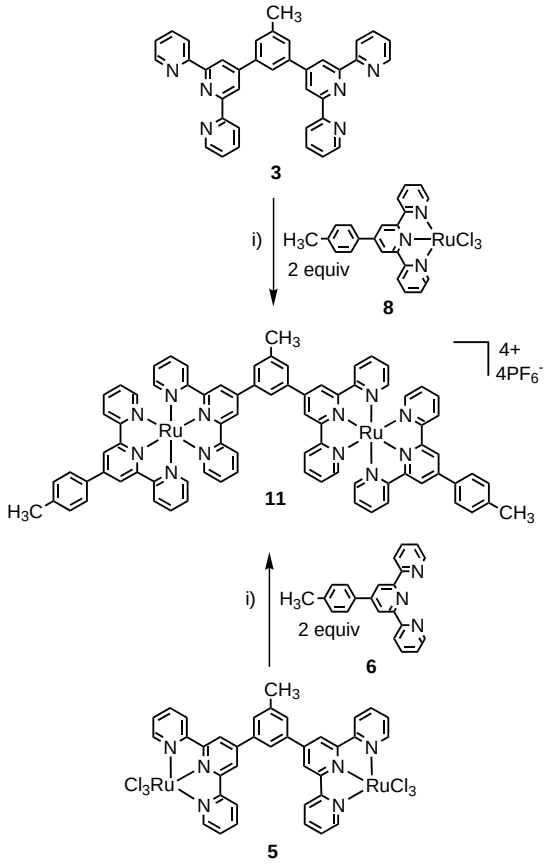
Confirmation of the specificity and stability of the $Ru(tpy)_2$ motif was obtained from a combination of selected simple ligands (**6** or **7**) and the Ru^{III} complex **8** (Scheme 2). The 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (**6**) was synthesized according to literature.[37] An ethanolic solution of toluylterpyridine **6** and $RuCl_3 \cdot 3H_2O$ was refluxed for 12 h to afford (87%) the metalated adduct **8**, which was used without further purification. Mono-complex **8** was then treated with mono(terpyridine) ligand **6** in MeOH and refluxed for 12 h under reducing conditions (*N*-ethylmorpholine) to give the desired homoleptic complex **9** [Ru(**6**)$_2$(PF_6)$_2$] (67%), which exhibited a downfield shift (^{1}H NMR) of the 3′,5′-pyr*H* singlet ($\delta = 9.19$ ppm; $\Delta\delta = +0.36$) and an upfield shift of the 6,6″-pyr*H* doublet ($\delta = 7.62$ ppm; $\Delta\delta = -1.15$) compared to the free ligand **6**; mass spectral data (ESI-MS) were also in accord with the assigned structure. Analogous treatment of the Ru^{III} complex **8** with free ligand **7**[38] afforded the heteroleptic complex **10** [Ru(**6**)(**7**)(PF_6)$_2$], which was evidenced by two close but still distinct singlets (^{1}H NMR) at $\delta = 8.99$ and 9.00 for the 3′,5′-pyr*H* and 3a′,5a′-pyr*H* characteristic of structural dissymmetry. Mass spectral data (ESI-MS) further supported the *heteroleptic* structure. There was no evidence of ligand scrambling, which would have been obvious by the presence of the Ru(**6**)$_2^{2+}$ (i.e., **9**) or Ru(**7**)$_2^{2+}$ complexes. This confirmed the previous report,[39] but also demonstrated the structural integrity of the molecular assembly.

To aid in the characterization of the resultant hexameric architecture in the self-assembled construct, formation and proof of the similar components for that used in a stepwise assembly process were undertaken. Thus, an ethanolic solution of bisterpyridine monomer **3** with two equivalents of $RuCl_3 \cdot 3H_2O$ was refluxed for 12 h, which produced (92%) the minimally soluble, paramagnetic bis(Ru^{III}) adduct **5** (Scheme 1), which when reacted with two equivalents of free monoterpyridine ligand **6** afforded the bis(ruthenium complex) **11** [Ru_2(**5**)(**6**)$_2$(PF_6)$_2$] (Scheme 3). The ^{1}H NMR spectrum for **11** showed a 1:2 proton integration ratio for the central ($\delta = 2.96$ ppm) and terminal ($\delta = 2.68$ ppm) methyl groups supporting the bis(capped) structure. As in the case of dimer **9**, complex **11** exhibited a downfield shift (^{1}H NMR) of the 3′,5′-proton resonance ($\delta = 9.17$ ppm; $\Delta\delta = +0.34$ ppm) and an upfield shift for the 6,6″-proton signal ($\delta = 7.62$ ppm; $\Delta\delta = -1.15$ ppm). Alternatively, treatment of the bis-ligand **3** with two equivalents of mono-complex **8** afforded the identical diamagnetic bis-complex **11**; no evidence for ligand scrambling was detected.

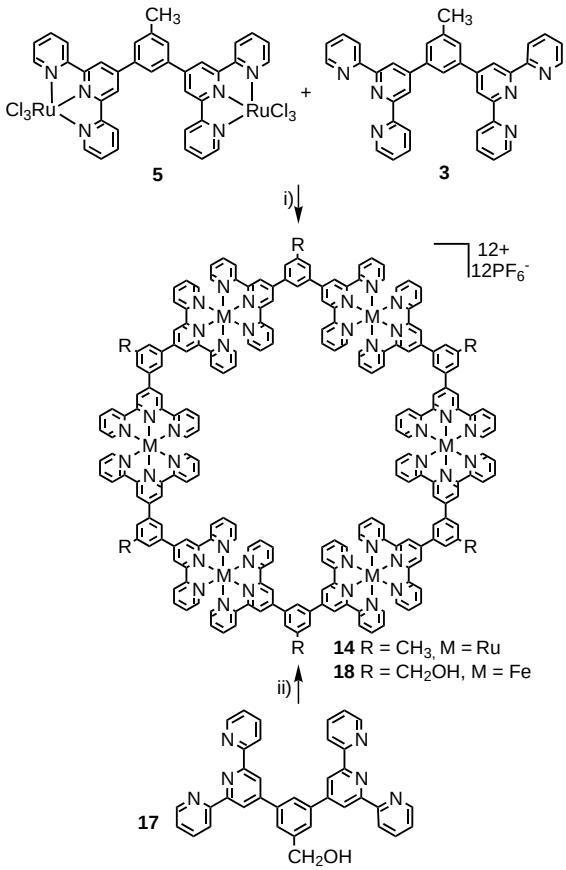
The self-assembled, diamagnetic, hexameric Ru^{II} complex **14** [Ru_6(**3**)$_6$(PF_6)$_{12}$] was prepared (Scheme 4) by reaction of the free bisterpyridine monomer **3** with one equivalent of the activated bis(Ru^{III}) adduct **5** in MeOH for 12 h at reflux under reducing conditions (*N*-ethylmorpholine). The hexamer was initially obtained in 85% yield but possessing chloride counterions which, after chromatography and counterion exchange (Cl^- to PF_6^-), afforded macrocycle **14** in an overall yield of 43% overall, that was structurally confirmed by diverse spectral methods. The ^{1}H NMR spectrum of **14** revealed a single absorption at $\delta = 2.93$ ppm (CH_3) suggesting the presence of a single monomeric unit in contrast to that of a linear oligomer such as in the case of bisruthenium complex **11**, which displayed two distinct methyl singlets in the ^{1}H NMR spectrum. Other diagnostic spectral attributes (^{1}H NMR) included the singlet at $\delta = 8.41$ ppm for the 4,6-Ar*H* as well as the notable upfield and downfield shifts for the



Scheme 2. Synthesis of mono(Ru^{II}) complexes **9** and **10**: i) $RuCl_3 \cdot 3H_2O$, EtOH, 12 h, reflux; ii) a) *N*-ethylmorpholine, MeOH, 12 h, reflux, b) methanolic $NH_4^+PF_6^-$.



Scheme 3. Synthesis of complex **11** by different routes to verify the structure of bis(Ru^{III}) adduct **5;** i) a) *N*-ethylmorpholine, MeOH, 12 h, reflux, b) methanolic $NH_4^+PF_6^-$.



Scheme 4. Synthesis of metallomacrocycles **14** by self- and directed-assembly; i) a) *N*-ethylmorpholine, MeOH, 12 h, reflux, b) methanolic $NH_4^+PF_6^-$.

doublet ($\delta = 7.62$ ppm; $\Delta\delta = -1.15$ ppm) of the 6,6″-pyr*H* and for the 3′,5′-pyr*H* signals ($\delta = 9.37$ ppm; $\Delta\delta = +0.54$ ppm), respectively, when compared to corresponding absorptions that characterize the uncomplexed bisterpyridine. COSY and HETCOR spectra of the bisterpyridine **3** and the self-assembled macrocycle **14** verified the peak assignments as well as coupling patterns. This hexameric structure was further established by MALDI-TOF mass spectrometry, which was measured in the linear mode with the use of a *trans*-3-indoleacrylic acid matrix. The peaks at *m*/*z* 5544 [$-1\,PF_5$], 5400 [$-1\,PF_6 - 1\,PF_5$], 5292[$-3\,PF_5$], 5166[$-4\,PF_5$], 5020[$-4\,PF_5 - 1\,PF_6$] were calculated as the loss of either PF_5 alone or as both PF_5 and PF_6 together, which is a known phenomena.[40] Hexamer **14**, initially isolated as the $12\,Cl^-$ salt, exhibited solubility in MeOH and hot H_2O, while conversion to the $12\,PF_6^-$ salt facilitated solubility in MeCN, acetone, and DMSO.

To further confirm and insure the structural characterization of macrocycle **14** [$Ru_6(\mathbf{3})_6(PF_6)_{12}$], an alternative stepwise, directed route was undertaken (Scheme 5). The diamagnetic bis-complex **12** was prepared by treatment of bis-complex **5** with two equivalents of unmetalated bisterpyridine **3**. The ^1H NMR spectrum of **12** showed a complex pattern of broadened absorptions in the aromatic region ($\delta = 9.76$–7.40 ppm) as well as two anticipated singlets arising from the nonequivalent methyl groups ($\delta = 2.79$, 2.94 ppm) present in the expected 1:2 ratio. Finally, reaction of oligomer **12** with two equivalents of $RuCl_3 \cdot 3\,H_2O$ afforded the corresponding paramagnetic bis(terminal Ru^{III}) adduct **13**, which when treated with one equivalent of **12** yielded (ca. 80%) a sample of crude hexamer, subsequent chromatography and counter-ion exchange generated **14** which possesses identical spectral and physical characteristics to those for **14** derived from the self-assembled procedure. The UV spectrum of **14** exhibited extinction coefficients (ε) of a 5.1-, 5.5-, and 5.8-fold increase for λ_{max} at 290, 312, and 496 nm, respectively (Table 1), when compared to coefficients for the mono(Ru^{II}) complex **9** measured analogously. The equilibrium analytical ultracentrifugation absorption profiles[41] for hexamer **14**, (obtained from the self-assembly procedure) at a concentration of 0.5% in MeCN has been conducted and further support the molecular weight range. It is also notable that the chromato-

Table 1. CV data for Ru^{II} complexes **9** and **14** (potentials versus ferrocene/ferrocenium; reversible signal experiments were carried out at 100 mV s^{-1} in 0.1 M nBu_4BF_4/DMF solution at 298 K).

Complex	E1/2(ΔEp), [V] terpyridines		Ru^{III}/Ru^{II}
9	– 1.800 (0.061)	– 1.580 (0.061)	0.832 (0.062)
14	adsorption peak	– 1.622 (0.075)	0.798 (0.091)

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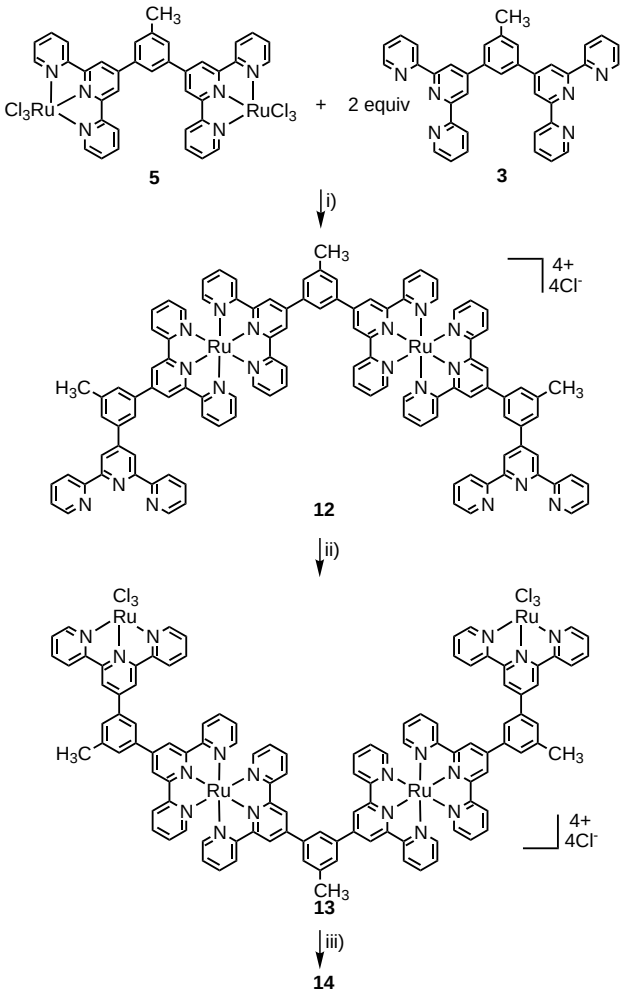


Scheme 5. Synthesis of trimeric precursors **12** and **13** for stepwise preparation of metallomacrocycle **14**: i) *N*-ethylmorpholine, MeOH, 12 h, reflux; ii) $RuCl_3 \cdot 3H_2O$, EtOH, 12 h, reflux; iii) a) **12**, *N*-ethylmorpholine, MeOH, 12 h, reflux, b) methanolic $NH_4^+PF_6^-$.

graphs measured by TLC of the self- versus the stepwise-assembled hexamers were identical and, as expected, different from all precursors.

Cyclic voltammetry (CV) experiments with macrocycle **14**, further supported its proposed structure (Figure 1). The electrochemical response of mono(Ru^{II}) complex **9** considered as a monomeric unit of **14**, showed two reversible waves (Figure 1a) that presumably correspond to the monoelectronic reduction of each one of the two terpyridine ligands surrounding the Ru atom. As expected, the electrochemical behavior of the Ru – tpy moieties of macrocyclic complex **14**, based on previous electrochemical experiments,[42, 43] was notably different from that of the simple complex **9**. In Figure 1b, the electrochemical response of hexamer **14** in the same potential region revealed that the most positive wave was quasi-reversible and that the most negative one was characterized by a sharp oxidation peak that increased its size as the switching potential became more negative. The observed sharpness of the oxidation peak is typical of adsorbed electroactive species at an electrode surface[44, 45] and therefore can reasonably be explained by assuming the formation of an insoluble reduction product at the second

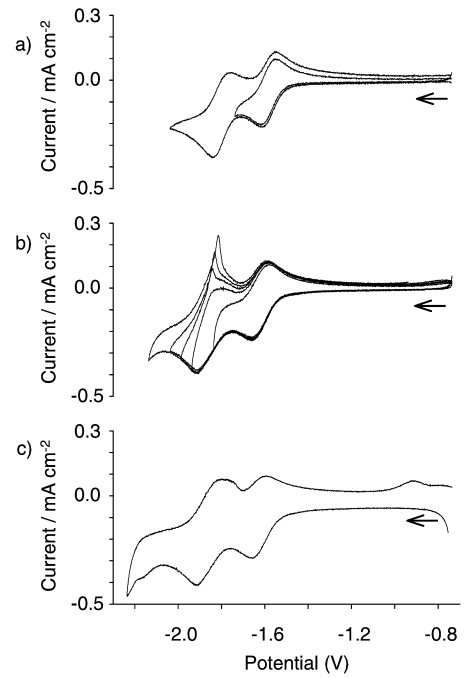


Figure 1. Cyclic voltammograms of 1 mM solutions of a) mono(Ru^{II}) complex **9**, and b) and c) macrocycle **14** (performed in 0.1 M nBu_4NBF_4 in DMF at 298 K with a scan rate of 100 $mV\,s^{-1}$).

reduction peak. In this way, the incorporation of a second electron into each one of the Ru – tpy moieties would form a large neutral species that, as opposed to its smaller counterpart (mono-complex **9**), would be readily adsorbed on the electrode surface. This idea was further supported by CV experiments in which the cathodic scan reached more negative potentials than those showed in Figure 1a and 1b. As can be observed in Figure 1c, the CV response of **14** in a slightly wider potential window is characterized by an irreversible reduction at very negative potentials that resulted in the absence of the sharp oxidation peak observed in Figure 1b during the anodic scan. This suggests that there is an irreversible reaction at about 2.1 V versus ferrocenium/ferrocene that, either disconnected some high percentage of metal complex, or formed a chemically different species that did not adsorb on the electrode surface. Another interesting comparison that could be made with the CV curves presented in Figure 1a and b is related to the half-wave potentials and to the peak-to-peak splitting that characterize them. Close inspection of the data (Table 2) for complexes **9** and **14**, reveals that the reduction of macrocycle **14** requires more energy than its smaller counterpart **9** and that macrocycle **14** has a slightly larger peak-to-peak separation. Whereas the improved basicity of the terpyridine ligands in **14** could be rationalized in terms of the "pseudo"-resonance stabilization energy provided by its chemical structure;[46] the larger peak-to-peak splitting of the waves may be due to the nonequivalence effect of the terpyridine units of **14** that, in turn, could be a consequence of a weak coupling between the electroactive units.[47–49]

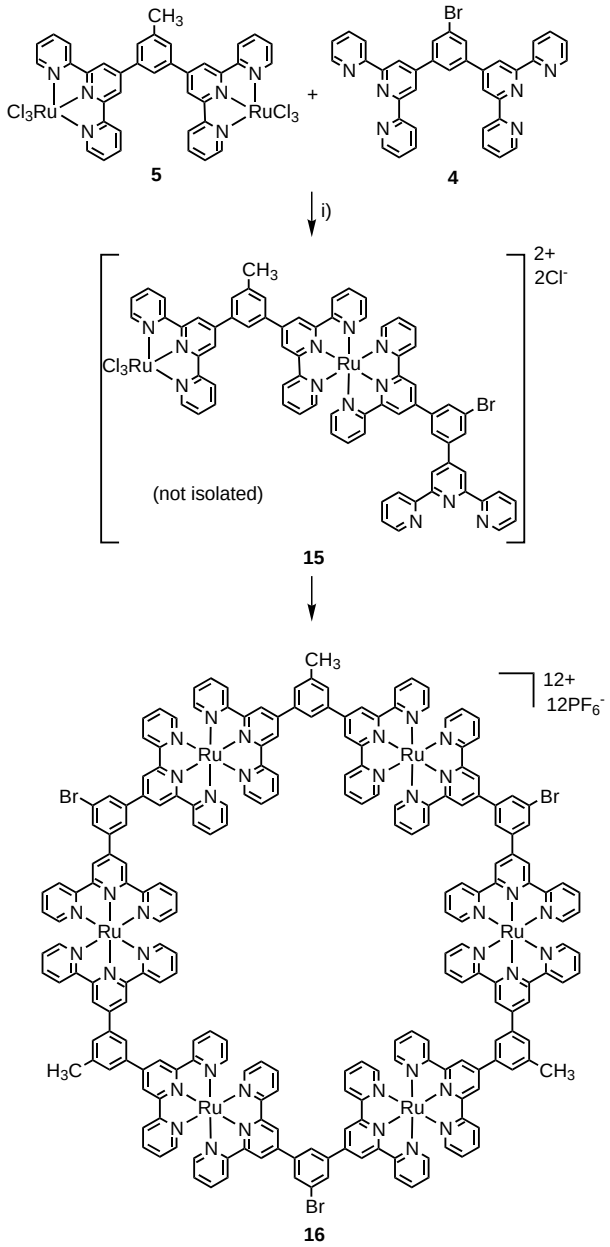
In an effort to modify the solubility of macrocycle **14** $[Ru_6(\mathbf{3})_6(PF_6)_{12}]$, as well as to probe its use as an organizational scaffolding for nonbonded network formation, the

Table 2. UV absorption data of complexes.

Complex	λ_{max} [nm]	Extinctioncoefficient (ε)
9	284	58900
	310	66100
	486	24800
10	286	56 000
	310	59700
	490	23680
11	290	113200
	496	120400
	490	47000
12	288	135530
	310	122480
	492	50490
14	290	322900
	312	336800
	496	143400
16	290	317100
	310	310200
	496	148150

counterions in $[Ru_6(\mathbf{3})_6(Cl)_{12}]$ were exchanged with a dodecacarboxylate-terminated dendrimer.[50] Thus, a 1:1 mixture of macrocycle **14** (dodecachloride) and the dodecacarboxylate sodium salt $[C(CH_2OCH_2CH_2CONHC(CH_2CH_2CO_2Na)_3)_4]$ was dialyzed to give a gelatinous precipitate that possessed no residual sodium or chloride ions based on elemental analysis; unfortunately, this 1:1 combination proved to be extremely insoluble in all common solvents. However, a 1:1 mixture of hexamer **14** (Cl^-) and a 3rd generation carboxylate-terminated dendrimer gave an analogous $[Ru_6(\mathbf{3})_6(G3\text{-}108\text{-}CO_2^-(ca.\ Na_{96}))]$ complex, which produced a deep red D_2O solution (25 °C), owing to the presence of the Ru^{II}, which allowed verification of the aqueous solubility by ^1H NMR spectroscopy due to the excess carboxylate component in the assembly.

To further investigate the Ru-based self-assembly technique, the construction of heteroleptic macrocycles was undertaken to ascertain the degree of order in the assembly process (Scheme 6). A suspension of monomer **4** and bis(Ru^{II}) complex **5** in MeOH was refluxed for 12 h to afford the alternating Me/Br-based macrocycle **16**, which was purified by preparative TLC (SiO_2, $R_f = 0.60$, eluent; MeCN:saturated aqueous KNO_3:water = 7:1:1, 36 %). Evidence for its formation includes a symmetrically similar, yet expectedly broadened, spectrum (^1H NMR) that corresponds to that of the hexamethyl analogue **14** except for two identical proton peaks on the benzene ring associated with ligand **4**, which were shifted downfield from those of free ligand **4** (($\delta = 8.75$ ppm, 2,6-Ar*H* ($\Delta\delta = +0.6$ ppm, **4**), $\delta = 9.18$ ppm, 4-Ar*H* ($\Delta\delta$ +0.88, **4**)) with the exact expected proton integration values, respectively. COSY and HETCOR NMR experiments further supported the assigned structure. A UV study of **16** gave extinction coefficients (ε) that exhibited a 5.7-, 5.2-, and 6.1-fold increase for λ_{max} at 290, 310, and 496 nm, respectively, when compared to coefficients measured for the mono(Ru^{II}) complex **10**. Since ligand scrambling has not been observed (as noted above), the stepwise complexation led to the in situ generation of intermediate **15**, which then assembled to give rise to macrocycle **16**, as supported by the spectral data.



Scheme 6. Synthesis of heteroleptic metallomacrocycle **16** by self-assembly: i) a) *N*-ethylmorpholine, MeOH, 12 h, reflux, b) methanolic $NH_4^+PF_6^-$.

Successful construction of homo- and heteroleptic macrocycles suggested the creation of rings with easily modifiable functionality, as well as with different metals, such as Fe^{II} (Scheme 4). Thus, the hydroxymethyl bisterpyridine monomer **17** was accessed starting 3,5-di(formyl)-1-hydroxymethylbenzene, derived from the incomplete reduction of 1,3,5-tris(chlorocarbonyl)benzene followed by its treatment under standard conditions.[34] Reaction of **17** with $FeCl_2$ (1:1, MeOH) gave the desired $[Fe_6(\mathbf{17})_6(Cl)_{12}]$ macrocycle **18** in 81 % yield. The complete absence (^1H NMR) of extraneous peaks excluded the presence of starting materials, intermediates, and oligomeric materials; whereas a slightly broadened singlet (^1H NMR) at $\delta = 5.65$ ppm (CH_2OH), the singlet at $\delta = 8.63$ ppm for the 4,6-Ar*H* as well as the diagnostic shifts for the doublet ($\delta = 7.30$ ppm, $\Delta\delta = -1.48$ ppm) of 6,6″-pyrH,

0947-6539/02/0813-2950 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 13

and the 3′,5′-pyrH ($\delta = 9.51$ ppm, $\Delta\delta = +0.67$ ppm) signals were in accord with that expected for ring formation. Transmission electron microscopy (TEM) images of **18** $[Fe_6(\mathbf{19})_6(Cl)_{12}]$ revealed single, hexagonal-shaped particles with the predicted diameter of about 37 Å, based on molecular modeling studies (Figure 2). Close inspection of

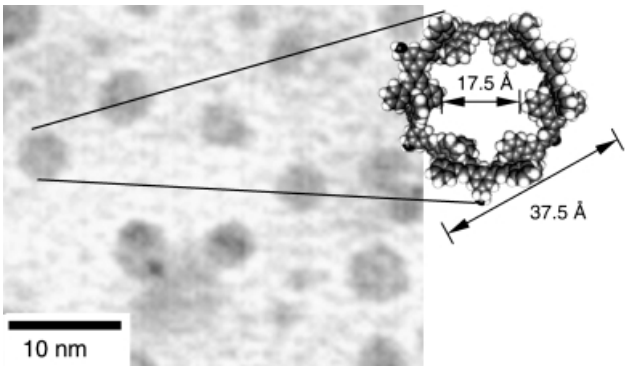


Figure 2. Transmission electron micrograph of $\mathbf{18}^{+12} \cdot 12\,PF_6^-$ (magnification of 200 000 ×) showing an individual, regular hexagon along with its computer generated CPK model for comparison Darkened metal centers in hexameric arrangement can be observed.

the TEM image reveals an inner star form and six, hexagonally juxtaposed dark regions (i.e., the metal centers), which are also consistent with predicted morphology. The H-bonding functionality and the intial water content were critical factors in sample preparation Thus, the external functionality may play an important role in aggregation processes; further studies are on-going to evaluate intermolecular interactions.

Conclusion

We have prepared novel, angular bis(terpyridine) derivatives (**3**, **4**, and **17**) as building blocks for the formation of stable, hexagonal metallomacrocycles. These ligands were employed for the synthesis of the homo- or heteroleptic hexa(bis(terpyridine)ruthenium) complexes **14** and **16** and the related Fe^{II} analogue **18**. The structures of these hexagonal architectures were characterized by means of ^1H and ^{13}C NMR, UV/Vis spectroscopy, mass spectrometry, and, in the case of the Fe_6 macrocycle, also by electron microscopy. Also it is envisioned that, based on the simple counterion exchange experiments, the use of compact, charge-concentrated (pseudo)spherical dendrimers possessing polyanionic surfaces will facilitate entry to better control counterion randomness at the organic – inorganic interface. Experiments are currently ongoing to access larger and more complex macrocycles possessing different metal connectivities as well as larger fractal architectures.

Experimental Section

Materials and methods: Chemicals were purchased from Aldrich and used as received. Thin layer chromatography (TLC) was conducted on flexible sheets precoated with aluminum oxide IB-F or silica gel IB2-F (Baker-flex) and visualized with UV light. Column chromatography was conducted using neutral/basic alumina, Brockman Activity I, 60–325 mesh, or silica gel (60–200 mesh) purchased from Fisher Scientific. Melting points were determined on an Electrothermal 9100 and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX250 NMR spectrometer. IR spectra were recorded on an ATI Matheson Genesis FTIR spectrophotometer. Absorption spectra were measured in MeCN at room temperature with a Hewlett Packard 8452A Diode Array spectrophotometer. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap mass spectrometer (ESI-MS) or a Bruker Reflex II MALDI-TOF mass spectrometer (MALDI-MS) with *trans*-3-indoleacrylic acid as the matrix. Molecular weights for **14** were measured by equilibrium analytical ultracentrifugation using a Beckman XLA analytical ultracentrifuge equipped with an AN60 Ti rotor and absorption optics. MeOH or MeCN served as solvents. A visible wavelength was selected for each sample to produce an average absorbance of about 0.5; concentration was varied over a wide range. Rotor speed (typically 25,000 RPM) was selected to produce a smooth, substantial gradient in concentration. For a single component in the dilute limit, the absorbance, A, profile is given by Equation (1),where ω is the circular frequency (rad s^{-1}), M is the molar mass, ρ the solvent density, the solute partial specific volume, r the radius from the center of the rotor, a the radius at the meniscus, R the gas constant, and T the Kelvin temperature.

$$A(r) = A(a)e^{\omega^2 M(1-\rho\bar{\nu})(r^2-a^2)/2RT}$$

The absorbance profile of a multicomponent system has additional exponential growth terms. A Parr DMA58 precision densitometer was used to determine the partial specific volume. The electrochemical experiments were conducted using a PGZ301 Potentiostat programmed and controlled by means of a computer loaded with the voltamaster 4 software (Radiometer-Copenhagen). Resistance compensation for all experiments was automatically computed and corrected by the software in the ″static automatic″ mode. All cyclic voltammetry measurements were conducted in anhydrous DMF solutions containing approximately a 1.0 mM concentration of the electroactive compound and 0.1M of tetrabutylammonium tetrafluoroborate (nBu$_4$NBF$_4$) as supporting electrolyte. The electrochemical cell consisted of a 2.0 mL conical vial fitted with a graphite working electrode (previously polished in sequential steps with diamond and alumina polishing compounds on a felt surface), a silver pseudo-reference electrode, and a platinum wire as a counter electrode (Cypress System, Lawrance, KS). Dry N_2 gas was bubbled carefully through the electroactive solution for at least 10 min before each measurement to deoxygenate the solution. All the potentials reported in this work were measured against the ferrocene/ferrocenium redox couple. Transmission electron micrographs were obtained by using a JEOL 200EXII electron microscope at a magnification of 200 000 ×. A 0.03 % methanolic solution of **18** was applied to a carbon-coated glass plate. After removal of the glass with HF (48 %), the coated carbon film was applied to the surface of a Ni grid and air-dried.

1,3-Bis(2,2′:6′,2″-terpyridin-4′-yl)-5-methylbenzene (3): 5-Methylbenzene-1,3-dicarbaldehyde[34] (**1**; 400 mg, 2.7 mmol) was dissolved in EtOH (50 mL) then 2-acetylpyridine (1.5 g, 12 mmol) was added, followed after 2 min by aqueous NaOH solution (5 mL, 1 M). After the dark pink solution had been stirred at 25 °C for 20 h, the solvent was evaporated in vacuo to yield a red oil, which was extracted with CH_2Cl_2. The combined extracts were washed with water, dried ($MgSO_4$), and concentrated in vacuo to give a pink solid, as an intermediate. Ammonium acetate (10 g, excess) and glacial AcOH (50 mL) were added; the mixture was refluxed for 4 h. The dark brown solution was cooled, and neutralized with aqueous Na_2CO_3 to afford a deep yellow precipitate, which was filtered, washed with hot EtOH, and purified by column chromatography (Al_2O_3). Elution with a mixture of EtOAc/hexane (1:1), followed by recrystallization gave pure bis(terpyridine) ligand **3** (320 mg, 22 % overall yield). M.p. 187–188 °C (decomp); ^1H NMR ($CDCl_3$) $\delta = 2.59$ (s, 3H; CH_3), 7.38 (dd, $J = 6$ Hz, 4H; $H^{5,5''}$), 7.82 (s, 2H; $H^{4,6}{}_{Ar}$), 7.91 (dd, $J = 8$ Hz, 4H; $H^{4,4''}$), 8.22 (s, 1H; $H^2{}_{Ar}$), 8.71 (d, $J = 8$ Hz, 4H; $H^{3,3''}$), 8.77 (d, $J = 4$ Hz, 4H; $H^{6,6''}$), 8.83 (s, 4H; $H^{3'5'}$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.60$ (CH_3), 119.24 ($C^{3'}$), 121.50 ($C^5{}_{Ar}$), 121.71 (C^3), 123.53 ($C^2{}_{Ar}$), 123.94 (C^5), 128.94 ($C^6{}_{Ar}$), 136.97 (C^4), 139.48 ($C^1{}_{Ar}$), 149.20 (C^6), 150.31 ($C^{4'}$), 155.97 (C^2), 156.20 ($C^{2'}$) ppm; IR (KBr): $\tilde{\nu} = 3051$, 3013, 2918, 2855, 1589, 1567, 1469, 1379 cm^{-1}; ESI-MS: m/z: 555 [$+H^+$]; calcd $C_{37}H_{26}N_6$ (554); elemental analysis (%): calcd: C 80.14, H 4.69, N 15.16; found: C 79.34, H 4.84, N 14.89.

3,5-Bis(2,2′:6′,2″-terpyridin-4′-yl)-1-bromobenzene (4): Bromo-bis(terpyridine) ligand **4** was synthesized (35% overall yield) by same procedure as for **3** by using 1-bromo-3,5-dicarboxaldehyde[34] as a starting material. M.p. 308–309 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.41$ (dd, $J = 6$ Hz, 4H; $H^{5,5''}$), 7.94 (dd, $J = 8$ Hz, 4H; $H^{4,4''}$), 8.15 (s, 2H; $H^{2,6}{}_{Ar}$), 8.30 (s, 1H; $H^{4}{}_{Ar}$), 8.73 (d, $J = 8$ Hz, 4H; $H^{3,3''}$), 8.78 (d, $J = 5$ Hz, 4H; $H^{6,6''}$), 8.81 (s, 4H; $H^{3',5'}$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 119.23$ ($C^{3'}$), 121.62 (C^{3}), 123.90 ($C^{4}{}_{Ar}$), 124.18 (C^{5}), 125.23 ($C^{1}{}_{Ar}$), 130.96 ($C^{2}{}_{Ar}$), 137.12 (C^{4}), 141.63 ($C^{3}{}_{Ar}$), 148.88 ($C^{4'}$), 149.33 (C^{6}), 156.10 (C^{2}), 156.33 ($C^{2'}$); ESI-MS: m/z: 620 [$+H^+$]; calcd for $C_{36}H_{23}N_6Br$ (619); IR (KBr): $\tilde{\nu} = 3050$, 3012, 1585, 1567, 1469, 1385 cm^{-1}; elemental analysis (%): calcd ($+1\,H_2O$): C 67.82, H 3.93, N 13.19; found: C 67.75, H 3.97, N 13.24.

[Ru$_2$(3)Cl$_6$] (5): *Method A*: Bis(terpyridine)ligand **3** (200 mg, 360 μmol) was added to a solution of $RuCl_3 \cdot 3H_2O$ (188 mg, 720 μmol) in EtOH (20 mL), then the suspension was refluxed for 12 h. After mixture had been cooled, the resultant dark brown solid was filtered, washed with cold EtOH, and dried in vacuo to yield the bis(Ru^{III}) adduct **5** as a dark brown solid: yield: 320 mg (92%); m.p. > 400 °C; IR (KBr): $\tilde{\nu} = 3062$, 2923, 2852, 1602, 1548, 1472, 1399 cm^{-1}. This material was used without further purification.

[Ru(6)Cl$_3$] (8): 4′-(4-Methylphenyl)-2,2′:6′,2″-terpyridine[37] (**6**; 200 mg, 620 μmol) was treated with one equivalent of $RuCl_3 \cdot 3H_2O$ (160 mg, 620 μmol) in EtOH (20 mL), as described in the above Method A, to give the desired **8** as a brown solid: yield 290 mg (87%); m.p. > 400 °C; IR (KBr): $\tilde{\nu} = 3066$, 3041, 2919, 2854, 1601, 1548, 1467, 1403 cm^{-1}. This material was used without further purification.

[Ru(6)$_2$][PF$_6$]$_2$ (9): *Method B*: Mono(terpyridine)ligand **6** (61 mg, 188 μmol) was added to a suspension of mono(Ru^{III}) adduct **8** (100 mg, 188 μmol) in MeOH (20 mL), then *N*-ethylmorpholine (500 μL) was added; the mixture was refluxed for 12 h. After the mixture had been cooled, 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, Et_2O, and aqueous acetone, then dried in vacuo to afford red microcrystals: yield: 130 mg (67%); m.p. > 400 °C; ^{1}H NMR (CD_3CN): $\delta = 2.74$ (s, 3H; CH_3), 7.37 (dd, 2H; $H^{5,5''}$), 7.62 (d, 2H; $H^{6,6''}$), 7.78 (d, 2H; $H^{3,5}{}_{Ar}$), 8.14 (dd, 2H; $H^{4,4''}$), 8.31 (d, 2H; $H^{2,6}{}_{Ar}$), 8.83 (d, 2H; $H^{3,3''}$), 9.19 (s, 2H; $H^{3',5'}$) ppm; ^{13}C NMR (CD_3CN): $\delta = 21.91$ (CH_3), 122.83 ($C^{3'}$), 125.94 (C^{3}), 128.89 (C^{5}), 129.14 ($C^{2}{}_{Ar}$), 131.77 ($C^{3}{}_{Ar}$), 135.39 ($C^{4}{}_{Ar}$), 139.47 (C^{4}), 142.52 ($C^{1}{}_{Ar}$), 149.75 ($C^{4'}$), 153.91 (C^{6}), 156.88 (C^{2}), 159.74 ($C^{2'}$) ppm; IR (KBr): 3086, 2924, 2854, 1607, 1550, 1479, 1428, 1407 cm^{-1}; UV/Vis (MeCN): $\lambda_{max} = 284$ (5.89×10^4), 310 (6.60×10^4), 486 nm (2.48×10^4); MALDI-TOF: m/z: 892 [$-PF_6$], 747 [$-2PF_6$], calcd for $C_{44}H_{34}N_6RuP_2F_{12}$ (1037); elemental analysis (%): calcd: C 50.91, H 3.28, N 8.10; found: C 50.83, H 3.36, N 8.03.

[(6)Ru(7)][PF$_6$]$_2$ (10): Bromo-mono(terpyridine)ligand **7**[38] (39 mg, 100 μmol) was added to suspension of mono(Ru^{III}) adduct **8** (53 mg, 100 μmol), following the above method B, to afford **10** as red microcrystals: yield: 95 mg (86%); m.p. > 400 °C; ^{1}H NMR (CD_3CN): $\delta = 2.56$ (s, 3H; **6**-CH_3), 7.19 (m, 4H; (**6** + **7**)-$H^{5,5''}$), 7.44 (dd, 4H; (**6** + **7**)-$H^{6,6''}$), 7.60 (d, 2H; **6**-$H^{3,5}{}_{Ar}$), 7.96 (m, 6H; (**6** + **7**)-$H^{4,4}$ + (**7**)-$H^{2,6}{}_{Ar}$), 8.11 (d, 2H; **7**-$H^{3,5}{}_{Ar}$), 8.66 (d, 4H; (**6** + **7**)-$H^{3,3''}$), 8.99 (s, 2H; **7**-$H^{3',5'}$), 9.00 (s, 2H; **6**-$H^{3',5'}$) ppm; ^{13}C NMR (CD_3CN): $\delta = 21.22$ (**6**-CH_3), 122.15 (**7**-$C^{3'}$), 122.29 (**6**-$C^{3'}$), 125.29 ((**6** + **7**)-C^3), 128.20 (**7**-C^5), 128.30 (**6**-C^5), 128.45 (**7**-$C^{3}{}_{Ar}$), 130.43 (**6**-$C^{2}{}_{Ar}$), 131.08 (**7**-$C^{2}{}_{Ar}$), 133.48 (**6**-$C^{3}{}_{Ar}$), 134.68 (**7**-$C^{1}{}_{Ar}$), 136.85 ((**6** + **7**)-$C^{4}{}_{Ar}$), 138.83 ((**6** + **7**)-C^4), 141.84 (**6**-$C^{1}{}_{Ar}$), 147.74 (**7**-$C^{4'}$), 149.20 (**6**-$C^{4'}$), 153.22 ((**6** + **7**)-C^6), 156.10 (**7**-C^2), 156.38 (**6**-C^2), 158.90 (**7**-$C^{2'}$), 159.90 (**6**-$C^{2'}$) ppm; IR (KBr): $\tilde{\nu} = 3085$, 2925, 2862, 1608, 1545, 1467, 1430, 1408 cm^{-1}; UV/Vis (MeCN): $\lambda_{max} = 286$ (5.60×10^4), 310 (5.97×10^4), 490 nm (2.38×10^4); ESI MS: m/z: 406 ($z = 2$, without counter ion) calcd for $C_{43}H_{31}N_6BrRuP_2F_{12}$ (1102); elemental analysis (%): calcd: C 46.82, H 2.77, N 7.62; found: C 46.72, H 2.82, N 7.52.

[(3)Ru$_2$(6)$_2$][PF$_6$]$_4$ (11): *Route 1*: Mono(terpyridine)ligand **6** (67 mg, 206 μmol) was added to suspension of bis(Ru^{III}) adduct **5** (100 mg, 103 μmol), following the above method B, to yield **11** as red microcrystals: yield: 130 mg (65%); m.p. 230 °C; ^{1}H NMR (CD_3CN): $\delta = 2.68$ (s, 6H; **6**-CH_3), 2.96 (s, 3H; **3**-CH_3), 7.35 (dd, 8H; (**6** + **3**)-$H^{5,5''}$), 7.62 (m, 8H; (**6** + **3**)-$H^{6,6''}$), 7.74 (d, 4H; **6**-$H^{3,5}{}_{Ar}$), 8.12 (m, 8H; (**6** + **3**)-$H^{4,4''}$], 8.28 (d, 4H; **6**-$H^{2,6}$), 8.49 (s, 2H; **3**-$H^{4,6}{}_{Ar}$), 8.82 (d, 4H; **6**-$H^{3,3''}{}_{Ar}$), 8.92 (d + s, 5H; **3**-$H^{3,3''} + H^{2}{}_{Ar}$), 9.17 (s, 4H; **6**-$H^{3',5'}$), 9.40 (s, 4H; **3**-$H^{3',5'}$) ppm; ^{13}C NMR (CD_3CN): $\delta = 20.41$, 20.77 ((**6** + **3**)-CH_3), 121.35, 121.83 ((**6** + **3**)-$C^{3'}$), 124.30, 124.51 ((**6** + **3**)-C^3), 127.50 ((**6** + **3**)-C^5), 127.70 ((**6** + **3**)-$C^{2}{}_{Ar}$), 130.26 (**6**-$C^{3}{}_{Ar}$ + **3**-$C^{6}{}_{Ar}$), 133.89 (**6**-$C^{4}{}_{Ar}$ + **3**-$C^{5}{}_{Ar}$), 138.03 ((**6** + **3**)-C^4), 141.02 ((**6** + **3**)-$C^{1}{}_{Ar}$), 147.55, 148.39 ((**6** + **3**)-$C^{4'}$), 152.46 ((**6** + **3**)-C^6), 155.34, 155.60 ((**6** + **3**)-C^2), 158.23 ((**6** + **3**)-$C^{2'}$) ppm; IR (KBr):$\tilde{\nu} = 3112$, 2923, 2856, 1606, 1547, 1467, 1429, 1405 cm^{-1}; UV/Vis (MeCN): $\lambda_{max} = 290$ (1.13×10^5), 310 (1.20×10^5), 490 nm (4.70×10^4); MALDI-TOF: m/z: 1837 [$-PF_6$], 1692 [$-2PF_6$], 1547 [$-3PF_6$], calcd for $C_{81}H_{60}N_{12}Ru_2P_4F_{24}$ (1982); elemental analysis (%): calcd ($+2\,H_2O$): C 48.16, H 3.17, N 8.32; found: C 48.14, H 3.54, N 8.52.

[(3)Ru$_2$(6)$_2$][PF$_6$]$_4$ (11): *Route 2*: Bis(terpyridine)ligand **3** (36 mg, 65 μmol) was added to a suspension of mono(Ru^{III}) adduct **8** (69 mg, 130 μmol), following the above method B, to afford **11** as red microcrystals: yield: 100 mg (77%). This sample was spectrally identical to the sample obtained by Route 1.

[Ru$_2$(3)$_3$][Cl]$_4$ (12): Bis(terpyridine)ligand **3** (114 mg, 200 μmol) was added to a suspension of the bis(Ru^{III}) adduct **5** (97 mg, 100 μmol), following the above method B, to yield the free bis(terpyridine)-terminated trimeric precursor **12** as red microcrystals: yield: 180 mg (89%); m.p. > 400 °C; ^{1}H NMR (CD_3OD): $\delta = 2.79$(s, 3H; **5**-CH_3), 2.94(s, 6H; **3**-CH_3), 7.40–9.76 (m, aromatics and terpyridines, 69H) ppm; ^{13}C NMR (CD_3OD): $\delta = 20.89$, 122.01, 122.60, 125.19, 125.69, 128.01, 130.54, 136.84, 138.51, 141.32, 148.76, 149.25, 152.40, 156.12, 158.97 ppm; IR (KBr): $\tilde{\nu} = 3069$, 2925, 2853, 1605, 1545, 1470, 1396 cm^{-1}; UV/Vis (MeCN, PF_6 counterion): $\lambda_{max} = 288$ (1.35×10^5), 310 (1.22×10^5), 492 nm (5.0×10^4); MALDI-TOF: m/z: 1864 [$-Cl_4$], calcd for $C_{111}H_{78}N_{18}Ru_2Cl_4$ (2006).

[Ru$_4$(3)$_3$][Cl]$_{10}$ (13): Trimeric precursor **12** (50 mg, 25 μmol) was added to a solution of $RuCl_3 \cdot 3H_2O$ (13 mg, 50 μmol) in EtOH (10 mL), and the suspension was refluxed for 12 h. After the mixture had been cooled, the dark red solid was filtered, washed with cold EtOH and dried in vacuo to yield **13** as a dark brown solid: yield: 45 mg (74%); m.p. > 400 °C; IR (KBr): $\tilde{\nu} = 3061$, 2923, 2866, 1604, 1540, 1469, 1395 cm^{-1}. This material was used without further purification.

One-pot synthesis of [Ru$_6$(3)$_6$][PF$_6$]$_{12}$ (14): Bis(terpyridine)ligand **3** (114 mg, 200 μmol) was added to a suspension of the bis(Ru^{III}) adduct **5** (190 mg, 200 μmol), following the above method B, to give (85%) a dark red solid, which was filtered, then purified by TLC (SiO_2; eluent: aqueous MeCN/saturated KNO_3 solution (1:7:1)). The major dark band was collected and extracted, then excess methanolic ammonium hexafluorophosphate was added to precipitate **14**, which was sequentially washed with MeOH, Et_2O, and aqueous acetone, and dried in vacuo to yield dark purple microcrystals: yield: 160 mg (43%); m.p. > 400 °C; $R_f = 0.55$; ^{1}H NMR (CD_3CN): $\delta = 2.93$ (s, 3H; CH_3), 7.31 (dd, 4H; $H^{5,5''}$), 7.62 (d, 4H; $H^{6,6''}$), 8.06 (dd, 4H; $H^{4,4''}$), 8.41 (s, 2H; $H^{4,6}{}_{Ar}$), 8.87 (d + s, 5H; $H^{3,3''} + H^{2}{}_{Ar}$), 9.37 (br, 4H; $H^{3',5'}$) ppm; ^{13}C NMR ([D_6]DMSO): $\delta = 21.54$ (CH_3), 121.83 ($C^{3'}$), 124.62 ($C^{5}{}_{Ar}$), 125.09 (C^3), 127.96 ($C^{2}{}_{Ar}$), 130.32 (C^5), 137.60 ($C^{4}{}_{Ar}$), 138.24 (C^4), 140.10 ($C^{1}{}_{Ar}$), 146.86 ($C^{4'}$), 152.24 (C^6), 155.25 (C^2), 158.14 ($C^{2'}$) ppm; IR (KBr):$\tilde{\nu} = 3074$, 2922, 2854, 1603, 1532, 1469, 1394 cm^{-1}; UV/Vis (MeCN): $\lambda_{max} = 290$ (3.22×10^5), 312 (3.37×10^5), 496 nm (1.43×10^5); MALDI-TOF: m/z: 5544 [$-1PF_5$], 5400 [$-1PF_6$—$1PF_5$], 5292[$-3PF_5$], 5166[$-4PF_5$], 5020[$-4PF_5$—$1PF_6$], calcd for $C_{222}H_{156}N_{36}Ru_6P_{12}F_{72}$ (5670); elemental analysis (%)($+8H_2O$): calcd: C 45.82, H 2.96, N 8.67; found: C 45.86, H 2.98, N 8.68.

Stepwise synthesis of [Ru$_6$(3)$_6$][PF$_6$]$_{12}$ (14): Trimeric precursor **12** (33 mg, 17 μmol) was added to a suspension of the bis(Ru^{III}) adduct **13** (40 mg, 17 μmol) in MeOH (20 mL), then *N*-ethylmorpholine (500 μL) was added and the mixture was refluxed for 12 h. The work-up afforded (ca. 80%) crude hexamer (chloride counterions), which was subjected to the above and purification processes (method B): yield: 40 mg (55% overall); the sample was identical in all respects to the above.

[(3)$_3$Ru$_6$(4)$_3$][PF$_6$]$_{12}$ (16): Bromo-bis(terpyridine)ligand **4** (43 mg, 70 μmol) was added to bis(Ru^{III}) adduct **5** (68 mg, 70 μmol), following the above method B, to give (ca. 85%) a dark red solid, which was filtered, then purified with TLC (SiO_2; eluent: aqueous MeCN/saturated KNO_3 solution (1:7:1)). The major dark band was collected and extracted, then excess methanolic ammonium hexafluorophosphate was added to precipitate **17**, which was sequentially washed with MeOH, Et_2O, and aqueous acetone, and dried in vacuo to yield dark purple microcrystals: yield: 50 mg (36%); m.p. > 400 °C; $R_f = 0.60$; ^{1}H NMR (CD_3CN): $\delta = 2.90$ (s, 3H; **3**-CH_3), 7.30 (m, 8H; (**3** + **4**)-$H^{5,5''}$), 7.60 (d, 8H; (**3** + **4**)-$H^{6,6''}$), 8.05 (dd, 8H; (**3** + **4**)-$H^{4,4''}$), 8.41 (s, 2H; **3**-$H^{4,6}{}_{Ar}$), 8.75 (s, 2H; **4**-$H^{2,6}{}_{Ar}$), 8.85 (d + s, 9H; (**3** + **4**)-

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$H^{3,3''}$ + **3**-H^{2}_{Ar}), 9.18 (s, 1H; **4**-H^{4}_{Ar}), 9.43 (s, 8H; (**3** + **4**)-$H^{3',5'}$) ppm; ^{13}C NMR ([D$_6$]DMSO): δ = 22.01 (**3**-CH_3), 122.79 ((**3** + **4**)-$C^{3'}$), 124.84 (**3**-C^{5}_{Ar}), 125.88 ((**3** + **4**)-C^{3}), 127.11 (**4**-C^{4}_{Ar}), 128.50 ((**3** + **4**)-C^{5} + **3**-C^{2}_{Ar}), 131.05 (**3**-C^{6}_{Ar}), 132.10 (**4**-C^{1}_{Ar}), 132.66 (**4**-C^{2}_{Ar}), 138.47 (**4**-C^{3}_{Ar}), 138.84 ((**3** + **4**)-C^{4}), 140.49 (**3**-C^{1}_{Ar}), 146.15 (**4**-$C^{4'}$), 147.99 (**3**-$C^{4'}$), 153.00 ((**3** + **4**)-C^{6}), 156.04 ((**3** + **4**)-C^{2}), 158.89 ((**3** + **4**)-C^{2}) ppm; IR (KBr): $\tilde{\nu}$ = 3124, 2929, 1605, 1533, 1471, 1396 cm^{-1}; UV/Vis (MeCN): λ_{max} = 290 (3.17 × 10^5), 310 (3.10 × 10^5), 496 nm (1.48 × 10^5); elemental analysis (%): ($C_{219}H_{147}N_{36}Br_3Ru_6P_{12}F_{72}\cdot 24H_2O$): calcd: C 41.73, H 3.09, N 8.00; found: C 41.62, H 2.81, N 8.29.

1,3-Diformyl-5-hydroxymethylbenzene: Lithium tri-*tert*-butoxyaluminum hydride (12.2 g, 48 mmol) was dissolved in dry THF (150 mL) and cooled to -78 °C, then a THF solution of 1,3,5-tris(chlorocarbonyl)benzene (**4**; 3.0 g, 12 mmol, 50 mL) was added dropwise over 30 minutes. The mixture was stirred for an additional 6 h at 25 °C with TLC monitoring; then water (ca. 20 mL) was added to the mixture to destroy the reducing agent, the solid was filtered and washed with EtOAc. The combined organic solution was evaporated in vacuo affording a solid, which was purified by column chromatography (SiO; elution with a (1:1) EtOAc/hexane mixture) to give **5** (33 %; 630 mg); R_f = 0.4; ^{1}H NMR: δ = 2.17 (br, 1H; CH_2OH), 4.94 (s, 2H; CH_2OH), 8.20 (s, 2H; Ar$H^{4,6}$), 8.33 (s, 1H; ArH^{2}), 10.15 (s, 2H; C*H*O); ^{13}C NMR δ 63.51 (*C*H$_2$OH), 130.03 (Ar*C*^{2}), 132.50 (Ar*C*^{4,6}), 137.01 (Ar*C*^{1,3}), 143.49 (Ar*C*^{5}), 191.25 (C=O); ESI-MS: *m*/*z*: 165 [*M* + H$^+$], calcd for $C_9H_8O_3$ (164).

1,3-Bis(2,2′:6′,2″-terpyridine-4′-yl)-5-(hydroxymethyl)benzene (17): 1,3-Diformyl-5-hydroxymethylbenzene (500 mg, 3.05 mmol) was dissolved in EtOH (50 mL), then 2-acetylpyridine (2.25 g, 18 mmol) was added, followed after 2 min by aqueous NaOH solution (5 mL, 1 M). After the dark pink solution had been stirred at 25 °C for 20 h, the solvent was evaporated in vacuo to yield a red oil, which was extracted with CH_2Cl_2. The combined extracts were washed with water, dried ($MgSO_4$), and concentrated in vacuo to give a pink solid to which a mixture of NH_4OAc (15 g) and glacial AcOH (50 mL) was added; the mixture was refluxed for 4 h. The dark brown solution was cooled, and neutralized with aqueous Na_2CO_3 to afford a deep yellow precipitate, which was filtered and purified by column chromatography (Al_2O_3; elution with a mixture (1:1) of EtOAc/hexane) to give pure bis(terpyridine) ligand **17** (23 %; 400 mg) as a colorless solid; ^{1}H NMR: δ = 5.34 (s, 2H; CH_2OH), 7.40 (dd, *J* = 6 Hz, 4H; $H^{5,5''}$), 7.94 (dd, *J* = 8 Hz, 4H; $H^{4,4''}$), 7.99 (s, 2H; $H^{4,6}_{Ar}$), 8.33 (s, 1H; H^{2}_{Ar}), 8.75 (d, *J* = 8 Hz, 4H; $H^{3,3''}$), 8.78 (d, *J* = 4 Hz 4H; $H^{6,6''}$), 8.84 (s, 4H; $H^{3',5'}$) ppm; ^{13}C NMR: δ = 66.01 (CH_3), 119.32 ($C^{3'}$), 121.53 (C^{5}_{Ar}), 123.98 (C^3), 126.24 (C^{2}_{Ar}), 128.10 (C^5), 137.15 (C^{6}_{Ar}), 137.45 (C^4), 139.93 (C^{1}_{Ar}), 148.94 (C^6), 149.81 ($C^{4'}$), 155.82 (C^2 + $C^{2'}$) ppm; IR (KBr): $\tilde{\nu}$ = 3055, 3014, 2917, 2853, 1586, 1567, 1471, 1375 cm^{-1}; ESI-MS: *m*/*z*: 571 [*M* + H$^+$], calcd for $C_{37}H_{26}N_6O$ (570); elemental analysis (%): calcd: C 77.89, H 4.56, N 14.74; found: C 77.44, H 4.54, N 14.69.

[Fe$_6$(17)$_6$][PF$_6$] (18): A MeOH solution of one equivalent of $FeCl_2\cdot 4H_2O$ (35 mg, 175 μmol, 1 mL) was added to a solution of 1,3-bis(2,2′:6′,2″-terpyridin-4′-yl)-5-(hydroxymethyl)benzene (**17**; 100 mg, 175 μmol) in MeOH/THF ((2:1) 20 mL) . The mixed solution was refluxed for 12 h. After the mixture had been cooled, the resultant deep purple solution was filtered (Celite), then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was purified by column chromatography (SiO_2; elution with a H_2O:MeCN:KNO_3 (1:7:1) solvent mixture) to afford **18** (81 %; 130 mg) as a purple solid; R_f = 0.6; ^{1}H NMR (CD_3CN): δ = 5.65 (s, 2H; CH_2OH), 7.15 (dd, 4H; $H^{5,5''}$), 7.30 (d, 4H; $H^{6,6''}$), 7.97 (dd, 4H; $H^{4,4''}$), 8.63 (s, 2H; $H^{4,6}_{Ar}$), 8.81 (d, 4H; $H^{3,3''}$), 9.46 (s, 1H; H^{2}_{Ar}), 9.51 (br, 4H; $H^{3',5'}$) ppm; ^{13}C NMR (DMSO): δ = 65.56 (CH_2OH), 121.65 ($C^{3'}$), 124.19 (C^{5}_{Ar} + C^3), 127.69 (C^{2}_{Ar}), 129.53 (C^5), 137.85 (C^{4}_{Ar}), 138.85 (C^4 + C^{1}_{Ar}), 148.51 ($C^{4'}$), 152.66 (C^6), 157.74 (C^2), 159.97 ($C^{2'}$) ppm; IR (KBr): $\tilde{\nu}$ = 3425, 3067, 2932, 1733, 1609, 1474, 1405, 1302, 1246, 1138, 842, 792 cm^{-1}; UV/Vis (MeCN): λ_{max} = 290 (3.05 × 10^5), 322 (2.11 × 10^5), 576 nm (1.29 × 10^5); elemtal analysis (%) calcd for $C_{222}H_{156}N_{36}O_6Fe_6P_{12}F_{72}$ (5495) + (16 H_2O): C 46.07, H 3.25, N 8.72; found: C 46.15, H 3.45, N 8.86.

Acknowledgements

We gratefully thank the National Science Foundation (G.R.N.: (DMR-9901393) and P.S.R.: (BIR-9420253)) and the Office of Naval Research (G.R.N.: (N00014 – 99 – 1 – 0082)). The Ohio Board of Regents are also acknowleged for financial support. Also acknowledged are the Louisiana Board of Regents Fellowship (R.C.) and a postdoctoral fellowship provided by the Korea Research Foundation (T.J.C.). We also thank Prof. Goeffrey A. Ozin and Dr. Srebri Petrov at the University of Toronto, Prof. Edwin Constable at the University of Birmingham, and Prof. Deiter Schubert of the Institute for Biophysics at JWG University in Frankfurt for insightful and helpful comments. Prof. Stephen Chang and Dr. Lei Zhu (University of Akron) are gratefully acknowledged for help with the TEM experiments.

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Received: August 24, 2001
Revised: February 18, 2002 [F3506]

  0947-6539/02/0813-2954 $ 20.00+.50/0