Towards Ordered Architectures: Self-Assembly and Stepwise Procedures to the Hexameric Metallomacrocycles [Arylbis(terpyridinyl)$_6$Fe$^{II}_{6-n}$-Ru$^{II}_n$] ($n = 0,2,3,5$)

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Abstract: Hexameric metallomacrocycles are a new class of ordered rigid-macromolecules which possess unique structural, electronic, and physical characteristics. Directed- and self-assembly methods for the construction of these stable bis(terpyridine)-based materials are investigated by using both Fe^{II} and Ru^{II} as the coordinating metals. These heterometallomacrocycles and their homocounterparts are structurally compared, and their attendant electrochemical properties are analyzed and evaluated. These studies demonstrate the potential to create stable, nanoscale, doughnut-shaped, molecular assemblies with envisioned ramifications for energy storage and release, as well as nanoscale molecular electronic and magnetic devices.

Keywords: iron · metallomacrocycles · ruthenium · self-assembly · terpyridine

Introduction

Construction of highly ordered, regularly repeating molecular architectures[1] through self-assembly techniques is of interest from a variety of supramolecular perspectives, which leads to utilitarian applications in molecular electronics,[2,5] catalysis,[6–11] luminescence,[12–15] advanced drugs,[16–22] unimolecular micelles,[21,23–28] nanoscale structures and devices,[23,29–32] and crystal engineering.[33–38] Access to such materials has been greatly facilitated by the arrival of "modular" synthetic methods[39] that allow the preparation of dendritic (fractal),[40] and other well-defined, specifically hexameric[41–51] constructs.[52–59] Primary focus of this strategy involves the use of similar monomers for the pre-determined assembly of "higher-ordered" structures that possess greater utility or differing properties to that of the monomers alone —a tenant professed by supramolecular chemistry[60] as envisioned by Lehn.[61–65]

Predicated on the stability and ubiquity of benzenoid architectures in classical carbon-chemistry, we surmised that 120° juxtaposed bis(terpyridine) moieties would facilitate the creation of "benzenoid-based" metallomacrocycles by the formation of well known pseudo-octahedral, terpyridine–metal–terpyridine [–< M >–] complexes. Development of the requisite building blocks was facilitated by standard procedures for terpyridine construction.[66,67]

Results

Recently, we reported an efficient, one-step, irreversible, high-yield assembly of stable hexagonal metallomacrocycles (**1**), based on [–< Ru >–] connectivity.[68–70] (Figure 1). In this report, we describe the extension of the synthetic procedure to mixed Fe^{II}- and Ru^{II}-based metallomacrocycles, which leads to predictable metal connectivity patterns that can be analyzed both spectroscopically and electrochemically. Benefits of using iron, as the connective metal center, include a more simplified synthetic procedure for the formation of the [–< Fe >–] complexes, without the need for the reduction step associated with the Ru^{III} to Ru^{II} transformation.

We employed the readily available bis(terpyridine) monomers that possess a 120° angle with respect to the two ligating moieties for the construction of hexagonal architectures, that possess different peripheral functional groups based on 3,5-bis(2,2′:6′,2″-terpyridin-4′-yl)toluene (**3**), which was previously reported (Scheme 1).[70] Also, as a prelude to the preparation of Fe-based hexamers, and for comparative purposes, a known [$(tpy)_2Fe^{II}$] complex[71] (**5**) was prepared

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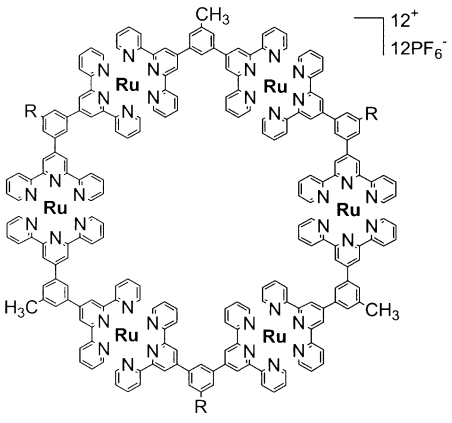
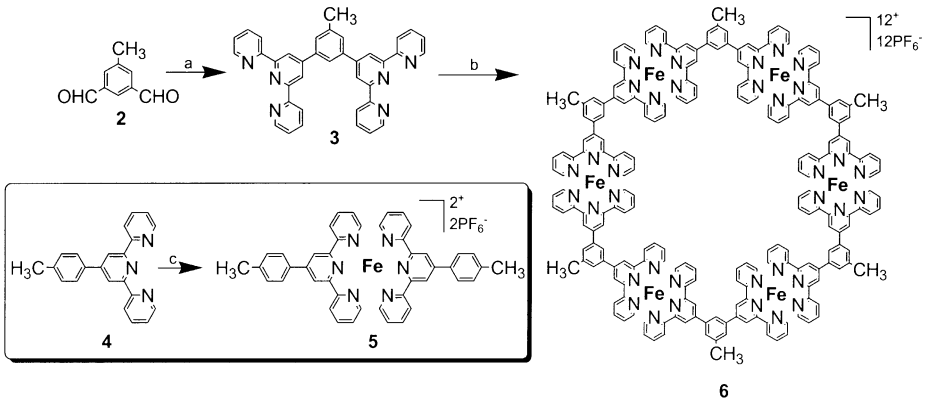


Figure 1. Hexa(Ru^{II}) complexes (–<Ru>$_6$–; **1a**, **1b**).



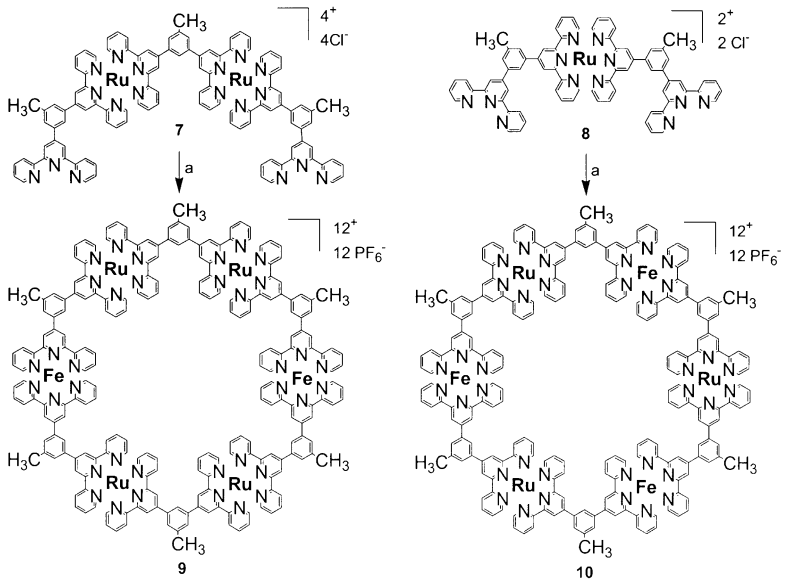
Scheme 1. a) Synthesis of a bis(terpyridine) monomer **3**: i) 4 equivs 2-acetylpyridine, NaOH, EtOH, 20 h, 25 °C; ii) NH_4OAc, AcOH, 4 h, reflux; b) Preparation of hexameric Fe^{II} complex (–<Fe>$_6$–; **6**) by a one-step procedure: i) 1 equiv $FeCl_2{\cdot}4H_2O$, MeOH/THF (4:1), 12 h, reflux; ii) MeOH, NH_4PF_6; c) Synthesis of a model terpyridine Fe^{II} complex **5**: i) 1 equiv $FeCl_2{\cdot}4H_2O$, MeOH, 12 h, reflux; ii) MeOH, NH_4PF_6.

(97 %) by using 4-(2,2′:6′,6″-terpyridin-4′-yl)toluene[72] (**4**). This complex exhibited (^{1}H NMR spectroscopy) a downfield shift for the 3′,5′-tpy*H* (s; $\delta = 9.15$, $\Delta\delta = +0.32$), and an upfield shift of the 6,6″-tpy*H* (d; $\delta = 7.17$, $\Delta\delta = -1.6$) relative to that of the starting ligand; MS (ESI-MS: 846.4, 351.1; calcd: 846.8 $[M-1PF_6]^+$, 351.1 $[M-2PF_6/z]^+$, $z = 2$) was in accord with the assigned structure.

The related diamagnetic, hexameric Fe^{II} metallomacrocycle (**6**) was prepared, through self-assembly, (>85 %) by reacting one equivalent of the corresponding bis(terpyridine) ligand[70] (**3**), with one equivalent of $FeCl_2{\cdot}4H_2O$ (Scheme 1). The spectra (^{1}H NMR) of macrocycle **6** revealed a singlet at $\delta = 2.92$ ppm for the external (peripheral) methyl moiety, which 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. Also present, was a spike at $\delta = 8.52$ for the 4,6-Ar*H* as well as notable upfield and downfield shifts for the doublets for 6,6″-tpy*H* ($\delta = 7.32$, $\Delta\delta = -1.45$) and 3′,5′-tpy*H* ($\delta = 9.48$, $\Delta\delta = +0.65$), respectively, relative to corresponding absorptions characterizing the uncomplexed (bis)terpyridine (**3**). COSY (correlation spectroscopy), NOESY (nuclear overhauser and exchange spectroscopy), and HETCOR (heteronuclear chemical-shift correlation spectroscopy) experiments were performed on the bis(terpyridine) monomer **3**, and the self-assembled metallomacrocycle **6** verifying the peak assignments and coupling patterns. UV absorption spectra of macrocycles (**6**) exhibited a 6.1 ($\varepsilon = 1.32 \times 10^5$) fold increase for measured extinction coefficients ($\lambda_{max} =$ 576 nm), due to metal-to-ligand charge-transfer (MLCT) bands,[73] relative to the analogous recorded coefficient for the Ar–<Fe>–Ar (**5**; Ar = *p*-tolyl; $\varepsilon = 2.1 \times 10^4$).

Access to more complex building blocks prompted the construction of heteronuclear (mixed Fe^{II} and Ru^{II} complexes) hexagonal macrocycles through a semi-self-assembly approach. Reaction of one equivalent of the diamagnetic bis-complex[70] **7** with one equivalent of $FeCl_2{\cdot}4H_2O$ gave macrocycle **9** (85 %), which exhibited (^{1}H NMR) two distinct singlets at $\delta = 2.89$ and 2.85 in a 2:1 ratio for the methyl groups flanked by either Ru/Fe or Ru/Ru, respectively; this was indicative of their *para*-type juxtaposition between the Fe metal centers, as well, the 6,6″-tpy*H* and 3′,5′-tpy*H* absorptions, which were also observed as two sets of resolved peaks due to the coordination spheres [$\delta = 7.55$, 8H (Ru); 7.27, 4H (Fe) and $\delta = 9.27$; 8H (Ru); 9.44, 4H (Fe)]. An additional supporting resonance that appeared at $\delta = 8.38$–8.44 (4,6-Ar*H*) was also observed as an asymmetric multiplet due to neighboring Fe and Ru coordination effects; this is in sharp contrast to the singlets recorded for the corresponding positions in the spectra of Fe hexamer **6** and the Ru hexamer **1a**.

Construction of the heteronuclear metallocycle **10** (Scheme 2), which possesses alternating Fe and Ru coordination centers was accomplished by preparation of the mono-Ru^{II}-[bis(diterpiridinyl)] dimer **8** (21 %), and reacting it with a 2:1 ratio of bis(terpyridine) (**3**) and $RuCl_3{\cdot}H_2O$ under high-dilution conditions; attempts to increase the yield of this precursor were unsuccessful, since the macrocyclization process that afforded the hexamer was competitive with simple dimer formation. The precursor **8** was purified by column chromatography (Al_2O_3), eluting a H_2O:MeCN:-KNO_3 (1:7:1) solvent mixture, to afford a pure red solid. Structural support for the bis(terpyridinyl) dimer (**8**) included (^{1}H NMR spectroscopy) resonances for the 6,6″-tpy*H* of coordinated terpyridine moiety ($\delta = 7.48$), and the analogous free-terpyridine protons ($\delta = 8.71$). Also, resonances attributed to the 4,6-Ar*H* and 3′,5′-tpy*H* positions of the singularly coordinated bis(terpyridine) units were observed as expected [$\delta = 7.96$ (1H, free), 8.48 (1H, coordinated), 8.95 (2H, free), and 9.15 ppm (2H, coordinated), respectively].



Scheme 2. Di- and mono(Ru^{II}) monomers, **7** and **8**, for the construction of heteronuclear macrocycles $-<Ru>_4-<Fe>_2$ (**9**), $-<Ru>_3-<Fe>_3-$ (**10**), respectively: a) i) 1 equiv $FeCl_2{\cdot}4H_2O$, MeOH, 12 h, reflux; ii) MeOH, NH_4PF_6.

The ESI-mass spectrum for **8** displayed a dominant molecular ion peak at $m/z = 605.0$, calcd 604.6 $[M-2Cl]^+$.

Reaction of one equivalent of $FeCl_2$ with the bis(diterpiridinyl)monoruthenium precursor **8** gave the desired alternating heteronuclear metallomacrocycle **10** (82%). The alternating architecture of **10** exhibited (^{1}H NMR, Figure 2) sig-

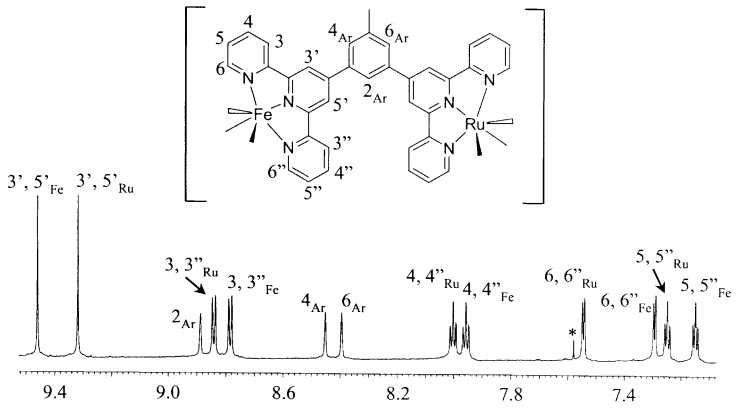


Figure 2. Aromatic region of the ^{1}H NMR (750 MHz) for the ($-<Ru>_3-<Fe>_3-$) hexamer **10** (* denotes a slight impurity).

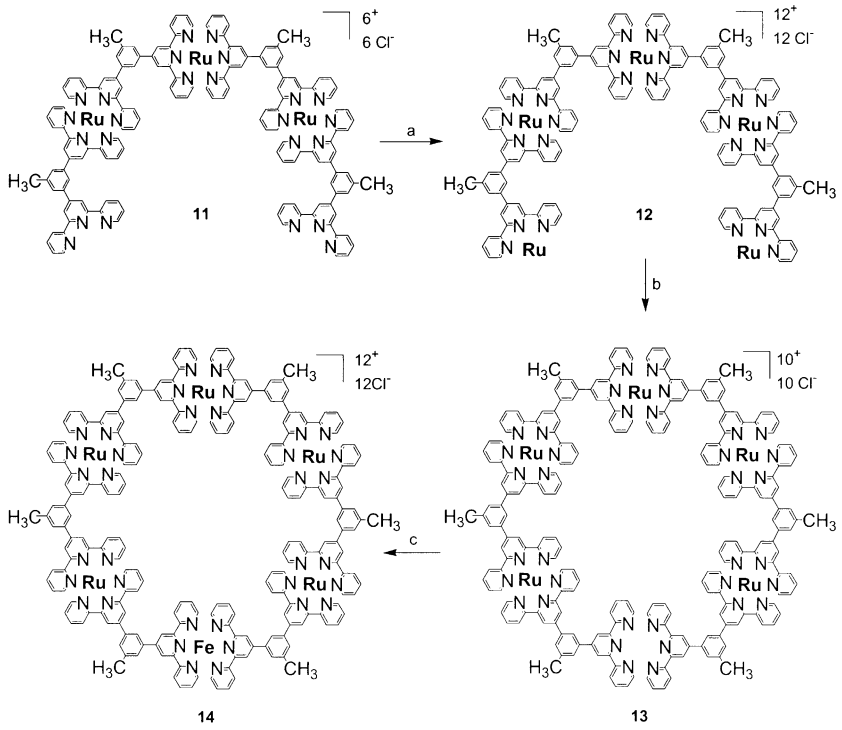
nals for the 6,6″-tpy*H* and 3′,5′-tpy*H* protons that were divided into two sets of peaks $\delta = 7.29$ (Fe), 7.55 (Ru) and 9.28 (Ru), 9.47 ppm (Fe) all integrating for two hydrogens with notable upfield (6,6“-tpy*H*, $\delta = 7.29$, Fe, $\Delta\delta = -1.42$) and downfield (3′,5′-tpy*H*, $\delta = 9.47$, Fe, $\Delta\delta = +0.52$) shifts relative to that observed for the free terpyridine moieties of **8**. Other characteristic resonances at $\delta = 8.40$–8.46, assigned to the 4,6-Ar*H*, were observed as two symmetric singlets due to neighboring Ru and Fe coordination; this is in contrast to the corresponding singlets of all Ru (**1a**) and Fe (**6**) hexamers. Proton data for the heteronuclear hexamers **9** and **10** are relative to that of the Ru (**1a**) and Fe (**6**) hexamers, as shown in Table 1.

Finally, construction, shown in Scheme 3, of the heteronuclear metallocycle **14**, which possesses one Fe and five Ru coordination centers was accomplished through preparation of the trisRu^{II}-bis(terpyridine)-tetramer (**11**, 14%) by a controlled stepwise assembly procedure of **8** with two equivalents of $RuCl_3{\cdot}H_2O$, and an excess of **3**. Structural support for the bis(terpyridinyl) tetramer (**11**) included (^{1}H NMR) two singlets at $\delta = 2.89$ and 2.75 ppm in a 1:1 ratio for the methyl groups, and two singlets at $\delta = 9.71$ and 9.45 ppm in a 3:1 ratio for the 3′,5′-tpy*H* positions. The ESI-mass spectrum displayed a peak at $m/z = 876.2$, calcd 876 $[M-3Cl]^{+3}$. Treatment of precursor **11** with two equivalents of $RuCl_3{\cdot}3H_2O$ gave the corresponding paramagnetic bis(Ru^{III}) adduct **12**, which when treated with two equivalents of **3** generated intermediate **13** whose spectral composition was complicated, but possessed terminal terpyridine signals ($\delta =$ 9.04, 8.95, 8.77, 8.69, 8.33, 7.90, 7.55 ppm). Since it would be easier to analyze the cyclic hexamer due to the instilled simplicity based on symmetry considerations, treatment of **13** with one equivalent of methanolic $FeCl_2$ gave the desired heteronuclear metallomacrocycle **14**, (85%, overall). Structural support for the metallomacrocycle **14** included (^{1}H NMR) two singlets at $\delta = 2.92$ and 2.89 ppm in a 1:2 ratio for the methyl groups flanked by either Ru/Fe or Ru/Ru, respectively, also, two singlets at $\delta = 9.91$ and 9.72 ppm in a 1:5 ratio for the 3′,5′-tpy*H* positions. The ESI-mass spectrum displayed a peak at $m/z = 682.8$, calcd 683 $[M-6Cl]^{+6}$.

Further support for the proposed structures of heteronuclear metallomacrocycles **9**, **10**, and **14** was provided by observation of their UV absorption spectra (MeCN at 25°C). All the macrocycles exhibited two MLCT bands attributed to the $-<Ru>-$ and $-<Fe>-$ complexes at λ_{max} 496 nm ($\varepsilon =$

Table 1. Correlated ^{1}H NMR data for complexes $-<Ru>_6-$ (**1a**), $-<Fe>_6-$ (**6**), $-<Ru>_4-<Fe>_2-$ (**9**), $Ru>_3<Fe>_2-$ (**10**).

	Ar_2	$Ar_{4,6}$	3′, 5′	3, 3″	4, 4″	5, 5″	6, 6″
1a	8.87, s	8.41, s	9.37, s	8.87, d	8.06, dd	7.31, dd	7.62, d
6	9.00, s	8.52, s	9.48, s	8.78, d	7.98, dd	7.17, dd	7.32, d
9	8.94, s	8.38~8.44,	9.27, s	8.79, m	8.00, m	7.27, m	7.55, d
	8.79, s		9.44, s			7.15, dd	7.27, m
10	8.89, s	8.40, s	9.28, s	8.85, d	8.00, dd	7.27, dd	7.55, d
		8.46, s	9.47, s	8.78, d	7.95, dd	7.19, dd	7.29, d



Scheme 3. Construction of the –<Ru>$_5$–<Fe>– Hexamer **14**: a) 2 equivs $RuCl_3 \cdot 3H_2O$, EtOH, 12 h, reflux; b) 2 equivs **3**, *N*-ethylmorpholine, MeOH, 12 h, reflux; c) 1 equiv $FeCl_2 \cdot 4H_2O$, MeOH, 12 h, 25 °C.

9.9×10^4, **9**; 7.44×10^4, **10**; 12.4×10^4, **14**) and 576 ($\varepsilon = 4.86\times10^4$, **9**; 5.82×10^4, **10**; 2.48×10^4, **14**), respectively. Extinction coefficients for the Ru-tpy MLCT bands of **9**, **10**, and **14** exhibited a 3.7, 3, and 5-fold increase for λ_{max} at 496 nm, respectively, relative to the analogous coefficient ($\varepsilon = 24\,800$) for the Ar–<Ru>–Ar complex (Ar = 4-tolyl, not shown). Similarly, extinction coefficients for the Ar–<Fe>–Ar MLCT bands of **9**, **10**, and **14** revealed a 2.2-, 2.7-, and 1-fold increase for λ_{max} at 576 nm, respectively, relative to the analogous coefficient for Ar–<Fe>–Ar.

An insight into the structural aspects of these stable metallohexamers is obtained by cyclic voltammetry (CV) experiments. The mono-(Fe^{II}) complex **5** and macrocycle **6** showed, as expected, very similar electrochemical responses. Figure 3b, for example, shows the voltammetric response of **6,** which exhibits two overlapped waves that according to Chow and co-workers,[74] did not correspond to the reduction of the terpyridine ligands, but to the sequential monoelectronic reduction of the iron atoms during the cathodic scan, and their corresponding oxidation processes in the anodic part of the voltammogram. Although the two waves were overlapped for the Fe redox processes, the values of the half-wave potentials for the couples Fe^{II}/Fe^{I} and Fe^{I}/Fe^{0} could be obtained by using the method of Myers and Shain.[75,76] The potential values are reported in Table 2, and revealed that the mono-(Fe^{II}) tpy complex was reduced at potentials about 25 mV more negative than their cyclic counterpart **6**, which suggests that the reduction of the macrocycle required less energy. Since the Fe reduction for both complexes was directly related to a decrease in the electrostatic interaction that holds the organometallic complexes together, less energy was required to diminish the electrostatic stability of macrocycle **6** relative to the mono com-

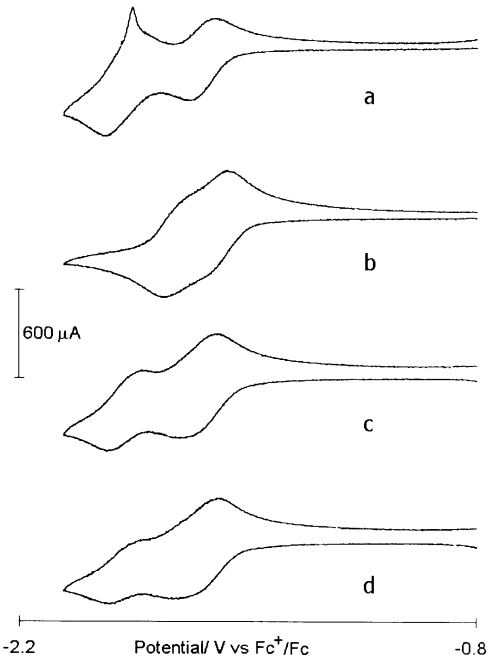


Figure 3. CV responses of approximately 1 mM solutions of a) **1a**, b) **6**, c) **9**, and d) **10** in 0.1 M Bu_4NBF_4 and DMF ($\tilde{\nu} = 100\ mV\,s^{-1}$, 298 K) by using a graphite-working electrode. All potentials are referenced against the potential of the ferrocenium/ferrocene couple.

Table 2. Cyclic voltammetry (CV) data for complexes –<Ru>$_6$– (**1a**), –<Fe>– (**5**), –<Fe>$_6$– (**6**), –<Ru>$_4$<Fe>$_2$– (**9**), –<Ru>$_3$<Fe>$_3$– (**10**), and <Ru>$_5$<Fe>– (**14**) in 0.1 M Bu_4NBF_4 and DMF ($\tilde{\nu}$ = 100 mV s^{-1}, 298 K).

	$E_{1/2}(\Delta Ep)$ [V]			
	Fe^I/Fe^0	Fe^{II}/Fe^I	Fe^{III}/Fe^{II}	Ru^{III}/Ru^{II}
5	−1.734 (0.058)	−1.594 (0.058)	0.766 (0.058)	
6	−1.709 (0.058)	−1.569 (0.058)	0.657 (0.083)	
9[a]			0.655 (0.081)	0.810 (0.091)
10[a]			0.655 (0.083)	0.808 (0.090)
14[a]			0.654 (0.083)	0.807 (0.090)
1a	adsorption, −1.622 (0.075)			0.798 (0.091)

[a] Combination of peaks due to the overlap of the Fe- and Ru-terpyridine responses.

plex. These results could be explained in terms of the macrocyclic rigidity of **6** which, relative to its smaller mono(Fe) counterpart, should favor the electrochemical reduction of the Fe cations.

Electrochemical experiments with the binuclear metallomacrocycles **9**, **10**, and **14** in the same potential region showed a voltammetric response with characteristics similar to homo-metallic constructs **6** and **1a**. The voltammogram of **9** (i.e., Figure 3c) shows two waves, of which the first is particularly wide. Comparison of this voltammogram with those of homo-metallic complexes (**1a** and **6**, Figure 3a and b, respectively) suggested that, since the most positive peak was actually a combination of three closely-spaced signals that corresponded to two Fe and one terpyridine related processes, the second wave should be due to the redox activity of one of the terpyridine units non-covalently bonded to the Ru atoms. Peak assignments were further supported by the voltammetric response of complex **10**, which as observed in Figure 3d, was characterized by two waves that appeared at roughly the same potentials of those for **9**, but displayed different relative sizes. The shape of the voltammetric response of **10** appeared as the sum of those showed by the homonuclear complexes, and the observed difference in the relative currents was consistent with the proposed chemical structures of the heterometallomacrocycles **9** and **10**. Thus, complex **10** has one less Ru atom than **9**, and therefore exhibited a smaller relative current in the most negative wave, which, according to the results obtained for **1a**, was a signal associated with the reduction of one of the terpyridine moieties that surrounds a Ru atom (see Figure 3a). Complementary to this observation, the most positive wave for **10** clearly showed a larger relative current that was consistent with the fact that this species had one more Fe atom than complex **9**.

Notably, substitution of two and three Ru atoms for Fe metallic centers changed the structure reduced products in such a way that, in contrast to **1a**, the resulting neutral species did not adsorb on the electrode surface (see Figure 3a).[70] The voltammetric behavior of these complexes was also explored in the potential region in which the metallic centers were oxidized to the M^{3+} state. The Ru and Fe atoms in complexes **1a** and **6** showed redox waves at potentials separated by about 140 mV. The corresponding data, presented in Table 2, further revealed that their half-wave potential was less positive than those of their smaller mono(Ru) (0.832 V)[70] and mono(Fe) counterparts, as well as, their peak-to-peak separation, which was larger than the ~60 mV ΔEp that characterized the reversible electron-transfer processes for the mono-metallic building blocks. These observations were consistent with the improved basicity that the resonant macrocyclic structure of **1a** and **6** supplied to the terpyridine units,[77] and a small chemical grouping between the electroactive centers; this consequently resulted in the larger peak-to-peak separation.[78] The CV experiments with the binuclear macrocycles **9** and **10** further confirmed their proposed chemical structure. The voltammetric response of these complexes showed two redox waves positioned at the potentials that characterized the electrochemical signals of the Ru and Fe metals. Furthermore, the relative currents associated with these waves clearly indicate that the relative amounts of Ru and Fe atoms in each complex correspond to those of their chemical structure. Thus, since **9** exhibited a larger relative Ru associated current at the more positive wave, macrocycle **10** showed approximately the same current for the Fe and Ru redox processes.

Conclusion

The self-assembly of hexameric architectures, which employ both –<Ru>– and –<Fe>– connectivity, and results in stable heteronuclear metallomacrocycles has been achieved. Their stepwise construction permits the specific introduction of different metal centers, coupled with the ability to tailor the periphery of the hexamacrocycles; this afforded entry into novel shape-persistent architectures and cores for dendritic construction. The reversible redox characteristics of this family of metallohexamers suggests that they are ideal candidates for electron storage. The intra- and intermolecular electron transfer and related supramolecular properties are currently being evaluated.

Experimental Section

Materials and methods: Chemicals were purchased from Aldrich and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets precoated with aluminum oxide IB-F or silica gel IB2-F (Baker-flex), and visualized by UV light. Column chromatography was conducted by using neutral/basic alumina, Brockman Activity I (60–325 mesh), or silica gel (60–200 mesh) from Fisher Scientific. Melting points were determined on an Electrothermal 9100 heater. ^1H and ^{13}C NMR spectra were recorded on Bruker DPX250 and Varian Unity Inova750 spectrometers; all samples were run in $CDCl_3$, except where noted. IR spectra were recorded on an ATI Matheson Genesis FTIR spectrophotometer. Absorption spectra were measured in MeCN solution at 25 °C with a Hewlett–Packard 8452A diode array spectrophotometer. Mass spectra were obtained on Bruker Esquire API Electrospray Ion-trap mass spectrometer. The electrochemical experiments were

performed by using a PGZ301 Potentiostat, which was programmed and controlled by means of a computer loaded with the Voltamaster 4 software (Radiometer, Copenhagen). Resistance compensation for all the experiments was automatically computed and corrected by the software in the "static automatic" mode. All the cyclic voltammetry measurements were conducted in anhydrous DMF solutions, that contained an electroactive compound (~1.0 mM) and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4, 0.1 M), as the 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 alumina and diamond polishing compound 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 minutes before each measurement in order to deoxygenate the solution. All the potentials reported in this work were measured against the ferrocene/ferrocenium redox couple.

[Fe(4)$_2$][PF$_6$]$_2$ (5): This compound was prepared in 97% yield by a reported procedure.[71]

[Fe$_6$(3)$_6$][PF$_6$]$_{12}$ (6): The MeOH solution of 1.0 equiv of $FeCl_2 \cdot 4H_2O$ (36 mg, 181 μmol, 1 mL) was added to a solution of 3,5-bis(2,2′:6′,2″-terpyridin-4′-yl)toluene[70] (**3**; 100 mg, 181 μmol) in MeOH/THF (4:1, 20 mL), then the mixed solution was refluxed for 12 h. After cooling, the resultant deep-purple solution was filtered (celite), and a slight excess of methanolic NH_4PF_6 was added to precipitate the complex, which was column chromatographed (SiO_2) by eluting a H_2O/MeCN/KNO_3 (1:7:1) solvent mixture. After chromatography, methanolic NH_4PF_6 was added to give **6** (86%) as a microcrystalline purple solid: 140 mg; m.p. >400 °C; R_f = 0.6; ^{1}H NMR (CD_3CN): δ = 2.92 (s, 3H; CH_3), 7.17 (dd, 4H, tpy$H^{5,5''}$), 7.32 (d, 4H, tpy$H^{6,6''}$), 7.98 (dd, 5H; tpy$H^{4,4''}$), 8.52 (s, 2H, Ar$H^{4,6}$), 8.78 (d, 4H; tpy$H^{3,3''}$), 9.00 (s, 1H; ArH^2), 9.48 ppm (br s, 4H, tpy$H^{3',5'}$); ^{13}C NMR (DMSO): δ = 22.16 (CH_3), 121.32 (tpy$C^{3'}$), 123.78 (ArC^5 + tpyC^3), 127.32 (ArC^2), 130.35 (tpyC^5), 137.05 (ArC^4), 138.52 (tpyC^4), 140.10 (ArC^1), 148.50 (tpy$C^{4'}$), 152.35 (tpyC^6), 157.48 (tpyC^2), 159.63 ppm (tpy$C^{2'}$); IR (KBr): $\tilde{\nu}$ = 3411, 3067, 2928, 1701, 1608, 1540, 1473, 1400, 1034, 840, 788 cm^{-1}; UV/Vis (MeCN) λ_{max} (ε) = 290 (3.21×10^5), 322 (2.13×10^5), 576 nm (1.32×10^5); elemental analysis calcd for (%) $C_{222}H_{156}N_{36}Fe_6P_{12}F_{72}$ (5399) + (12 H_2O): C 47.44; H 3.20; N 8.97; found: C 46.94, H 3.02, N 8.82.

[Ru(3)$_2$]Cl$_2$ (8): Bis(terpyridine)ligand (**3**) (200 mg, 360 μmol) was dissolved in *n*-pentanol (600 mL) at 110 °C, then a solution of $RuCl_3 \cdot 3H_2O$ (74 mg, 360 μmol) in *n*-pentanol (225 mL) was added drop wise. The mixture was heated for 12 h at 110 °C. After the solvent was removed in vacuo, a solution of bis(terpyridine) (**3**) (200 mg, 360 μmol) and *N*-ethylmorpholine (0.1 mL) in MeOH (500 mL) was added, and then refluxed for another 12 h. After the solvent and volatiles were removed in vacuo, the residue was column chromatographed (Al_2O_3) eluting a H_2O/MeCN/KNO_3 (1:7:1) solution to give red solid **8** (21%), which was dried: 50 mg; 320 °C; ^{1}H NMR (CD_3CN): δ = 2.70 (s, 3H, CH_3), 7.21 (dd, 2H; tpy$H^{5,5''}$, coordinated), 7.48 (m, 4H; tpy$H^{5,5''}$, free + tpy$H^{6,6''}$, coordinated), 7.96 (m, 5H; tpy$H^{4,4''}$, both + Ar$H^{4,6}$, free), 8.19 (s, 1H; ArH^2), 8.48 (s, 1H; Ar$H^{4,6}$, coordinated), 8.71 (d, 2H; tpy$H^{6,6''}$, free), 8.74 (br, 4H; tpy$H^{3,3''}$, both), 8.95 (s, 2H; tpy$H^{3',5'}$, free), 9.15 ppm (s, 2H, tpy$H^{3',5'}$, coordinated); ^{13}C NMR (CD_3CN) δ = 21.78, 119.73, 122.12, 122.85, 124.79, 125.42, 125.67, 128.38, 130.32, 131.20, 138.38, 138.88, 140.52, 141.46, 148.60, 150.19, 151.30, 153.31, 156.31, 157.04, 159.17 ppm; ESI-MS: *m*/*z*: 605.0 ([*M* − 2Cl], *z* = 2, calcd 604.6).

[Ru$_4$(3)$_6$Fe$_2$][PF$_6$]$_{12}$ (9) The MeOH solution of 1.0 equiv of $FeCl_2 \cdot 4H_2O$ (5.4 mg, 27 μmol, 1 mL) was added to a solution of $[Ru_2(\mathbf{3})_3][Cl]_4$[70] (**7**; 55 mg, 27 μmol) in MeOH (10 mL), then following the above general procedure, gave precipitate **9** (85%) as a microcrystalline purple solid: 55 mg; m.p. >400 °C; R_f = 0.6; ^{1}H NMR (CD_3CN): δ = 2.85 (s, 3H; CH_3, Ru/Ru), 2.89 (s, 6H; CH_3, Ru/Fe), 7.15 (dd, 4H; tpy$H^{5,5''}$, Fe), 7.27 (m, 12H, tpy$H^{5,5''}$, Ru + tpy$H^{6,6''}$, Fe), 7.55 (d, 8H; tpy$H^{6,6''}$, Ru), 8.00 (m, 12H; tpy$H^{4,4''}$), 8.38–8.44 (m, asymm., 6H; Ar$H^{4,6}$), 8.79 (br, m + s, 14H; tpy$H^{3,3''}$ + ArH^2, Ru/Fe), 8.94 (s, 1H; ArH^2, Ru/Ru), 9.27 (s, 8H; tpy$H^{3',5'}$, Ru), 9.44 ppm (s, 4H, tpy$H^{3',5''}$, Fe); ^{13}C NMR (DMSO): δ = 21.75 (CH_3), 121.89 (tpy$C^{3'}$), 124.41 (ArC^5 + tpyC^3, Fe), 125.19 (ArC^5 + tpyC^3, Ru), 128.04 (ArC^2), 130.33 (tpyC^5), 137.78 (ArC^4), 138.40 (tpyC^4, Ru), 139.16 (tpyC^4, Fe), 140.31 (ArC^1), 147.00 (tpy$C^{4'}$, Ru), 148.85 (tpy$C^{4'}$, Fe), 152.36 (tpyC^6), 155.41 (tpyC^2, Ru), 158.27 (tpyC^2, Fe + tpy$C^{2'}$, Ru), 160.27 ppm (tpy$C^{2'}$, Fe); IR (KBr): $\tilde{\nu}$ = 3429, 3071, 2920, 1605, 1538, 1471, 1396, 1302, 1140, 839, 786 cm^{-1}; UV/Vis (MeCN) λ_{max} (ε) = 290 (3.10×10^5), 310 (3.10×10^5), 496 (9.20×10^4), 576 nm (4.86×10^4); elemental analysis calcd (%) for $C_{222}H_{156}N_{36}Ru_4Fe_2P_{12}F_{72}$ (5580): C 47.74, H 2.80, N 9.03; found. C 48.01, H 3.16, N 8.72.

[Ru$_3$(3)$_6$Fe$_3$][PF$_6$]$_{12}$ (10): The MeOH solution of 1.0 equiv of $FeCl_2 \cdot 4H_2O$ (15.5 mg, 78 μmol, 1 mL) was added to a solution of $[Ru(\mathbf{3})_2][Cl]_2$ (**8**; 100 mg, 78 μmol) in MeOH (20 mL), then following the above general procedure, gave **10** (82%), as a microcrystalline purple solid: 100 mg; m.p. >400 °C; R_f = 0.6; ^{1}H NMR (CD_3CN): δ = 2.86 (s, 3H; CH_3), 7.19 (dd, 2H; tpy$H^{5,5''}$, Fe), 7.27 (dd, 2H; tpy$H^{5,5''}$, Ru), 7.29 (d, 2H; tpy$H^{6,6''}$, Fe), 7.55 (d, 2H; tpy$H^{6,6''}$, Ru), 7.95 (dd, 2H; tpy$H^{4,4''}$, Fe), 8.00 (dd, 2H; tpy$H^{4,4''}$, Ru), 8.40 (s, 1H; Ar$H^{4,6}$, Ru), 8.46 (s, 1H; Ar$H^{4,6}$, Fe), 8.78 (d, 2H; tpy$H^{3,3''}$, Fe), 8.85 (d, 2H; tpy$H^{3,3''}$, Ru), 8.89 (s, 1H; ArH^2), 9.28 (s, 2H; tpy$H^{3',5''}$, Ru), 9.47 ppm (s, 2H; tpy$H^{3',5'}$, Fe); ^{13}C NMR (DMSO): δ = 21.55 (CH_3), 121.75 (tpy$C^{3'}$), 124.34 (ArC^5 + tpyC^3, Fe), 125.02 (ArC^5 + tpyC^3, Ru), 127.93 (ArC^2), 130.63 (tpyC^5), 137.53 (ArC^4), 138.28 (tpyC^4, Ru), 138.95 (tpyC^4, Fe), 140.23 (ArC^1), 146.83 (tpy$C^{4'}$, Ru), 148.96 (tpy$C^{4'}$, Fe), 152.77 (tpyC^6), 155.24 (tpyC^2, Ru), 158.27 (tpyC^2, Fe), 158.08 (tpy$C^{2'}$, Ru), 160.11 ppm (tpy$C^{2'}$, Fe); IR (KBr): $\tilde{\nu}$ = 3426, 3077, 2921, 1606, 1540, 1471, 1397, 1300, 1140, 840, 787 cm^{-1}; UV/Vis (MeCN) λ_{max} (ε) = 290 (2.56×10^5), 310 (2.49×10^5), 496 (7.44×10^4), 576 nm (5.82×10^4); elemental analysis calcd (%) for $C_{222}H_{156}F_{72}Fe_3N_{36}P_{12}Ru_3$ (5538.17) + (6 H_2O): C 47.22, H 2.99, N, 8.93; found: C 47.20, H 2.93, N 8.97.

[Ru$_3$(3)$_4$]Cl$_6$ (11): $RuCl_3 \cdot 3H_2O$ (37 mg, 180 μmol) was added to a solution of bis(terpyridine)ligand (**3**) (200 mg, 360 μmol) in MeOH/THF (2:1, 100 mL), then the solution was refluxed for 12 h. After concentration in vacuo, the residue was column chromatographed (Al_2O_3) eluting MeOH to give the product upon solvent removal. The solid was washed with hot $CHCl_3$, then dried in vacuo to yield **11** (14%), as a red solid: 140 mg; m.p. >400 °C; ^{1}H NMR (CD_3OD): δ = 2.75 (s, 6H; CH_3, coordinated), 2.89 (s, 6H; CH_3, free), 7.33–7.38 (dd, 12H; tpy$H^{5,5''}$, coordinated), 7.54 (br, 4H; tpy$H^{5,5''}$, free), 7.63–7.65 (d, 4H; tpy$H^{6,6''}$, coordinated-inside), 7.68–7.69 (d, 8H; tpy$H^{6,6''}$, coordinated-outside), 8.06–8.08 (d, 16H; tpy$H^{4,4''}$, both), 8.35 (s, 2H; ArH^2, free), 8.47 (s, 2H; ArH^4, free), 8.69 (s, 2H; ArH^6, free), 8.75 (d, 4H; tpy$H^{3,3''}$, free), 8.94 (s, 4H; Ar$H^{4,6}$, coordinated), 9.02–9.04 (d, 4H; tpy$H^{6,6''}$, free), 9.20 (s, 2H; ArH^2, coordinated), 9.24–9.27 (d, 12H; tpy$H^{3,3''}$, coordinated), 9.45 (s, 4H; tpy$H^{3',5'}$, free), 9.71 ppm (s, 12H, tpy$H^{3',5'}$, coordinated); ^{13}C NMR (CD_3OD): δ = 21.92, 22.03, 120.21, 123.14, 123.32, 123.76, 125.16, 125.94, 126.39, 126.84, 129.15, 129.68, 130.70, 131.68, 139.27, 139.65, 139.82, 141.11, 142.30, 142.48, 149.95, 150.35, 151.34, 153.50, 157.24, 157.64, 159.97, 160.09 ppm. ESI-MS: *m*/*z*: 876.2 ([*M* − 3Cl], *z* = 3; calcd 876).

[Ru$_5$(3)$_4$]Cl$_{12}$ (12): The tetrameric precursor **11** (30 mg, 10 μmol) was added to a solution of $RuCl_3 \cdot 3H_2O$ (4 mg, 20 μmol) in EtOH (30 mL), and the mixture was refluxed for 12 h. After cooling, the dark red solid was filtered, washed with cold EtOH, and dried in vacuo to yield **14** as a dark brown solid: yield: 33 mg (98%); m.p. >400 °C; IR (KBr) $\tilde{\nu}$ = 3061, 2923, 2866, 1604, 1540, 1469, 1395 cm^{-1}. This material was used without further purification.

[Ru$_5$Fe(3)$_6$]Cl$_{12}$ (14): Bis(terpyridine)ligand **3** (12 mg, 20 μmol), was added to a suspension of bis(Ru^{III}) adduct **12** (33 mg, 10 μmol) in MeOH, then *N*-ethylmorpholine (100 μL) was added; the mixture was then refluxed for 12 h. After cooling, the resulting deep red solution was concentrated and dialyzed with a 3500 MWCO RC dialysis membrane in 98% MeOH. After two days, the red solution inside the membrane was evaporated and dried in vacuo to give intermediate **13** (95%) as a red solid (42 mg); this showed a complex NMR pattern, but indicated the presence of the terpyridine termini, and thus was used without further characterization. An MeOH solution of 1.0 equiv of $FeCl_2 \cdot 4H_2O$ (2 mg, 10 μmol, 1 mL) was added to a stirred solution of the linear penta(Ru^{II}) complex **13** (42 mg, 10 μmol) in MeOH (20 mL), and was maintained at 25 °C for 12 h. By following the above procedure, **14** (90%) was produced as a red solid: 36 mg; m.p. > 400 °C; R_f = 0.5; ^{1}H NMR (CD_3OD): δ = 2.89 (s, 12H; CH_3, Ru/Ru), 2.92 (s, 6H; CH_3, Ru/Fe), 7.37 (m, 24H, tpy$H^{5,5''}$, both), 7.68 (br, 24H; tpy$H^{6,6''}$, both), 8.10 (br, 24H, tpy$H^{4,4''}$, both), 8.48 (s, 8H; Ar$H^{4,6}$, Ru/Ru), 8.53–8.60 (2 s, 4H; Ar$H^{4,6}$, Ru/Fe), 9.25 (d + s, 30H; tpy$H^{3,3''}$ + ArH^2, both), 9.72 (s, 20H; tpy$H^{3',5'}$, Ru), 9.91 ppm (s, 4H; tpy$H^{3',5'}$, Fe); ^{13}C NMR (DMSO): δ = 22.02 (CH_3, Ru/Ru), 30.84 (CH_3, Ru/Fe), 123.71 (C$^{3'}$), 126.80 (ArC^5 + tpyC^3, Fe), 129.12 (ArC^2), 131.62 (tpyC^5), 139.64 (ArC^4), 139.78 (tpyC^4), 142.48 (ArC^1), 149.89 (tpy$C^{4'}$, Ru), 153.42 (tpyC^6), 157.20 (tpyC^2, Ru), 160.02 (tpy$C^{2'}$, Ru),

162.11 (tpyC^2, Fe), 165.79 ppm (tpy$C^{2'}$, Fe); ESI-MS: m/z: 682.8 ([$M-6$Cl], $z=6$; calcd 683).

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