Construction of triangular metallomacrocycles: [M_3(1,2-bis(2,2′:6′,2″-terpyridin-4-yl-ethynyl)benzene)$_3$] [M = Ru(II), Fe(II), 2Ru(II)Fe(II)]†

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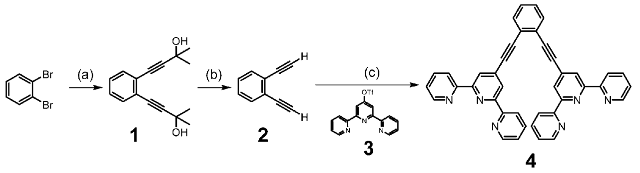
Complexation of a predesigned (1,2-bis(2,2′:6′,2″-terpyridin-4-yl-ethynyl)benzene) ligand possessing a 60° angle between two terpyridines with transition metals [Fe(II) and Ru(II)] afforded the self-assembled, triangular metallomacrocycles.

It has been well documented that the self-assembly of supramolecular species[1] is based on a combination of the inherent structural information, such as the ligand juxtapositioning, incorporated within the polytopic building blocks. Stang,[2] Fujita,[3] Atwood,[4] and others[5–7] 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 metallohexamers[8–10] based on the formation of six tpy–Ru(II)–tpy (where tpy = terpyridine) bonds, especially since this mode of connectivity is not reversible under normal reaction conditions; in general, intramolecular reactions were found to be favored over intermolecular. Rigid cyclic trimetallic complexes with metal–metal bonds or bridging ligands are known[11] and their formation has been shown to be influenced by several factors, including concentration,[12,13] stoichiometry[14] or the presence of a template.[13] Metallotriangles utilizing tpy–metal(II)–tpy connectivity are largely unknown.

Herein, we report the logical extension of this metallomacrocycle formation involving the preparation of bis(terpyridine) monomer **4** whereby 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.

Construction (Scheme 1) of the desired angular building block, 1,2-bis(2,2′:6′,2″-terpyridin-4-yl-ethynyl)benzene **4** started with ethynylation of 1,2-dibromobenzene to give diol **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[15] (4-tpyOTf; **3**) *via* a palladium-catalyzed cross coupling using [$(C_6H_5)_3]_4$Pd(0) in base solvent, to yield (41%) **4**, as an air-stable, off-white solid. Vapor diffusion of hexane into a $CHCl_3$ solution of **4** afforded a single crystal for X-ray analysis.‡ The ORTEP representation of **4** (Fig. 1) confirms the desired angle of directionality (*ca.* 62°) between the ligands. One terpyridine lies approximately in the same plane as the benzene moiety; the other terpyridine is tilted *ca.* 30° out of this plane and the alkyne connections are linear.



Scheme 1 *Reagents and conditions*: (a) 2-methyl-3-butyn-2-ol, $Pd(dba)_2$, PPh_3, CuI, Et_3N; (b) KOH, MeOH/toluene; (c) $Pd(PPh_3)_4$, $^iPr_2NH$/toluene.

Reaction of a 1 : 1 mixture of ligand **4** and $FeCl_2·4H_2O$ in MeOH for 24 h at 25 °C (Scheme 2) gave the self-assembled triangular Fe(II) metallomacrocycle **5**, which revealed (^{1}H 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, $\Delta\delta$ = −1.48) arising from the 6,6″-tpy*H*s and downfield shift for the 3′,5′-tpy*H* signals (δ = 9.19, $\Delta\delta$ = 0.54). Other diagnostic spectral attributes (^{13}C NMR) included the two distinct peaks at δ = 91.5 and 96.3 for the acetylene carbons. COSY and HETCOR spectra of the bis(terpyridine) **4** and the self-assembled macrocycle **5** further verified the peak assignments and the coupling patterns. This

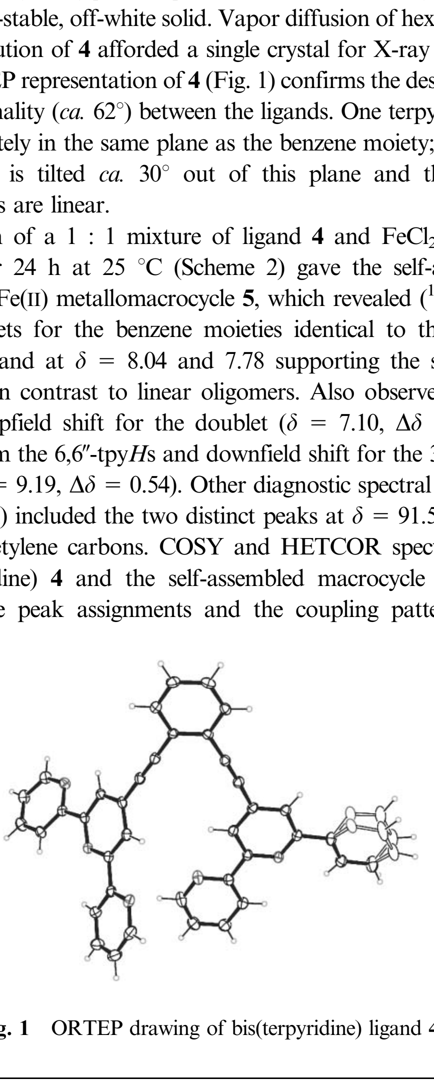


Fig. 1 ORTEP drawing of bis(terpyridine) ligand **4**.

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† Electronic supplementary information (ESI) available: NMR, Mass, UV and elemental analysis data for **4**, **5**, **6** and **9**. See http://www.rsc.org/suppdata/cc/b4/b409348h/

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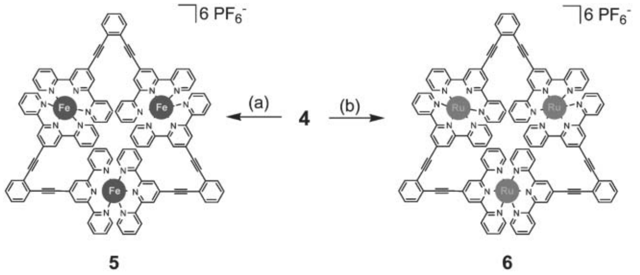
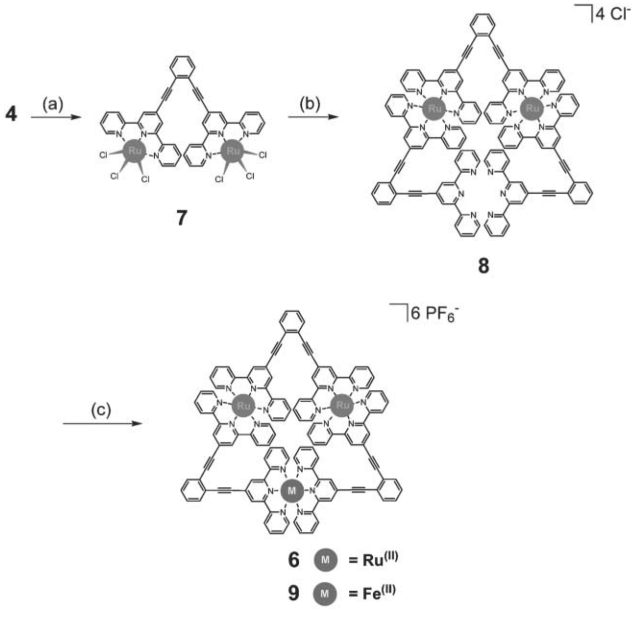


Scheme 2 *Reagents and conditions*: (a) i) $FeCl_2·4H_2O$, MeOH, ii) NH_4PF_6/MeOH; (b) i) $RuCl_2·(DMSO)_4$, MeOH, reflux, ii) NH_4PF_6/MeOH.

triangular structure was further established by ESI-MS by 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 phenomenon.[16] While metallomacrocycle **5**, initially isolated as the 6 Cl^- salt, exhibited solubility in MeOH and hot H_2O, its conversion to the 6 PF_6^- salt facilitated solubility in MeCN, acetone, DMF, and DMSO.

The self-assembled Ru(II) counterpart **6** was prepared by treatment of MeOH solution of monomer **4** with one equiv. of $RuCl_2·(DMSO)_4$ over 36 h at 50 °C. The initial desired trimer was obtained in approximately 70% yield, but after column chromatography followed by counterion exchange (Cl^- to PF_6^-), pure macrocycle **6** 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 (δ = 7.35, $\Delta\delta$ = −1.23) of 6,6″-tpy*H*s, and the 3′,5′-tpy*H*s (δ = 9.01, $\Delta\delta$ = 0.36), along with definitive ESI-MS data (*m*/*z* = 2796.4 $[M + H - PF_6^-]^+$), all support the structural assignment.

A stepwise approach (Scheme 3) was also undertaken, in which the diamagnetic $[Ru_2(\mathbf{4})_2][4Cl^-]$, **8**, was prepared by treatment of bis-Ru(III) adduct **7** 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 $RuCl_2·(DMSO)_4$ with refluxing afforded the corresponding metallomacrocycle **6**. Structural supports (^{1}H NMR, ^{13}C NMR, mass spectrometry) for the metallomacrocycle were obtained giving the same results as with previous **6** made by the self-assembly method. This procedure might also permit the specific introduction of different metal centers (*i.e.*, Os, Fe, Zn) in the periphery. In order to show another example, reaction of one equiv. of $FeCl_2·4H_2O$ with the diamagnetic bis-complex **8** has been conducted to obtain the desired heteronuclear metallomacrocycle **9**. The heteronuclear architecture of **9** exhibited (^{1}H NMR) signals for the 3′,5′-tpy*H* protons that were split into three kinds of peaks at δ = 9.18 (Fe), 9.05 (Fe/Ru), 9.01 (Ru) ppm in a 1 : 1 : 1 ratio. Also, there were two doublets at δ = 6.93 (Ru), 6.87 (Fe) ppm in a 2 : 1 ratio for the 5,5″-tpy*H*s position as additional supporting resonance. The mass spectrum displayed the signals of multiple-charged entities ranging from *m*/*z* = 1302.1 $[M - 2PF_6^-]^{2+}$ to 337.3 $[M - 6PF_6^-]^{6+}$charge states.



Scheme 3 *Reagents and conditions*: (a) $RuCl_3·3H_2O$, MeOH, reflux; (b) 2 equiv. **4**, *N*-ethylmorpholine, MeOH, reflux; (c) i) $RuCl_2·(DMSO)_4$ or $FeCl_2·4H_2O$, MeOH, reflux, ii) NH_4PF_6/MeOH.

Absorption spectra recorded for ethynyl-substituted complexes in dilute CH_3CN solution exhibit the expected absorption transitions; in the case of **5**, an intense ligand-centered π–π* transition of terpyridine moieties is clearly apparent at λ_{max} = 283 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 as the promotion of an electron from the metal-centered *d*-orbitals to an unfilled ligand-centered π* orbital[17] has a maximum (λ_{max}) around 578 nm with molar absorption coefficients at the peak of *ca.* 6.43×10^4 dm^3 mol^{-1} cm^{-1} per Fe(II)-triangle. Similarly, triangle **6** exhibited two ligand-centered π–π* transitions of terpyridine moieties and an MLCT at λ_{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 compound **9** exhibited two metal–ligand charge transfer (MLCT) bands attributed to the Ru(II)- and Fe(II)-complexes at λ_{max} = 499 nm ($\varepsilon = 5.86 \times 10^4$), 582 nm ($\varepsilon = 2.38 \times 10^4$), respectively. This observation of its UV absorption spectrum may serve the proposed structure of heteronuclear metallomacrocycle **9** as further supporting information.

The cyclic voltammogram (CV) of a 0.11 mM solution of the Ru(II) triangle **6** in MeCN is shown in Fig. 2(b). Two terpyridine ligand-centered reductions and one oxidation of the ruthenium

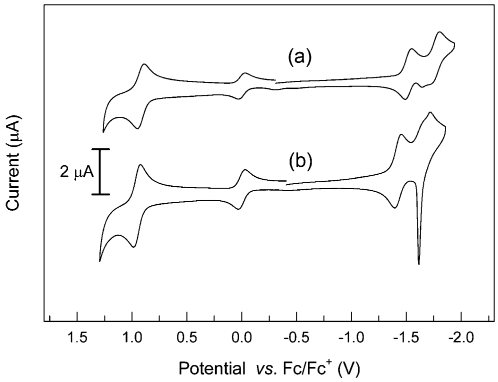


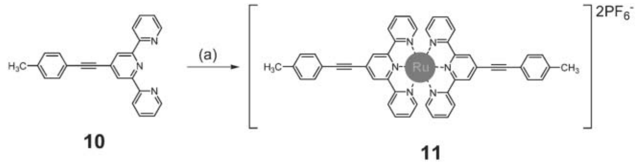
Fig. 2 CV responses of 1 mM solutions of (a) Ru(II)–terpyridine monocomplex **11**; (b) triangular Ru(II) metallomacrocycle **6**.

Table 1 Redox potentials (V *vs.* Fc/Fc$^+$) of triangular Ru(II) metallomacrocycle **6** and model compound **11** in 0.1 M TBAPF$_6$–MeCN at glassy carbon electrode; scan rate = 100 mV s^{-1}

Complex		E_{red} (I)	E_{red} (II)	E_{ox} (I)
6	E_{pc}	−1.46	−1.72	0.92
	E_{pa}	−1.39	−1.61	0.98
	$E_{1/2}$	−1.43	—	0.95
11	E_{pc}	−1.55	−1.80	0.89
	E_{pa}	−1.49	−1.65	0.95
	$E_{1/2}$	−1.52	—	0.92

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 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.

For comparison, the CV of model compound [Ru(tpy)$_2$][2PF$_6^-$] (Scheme 4) exhibits similar behaviour to the CV of **6**. From an analysis of the CV of the first reduction peak intensities of **11** (I_p^{mono}) and triangle **6** (I_p^{tri}), the peak current ratio ($I_p^{mono} : I_p^{tri}$ = 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 Ru centers. The presence of a single oxidation potential for the Ru(II/III) couple within the solvent window at all scan rates suggests that three ruthenium centers in the macrocycle are oxidized at the same potential, as expected for non-interacting centers in identical environments.



Scheme 4 Model compound of triangular metallomacrocycle **6**. *Reagents and conditions*: (a) i) RuCl$_2$·(DMSO)$_4$, MeOH, reflux, ii) NH$_4$PF$_6$/MeOH.

These metallomacrocycles possess potential internal steric interactions that can be observed in the CPK representations. Variable temperature ^{1}H NMR spectra of [Fe$_3$(**4**)$_3$][6PF$_6^-$] support this observation in that peaks begin to broaden and shift as the temperature is decreased and bis(terpyridine) complex rotation is slowed.

In conclusion, we have demonstrated the formation and characterization of a unique, self-assembled, triangle metallomacrocycle by using tpy–metal(II)–tpy connectivity, which is stable and irreversible under the reaction conditions. This coordination-directed triangle gave entry into shape-persistent, densely packed architecture. Also, the stepwise contruction permits specific introduction of different metal centers. Therefore, the reversible redox characteristics and the heterogeneous metal core structure suggest that they are ideal candidates for energy storage devices and nanomachinery.

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Notes and references

‡ Crystal data for **4**: C$_{40}$H$_{24}$N$_6$, M = 588.65, triclinic, space group $P\bar{1}$, a = 10.8137(10), b = 12.4510(10), c = 13.061(2) Å, α = 68.247(5), β = 75.799(5), γ = 66.262(7), V = 1485.6(3) Å^3, T = 102 K, Z = 2, μ(Mo–Kα) = 0.080 mm^{-1}, 10773 independent reflections, R_{int} = 0.038, R_1 = 0.054, wR_2 = 0.141 (all data). CCDC 252799. See http://www.rsc.org/suppdata/cc/b4/b409348h/ for crystallographic data in .cif or other electronic format.

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