NJC

Cite this: *New J. Chem.*, 2011, **35**, 2130–2135

www.rsc.org/njc

PAPER

A rigid metallohexameric macrocycle composed of *endo*- and *exo*-cyclic bisterpyridine-metal complexes†

Sinan Li,[a] Charles N. Moorefield,[b] Carol D. Shreiner,[c] Pingshan Wang,[d] Rajarshi Sarkar[e] and George R. Newkome*[be]

Received (in Montpellier, France) 2nd March 2011, Accepted 9th May 2011
DOI: 10.1039/c1nj20195f

Synthesis of terpyridine-based building blocks has allowed the self-assembly of a nanosized metallomacrocycle with precisely positioned, peripheral metal complexes. Construction of the precursors included the assembly of a heteroleptic bisterpyridine-Ru(II) complex possessing a diiodoaryl moiety that was subsequently reacted with two equivalents of 4′-ethynyl-2,2′:6′,2″-terpyridine *via* a Pd(0)-catalyzed Sonagashira coupling, to generate the requisite monomer with two, 120°-juxtaposed metal coordination sites. Addition of one equivalent of Fe(II) to one equivalent of the bisligand afforded the metallocycle with 12 metals [6 internal Fe(II) ions and 6 external Ru(II) ions] measuring *ca.* 7 nm in diameter.

Introduction

The construction of shape-persistent architectures is of great interest to the design and creation of supramolecular nanodevices,[1–4] as well as smart materials.[5] In part, rigid macrocycles possessing dimensions within the nanoregime, in contrast to their open-ended chain/hyperbranched analogues,[6,7] are playing an increasingly important role in the supramolecular construction of molecular building blocks as well as affording easy access to the development of new versatile synthetic methodologies.[8–12]

Stang[13–16] and Lehn[17–19] have prompted an extensive and continuing examination of transition metal binding self-assembling precursors to form shape-persistent macrocycles[20–22] possessing unique electronic and photonic properties. In the 1930s, Morgan and Bustall[23,24] synthesized the first terpyridines; however, more recently these monomers have been used in predesigned macromolecular constructs.[25,26] Their stable coordination chemistry is a particularly powerful tool for the assembly of supramolecular architectures, due to their pseudo-octahedral geometry that easily imparts framework directionality. Additionally, novel utilitarian properties, based on metal ion selection, can be instilled.[26] Notably, some of these terpyridine-metal complexes are reversible under specific conditions, suggesting their use as protecting groups;[27] whereas, others are totally irreversible under typical environmental conditions.

Most shape-persistent macrocycles are constructed as regular convex polygons that include triangles, rectangles, pentagons, and hexagons, to mention but a few.[28] Based on a purely geometric viewpoint, regular polygons can be divided into subunits that possess identical shape and size; these subunits provide the design criteria for the building blocks used in their construction. For example, a regular triangle consists of three objects each possessing two terminally connected arms juxtaposed to form a 60° angle. Analogously, a regular hexagon possesses six identical subunits characterized by 120° angles forming a hexameric cycle, or three subunits each possessing a net 60° between terminal ligands. Notably, in some cases, the polygons are only equiangular, and not equilateral, but are still geometrically symmetric.[14]

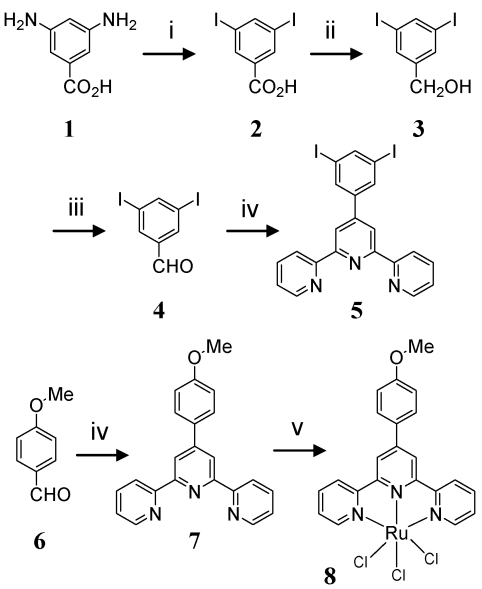
Our strategy for macrocycle self-assembly is predicated on this geometric "retroconstruction" and is ideally suited for bis(terpyridinyl) monomers that can be designed and constructed with angles up to 180° with respect to the two ligating termini.[29] Hence, our previous work has focused predominately on the synthesis of triangular-,[30] pentagonal-,[31] hexagonal-,[32–35] and decameric-macrocycles.[36] Herein, we report the design and construction of a hexagon-based, star-shaped macrocycle possessing *both exo*- and *endo*-cyclic bisterpyridinyl-metal ion complexes; six Fe(II) ions bind the cyclic core and six bisterpyridine-Ru(II) complexes radiate from the hexagonal vertices.

[a] *Lubrizol Advanced Materials, 9911 Brecksville Rd., Cleveland, OH 44141-3201, USA*
[b] *Maurice Morton Institute for Polymer Science, 170 University Cr., The University of Akron, Akron, OH 44325. Fax: 330-972-2368*
[c] *Chemistry Department, Hiram College, P.O. Box 67, Hiram, OH 44234. Fax: 330-569-5448*
[d] *ChemNano Materials, 2220 High St., Suite 605, Cuyahoga Falls, OH 44221*
[e] *Departments of Polymer Science and Chemistry, 170 University Cr., The University of Akron, Akron, OH 44325. E-mail: newkome@uakron.edu; Fax: 330-972-2368*
† Dedicated to Professor Didier Astruc on the occasion of his 65th birthday.

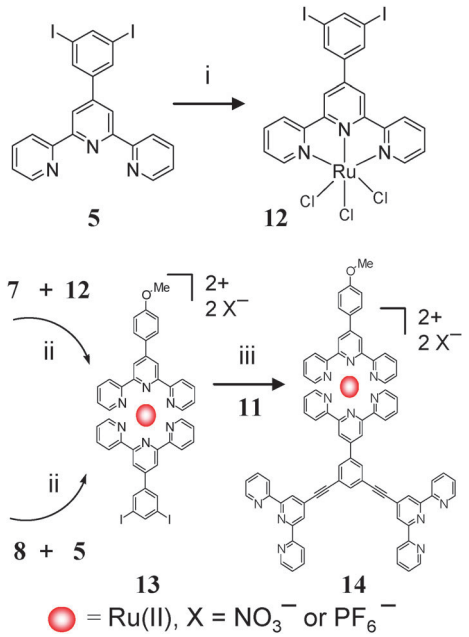
Results and discussion

Assembly (Scheme 1) began with commercially available 3,5-diaminobenzoic acid (**1**) that was initially transformed (70%) to 3,5-diiodobenzoic acid (**2**),[37] which was subsequently reduced with BH_3·THF to give (88%) the intermediate alcohol **3**[38] that was then oxidized with PCC to afford (>90%) the desired 3,5-diiodobenzaldehyde (**4**);[39] their ^{1}H and ^{13}C NMR data were identical to literature. 3,5-Diiodobenzaldehyde **4** was subsequently treated with 2.1 eq. of 2-acetylpyridine at 25 °C under basic conditions (NaOH) for 12 h, followed by refluxing with excess NH_4OAc in HOAc for 8 h. The desired 4′-(3,5-diiodophenyl)-2,2′ : 6′,2″-terpyridine (**5**) was isolated in 34% yield and confirmed by peaks (^{1}H NMR) at 8.64 (3′,5′-tpy*H*) and 8.76 ppm (6,6″-tpy*H*) along with an absorption (^{13}C NMR) at 95.05 ppm assigned to the C_{Ar}-I, and the mass signal at m/z = 561.9 $(M+H)^+$ supported the assignment. The paramagnetic, Ru(III) capping agent adduct 4′-(*p*-methoxyphenyl)-2,2′ : 6′,2″-terpyridine (**8**) was then obtained by refluxing (EtOH, 4 h) a mixture of 4′-(*p*-methoxyphenyl)-2,2′ : 6′,2″-terpyridine[40] (**7**), generated from *para*-methoxybenzaldehyde (**6**) with 2-acetylpyridine and excess NH_4OAc in HOAc, with $RuCl_3$·nH_2O.

Two routes to produce the intermediate diiodo complex **13** were employed (Scheme 2). To a mixture of methoxy adduct **8** (1 eq.) and diiodoterpyridine **5** (1 eq.) in MeOH, *N*-ethylmorpholine, as a reducing agent, was added. After refluxing, the desired dimer **13** was isolated (84%), as a dark red solid; however, for structural verification, it was also prepared (77%) by refluxing the diiodoRu(III) adduct **12** (1 eq.; accessed by treatment of diiodo-terpyridine ligand **5** with $RuCl_3$·nH_2O) with methoxyterpyridine **7** in MeOH with added *N*-ethylmorpholine. In each instance, the structure of the Ru(II) complex **13** was characterized (^{1}H NMR) by signals at 8.98 and 8.96 ppm, which were assigned to 3′,5″-tpy*H*s of the diiodo (**5**) and methoxy (**7**) components, respectively; while the ^{13}C NMR



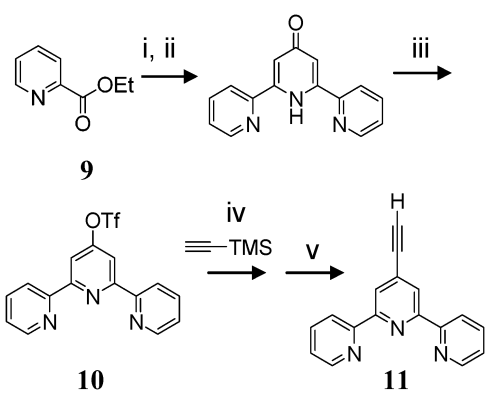
Scheme 1 (i) $NaNO_2$, H_2SO_4, urea, H_2O, 0 °C, 2 h, then KI, 5 h, 25 °C; (ii) BH_3·THF; (iii) PCC; (iv) 2-acetylpyridine, NaOH, then NH_4OAc, HOAc; (v) $RuCl_3$·nH_2O, MeOH, Δ.



Scheme 2 (i) $RuCl_3$·nH_2O, MeOH, reflux; (ii) *N*-ethylmorpholine, MeOH, reflux; (iii) Pd^0, CuI, Et_3N.

spectrum displayed a prominent absorption at 96.78 ppm for C_{Ar}-I. Further confirmation of the structure of complex **13** was provided by the ESI-MS data [1146.9 $(M - PF_6)^{1+}$, 501.0 $(M - 2PF_6)^{2+}$].

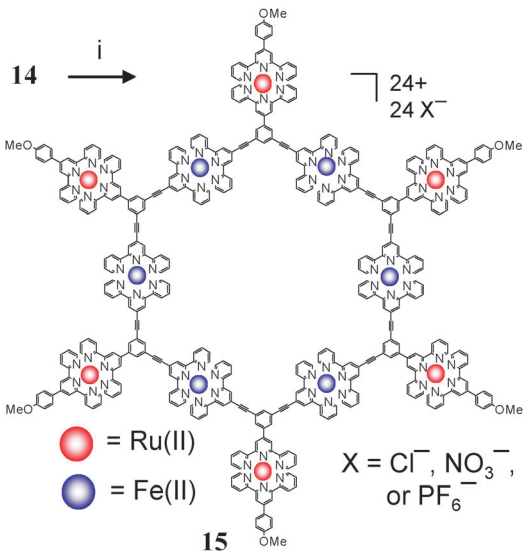
The key bisterpyridine ligand **14** for the desired heteronuclear macrocycle was synthesized *via* the Sonagashira coupling[41–43] of diiodoaryl complex **13** with 4′-ethynyl-2,2′ : 6′,2″-terpyridine[44,45] (**11**), which was prepared (Scheme 3) by the transformation of 2-carboethoxypyridine (**9**) to the terpyridine triflate **10**, then treatment with trimethylsilylacetylene and deprotection. The solubility of bis-ligand-Ru(II) complex **14** was poor in most common organic solvents. The ^{1}H NMR spectrum of complex **14** showed the expected downfield shifts for the complexed 3′,5′-tpy*H*s (9.19 ppm, $\Delta\delta$ = +0.21) for the dialkynylterpyridine portion and (9.04 ppm, $\Delta\delta$ = +0.08) for the methoxyterpyridine portion along with additional esonances at 8.86–8.70 ppm assigned to the 3′,5′-tpy*H*s, 6,6″-tpy*H*s, and 3,3″-tpy*H*s of the two free terpyridines.



Scheme 3 (i) acetone, NaH, anh. THF, reflux, 2 h; (ii) NH_4OAc, EtOH, reflux, 8 h; (iii) $(CF_3SO_2)_2O$, anh. pyridine, 25 °C, 48 h; (iv) Pd^0; (v) KF.

The ^{13}C NMR spectrum displayed distinct signals at 94.10, 89.72, and 56.84 ppm assigned to the unsymmetrical $C\equiv C$ and OCH_3 moieties, respectively. The structure of bisterpyridine **14** was further confirmed by the ESI-MS data [m/z 1405.6 $(M - PF_6)^{1+}$ and 630.6 $(M - 2PF_6)^{2+}$].

Complex **14** was subsequently subjected to macrocyclicization,[27,29,33,34,46] in which **14** was treated with 1 eq. of $FeCl_2$ in refluxing MeOH for 24 h to afford the desired homonuclear hexameric macrocycle **15**, which was isolated in 36% as a purple solid (Scheme 4). The resultant hexamer **15**, possessing 24 positive charges, exhibited improved solubility compared to that of the starting ligand **14**; it was freely soluble in MeCN (PF_6^- counterion) and MeOH (NO_3^- or Cl^- counterion). Pertinent observations confirming the structure included a downfield ^1H NMR shift of the singlet assigned to the Fe(II)-complexed, 3′,5′-tpy*H*s (9.25 ppm, $\Delta\delta = +0.45$) and the presence of signals (^{13}C NMR) at 96.67, 89.31, and 56.50 ppm corresponding to the unsymmetrical $C\equiv C$ and OCH_3 moieties, respectively.



Scheme 4 (i) $FeCl_2$, MeOH, Δ, 8 h.

The UV-vis spectrum of hexamer **15** exhibited the expected absorbance pattern at 582 and 493 nm in MeCN, which was attributed to the MLCT transitions[25] in the two different complexes, ⟨tpy-Fe-tpy⟩ and ⟨tpy-Ru-tpy⟩, respectively (Fig. 1A).

X-Ray photoelectron spectroscopy (XPS, using monochromatic Mg-Kα radiation at a power of 250 W; Fig. 1B) was performed to verify the presence of the coordinated metals. Since the electron binding energies that are commonly used to characterize Ru ($3d^1$ and $3d^5$ at ~285 eV) and Fe ($2p^1$ and $2p^3$ at 705–720 eV) are very close to the binding energy peaks of C 1s (~284 eV) and F 1s (~690 eV), we choose Ru $3p^3$ as the characteristic binding energy and the NO_3^- counterion rather than the more common PF_6^-. The XPS measurements of this heteronuclear-polymetal macrocycle showed a binding energy peak at 462.52 eV attributed to Ru $3p^3$, as well as peaks assigned to Fe ($2p^1$ and $2p^3$ at 720.57 and 707.65 eV, respectively). As expected, the appearance of two N 1s peaks at 407.98 eV and 401.62 eV was observed; there was no evidence of any residual PF_6^- (specifically P 2p at 130.6eV and F 1s at 690 eV). The higher binding energy of N 1s (407.98 eV), which is the higher oxidation state of N, was attributed to the presence of the NO_3^- counterion. The exact atomic Fe : Ru ratio of 1 : 1 provided excellent support for hexamer **15**.

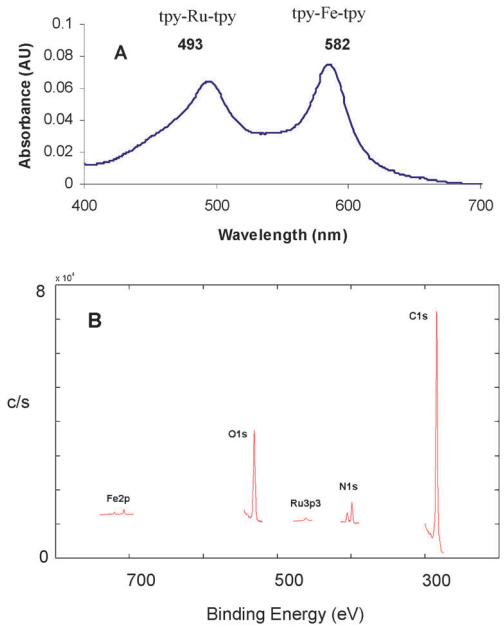


Fig. 1 UV-vis and XPS spectra of metallomacrocycle **15**.

Based on initial molecular modeling, the predicted structure of heteronuclear-Fe(II)Ru(II) macrocycle **15** possesses 7 nm and 2.5 nm outer and internal diameters, respectively (Fig. 2A). As a consequence of the high symmetry in hexamer **15** as well as the repeating ⟨tpy-metal(II)-tpy⟩ moieties, the NMR, UV, and XPS data confirm its macrocyclic architecture. Hence to better envision its uniformity, atomic force microscopy (AFM) was conducted. A droplet of a dilute MeCN solution of hexamer **15** (1 μg mL^{-1}) was deposited on a freshly cleaved, mica surface, dried under N_2. Using a super sharp silicon probe possessing a typical radius-of-curvature of ~2 nm on the AFM, the collected topographic image of **15** revealed an obvious ring structure with a discernible central hole, which has an outer diameter ~11 nm supporting both the shape and size of the modeled macrocycle (Fig. 2B).

The heteronuclear macrocycle **15** (with PF_6^-) was observed to possess moderate thermal stability as measured by thermal gravimetric analysis (TGA). Unlike that of other related metallomacromolecules, the TGA trace of **15** did not exhibit a sharp decomposition temperature (Fig. 3A). The overall decomposition process was observed as a curve with a small slope and two onset temperatures recorded at 174.2 and 591.8 °C. The cyclic voltammetry (CV) was also conducted to characterize the electrochemical properties of **15** (Fig. 3B). Interestingly, the recorded CV trace did not reveal the expected two oxidative couples of Ru and Fe,[47] but only one at 1.29 V ($\Delta E = 18$ mV), presumably due to the very close redox potentials of Fe and Ru.

Conclusions

Geometrical "retroconstruction" of a 2D hexagon has been employed for the design and synthesis of a heteronuclear-Fe(II)Ru(II) structure in the nanometre size regime. The observed

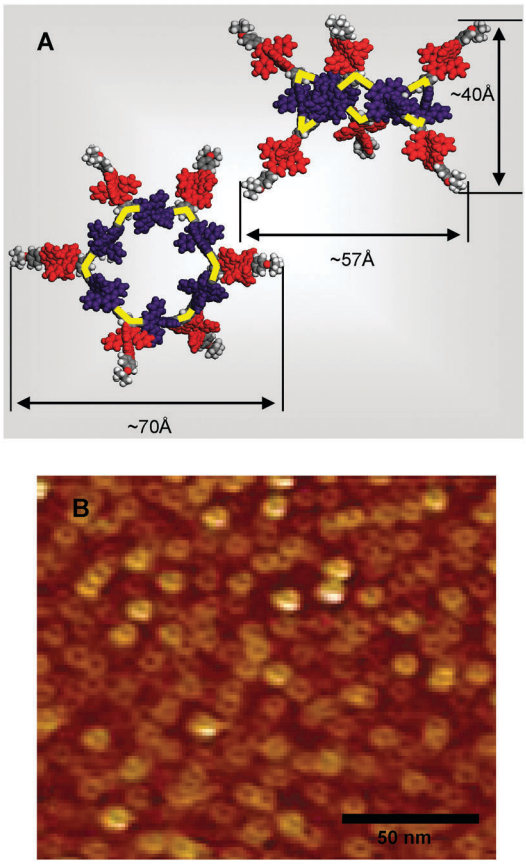


Fig. 2 (A) Top and side views of an optimized molecular model of **15** with the counterions omitted for clarity and (B) a tapping mode AFM image of macrocycle **15** (scale bar: 50 nm).

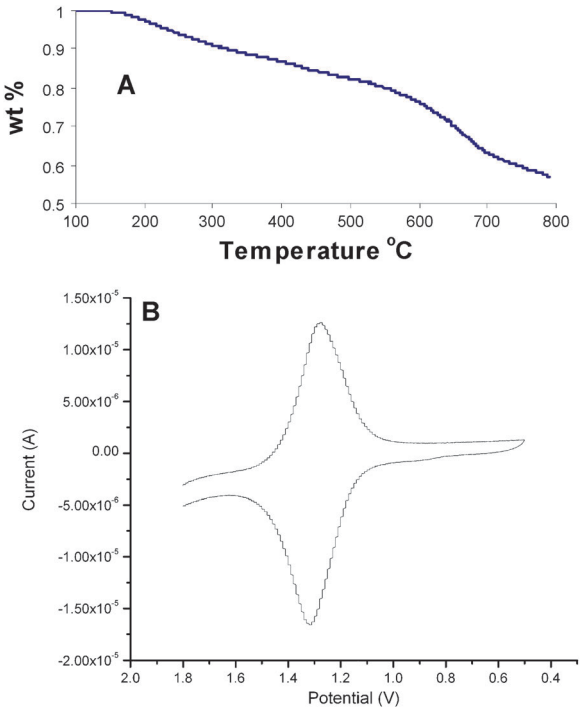


Fig. 3 Thermogravimetric analysis (A) and cyclic voltammetry (B) recordings for macrocycle **15** (PF_6^-). The CV was conducted in $MeCN/Bu_4NPF_6$ with 0.1 M Bu_4NPF_6 at 25 °C using a NaCl reference electrode.

NMR spectra coupled with the AFM imaging and measured physical properties provide direct evidence for the proposed structure. Investigations into the potential to employ and fine-tune the electronic properties of these unique materials are currently ongoing.

Experimental section

General comments

3,5-Diaminobenzoic acid, 2-acetylpyridine, trimethylsilyl acetylene, palladium catalysts $[Pd(PPh_3)_4]$, $Pd(PPh_3)_2Cl_2$, and $Pd(dppf)Cl_2]$, 4-methoxy-benzaldehyde, ammonium acetate (NH_4OAc), BH_3·THF, pyridinium chlorochromate (PCC), $RuCl_3$, $FeCl_2$, CuI, and NH_4PF_6 were purchased from either Aldrich or Acros and were used directly without further purification. Both **7**[40] and **11**[44,45] were prepared following literature procedures and their structures were fully characterized. Column chromatography was performed using SiO_2 (60–200 mesh) or basic Al_2O_3, Brockman Activity I (60–325 mesh).

^1H and ^{13}C NMR spectra were recorded using a Mercury 300 MHz (75 MHz) NMR spectrometer using CD_3CN, as solvent, unless otherwise noted. Mass spectra were obtained using a Bruker Esquire Electrospray Ion Trap mass spectrometer (ESI-MS). Hewlett-Packard 8452A diode array spectrophotometer for UV/Vis absorption measurement; CHI 440 Electrochemical Workstation for cyclic voltammetry measurements; and X-ray photoelectron spectroscopic (XPS, monochromatic Mg-Kα radiation at power 250 W, 93.90 eV) measurements were used. Molecular modeling was performed using Material Studio software available from Accelyrs. Geometry optimization was achieved using the Forcite module and the conjugate gradient algorithm with convergence tolerances of 0.0001 kcal mol^{-1} (energy) and 0.005 kcal mol^{-1}/Å. Energy minimization employed a universal forcefield with an atom-based summation method and cubic spline truncation for both the electrostatic and non-bonded interactions. AFM was conducted in the tapping mode by adding droplets of dilute solutions of the macrocycle on the surface of freshly cleaved mica, then dried at 25 °C for 8 h; a super sharp silicon probe possessing a typical radius-of-curvature of ~2 nm (SSS-NCH-SPL from NANOSENSORS) was used.

4′-(3,5-Diiodophenyl)-2,2′:6′,2″-terpyridine (5)

To an aqueous solution of $NaNO_2$ (2.5 M), a H_2SO_4 solution of 3,5-diaminobenzoic acid (**1**; 3 g, 20 mmol) was added at 0 °C. Urea (3 g) and KI (7 g) were added and the mixture was stirred for 2 h, then poured into ice-cold water. The solid was filtered and shown to be 3,5-diiodobenzoic acid (**2**; 5.1 g, 70%),[37] which was reduced with BH_3·THF to give (88%) 3,5-diiodobenzyl alcohol (**3**).[38] Subsequent PCC-oxidation of **3** in CH_2Cl_2 at 25 °C gave (>90%) 3,5-diiodobenzaldehyde (**4**), as a yellowish solid.[39]

To a stirred mixture of aldehyde **4** (2.5 g, 7 mmol) and 2-acetylpyridine (1.78 g, 2.1 eq.) in EtOH (80 mL, 95%), aqueous NaOH (1.5 mL, 2.1 eq., 1.0 M) was added dropwise. The mixture was stirred at 25 °C for 12 h, then the solvent was evaporated *in vacuo* to give a dark red solid. Excess NH_4OAc

(5.5 g) in HOAc (50 mL) was added and the resultant mixture was refluxed for 8 h, after which the HOAc was removed *in vacuo* leaving a brown residue that was partitioned between $CHCl_3$ and H_2O (1 : 1, 600 mL). The organic layer was washed twice with H_2O, dried ($MgSO_4$), and concentrated *in vacuo* to give the crude product, which was chromatographed (Al_2O_3) by elution with an $EtOAc/C_6H_{12}$ (1 : 1) solvent mixture. Lastly, recrystallization (MeOH) gave pure 4′-(3,5-diiodophenyl)-2,2′ : 6′,2″-terpyridine (**5**), as a yellowish solid: 1.33 g (34%); mp 230 °C; ^{1}H NMR ($CDCl_3$): δ 8.76 (d, J = 4 Hz, 2H, 6,6″-tpy*H*), 8.70 (d, J = 8 Hz, 2H, 3,3″-tpy*H*), 8.64 (s, 2H, 3′,5′-tpy*H*), 8.17 (s, 2H, 2,6-Ar*H*), 8.15 (s, 1H, 4-Ar*H*), 7.93 (t, J = 6 Hz, 2H, 4,4″-tpy*H*), 7.41 (t, J = 6 Hz, 2H, 5,5″-tpy*H*); ^{13}C NMR ($CDCl_3$): δ 156.00, 155.59, 149.03, 147.70, 145.74, 142.31, 137.67, 135.72, 124.46, 121.89, 119.12, 95.51; ESI-MS (560.92 calcd. for $C_{21}H_{13}I_2N_3$): m/z 561.9 $(M+H)^+$.

4′-(3,5-Diiodophenyl)-2,2′ : 6′,2″-terpyridine-Ru(III) adduct (12)

Was prepared from a stirred solution of 4′-(3,5-diiodophenyl)-2,2′ : 6′,2″-terpyridine (**5**; 77 mg, 137 μmol), $RuCl_3$ (36.4 mg, 14 μmol) in MeOH (20 mL). After stirring at 25 °C for 1 h, the mixture was refluxed for additional 8 h. After cooling to 25 °C, the black precipitate was filtered and washed thoroughly with MeOH and $CHCl_3$ to give 4′-(3,5-diiodophenyl)-2,2′ : 6′,2″-terpyridine-Ru(III) adduct **12**, as a black solid (30 mg, 29%), which was used directly.

4′-(*p*-Methoxyphenyl)-2,2′ : 6′,2″-terpyridine-Ru(III) adduct (8)

To a solution of $RuCl_3$ (128 mg, 490 μmol) in MeOH (20 mL), **7**[40] (157 mg, 463 μmol) was added. After being stirred at 25 °C for 1 h, the solution was refluxed for 4 h to afford 4′-(*p*-methoxy-phenyl)-2,2′ : 6′,2″-terpyridine-Ru(III) adduct **8**, as black solid (247 mg, 88%), which was used directly.

4′-(3,5-Diiodophenyl)-2,2′ : 6′,2″-terpyridine-Ru(II)-4′-(*p*-methoxyphenyl)-2,2′ : 6′,2″-terpyridine ⟨5-Ru(II)-7⟩ (13)

Method A. To a mixture of **5** (139 mg, 250 μmol) and **8** (137.5 mg, 250 μmol) in MeOH (50 mL), *N*-ethylmorpholine (5 drops) was added. After stirring for 1 h at 25 °C, the mixture was refluxed for additional 12 h. The solvent was evaporated *in vacuo* to give a residue that was chromatographed (SiO_2) by eluting with a H_2O/KNO_3 (conc.)/MeCN (1 : 1 : 10) solvent mixture to afford ⟨**5**-Ru(II)-**7**⟩ (**13**), which was treated with methanolic NH_4PF_6 in order to prepare the desired **13** (PF_6^-), as a dark red solid (271 mg, 84%), which was identical in all respects to the sample derived from Method B.

Method B. To a mixture of **12** (16 mg, 20 μmol) and **7** (7 mg, 20 μmol) in MeOH (10 mL), 2 drops of *N*-ethylmorpholine was added. After refluxing for 12 h, the solution was concentrated *in vacuo* and the residue was chromatographed (SiO_2) by eluting with a H_2O/KNO_3(conc.)/MeCN (1 : 1 : 10) solvent mixture to afford ⟨**5**-Ru(II)-**7**⟩ (**13**), which was treated with methanolic NH_4PF_6 in order to prepare the desired **13** (PF_6^-), as a dark red solid: 19.9 mg (77%); ^{1}H NMR (CD_3CN): δ 8.98 [s, 2H, 3′,5′-tpy(**7**)*H*], 8.96 [s, 2H, 3′,5′-tpy(**5**)*H*], 8.65 [brd, 4H, 3,3″-tpy(**7**)*H* and 3,3″-tpy(**5**)*H*], 8.59 [s, 2H, 2,6-(**7**)Ar*H*], 8.42 [s, 1H, 4-(**7**)Ar*H*], 8.21 [d, J = 9 Hz, 2H, 2,6-(**5**)Ar*H*], 7.98 [m, 4H, 4,4″-tpy(**7**)*H* and 4,4″-tpy(**5**)*H*], 7.45 [d, J = 5 Hz, 2H, 6,6″-tpy(**7**)*H*], 7.37 [d, J = 5 Hz, 2H, 6,6″-tpy(**5**)*H*], 7.32 [d, J = 8 Hz, 2H, 3,5-(**5**)Ar*H*], 7.21-7.14 [m, 4H, 5,5″-tpy(**7**)*H* and 5,5″-tpy(**5**)*H*], 3.97 [s, 3H, (**5**)ArOCH_3]; ^{13}C NMR (CD_3CN): δ 163.22, 159.64, 159.44, 157.10, 156.54, 153.80, 149.61, 147.70, 146.03, 141.85, 139.46, 139.43, 137.43, 130.61, 130.17, 128.96, 128.77, 126.01, 125.88, 123.10, 122.32, 116.44, 96.78, 56.79; ESI-MS Calcd. 1291.9 ($C_{43}H_{30}F_{12}I_2N_6OP_2Ru$): found: m/z 1146.9 $(M–PF_6)^{1+}$, 501.0 $(M–2PF_6)^{2+}$.

Terpyridine-Ru(II) dimer (14)

To a degassed mixture of **13** (189 mg, 146 μmol), **11**[44,45] (94.1 mg, 366 μmol), $Pd(PPh_3)_2Cl_2$ (7.1 mg,10 μmol), and CuI (4.3 mg, 23 μmol) in a mixed solution of THF/MeCN (50 mL, 20/30), $(Me_2CH)_2NH$ (10 mL) was added. After degassing five times with Argon, the mixture was stirred at 80 °C for 3 d. The solution was concentrated *in vacuo* to give a red residue, which was chromatographed (Al_2O_3) by eluting with a H_2O/KNO_3(conc.)/MeCN (1 : 1 : 10) solvent mixture to afford terpyridine-Ru(II) dimer **14**, which was treated with an NH_4PF_6 MeOH solution in order to prepare the desired **14** (PF_6^-), as a light red solid: mp >350 °C, 138 mg (61%); ^{1}H NMR (CD_3CN): δ 9.19 [s, 2H, 3′,5′-tpy(**7**)*H*], 9.04 [s, 2H, 3′,5′-tpy(**5**)*H*], 8.86-8.70 [m, 15H, 3,3″-tpy(**7**)*H*, 3,3″-tpy(**5**)*H*, 3,3″-tpy(**11**)*H*, 6,6″-tpy(**11**)*H*, 3′,5′-tpy(**11**)*H* and 2,4,6-(**7**)Ar*H*], 8.27-8.24 [m, 6H, 4,4″-tpy(**11**)*H* and 2,6-(**5**)Ar*H*], 8.07-7.99 [m, 2H, 4,4″-tpy(**5***H* and 4,4″-tpy(**7**)*H*], 7.73 [t, J = 6 Hz, 4H, 5,5″-tpy(**11**)*H*], 7.54 [d, J = 5 Hz, 2H, 6,6″-tpy(**7**)*H*], 7.49 [d, J = 6 Hz, 2H, 6,6″-tpy(**5**)*H*], 7.37 [d, J = 8 Hz, 2H, 3,5-(**5**)Ar*H*], 7.30-7.23 [m, 4H, 5,5″-tpy(**7**)*H* and 5,5″-tpy(**5**)*H*], 4.03 [s, 3H, (**5**)ArOCH_3]; ^{13}C NMR (CD_3CN): δ 163.24, 159.63, 159.42, 157.23, 156.53, 155.36, 154.12, 153.83, 149.68, 149.30, 146.77, 141.20, 139.55, 137.46, 134.64, 133.50, 130.63, 130.09, 129.11, 128.89, 126.99, 125.97, 125.35, 124.93, 123.40, 122.89, 122.31, 116.44, 94.10, 89.72, 56.84; ESI-MS Calcd.1550.3 ($C_{77}H_{50}F_{12}N_{12}OP_2Ru$); found: m/z 1405.6 $(M–PF_6)^{1+}$, 630.6 $(M–2PF_6)^{2+}$.

Heteronuclear-Fe(II)Ru(II) hexameric macrocycle 15

A mixture of bisterpyridine ligand **14** (30 mg, 19 μmol) and $FeCl_2$ (3.8 mg, 1 eq.) in MeOH (30 mL) was refluxed for 12 h. After the solvent was removed *in vacuo*, the residue was chromatographed (SiO_2) by eluting with a H_2O/KNO_3 (conc.)/MeCN (1 : 1 : 10) solvent mixture. After removal of the solvent *in vacuo*, the residue was washed with water, dissolved in MeOH, and excess methanolic NH_4PF_6 was added to precipitate the complex. The collected dark purple solid was washed thoroughly with MeOH to afford the desired hexameric macrocycle **15**, as purple solid: 10.2 mg (36%); ^{1}H NMR (CD_3CN): δ 9.25-9.20 [m, 36H, 3′,5′-tpy(**Fe**)*H* and 3′,5′-tpy(**7**)*H*], 9.03 [s, 12H, 3′,5′-tpy(**5**)*H*], 8.85 [m, 24H, 3,3″-tpy(**Fe**)*H*], 8.81 [s, 6H, 4-(**7**)Ar*H*], 8.71 [d, J = 5 Hz, 12H, 3,3″-tpy(**7**)*H*], 8.65 [m, 24H, 3,3″-tpy(**5**)*H* and 2, 6-(**7**)Ar*H*], 8.24 [d, J = 5 Hz, 12H, 2,6-(**5**)Ar*H*], 7.99 [m, 48H, 4,4″-tpy(**5**)*H*, 4,4″-tpy(**7**)*H*, and 4,4″-tpy(**Fe**)*H*], 7.55 [m, 36H, 6,6″-tpy(**Fe**)*H* and 3,5-(**5**)Ar*H*] 7.34-7.17 [m, 72H, 6,6″-tpy(**7**)*H*, 6,6″-tpy(**5**)*H*, 5,5″-tpy(**7**)*H*, 5,5″-tpy(**5**)*H*, and 5,5″-tpy(**Fe**)*H*], 3.99 [s, 18H, (**5**)ArOCH_3]; ^{13}C NMR (CD_3CN): δ 162.95, 161.51, 159.41,

159.21, 158.45, 157.09, 156.30, 154.34, 153.60, 149.39, 146.68, 140.46, 140.16, 139.22, 137.39, 133.06, 130.34, 129.88, 128.85, 128.56, 126.42, 125.68, 125.30, 124.97, 122.95, 122.08, 116.16, 96.67, 89.31, 56.50; ESI MS 1480.6 $(M\text{-}7PF_6)^{7+}$, 1277.4 $(M\text{-}8PF_6)^{8+}$, 1119.5 $(M\text{-}9PF_6)^{9+}$, 992.9 $(M\text{-}10PF_6)^{10+}$, 889.6 $(M\text{-}11PF_6)^{11+}$, 803.4 $(M\text{-}12PF_6)^{12+}$, 730.3 $(M\text{-}13PF_6)^{13+}$, 667.9 $(M\text{-}14PF_6)^{14+}$.

Acknowledgements

We thank the generous support of the National Science Foundation (DMR-0705015 and DMR-0812337), the Ohio Board of Regents, and Mr Joshua Chavez for his summer assistance.

Notes and references

1 L. Zang, Y. Che and J. S. Moore, *Acc. Chem. Res.*, 2008, **41**, 1596.
2 U. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605.
3 Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, 2010, **110**, 3479.
4 B. H. Northrop, Y. R. Zheng, K. W. Chi and P. J. Stang, *Acc. Chem. Res.*, 2009, **42**, 1554.
5 L. Dai, *Intelligent Macromolecules for Smart Devices: From Materials Synthesis to Device Applications*, Springer-Verlag, London, 2004.
6 S. Höger, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 2685.
7 P. Wang, C. N. Moorefield, K. U. Jeong, S.-H. Hwang, L. Sinan, S. Z. D. Cheng and G. R. Newkome, *Adv. Mater.*, 2008, **20**, 1381.
8 S. Höger, *Chem.–Eur. J.*, 2004, **10**, 1320.
9 J. S. Moore, *Acc. Chem. Res.*, 1997, **30**, 402.
10 J. M. Tour, *Chem. Rev.*, 1996, **96**, 537.
11 Y.-F. Han, H. Li and G.-X. Jin, *Chem. Commun.*, 2010, **46**, 6879.
12 A.-M. Caminade, Y. Wei and J.-P. Majoral, *C. R. Chim.*, 2009, **12**, 105.
13 P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502.
14 P. J. Stang, *Chem.–Eur. J.*, 1998, **4**, 19.
15 P. J. Stang, *J. Org. Chem.*, 2009, **74**, 2.
16 B. H. Northrop, H.-B. Yang and P. J. Stang, *Chem. Commun.*, 2008, 5896.
17 P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, G. Baum and D. Fenske, *Chem.–Eur. J.*, 1999, **5**, 113.
18 M. Ruben, J.-M. Lehn and P. Müller, *Chem. Soc. Rev.*, 2006, **35**, 1056.
19 J.-M. Lehn, *Aust. J. Chem.*, 2010, **63**, 611.
20 P. Thanasekaren, R.-T. Liao, Y.-H. Liu, T. Rajendran, S. Rajagopal and K.-L. Lu, *Coord. Chem. Rev.*, 2005, **249**, 1085.
21 W. Zhang and J. S. Moore, *Angew. Chem., Int. Ed.*, 2006, **45**, 4416.
22 T. J. Cho, C. N. Moorefield, P. Wang and G. R. Newkome, *ACS Symp. Ser.*, 2006, **921**, 186.
23 G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1931, 20.
24 G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1937, 1649.
25 U. S. Schubert, H. Hofmeier and G. R. Newkome, *Modern Terpyridine Chemistry*, Wiley-VCH, Weinheim, 2006.
26 U. S. Schubert, A. Winter and G. R. Newkome, *Terpyridine-Based Materials-For Catalytic, Optoelectronic and Life Science Applications*, Wiley-VCH, Weinheim, 2011.
27 P. Wang, C. N. Moorefield and G. R. Newkome, *Angew. Chem., Int. Ed.*, 2005, **44**, 1679.
28 M. Soler, C. N. Moorefield and G. R. Newkome, *Hexameric Macrocyclic Architectures in Heterocyclic Chemistry*, ed. A. R. Katritzy, Elsevier, New York, 2010, vol. 101.
29 G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, M. J. Saunders, R. Cush and P. S. Russo, *Angew. Chem., Int. Ed.*, 1999, **38**, 3717.
30 S.-H. Hwang, C. N. Moorefield, F. R. Fronczek, O. Lukoyanova, L. Echegoyen and G. R. Newkome, *Chem. Commun.*, 2005, 713.
31 S.-H. Hwang, P. Wang, C. N. Moorefield, L. A. Godínez, J. Manríquez, E. Bustos and G. R. Newkome, *Chem. Commun.*, 2005, 4672.
32 S.-H. Hwang, C. N. Moorefield, P. Wang, F. R. Fronczek, B. H. Courtney and G. R. Newkome, *Dalton Trans.*, 2006, 3518.
33 G. R. Newkome, T. J. Cho, C. N. Moorefield, R. Cush, P. S. Russo, L. A. Godínez, M. J. Saunders and P. Mohapatra, *Chem.–Eur. J.*, 2002, **8**, 2946.
34 G. R. Newkome, T. J. Cho, C. N. Moorefield, P. P. Mohapatra and L. A. Godínez, *Chem.–Eur. J.*, 2004, **10**, 1493.
35 S. Perera, X. Li, M. Soler, A. Schlutz, C. Wesdemiotis, C. N. Moorefield and G. R. Newkome, *Angew. Chem., Int. Ed.*, 2010, **49**, 6539.
36 Y.-T. Chan, X. Li, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *Chem.–Eur. J.*, 2011, DOI: 10.1002/chem.201100559.
37 A. Enders and G. Maas, *Tetrahedron*, 2002, **58**, 3999.
38 M. H. Todd and C. Abell, *J. Comb. Chem.*, 2001, **3**, 319.
39 M. Beinhoff, W. Weigel, W. Rettig, I. Bruedgam, H. Hartl and A. D. Schlueter, *J. Org. Chem.*, 2005, **70**, 6583.
40 T. Mutai, J.-D. Cheon, S. Arita and K. Araki, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1045.
41 R. Chinchilla and C. Nájera, *Chem. Rev.*, 2007, **107**, 874.
42 K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467.
43 K. Sonogashira, *J. Organomet. Chem.*, 2002, **653**, 46.
44 R. Ziessel, J. Suffert and M.-T. Youinou, *J. Org. Chem.*, 1996, **61**, 6535.
45 V. Grosshenny, F. M. Romero and R. Ziessel, *J. Org. Chem.*, 1997, **62**, 1491.
46 G. R. Newkome, P. Wang, C. N. Moorefield, T. J. Cho, P. Mohapatra, S. Li, S.-H. Hwang, O. Lukoyanova, L. Echegoyen, J. A. Palagallo, V. Iancu and S.-W. Hla, *Science*, 2006, **312**, 1782.
47 I. Eryazici and G. R. Newkome, *New J. Chem.*, 2009, **33**, 345.