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Synthesis of achiral and racemic catenanes based on terpyridine and a directionalized terpyridine mimic, pyridyl-phenanthroline

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Concatenated macrocycles containing manisyl-substituted tridentate ligands 2,2′:6′,2″-terpyridine and 2-pyridin-2-yl-1,10-phenanthroline (simply referred to as terpyridine and pyridyl-phenanthroline herein) have been prepared *via* dual cyclization procedures. The manisyl derivative (manisyl = 4-methoxy-2,6-dimethylphenyl) was chosen for its ability to improve solubility while simultaneously incorporating functionality. Deprotection of the methoxy groups provided a soluble ligand that was re-alkylated with an array of terminal alkyne and alkene linkers. The tridentate coordinating ability of these ligands enabled complexation with Ru(II) and Fe(II), generating achiral and racemic octahedral complexes for terpyridine and pyridyl-phenanthroline, respectively. Subsequent macrocyclization *via* olefin metathesis or copper-mediated alkyne coupling afforded the corresponding catenanes, and in some cases a figure-eight macrocycle. The difference in symmetry and the presence of the manisyl group allowed the distinction between the catenane and the undesired figure-eight to be made directly by ^{1}H NMR. Metal-free achiral and racemic catenanes were obtained by liberating Fe(II) from the octahedral bound title ligands by treatment with hydrogen peroxide.

Introduction

Molecular representations of complex topologies are aesthetically attractive constructs that present challenges in structural design and synthesis.[1,2] Borromean Links,[2a] catenanes,[2b] and knots[2b] are representative of this class of structures, and along with their precursors, have been noticed for their potential applications.[3] Many of these assemblies rely on pre-organized templates[4] that include rigid complexes between chelating ligands and transition metals.[5] This approach, termed metal-templated, requires a coordinating component, of which the polypyridines, 2,2′-bipyridine,[6] 1,10-phenanthroline,[7] and 2,2′:6′,2″-terpyridine[8] are commonly employed and are of considerable interest to our research group.[9,10]

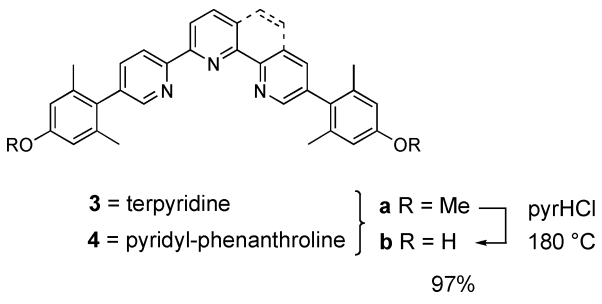
The bidentate ligand 1,10-phenanthroline and its tetrahedral coordination complex with copper(I) is the pioneering model for metal-templated synthesis of molecular catenanes.[11] The ease of introducing alkyl- and aryl-substituents into the 2- and 9-positions of commercially available 1,10-phenanthroline makes this ligand synthetically desirable for scaffolding.[12] In contrast, there are fewer examples of catenanes where the template is an octahedral center,[13–15] or that include terpyridine within their framework.[16,17] The first catenane built solely around terpyridine precluded removal of the templating metal,[15] while subsequent attempts to prepare a template-free version resulted in exclusive formation of a figure-eight macrocycle.[18]

Chiral variants of a catenane can be made by introducing asymmetry in the tethering or ring-closing steps,[14,19] or by incorporating directionality within the macrocycles.[20] For example, coordination complexes of the directionalized terpyridine mimic, pyridyl-phenanthroline,[21] are chiral and make practical building blocks for concatenated species.

Advances in poly-pyridine ligand synthesis, *via* cross-coupling methods, makes terpyridine and pyridyl-phenanthroline readily accessible;[9,22,23] and thus, prime candidates for the synthesis of achiral and racemic catenanes, respectively. To broaden the family of concatenated topological isomers and demonstrate proof-of-principle, a series of catenanes from octahedral Ru(II) and Fe(II) templates of manisyl-substituted terpyridine and pyridyl-phenanthroline were targeted.[24] Olefin metathesis[25] and copper-mediated alkyne coupling[26] for macrocyclization were implemented, and the relative advantages of each method are discussed. Symmetry analysis for the identification of catenane *vs.* figure-eight isomeric products by counting manisyl signals in the ^{1}H or ^{13}C NMR is presented as confirmation of the stereoselective synthesis. To our knowledge, the synthesis of metal-free achiral/racemic catenanes from these ligands has not been reported.[17]

Results and discussion

The metal-templated synthesis of catenanes commences with tridentate ligands **3a** and **4a**, previously prepared from commercially available and literature-known intermediates in two and three steps, respectively.[23] Deprotection of the methoxy groups with molten pyridinium hydrochloride provides soluble phenolic derivatives, **3b** and **4b**, that serve as backbones to the chiral and racemic catenanes presented here (Scheme 1). The terminal acetylene and olefin linkers used for macrocyclization, **21**–**24b**, were prepared in two steps as indicated from commercially available materials (Scheme 2).[27]



Scheme 1

Ru(II)-templated catenanes

Coordination of ligand **3b** with Ru(II) was achieved by reaction with $RuCl_2(DMSO)_4$ in refluxing ethylene glycol.[28] Aqueous workup with potassium hexafluorophosphate provided the

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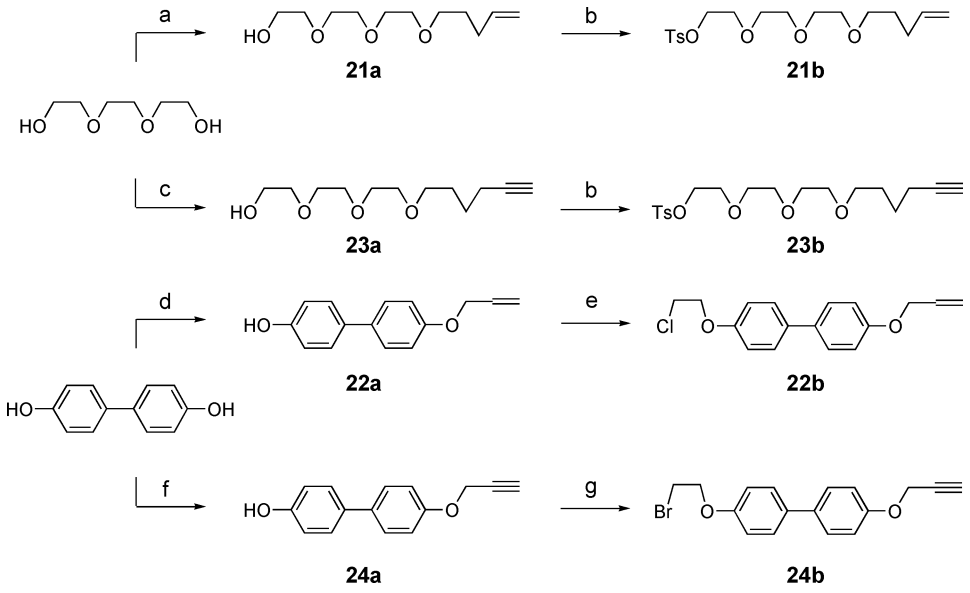
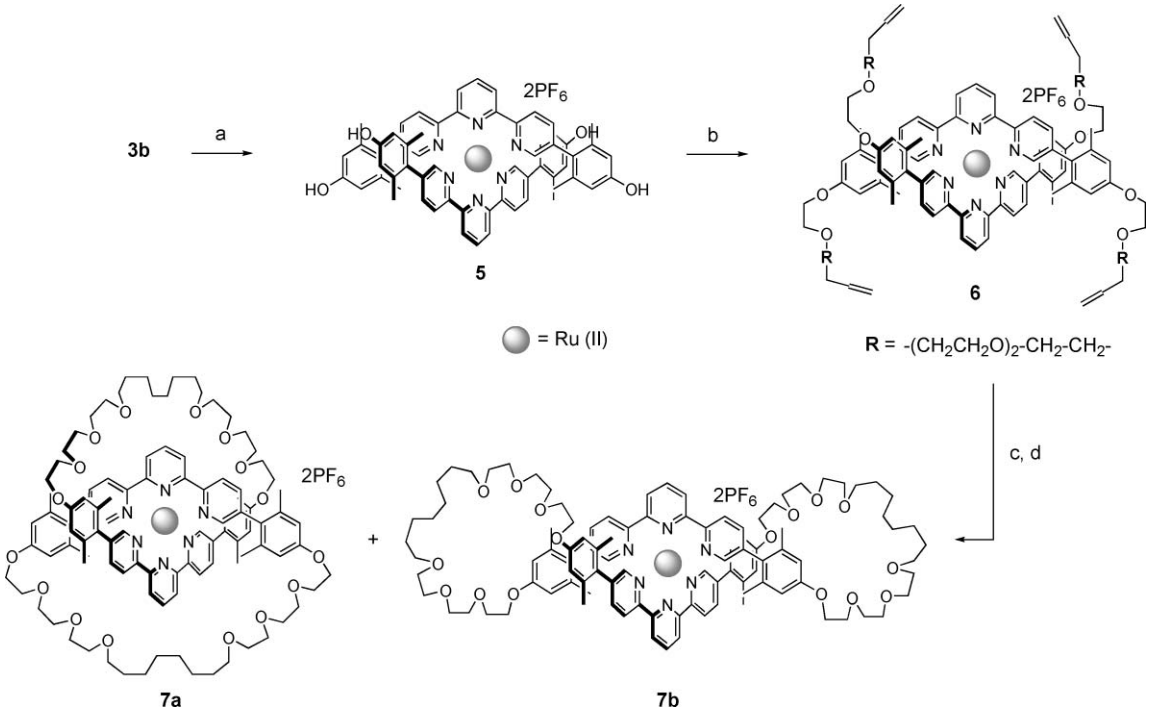


Scheme 2 *Reagents and conditions*: a) NaH, 0 °C → RT, 5-bromopentene, reflux, 12 h, 55%. b) Triethylamine, tosyl chloride, DMAP, dichloromethane, 0 °C → RT, 87% for **21b** and 78% for **23b**. c) NaH, 0 °C → RT, 6-chlorohexyne, reflux, 15 h, 56%. d) NaH, 0 °C → RT, allyl bromide, reflux, 12 h, 76%. e) NaH, 0 °C → RT, 1,2-dichloroethane, reflux, 15 h, 67%. f) NaH, 0 °C → RT, propargyl bromide, reflux, 10 h, 56%. g) NaH, 0 °C → RT, 1,2-dibromoethane, reflux, 8 h, 70%.



Scheme 3 *Reagents and conditions*: a) $RuCl_2(DMSO)_4$, ethylene glycol, 160 °C, 12 h, 91%. b) **21b**, Cs_2CO_3, CH_3CN, reflux, 12 h, 66%. c) $RuCl_2(PCy_3)_2CHPh$, CH_2Cl_2, 60 h, 74%. d) H_2, 10% Pd/carbon, CH_2Cl_2–EtOH, 12 h, 95%.

octahedral complex **5** as a deep red crystalline solid. As a result of the C_{2v} symmetry of **3b**, complex **5** has D_{2d} symmetry and is the template to the Ru(II) achiral catenanes. Alkylation of the tetra-phenolate of **5** with the terminal olefin linker **21b** using cesium carbonate in acetonitrile afforded pre-catenane **6**. Exposure of **6** to high dilution olefin metathesis conditions with Grubbs catalyst,[29] $RuCl_2(PCy_3)_2CHPh$, followed by immediate catalytic hydrogenation, generated both the catenane **7a** and the unexpected figure-eight macrocycle **7b** in a 1 : 2 ratio (Scheme 3).

Distinction between **7a** and **7b** was made directly by ^1H NMR due to the difference in molecular symmetry (D_{2d} and D_2, respectively) and the orthogonal conformation of the manisyl–pyridyl plane. Comparison of the signal for the manisyl aromatic proton **f** (~6.6 ppm), in compounds **6**, **7a** and **7b** is displayed in Fig. 1. After cyclization, this signal remains a singlet of isochronous enantiotopic signals for catenane **7a**, and splits into two diastereotopic singlets, **f** and **f'**, for figure-eight **7b** due to a reduced local symmetry, C_s to C_1, in the manisyl group. This is also observed for the protons of the methyl groups on manisyl (not pictured here). Additionally, the slight up-field shift in the peripheral pyridyl proton **a** associated with catenane formation is also observed for **7a** while those signals for **7b** remain relatively unchanged.

An undesired feature of olefin metathesis was the lack of thermodynamic drive to produce products and consume starting materials or intermediates. Tedious chromatographic separation was required in order to remove unreacted **6**, as well as the mono-ring-closed adducts of catenane as well as figure-eight. To circumvent this matter and to eliminate the need for hydrogenation we opted for a copper-mediated acetylenic

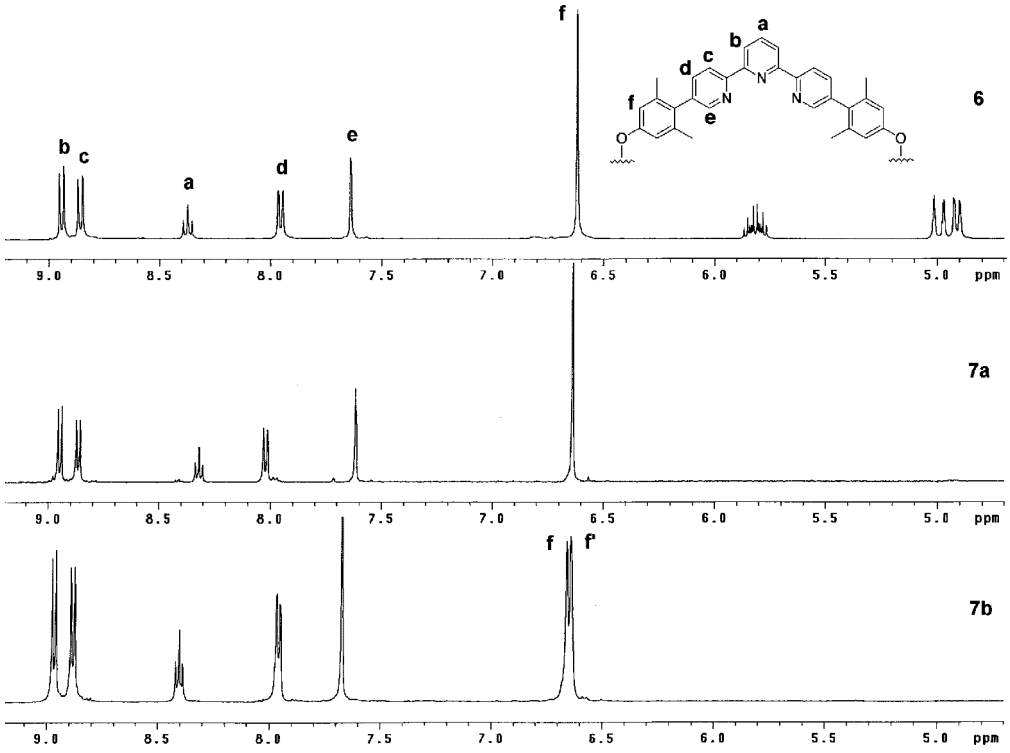
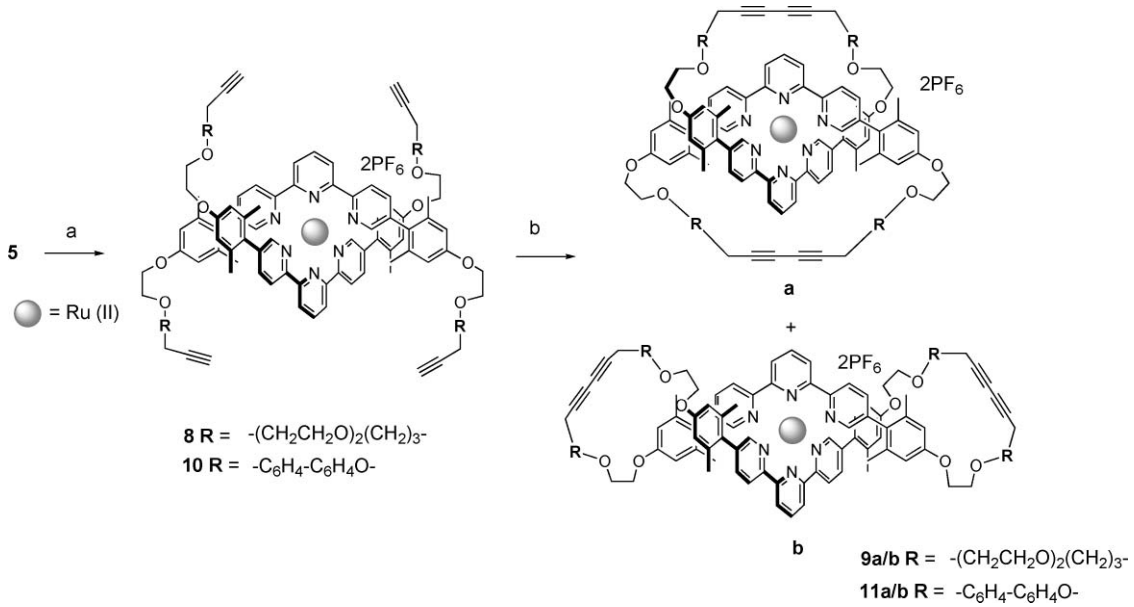


Fig. 1 500 MHz ^{1}H NMR spectra of compounds **6**, **7a**, and **7b**.



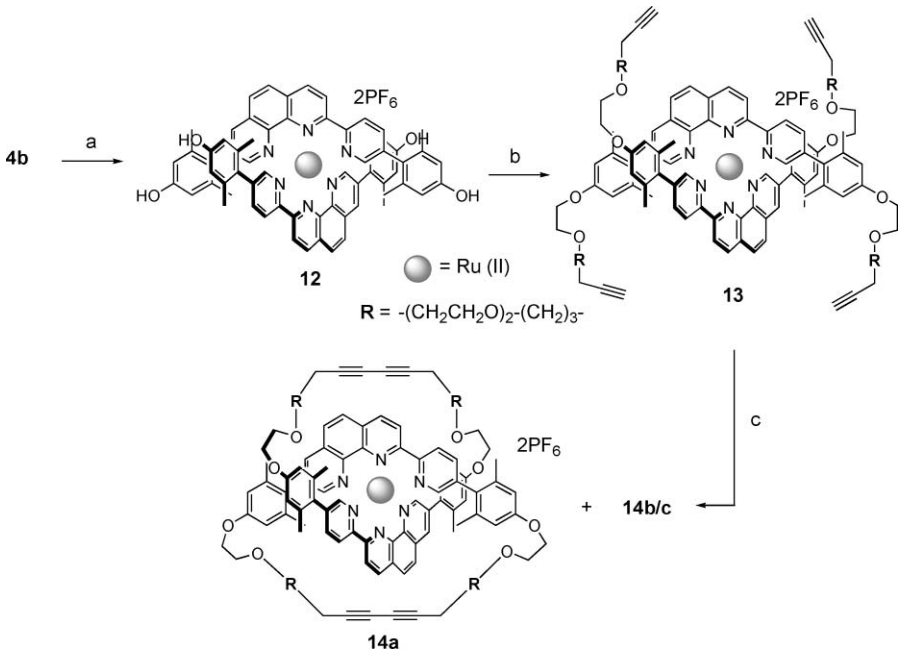
Scheme 4 *Reagents and conditions*: a) **23b** or **24b**, Cs_2CO_3, CH_3CN, reflux, 12 h, 54% for **8** and 70% for **10**. b) $Cu(OAc)_2$, CH_3CN, reflux, 12–15 h, 61% for **9a/b** and 57% for **11a/b**.

coupling using modified Eglington conditions as the cyclization step.

Pre-catenane **8** was prepared in an analogous manner to **6** using linker **23b**, which replaces the terminal olefins by terminal acetylenes. High dilution acetylenic coupling with excess copper(II) acetate gave the catenane **9a** and the figure-eight **9b** in approximately the same 1 : 2 ratio obtained for **7a** and **7b** by the olefin metathesis–hydrogenation procedure; however, precursor **8** was completely consumed to give **9a** and **9b** as monomeric products that are easily separable by column chromatography (Scheme 4). A similar symmetry analysis to that described above allowed the structural assignment.

Synthesis of the racemic modification of a chiral catenane was achieved using an analogous coupling strategy to that which afforded **9a** and **9b**. Coordination of the asymmetric tridentate ligand **4b** with Ru(II) using $RuCl_2(DMSO)_4$ in ethylene glycol gave complex **12** in racemic form (Scheme 5). Here the C_s symmetry of **4b** renders complex **12** with C_2 symmetry and provides the template for a racemic catenane. Alkylation of the racemic tetra-phenolate of **12** with linker **23b** gave pre-catenane **13**. Exposure of **13** to excess copper(II) acetate under high dilution conditions provided the chiral catenane **14a** and a set of diastereomeric figure-eights **14b/c** (not reported in detail due to the difficulties in their separation) in a 1 : 2 ratio.

The chiral nature of the pyridyl-phenanthroline Ru(II) complex makes distinction between catenane and figure-eight more difficult. The local symmetry of the manisyl group is lost upon coordination to Ru(II) and requires the distinction to be made on the basis of chemical shift changes in the ^{1}H NMR after cyclization. As in the reaction to form **9a** and **9b**, this reaction



Scheme 5 *Reagents and conditions*: a) $RuCl_2(DMSO)_4$, ethylene glycol, 160 °C, 12 h, 87%. b) **23b**, Cs_2CO_3, CH_3CN, reflux, 12 h, 56%. c) $Cu(OAc)_2$, CH_3CN, reflux, 12 h, 51% for **14a** and **14b/c**.

yields two sets of products that are easily separable by column chromatography from each other and from polymeric material. The racemic catenane **14a** product displays a single set of ^{1}H NMR aromatic signals with the expected up-field shift in the pyridyl-phenanthroline peripheral protons; whereas product composed of the diastereomeric mixture **14b/c** displays two sets of ^{1}H NMR signals in the aromatic region with little change in the chemical shift of the peripheral protons. High-resolution MALDI mass spectroscopy confirms that **14a** and **14b/c** are isomers with the expected monomeric mass.

Selective formation of the catenane was attempted by incorporating a biphenyl linker with the hope of sterically discouraging figure-eight formation. Alkylation of **5** with linker **24b** provided precursor **10**.[30] Exposure of **10** to acetylenic coupling conditions unfortunately still provided catenane **11a** and figure-eight **11b**, albeit in an improved 1 : 1 ratio (Scheme 4). Incorporating the biphenyl linker coincided with formation of X-ray quality crystals of **11a**, providing proof of structure and confirmation to our ^{1}H NMR assignment of the catenanes (Fig. 2).[31] Due to the thermodynamic stability of the octahedral Ru(II) complexes, removal of the ruthenium atom to form the metal-free catenanes was not effected.

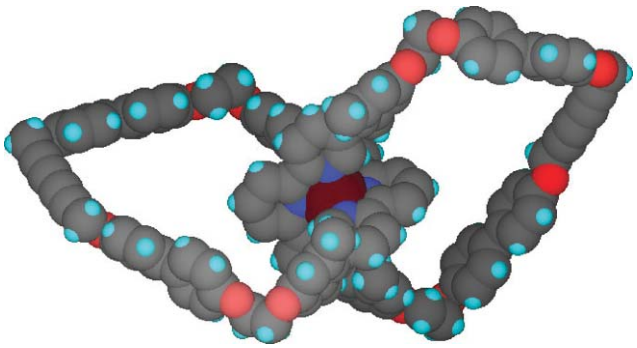


Fig. 2 X-Ray crystal structure of Ru(II) [2]catenane **11a**. Solvent molecules and PF_6^- counter-ion omitted for clarity.

Fe(II)-templated catenanes

Octahedral coordination complexes between Fe(II) and tridentate ligands produce complexes that are stable under mild conditions, but are labile under basic and oxidative conditions by way of Fe(III). To avoid complications possibly arising from a more labile metal system, alkylations were completed prior to coordination with Fe(II), and cyclization *via* copper-mediated actylenic coupling was not explored fully. Alkylation of **3b** with biphenyl linker **22b** using cesium carbonate gave ligand **15** (Scheme 6). Coordination of **15** with Fe(II) was achieved by treatment with iron(II) sulfate in acetone–water. Aqueous workup with potassium hexafluorophosphate gave pre-catenane **16** in its pure form. The mild conditions of olefin metathesis allowed for cyclization and preserved the Fe(II) complex. High dilution olefin metathesis of **16** surprisingly resulted in exclusive formation of the catenane and its mono-ring closed adduct as the only monomeric products; no figure-eight isomer was detected. The catenane was isolated as a mixture of *cis*/*trans* isomers in a 30% yield and immediately hydrogenated with catalytic Pt/alumina to afford **17**. As in the analysis of **7a**, **9a**, and **11a**, the symmetry of the manisyl group aids in the ^{1}H NMR identification of the catenane isomer. The expected up-field shifts in the pyridyl-proton aromatic signals are also observed. Removal of the Fe(II) template was achieved by the slow addition of aqueous hydrogen peroxide to a basic solution of **17** in acetonitrile–water. The purified achiral catenane **1** was isolated in 59% yield. The characteristic fragmentation pattern in the high resolution MALDI mass spectrum of **1** confirms formation of the catenane (Fig. 3).

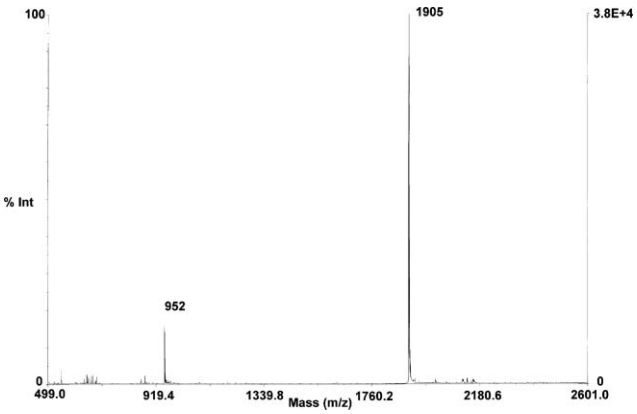
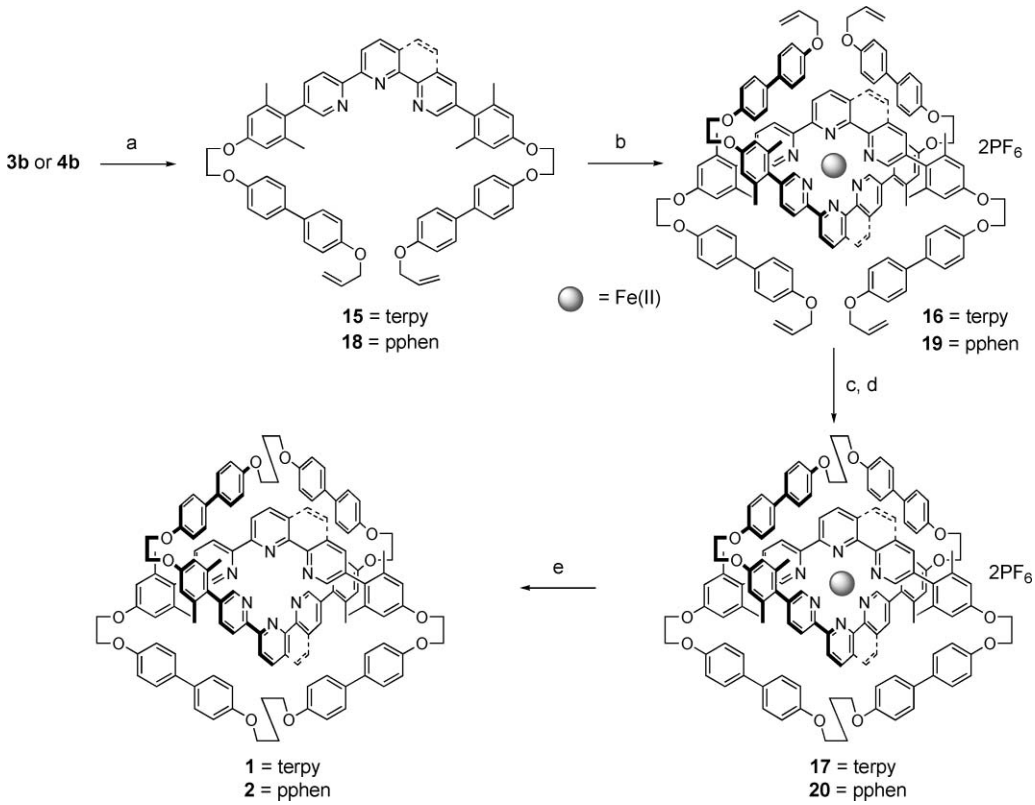


Fig. 3 MALDI high resolution mass spectrum of the template-free catenane **1**.



Scheme 6 Terpyridine = terpy; pyridyl-phenanthroline = pphen. *Reagents and conditions*: a) **22b**, Cs_2CO_3, DMF, 80 °C, 12 h, 88% for **15** and 92% for **18**. b) $FeSO_4 \cdot 7H_2O$, acetone–H_2O, 98% for **16** and 91% for **19**. c) $RuCl_2(PCy_3)_2CHPh$, CH_2Cl_2, 72 h, 30% for **17**-(*cis*/*trans*) and 21% for **20**-(*cis*/*trans*). d) Pt/alumina, CH_2Cl_2–EtOH, 16 h, 91% for **17** and 96% for **20**. e) H_2O_2, NaOH, CH_3CN–H_2O 1 : 1, 59% for **1** and 20% for **2**.

Racemic Fe(II)-templated catenane was prepared in an analogous fashion to that used to prepare **17**. Alkylation of **4b** with linker **22b** afforded **18**. Complex **19** was prepared by coordination between **18** and Fe(II) using iron(II) sulfate. High dilution olefin metathesis of **19** yields similar results to those seen for the reaction of **16**; only the catenane is produced in a 21% yield as a mixture of *cis*/*trans* isomers. Unreacted starting material and the mono-ring closed adduct comprise the majority of recovered materials and could be resubmitted to the reaction conditions to produce more product. Immediate hydrogenation of the *cis*/*trans* mixture with catalytic Pt/alumina gave the catenane **20**. Identification of **20** can be made by the characteristic up-field shifts in the aromatic region of the ^1H NMR spectrum. Removal of the Fe(II) was achieved by oxidation with hydrogen peroxide under basic conditions to give the racemic catenane **2** in 20% yield.

We conjecture that the absence of the figure-eight macrocycle arises from the decreased bite angle that the tridentate ligands form around Fe(II) relative to Ru(II). CPK modeling of **16** indicates that with enough pinching of the ligand around the metal center, the terminal olefins on opposing ligands become distant enough to prevent figure-eight formation, resulting in the preferential formation of the catenane.

To test this conjecture, the parent homoleptic complexes $Ru(\mathbf{3a})_2 \cdot 2PF_6$ and $Fe(\mathbf{3a})_2 \cdot 2PF_6$ were prepared and suitable crystals for X-ray crystallography were grown from slow evaporation of a dichloromethane solution in the presence of benzene (Fig. 4).[32]

X-Ray analysis reveals the N_1–M–N_3 ligand–metal bite angles for $Ru(\mathbf{3a})_2 \cdot 2PF_6$ and $Fe(\mathbf{3a})_2 \cdot 2PF_6$ to be 158.4(2) and 161.7(2)° respectively. Furthermore, the distances between opposing manisyl oxygen atoms of the same ligand are 16.646(6) and 16.481(6) Å for $Ru(\mathbf{3a})_2 \cdot 2PF_6$ and $Fe(\mathbf{3a})_2 \cdot 2PF_6$ respectively, and indicate an increased pinching of the ligands around Fe(II) relative to the Ru(II) cognate. This is further supported by the difference in N_1–N_3 distances, roughly 0.15 Å. Finally, the

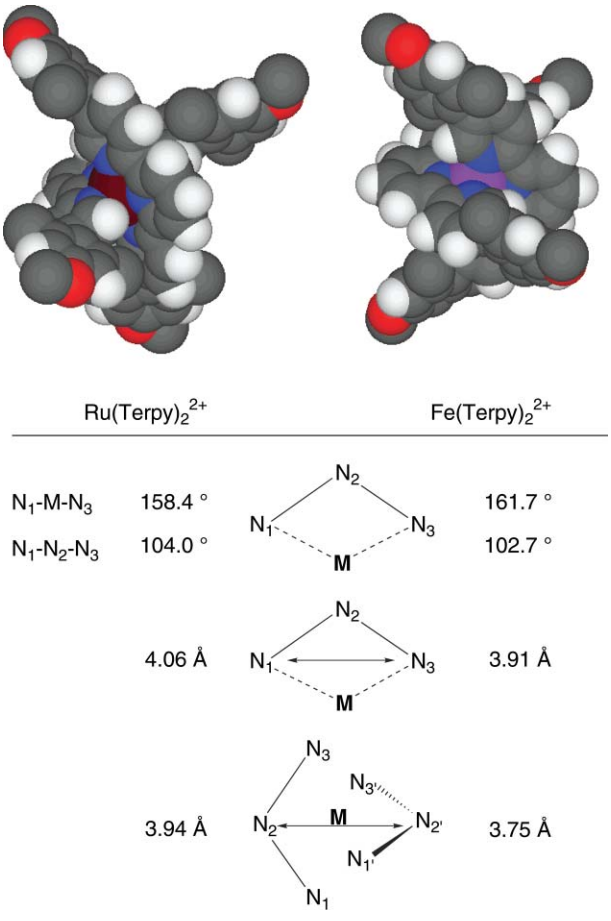


Fig. 4 X-Ray crystal structure and selected data for $Ru(\mathbf{3a})_2 \cdot 2PF_6$ (left) and $Fe(\mathbf{3a})_2 \cdot 2PF_6$ (right). Counter-ions omitted for clarity.

smaller ligand proximity around Fe(II) is demonstrated by the distances between central nitrogen atoms on terpyridine, N_2–$N_{2'}$, which vary by 0.19 Å and are consistent with our notion about the basis for the absence of figure-eight macrocycle formation with the Fe(II) templates.

Conclusions

We have demonstrated successfully that achiral and racemic catenanes can be synthesized using a metal-templated approach with terpyridine and pyridyl-phenanthroline ligands with either Ru(II) or Fe(II). Moreover, we have debuted pyridyl-phenanthroline in its first racemic templated topological isomer synthesis. Macrocyclization *via* olefin metathesis or copper-mediated alkyne coupling with Ru(II)-templated pre-catenanes resulted in both the catenane and the undesired figure-eight macrocycle, while olefin metathesis with Fe(II)-templated pre-catenanes resulted in preferential formation of a catenane. The labile Fe(II) core could easily be liberated to yield template-free achiral and racemic catenanes. Additionally, the aryl substituent manisyl served as an internal ^{1}H NMR probe for topological isomer identification of the achiral catenane.

Experimental

Materials and methods

^{1}H and ^{13}C NMR spectra were recorded on Varian (Mercury 300/400 MHz and Unity 500 MHz) spectrometers with tetramethylsilane (TMS) as an internal standard. High-resolution mass spectral (HRMS) analyses were performed by the University California Riverside mass spectrometry facility in either MALDI or EI mode, as indicated for each compound. All experiments were carried out under argon in freshly distilled anhydrous solvents unless otherwise noted. Commercial chemicals were used as supplied. Column chromatography was performed on neutral aluminum oxide (Brockmann II) and silica gel (230–425 mesh) from Fisher Scientific Co. Centrifugal chromatography was performed on a Harrison Research Chromatotron with 1 mm silica gel plates. UV–Vis spectra were recorded on a Perkin–Elmer UV/VIS/NIR spectrometer Lambda 19. Melting points were recorded on a Mel-Temp Laboratory Device and are uncorrected. Overlapping, non-symmetry-equivalent ^{13}C NMR signals for pyridyl-phenanthroline adducts are indicated by *.

5′,5″-Bis(4-hydroxy-2,6-dimethylphenyl)-2,2′:6′,2″-terpyridine (3b). To anhydrous molten pyridine hydrochloride (11.00 g, 90 mmol) at 150 °C was added **3a** (1.00 g, 2.1 mmol) and heated to 185 °C for 4 h. The hot solution was quenched with boiling water (20 mL). The resulting yellow precipitate was filtered, washed thoroughly with water, aqueous NH_4OH, and dried under vacuum overnight to yield a tan solid (0.92 g, 97%). Mp 212 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.75 (d, J = 8.0 Hz, 2H), 8.53 (d, J = 2.0 Hz, 2H), 8.52 (d, J = 8.0 Hz, 2H), 8.03 (t, J = 8.0 Hz, 1H), 7.70 (dd, J = 2.0, 8.0 Hz, 2H), 6.68 (s, 4H), 2.07 (s, 12H). ^{13}C NMR (100 MHz, CH_3OD, δ): 158.43, 152.93, 151.27, 148.22, 144.49, 140.85, 140.64, 138.45, 128.12, 124.05, 124.02, 115.57, 21.21. EI HRMS m/z: found 473.2111 (M^+); calcd ($C_{31}H_{27}N_3O_2$) 473.2103.

8-(4-Hydroxy-2,6-dimethylphenyl)-2-[5-(4-hydroxy-2,6-dimethylphenyl)pyridin-2-yl]-1,10-phenanthroline (4b). To anhydrous molten pyridine hydrochloride (11.00 g, 90 mmol) at 150 °C was added **4a** (1.00 g, 2.0 mmol) and heated to 185 °C for 4 h. The hot solution was quenched with boiling water (20 mL). The resulting yellow precipitate was filtered, washed thoroughly with water, aqueous NH_4OH, and dried under vacuum overnight to yield a yellowish solid (0.84 g, 93%). Mp 264–266 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 9.42 (bs, 1H), 9.37 (bs, 1H), 8.96 (d, J = 2.0 Hz, 1H), 8.91 (d, J = 8.0 Hz, 1H), 8.81 (d, J = 8.0 Hz, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.54 (d, J = 2.0 Hz, 1H), 8.35 (d, J = 2.0 Hz, 1H), 8.09 (d, J = 9.0 Hz, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.87 (dd, J = 2.0, 8.0 Hz, 1H), 6.64 (s, 2H), 6.60 (s, 2H), 1.99 (s, 6H), 1.98 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 156.98, 156.84, 155.14, 153.86, 151.42, 150.12, 145.06, 143.89, 138.92, 137.56, 137.26, 137.09, 137.04, 137.01, 135.84, 128.79, 128.59, 128.38, 128.26, 127.22, 126.83, 121.42, 119.95, 114.57, 114.51, 20.85, 20.77. EI HRMS m/z: found 498.2192 (MH^+); calcd ($C_{33}H_{28}N_3O_2$) 498.2182.

2-[2-(2-Pent-4-enyloxyethoxy)ethoxy]ethanol (21a). To a solution of triethylene glycol (15.0 g, 100 mmol) in THF (300 mL) at 0 °C was slowly added NaH (2.8 g, 70 mmol, 60% in mineral oil) as a solid. The resulting solution was allowed to reach room temperature while stirring over 1 h. Subsequently, 5-bromopentene (11.2 g, 75 mmol) was added *via* syringe and the contents heated at reflux for 12 h. The reaction was cooled to room temperature and the solvent was reduced to one half on a rotary evaporator. The residue was extracted with ether (200 mL) and water (100 mL). The organic layer was separated, dried over magnesium sulfate, filtered, and solvent evaporated to give an oil. The crude oil was purified by column chromatography on silica gel with hexane–ethyl acetate 1 : 3 as the eluant to yield a clear yellow viscous oil, R_f = 0.30 (8.43 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.74 (m, 1H), 4.94 (d, J = 17.0 Hz, 1H), 4.88 (d, J = 10.0 Hz, 1H), 3.65 (bs, 2H), 3.60–3.58 (m, 6H), 3.56–3.52 (m, 4H), 3.40 (t, J = 8.0 Hz, 2H), 2.95 (bs, 1H), 2.04 (q, J = 7.0 Hz, 2H), 1.62 (q, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 137.85, 114.39, 72.33, 70.49, 70.39, 70.34, 70.11, 69.83, 61.43, 30.08, 28.59. EI HRMS m/z: found 219.1593 (MH^+); calcd ($C_{11}H_{23}O_4$) 219.1596.

Toluene-4-sulfonic acid 2-[2-(2-pent-4-enyloxyethoxy)ethoxy] ethyl ester (21b). To an anhydrous solution of **21a** (8.43 g, 39 mmol), triethylamine (8.07 mL, 58 mmol) and 4-(dimethylamino)pyridine (0.47 g, 3.9 mmol) in dichloromethane (500 mL) at 0 °C was added *p*-toluenesulfonyl chloride (7.35 g, 39 mmol) as a solid. The reaction was slowly warmed to room temperature and stirred for an additional 8 h. The crude reaction mixture was quenched with water (150 mL), the organic layer separated, and the aqueous layer extracted with fresh dichloromethane (2 × 50 mL). The combined organic layers were dried over magnesium sulfate, filtered, and reduced to dryness to yield a viscous oil. The crude oil was purified by column chromatography on silica gel with hexane–ethyl acetate 1 : 1 as the eluant to yield a clear and colorless viscous oil, R_f = 0.50 (3.50 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.79 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.80 (m, 1H), 4.99 (d, J = 17.0 Hz, 1H), 4.94 (d, J = 10.0 Hz, 1H), 4.15 (t, J = 5.0 Hz, 2H), 3.68 (t, J = 5.0 Hz, 2H), 3.62–3.54 (m, 8H), 3.46 (t, J = 6.0 Hz, 2H), 2.44 (s, 3H), 2.10 (q, J = 7.0 Hz, 2H), 1.67 (q, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.41, 137.85, 132.54, 129.47, 127.58, 114.37, 70.47, 70.41, 70.38, 70.27, 69.83, 69.09, 68.40, 30.09, 28.62, 21.52. EI HRMS m/z: found 390.1952 (MNH_4^+); calcd ($C_{18}H_{32}NO_6S$) 390.1950.

4′-Allyloxybiphenyl-4-ol (22a). To a 0 °C solution of 4,4′-biphenol (10.0 g, 54 mmol) in THF (125 mL) was added NaH (1.5 g, 38 mmol, 60% in mineral oil) as a solid. The resulting solution was allowed to reach room temperature while stirring over 1 h. Subsequently, allyl bromide (4.88 g, 40 mmol) was added *via* syringe and the contents heated at reflux for 12 h. The crude reaction mixture was cooled to room temperature, filtered, and reduced to dryness. The crude white solid was purified by column chromatography on silica gel with dichloromethane–methanol 50 : 1 as the eluant to yield a white crystalline solid, R_f = 0.25 (5.72 g, 66%). Mp 172–173 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.45 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 9.0 Hz, 2H), 6.97 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.08 (m, 1H), 5.43 (dd, J = 2.0, 18.0 Hz, 1H), 5.30 (dd, J = 2.0, 11.0 Hz, 1H), 4.75 (s, 1H), 4.58 (d, J = 5.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 157.83, 154.68, 133.78, 133.64, 133.38, 128.03, 127.76, 117.78,

115.63, 115.05, 68.90. EI HRMS *m/z*: found 226.1000 (M^+); calcd ($C_{15}H_{14}O_2$) 226.0994.

4′-Allyloxy-4-(2-chloroethoxy)biphenyl (22b). To an anhydrous solution of **22a** (2.84 g, 13 mmol) in THF (150 mL) at 0 °C was added NaH (0.53 g, 13 mmol, 60% in mineral oil) as a solid. The resulting solution was stirred for 1 h while warming to room temperature. Subsequently, an excess of 1,2-dichloroethane (50 mL) was added and the contents heated to reflux for 15 h. After cooling the reaction to room temperature, diethyl ether (100 mL), and water (50 mL) were added. The organic layer was separated and the aqueous layer extracted with fresh diethyl ether (2 × 50 mL). The combined organic layers were dried over magnesium sulfate, filtered, and the solvent removed to yield a crude yellow solid. The crude product was purified by column chromatography on silica gel with hexane–dichloromethane 1 : 3 as the eluant to yield a white crystalline solid, $R_f = 0.75$ (1.70 g, 47%). Mp 142–144 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.49 (d, $J = 8.0$ Hz, 2H), 7.46, (d, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.08 (m, 1H), 5.44 (dd, $J = 2.0$, 17.0 Hz, 1H), 5.31 (d, $J = 2.0$, 10.0 Hz, 1H), 4.58 (d, $J = 4.0$ Hz, 2H), 4.26 (t, $J = 6.0$ Hz, 2H), 3.83 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 157.92, 157.39, 134.26, 133.47, 133.36, 127.87, 127.78, 117.74, 115.05, 115.04, 68.86, 68.10, 41.83. EI HRMS *m/z*: found 288.0927 (M^+); calcd ($C_{17}H_{17}O_2Cl$) 288.0917.

2-[2-(2-Hex-5-ynyloxyethoxy)ethoxy]ethanol (23a). To a solution of triethylene glycol (6.22 g, 40 mmol) in THF (250 mL) at 0 °C was added NaH (1.58 g, 40 mmol, 60% in mineral oil) as a solid. The solution was stirred for 1 h and slowly warmed to room temperature. Subsequently, 6-chlorohexyne (4.81 g, 40 mmol) was added *via* syringe and the reaction was heated at reflux for 15 h. The reaction was cooled to room temperature and solvent was reduced to one half on a rotary evaporator. The residue was extracted with ether (300 mL) and water (100 mL). The organic layer was separated, dried over magnesium sulfate, filtered, and solvent evaporated. The crude oil was purified by column chromatography on silica gel with ethyl acetate–hexane 3 : 1 as the eluant to yield a clear viscous oil, $R_f = 0.30$ (3.28 g, 36%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.73 (bs, 2H), 3.67–3.65 (m, 6H), 3.63–3.59 (m, 4H), 3.49 (t, $J = 7.0$ Hz, 2H), 2.71 (bs, 1H), 2.22 (dt, $J = 2.0$, 7.0 Hz, 2H), 1.95 (t, $J = 2.0$ Hz, 1H), 1.71 (q, $J = 7.0$ Hz, 2H), 1.60 (q, $J = 7.0$ Hz, 2H). ^{13}C NMR (125 MHz, $CHCl_3$, δ): 84.31, 72.45, 70.72, 70.60, 70.55, 70.33, 70.02, 68.35, 61.69, 28.50, 25.04, 18.10. EI HRMS *m/z*: found 248.1853 (MNH_4^+); calcd ($C_{12}H_{26}NO_4$) 248.1862.

Toluene-4-sulfonic acid 2-[2-(2-hex-5-ynyloxyethoxy)ethoxy] ethyl ester (23b). To an anhydrous solution of **23a** (1.67 g, 7 mmol), triethylamine (1.52 mL, 11 mmol) and 4-(dimethylamino)pyridine (0.09 g, 0.7 mmol) in dichloromethane (200 mL) at 0 °C was added *p*-toluenesulfonyl chloride (1.39 g, 7 mmol) as a solid. The reaction was slowly warmed to room temperature and stirred for an additional 8 h. The crude reaction mixture was quenched with water (75 mL). The organic layer was separated and the aqueous layer extracted with fresh dichloromethane (2 × 20 mL). The combined organic layers were dried over magnesium sulfate, filtered, and reduced to dryness to yield a viscous oil. The crude oil was purified by column chromatography on silica gel with hexane–ethyl acetate 1 : 1 as the eluant to yield a clear and colorless oil, $R_f = 0.50$ (2.29 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.80 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.16 (t, $J = 5.0$ Hz, 2H), 3.69 (t, $J = 5.0$ Hz, 2H), 3.61–3.56 (m, 8H), 3.47 (t, $J = 8.0$ Hz, 2H), 2.45 (s, 3H), 2.21 (dt, $J = 2.0$, 8.0 Hz, 2H), 1.94 (t, $J = 2.0$ Hz, 1H), 1.68 (q, $J = 7.0$ Hz, 2H), 1.59 (q, $J = 7.0$ Hz, 2H). ^{13}C NMR (100 MHz, $CHCl_3$, δ): 144.55, 132.93, 129.64, 127.82, 84.30, 70.77, 70.72, 70.65, 70.56, 70.08, 69.23, 68.70, 68.37, 28.74, 25.27, 21.74, 18.32. EI HRMS *m/z*: found 402.1938 (MNH_4^+); calcd ($C_{19}H_{32}NO_6S$) 402.1950.

4′-Prop-2-ynyloxybiphenyl-4-ol (24a). To a 0 °C solution of 4,4′-biphenol (3.0 g, 16 mmol) in THF (100 mL) was added NaH (0.71 g, 17 mmol, 60% in mineral oil) as a solid. The resulting solution was allowed to reach room temperature while stirring over 1 h. Subsequently, propargyl bromide (2.11 g, 18 mmol) was added *via* syringe and the contents heated at reflux for 10 h. The crude reaction mixture was cooled to room temperature, filtered, and reduced to dryness. The crude solid was purified by column chromatography on silica gel with dichloromethane as the eluant to yield a white crystalline solid, $R_f = 0.40$ (1.30 g, 36%). Mp 133–136 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.47 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 4.73 (d, $J = 2.5$ Hz, 2H), 2.54 (t, $J = 2.5$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.39, 154.55, 134.18, 133.29, 127.87, 127.58, 115.50, 115.03, 78.55, 75.56, 55.92. EI HRMS *m/z*: found 224.0835 (M^+); calcd ($C_{15}H_{12}O_2$) 224.0837.

4′-(2-Bromoethoxy)-4-prop-2-ynyloxybiphenyl (24b). To an anhydrous solution of **24a** (0.572 g, 3 mmol) in THF (50 mL) at 0 °C was added NaH (0.15 g, 4 mmol, 60% in mineral oil) as a solid. The resulting solution was stirred for 1 h while warming to room temperature. Subsequently, an excess of 1,2-dibromoethane (6 mL) was added and the contents heated to reflux for 8 h. The reaction was cooled to room temperature, filtered, and solvent evaporated. The crude product was purified by column chromatography on silica gel with hexane–dichloromethane 1 : 3 as the eluant to yield a white crystalline solid, $R_f = 0.60$ (0.60 g, 70%). Mp 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.49 (d, $J = 8.7$ Hz, 2H), 7.48 (q, $J = 8.7$ Hz, 2H), 7.03 (d, $J = 8.7$ Hz, 2H), 6.97 (d, $J = 8.7$ Hz, 2H), 4.73 (d, $J = 2.4$ Hz, 2H), 4.33 (t, $J = 6.0$ Hz, 2H), 3.66 (t, $J = 6.0$ Hz, 2H), 2.54 (t, $J = 2.4$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.05, 156.49, 134.02, 133.89, 127.76, 127.63, 115.05, 114.93, 78.54, 75.57, 67.96, 55.90, 29.23. EI HRMS *m/z*: found 330.0248 (M^+); calcd ($C_{17}H_{15}O_2Br$) 330.0255.

Ru[5′,5″-bis(4-hydroxy-2,6-dimethylphenyl)-2,2′:6′,2″-terpyridine]$_2$·2PF$_6$ (5). A degassed solution of ethylene glycol (30 mL), **3b** (0.500 g, 1.1 mmol) and $RuCl_2(DMSO)_4$ (0.255 g, 0.5 mmol) was heated to 160 °C for 12 h to produce a deep red solution. The reaction was cooled to room temperature, poured into aqueous KPF_6 (50 mL) and filtered over Celite. The red precipitate was washed with water and dissolved into a clean flask with acetone. The resulting red solution was dried over magnesium sulfate, filtered, and the solvent evaporated. Purification by column chromatography on silica gel with CH_3CN–H_2O–aqueous KPF_6 96 : 4 : 0.04 as the eluant yielded a red solid, $R_f = 0.40$ (0.59 g, 84%). Mp >350 °C. ^{1}H NMR (300 MHz, CD_3CN, δ): 8.81 (d, $J = 8.0$ Hz, 4H), 8.63 (d, $J = 8.0$ Hz, 4H), 8.43 (t, $J = 8.0$ Hz, 2H), 7.89 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.30 (d, $J = 2.0$ Hz, 4H), 7.08 (bs, 4H), 6.61 (s, 8H), 1.67 (s, 24H). ^{13}C NMR (100 MHz, acetone-d_6, δ): 157.88, 157.07, 155.93, 153.51, 141.29, 140.34, 137.47, 136.71, 126.91, 124.61, 124.19, 115.16, 20.49. MALDI HRMS *m/z*: found 1048.3250 (M^+); calcd ($C_{62}H_{54}N_6O_4$ Ru) 1048.3250. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 201 (5.4), 272 (4.7), 312 (4.8), 478 (4.1).

Ru[8-(4-hydroxy-2,6-dimethylphenyl)-2-[5-(4-hydroxy-2,6-dimethylphenyl)pyridin-2-yl]-1,10-phenanthroline]$_2$·2PF$_6$ (12). A degassed solution of ethylene glycol (30 mL), **4b** (0.500 g, 1.0 mmol) and $RuCl_2(DMSO)_4$ (0.243 g, 0.5 mmol was heated to 160 °C for 12 h to produce a deep red solution. The reaction was cooled to room temperature, poured into aqueous KPF_6 (50 mL) and filtered over Celite. The red precipitate was washed with water and dissolved into a clean flask with acetone. The resulting red solution was dried over magnesium sulfate, filtered, and the solvent removed. Purification by column chromatography on silica gel with CH_3CN–H_2O–aqueous KPF_6 95 : 5 : 0.05 as the eluant yielded a red solid, $R_f = 0.40$ (0.61 g, 87%). Mp >350 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 9.20 (d, $J = 8.5$ Hz, 4H), 9.00 (d, $J = 8.0$ Hz, 4H), 8.94

(d, $J = 8.5$ Hz, 4H), 8.52 (d, $J = 9.0$ Hz, 4H), 8.46 (d, $J = 2.0$ Hz, 4H), 8.40 (s, 4H), 8.39 (s, 4H), 8.37 (d, $J = 9.0$ Hz, 4H), 7.98 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.90 (d, $J = 2.0$ Hz, 4H), 7.70 (d, $J = 2.0$ Hz, 4H), 6.49 (s, 4H), 6.46 (s, 4H), 6.42 (s, 4H), 6.39 (s, 4H), 1.57 (s, 12H), 1.56 (s, 12H), 1.34 (s, 12H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 158.34*, 158.11, 156.35, 156.14, 155.41, 149.55, 147.30, 141.73, 140.92, 140.42, 138.29, 137.98, 137.90, 137.81, 137.72, 135.12, 131.76, 130.97, 129.97, 128.89, 127.65, 127.18, 125.60, 123.12, 115.44*, 115.38*, 20.59, 20.51, 20.33, 20.21. MALDI HRMS m/z: found 1096.3292 (M^+); calcd ($C_{66}H_{54}N_6O_4$ Ru) 1096.3250. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 201 (5.5), 239 (5.0), 296 (5.0), 343 (4.8), 499 (4.2).

Ru(5,5″-bis-(2,6-dimethyl-4-{2-[2-(2-pent-4-enyloxyethoxy)-ethoxy]ethoxy}phenyl)-[2,2′;6′,2″]-terpyridine)$_2$·2PF$_6$ (6). To an anhydrous solution of **5** (0.222 g, 0.17 mmol) in acetonitrile (35 mL) was added anhydrous cesium carbonate (0.61 g, 1.9 mmol) and **21b** (0.418 g, 1.1 mmol). The contents were heated at reflux for 10 h. The reaction was cooled to room temperature, poured into aqueous KPF_6 (50 mL) and filtered over Celite. The red oily precipitate was washed with water and transferred to a clean flask with dichloromethane. The resulting red solution was dried over magnesium sulfate, filtered, and the solvent removed. Purification by column chromatography on silica gel eluted with CH_3CN–H_2O–aqueous KPF_6 96 : 4 : 0.04 afforded a red glassy solid, $R_f = 0.70$ (0.23 g, 66%). Mp 49–52 °C. ^{1}H NMR (400 MHz, acetone-d_6, δ): 8.94 (d, $J = 8.0$ Hz, 4H), 8.86 (d, $J = 8.0$ Hz, 4), 8.37 (t, $J = 8.0$ Hz, 2H), 7.95 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.64 (d, $J = 2.0$ Hz, 4H), 6.62 (s, 8H), 5.81 (m, 4H), 4.99 (dd, $J = 2.0$, 17.0 Hz, 4H), 4.91 (dd, $J = 2.0$, 10.0 Hz, 4H), 4.08 (t, $J = 5.0$ Hz, 8H), 3.78 (t, $J = 5.0$ Hz, 8H), 3.65–3.57 (m, 24H), 3.52 (t, $J = 5$ Hz, 8H), 3.43 (t, $J = 6.0$ Hz, 8H), 2.14 (q, $J = 7.0$ Hz, 2H), 1.61 (s, 24H), 1.60 (q, $J = 7.0$ Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6, δ): 159.40, 157.17, 155.88, 153.36, 141.05, 140.29, 138.98, 137.46, 136.75, 128.01, 124.68, 124.25, 114.70, 114.28, 71.15, 71.05, 71.01, 70.68, 70.66, 70.15, 68.01, 30.93, 29.68, 20.61. MALDI HRMS m/z: found 1848.8969 (M^+); calcd ($C_{106}H_{134}N_6O_{16}$Ru) 1848.8900. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 202 (5.5), 234 (sh, 4.8), 272 (4.7), 312 (4.8), 478 (4.1).

Ru(5,5″-bis-(4-{2-[2-(2-hex-5-ynyloxyethoxy)ethoxy]ethoxy}-2,6-dimethylphenyl)-[2,2′;6′,2″]-terpyridine)$_2$·2PF$_6$ (8). To an anhydrous solution of **5** (0.100 g, 0.075 mmol) in acetonitrile (15 mL) was added anhydrous cesium carbonate (0.243 g, 0.74 mmol) and **23b** (0.229 g, 0.60 mmol). The contents were heated at reflux for 12 h. The reaction was cooled to room temperature, poured into aqueous KPF_6 (25 mL) and filtered over Celite. The red oily precipitate was washed with water and transferred to a clean flask with dichloromethane. The resulting red solution was dried over magnesium sulfate, filtered, and the solvent removed. Purification by column chromatography on silica gel eluted with CH_3CN–H_2O–aqueous KPF_6, 96 : 4 : 0.04 afforded a red glassy solid (0.09 g, 56%). Mp 54–58 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.97 (d, $J = 8.0$ Hz, 4H), 8.87 (d, $J = 8.0$ Hz, 4H), 8.39 (t, $J = 8.0$ Hz, 2H), 7.97 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.65 (d, $J = 2.0$ Hz, 4H), 6.63 (s, 8H), 4.09 (t, $J = 4.5$ Hz, 8H), 3.79 (t, $J = 4.5$ Hz, 8H), 3.65–3.58 (m, 24H), 3.53 (t, $J = 4.5$ Hz, 8H), 3.45 (t, $J = 5.0$ Hz, 8H), 2.31 (t, $J = 2.5$ Hz, 4H), 2.18 (dt, $J = 2.5$, 5.0 Hz, 8H), 1.65–1.62 (m, 8H), 1.62 (s, 24H), 1.57–1.54 (m, 8H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 159.03, 156.78, 155.51, 152.98, 140.65, 139.82, 137.03, 136,20, 127.51, 124.14, 123.71, 113.81, 84.01, 70.44, 70.32, 70.29, 70.10, 69.91, 69.32, 69.06, 67.33, 25.14, 19.74, 19.67, 17.56. MALDI HRMS m/z: found 1896.8874 (M^+); calcd ($C_{110}H_{134}N_6O_{16}$Ru) 1896.8900. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 201 (5.6), 273 (4.9), 312 (5.0), 478 (4.3).

Ru(5,5″-bis-{2,6-dimethyl-4-[2-(4′-prop-2-ynylbiphenyl-4-yloxy)ethoxy]phenyl}-[2,2′;6′,2″]-terpyridine)$_2$·2PF$_6$ (10). To an anhydrous solution of **5** (0.100 g, 0.075 mmol) in acetonitrile (5 mL) was added anhydrous cesium carbonate (0.192 g, 0.59 mmol), **24b** (0.123 g, 0.37 mmol), and triglyme (100 μL). The contents were heated at reflux for 36 h. The reaction was cooled to room temperature, poured into aqueous KPF_6 (25 mL) and filtered over Celite. The red oily precipitate was washed with water and transferred to a clean flask with dichloromethane. The resulting red solution was dried over magnesium sulfate, filtered, and the solvent removed. Purification by column chromatography on silica gel eluted with CH_3CN–H_2O–aqueous KPF_6 96 : 4 : 0.04 afforded a red solid (0.12 g, 70%). Mp 154–155 °C. ^{1}H NMR (400 MHz, acetone-d_6, δ): 8.95 (d, $J = 8.0$ Hz, 4H), 8.70 (d, $J = 8.0$ Hz, 4H), 8.38 (t, $J = 8.0$ Hz, 2H), 7.98 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.66 (d, $J = 2.0$ Hz, 4H), 7.56 (d, $J = 8.0$ Hz, 16H), 7.07 (d, $J = 8.0$ Hz, 8H), 7.04 (d, $J = 8.0$ Hz, 8H), 6.69 (s, 8H), 4.83 (d, $J = 2.4$ Hz, 8H), 4.36 (bd, $J = 4.5$ Hz, 16H), 3.12 (t, $J = 2.4$ Hz, 4H), 1.63 (s, 24H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 159.78, 158.99, 157.90, 157.70, 156.39, 153.86, 141.52, 140.74, 138.07, 137.17, 134.71, 134.20, 128.63, 128.46, 128.32, 125.06, 124.63, 116.11, 115.80, 114.72, 79.82, 77.05, 67.43, 67.39, 56.32, 20.62. MALDI HRMS m/z: found 2048.7409 (M^+); calcd ($C_{130}H_{110}N_6O_{12}$Ru) 2048.7220. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 201 (5.9), 266 (5.3), 312 (4.9), 478 (4.1).

Ru(8-(4-{2-[2-(2-hex-5-ynyloxyethoxy)ethoxy]ethoxy}-2,6-dimethylphenyl)-2-[5-(4-{2-[2-(2-hex-5-ynyloxyethoxy)ethoxy]-ethoxy}-2,6-dimethylphenyl)pyridin-2-yl]-[1,10]-phenanthroline)$_2$·2PF$_6$ (13). To an anhydrous solution of **12** (0.70 g, 0.051 mmol) in acetonitrile (10 mL) was added anhydrous cesium carbonate (0.132 g, 0.40 mmol) and **23b** (0.155 g, 0.40 mmol). The contents were heated at reflux for 12 h. The reaction was cooled to room temperature, poured into aqueous KPF_6 (15 mL) and filtered over Celite. The red oily precipitate was washed with water and transferred to a clean flask with dichloromethane. The resulting red solution was dried over magnesium sulfate, filtered, and the solvent removed. Purification by column chromatography on silica gel eluted with CH_3CN–H_2O–aqueous KPF_6 96 : 4 : 0.04 afforded a red glassy solid (63 mg, 56%). Mp 58–62 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 9.22 (d, $J = 8.0$ Hz, 2H), 9.02 (d, $J = 8.0$ Hz, 2H), 8.95 (d, $J = 8.0$ Hz, 2H), 8.53 (d, $J = 8.0$ Hz, 2H), 8.49 (d, $J = 2.0$ Hz, 2H), 8.39 (d, $J = 8.0$ Hz, 2H), 8.01 (dd, $J = 2.0$, 8.0 Hz, 2H), 7.93 (d, $J = 2.0$ Hz, 2H), 7.72 (d, $J = 2.0$ Hz, 2H), 6.62 (s, 2H), 6.59 (s, 2H), 6.55 (s, 2H), 6.53 (s, 2H), 4.05$_2$ (t, $J = 5.0$ Hz, 4H), 4.05 (t, $J = 5.0$ Hz, 4H), 3.76 (t, $J = 5.0$ Hz, 4H), 3.75 (t, $J = 5.0$ Hz, 4H), 3.63–3.51 (m, 32H), 3.45 (t, $J = 6.0$ Hz, 8H), 2.31 (t, $J = 2.0$ Hz, 4H), 2.18 (dt, $J = 2.0$, 7.0 Hz, 8H), 1.64–1.62 (m, 8H), 1.63 (s, 12H), 1.57–1.54 (m, 8H), 1.40 (s, 6H), 1.37 (s, 6H). ^{13}C NMR (100 MHz, acetone-d_6, δ): 159.42*, 157.76, 155.75, 155.67, 154.84, 149.19, 146.84, 141.10, 140.49, 139.79, 137.88, 137.64, 137.57, 137.46, 137.37, 134.79, 131.39, 130.64, 129.65, 128.59, 128.44, 127.97, 125.33, 122.84, 114.31*, 114.24*, 84.71*, 71.17*, 71.06*, 71.02*, 70.84*, 70.66*, 70.04*, 69.84*, 68.05*, 29.44*, 26.04*, 20.75, 20.66, 20.49, 20.36, 18.48*. MALDI HRMS m/z: found 1944.8859 (M^+); calcd ($C_{114}H_{134}N_6O_{16}$Ru) 1944.8894. UV–Vis (CH_3CN), λ_{max}/nm (log ε): 202 (5.4), 273 (5.2), 349 (4.7), 499 (4.0).

Ru(terpy-catenane)·2PF$_6$ (7a). To a solution of $RuCl_2$-$(PCy_3)_2CH_2Ph$ (3 mg, 3.5 μmol) in degassed dichloromethane (50 mL) at room temperature was added a solution of **6** (0.15 g, 0.07 mmol) in dichloromethane (10 mL) *via* syringe pump over 12 h. After stirring for an additional 48 h, the red solution was reduced to dryness and purified by column chromatography on silica gel with CH_3CN–H_2O–aqueous KPF_6 95 : 5 : 0.05 as the eluant to yield a red glassy solid (0.04 g, 27%) as a mixture of *cis*/*trans* isomers. This mixture was dissolved in dichloromethane–ethanol (1 : 1, 4 mL) and to it was added Pd/C (10 mol%). The suspension was stirred for 20 h under a hydrogen atmosphere. The slurry was filtered and reduced to dryness to yield a red glassy solid (0.04 g, 98%). Mp 118–120 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.94 (d, $J = 8.0$ Hz, 4H),

8.86 (d, $J = 8.0$ Hz, 4H), 8.32 (t, $J = 8.0$ Hz, 2H), 8.02 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.61 (d, $J = 2.0$ Hz, 4H), 6.64 (s, 8H), 4.13 (bt, $J = 5.0$ Hz, 8H), 3.77 (bt, $J = 5.0$ Hz, 8H), 3.64–3.56 (m, 32H), 3.49 (t, $J = 7.0$ Hz, 8H), 1.63 (bs, 8H), 1.60 (s, 24H), 1.44 (bs, 16H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 160.02, 157.58, 156.43, 154.01, 141.69, 140.49, 137.87, 136.85, 128.30, 125.08, 124.58, 114.77, 71.93, 71.52, 71.29, 71.24, 70.88, 70.33, 68.48, 30.75, 30.56, 27.11, 20.59. MALDI HRMS m/z: found 1796.8537 (M^+); calcd ($C_{102}H_{130}N_6O_{16}Ru$) 1796.8587. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 202 (5.5), 235 (sh, 5.0), 272 (4.9), 312 (5.0), 479 (4.2).

Ru(terpy-macrocycle)·2PF$_6$ (7b). Prepared simultaneously and hydrogenated in an identical manner to compound **7a** (0.068 g, 47%) *cis*/*trans* isomers. Hydrogenation yielded a red glassy solid, **7b** (0.065 g, 97%). Mp 132–134 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.96 (d, $J = 8.0$ Hz, 4H), 8.88 (d, $J = 8.0$ Hz, 4H), 8.40 (t, $J = 8.0$ Hz, 2H), 7.96 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.67 (d, $J = 2.0$ Hz, 4H), 6.66 (s, 4H), 6.64 (s, 4H), 4.13 (t, $J = 5.0$ Hz, 8H), 3.77 (t, $J = 5.0$ Hz, 8H), 3.62 (t, $J = 5.0$ Hz, 8H), 3.57–3.53 (m, 16H), 3.45 (t, $J = 5.0$ Hz, 8H), 3.33 (t, $J = 7.0$ Hz, 8H), 1.73 (s, 12H), 1.51 (s, 12H), 1.43 (q, $J = 7.0$ Hz, 8H), 1.19 (bs, 16H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 160.13, 157.73, 156.45, 153.91, 141.61, 140.83, 137.89, 137.70, 137.26, 128.41, 125.07, 124.67, 115.16, 115.06, 71.81, 71.61, 71.39, 71.28, 70.83, 70.35, 68.54, 30.65, 30.40, 26.99, 20.82, 20.62. MALDI HRMS m/z: found 1796.8624 (M^+); calcd ($C_{102}H_{130}N_6O_{16}Ru$) 1796.8581. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 203 (5.4), 236 (sh, 4.9), 273 (4.8), 311 (4.9), 479 (4.1).

Standard reaction conditions for copper-mediated coupling (compounds 9, 11, and 14a–b). To enough acetonitrile to generate a 1.0 mM solution of the corresponding pre-catenane Ru(II) complex (1.0 mol eq.) was added copper(II) acetate monohydrate (20 mol eq.), and the mixture heated at reflux for 12–32 h, or until no starting material was visible by TLC (SiO_2, CH_3CN–H_2O–aqueous KPF_6 95 : 5 : 0.05). The reactions were cooled and reduced to dryness. The residues were suspended in dichloromethane, filtered and the solvent evaporated to yield the crude red compounds. The crude mixtures were purified by column chromatography on silica gel with 100% CH_3CN → CH_3CN–H_2O–aqueous KPF_6 95 : 5 : 0.05 as the eluant, except for compounds **11a–b** which required centrifugal chromatography on silica gel with 100% CH_2Cl_2 → 2% MeOH as the eluant.

Ru(terpy-acteylcatenane)·2PF$_6$ (9a). A red glassy solid (0.012 g, 25%). Mp 65–70 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.95 (d, $J = 8.0$ Hz, 4H), 8.87 (d, $J = 8.0$ Hz, 4H), 8.36 (t, $J = 8.0$ Hz, 2H), 8.01 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.62 (d, $J = 2.0$ Hz, 4H), 6.34 (s, 8H), 4.12 (t, $J = 5.0$ Hz, 8H), 3.78 (t, $J = 5.0$ Hz, 8H), 3.64–3.60 (m, 24H), 3.55 (t, $J = 5.0$ Hz, 8H), 3.50 (t, $J = 6.0$ Hz, 8H), 2.36 (t, $J = 6.0$ Hz, 8H), 1.69–1.63 (m, 16H), 1.62 (s, 24H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 159.11, 156.71, 155.51, 153.07, 140.75, 139.72, 136.98, 136.21, 127.43, 124.16, 123.69, 113.85, 77.50, 70.60, 70.40, 70.31, 70.07, 69.99, 69.36, 67.56, 65.54, 25.06, 19.73, 19.69, 18.35. MALDI HRMS m/z: found 1892.8710 (M^+); calcd ($C_{110}H_{130}N_6O_{16}Ru$) 1892.8581. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 201 (5.2), 235 (sh, 4.7), 272 (4.6), 312 (4.7), 480 (3.9).

Ru(terpy-acetylmacrocycle)·2PF$_6$ (9b). A red glassy solid (0.017 g, 36%). Mp 79–84 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.98 (d, $J = 8.0$ Hz, 4H), 8.88 (d, $J = 8.0$ Hz, 4H), 8.42 (t, $J = 8.0$ Hz, 2H), 7.98 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.65 (d, $J = 2.0$ Hz, 4H), 6.66 (s, 4H), 6.65 (s, 4H), 4.12 (t, $J = 5.0$ Hz, 8H), 3.79 (t, $J = 5.0$ Hz, 8H), 3.64 (t, $J = 5.0$ Hz, 8H), 3.58, (t, $J = 5.0$ Hz, 8H), 3.56 (t, $J = 5.0$ Hz, 8H), 3.48 (t, $J = 5.0$ Hz, 8H), 3.37 (t, $J = 7.0$ Hz, 8H), 2.15 (t, $J = 7.0$ Hz, 8H), 1.69 (s, 12H), 1.59 (s, 12H), 1.52 (q, $J = 7.0$ Hz, 8H), 1.44 (q, $J = 7.0$ Hz, 8H). ^{1}H NMR (125 MHz, acetone-d_6, δ): 160.09, 157.67, 156.45, 153.95, 141.60, 140.85, 137.92, 137.86, 137.31, 128.37, 125.12, 124.68, 115.02, 114.88, 78.20, 71.59, 71.44, 71.32, 70.89, 70.86, 70.29, 68.47, 66.28, 29.65, 25.90, 20.81, 20.64, 19.18. MALDI HRMS m/z: found 1892.8663 (M^+); calcd ($C_{110}H_{130}N_6O_{16}Ru$) 1892.8581. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 202 (5.2), 236 (4.8), 272 (4.9), 311 (4.8), 478 (4.0).

Ru(terpy-biphencatenane)·2PF$_6$ (11a). A red solid (0.021 g, 29%). Mp >340 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.78 (d, $J = 8.0$ Hz, 4H), 8.76 (d, $J = 8.5$ Hz, 4H), 8.19 (t, $J = 8.0$ Hz, 2H), 7.93 (dd, $J = 2.0$, 8.5 Hz, 4H), 7.60 (d, $J = 9.0$ Hz, 8H), 7.58 (d, $J = 2.0$ Hz, 4H), 7.57 (d, $J = 9.0$ Hz, 8H), 7.12 (d, $J = 9.0$ Hz, 8H), 7.03 (d, $J = 9.0$ Hz, 8H), 6.64 (s, 8H), 5.01 (s, 8H), 4.41 (bd, $J = 8.0$ Hz, 16H), 1.55 (s, 24H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 159.34, 158.58, 157.69, 157.05, 156.24, 153.84, 141.50, 140.50, 137.94, 135.05, 134.20, 128.54, 128.50, 128.47, 124.95, 124.55, 116.22, 116.17, 114.72, 106.00, 76.50, 71.12, 66.90, 66.55, 56.72, 20.53. MALDI HRMS m/z: found 2044.6826 (M^+); calcd ($C_{130}H_{106}N_6O_{12}Ru$) 2044.6907. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 202 (5.6), 268 (5.2), 314 (4.8), 478 (4.0).

Ru(terpy-biphenmacrocyle)·2PF$_6$ (11b). A red solid (0.021 g, 21%). Mp > 340 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.96 (d, $J = 8.0$ Hz, 4H), 8.85 (d, $J = 8.0$ Hz, 4H), 8.40 (t, $J = 8.0$ Hz, 2H), 7.93 (dd, $J = 2.0$, 8.5 Hz, 4H), 7.65 (d, $J = 2.0$ Hz, 4H), 7.52 (d, $J = 8.5$ Hz, 8H), 7.50 (d, $J = 8.5$ Hz, 8H), 7.04 (d, $J = 8.5$ Hz, 8H), 7.00 (d, $J = 8.5$ Hz, 8H), 4.98 (s, 8H), 4.41 (bd, 16H), 1.73, (s, 12H), 1.45 (s, 12H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 159.70, 158.87, 157.72, 157.64, 156.48, 153.89, 141.46, 140.85, 138.01, 137.89, 137.19, 135.03, 134.33, 128.68, 128.44, 128.40, 125.04, 124.64, 116.31, 116.18, 115.69, 115.03, 76.54, 70.99, 67.54, 65.02, 56.58, 20.78, 20.62. MALDI HRMS m/z: found 2044.7012 (M^+); calcd ($C_{130}H_{106}N_6O_{12}Ru$) 2044.6907. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 202 (5.5), 266 (5.1), 311 (4.7), 479 (4.0).

Ru(pherpy-catenane)·2PF$_6$ (14a). A red glassy solid (0.012 g, 20%). Mp 122–128 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 9.12 (d, $J = 9.0$ Hz, 2H), 9.00 (d, $J = 8.0$ Hz, 2H), 8.93 (d, $J = 9.0$ Hz, 2H), 8.53 (d, $J = 9.0$ Hz, 2H), 8.53 (d, $J = 2.0$ Hz, 2H), 8.41 (d, $J = 9.0$ Hz, 2H), 8.04 (dd, $J = 2.0$, 8.0 Hz, 2H), 7.89 (d, $J = 2.0$ Hz, 2H), 7.69 (d, $J = 2.0$ Hz, 2H), 6.62 (s, 2H), 6.60 (s, 2H), 6.55 (s, 2H), 6.52 (s, 2H), 4.08 (bt, $J = 6.0$ Hz, 8H), 3.74 (bt, $J = 6.0$ Hz, 8H), 3.61–3.59 (m, 24H), 3.55 (bt, $J = 6.0$ Hz, 8H), 3.49 (bt, $J = 6.0$ Hz, 8H), 2.39 (bt, $J = 6.0$ Hz, 8H), 1.70–1.664 (m, 16H), 1.62 (s, 6H), 1.61 (s, 6H), 1.39 (s, 6H), 1.36 (s, 6H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 160.00, 159.98, 158.15, 156.36, 156.13, 155.46, 149.63, 147.31, 141.65, 140.74, 140.32, 138.11, 138.01, 137.95, 137.84, 137.76, 135.05, 131.82, 130.98, 130.14, 128.87, 128.71, 128.24, 125.67, 123.14, 114.77*, 114.71*, 78.53*, 71.50*, 71.31*, 71.22*, 70.99*, 70.91*, 70.26*, 68.49*, 66.56*, 29.72*, 26.01*, 20.74, 20.65, 20.48, 20.35, 19.32*. MALDI HRMS m/z: found 1940.8534 (M^+); calcd ($C_{114}H_{130}N_6O_{16}Ru$) 1940.8581. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 202 (5.3), 236 (4.9), 297 (4.8), 343 (4.6), 501 (4.0).

5–5″-Bis{4-[2-(4′-allyloxybiphenyl-4-yloxy)ethoxy]-2,6-dimethylphenyl}-[2,2′:6′2″]-terpyridine (15). An anhydrous solution of **3b** (0.197 g, 0.42 mmol), **22b** (0.330 g, 1.14 mmol), and cesium carbonate (0.689 g, 2.11 mmol) in DMF (10 mL) was heated at 80 °C for 12 h with an oil bath. The crude reaction mixture was quenched with water (30 mL) and extracted with chloroform (30 mL). The organic layer was separated, washed with water (3 × 20 mL), dried over magnesium sulfate, filtered and reduced to dryness. Purification by column chromatography on alumina with dichloromethane–hexane 3 : 1 as the eluant afforded a white solid (0.357 g, 88%). Mp 188–189 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.73 (d, $J = 8.0$ Hz, 2H), 8.53 (d, $J = 2.0$ Hz, 2H), 8.52 (d, $J = 8.0$ Hz, 2H), 8.02 (t, $J = 8.0$ Hz, 1H), 7.69 (dd, $J = 2.0$, 8.0 Hz, 2H), 7.50 (d, $J = 9.0$ Hz, 4H), 7.48 (d, $J = 9.0$ Hz, 4H), 7.03 (d, $J = 9.0$ Hz, 4H), 6.98 (d, $J = 9.0$ Hz, 4H), 6.80 (s, 4H), 6.09 (m, 2H), 5.44 (dd, $J = 2.0$, 18.0 Hz,

2H), 5.31, (dd, $J = 2.0$, 12.0 Hz, 2H), 4.58 (d, $J = 6.0$ Hz, 4H), 4.39 (bs, 8H), 2.10 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 158.08, 157.83, 157.80, 155.40, 154.67, 150.03, 138.35, 138.09, 138.01, 136.69, 133.91, 133.56, 133.34, 130.88, 127.79, 127.75, 125.55, 120.90, 117.74, 115.03, 115.00, 113.79, 68.88, 66.61, 66.42, 21.19. MALDI HRMS *m/z*: found 978.4525 (M^+); calcd ($C_{65}H_{60}N_3O_6$) 978.4477.

8-{4-[2-(4′-Allyloxybiphenyl-4-yloxy)ethoxy]-2,6-dimethylphenyl}-2-(5-{4-[2-(4′-allyloxybiphenyl-4-yloxy)ethoxy]-2,6-dimethylphenyl}pyridin-2-yl)-[1,10]-phenanthroline (18). An anhydrous solution of **4b** (0.256 g, 0.52 mmol), **22b** (0.447 g, 1.55 mmol), and cesium carbonate (0.840 g, 2.58 mmol) in DMF (13 mL) was heated at 80 °C for 12 h with an oil bath. The crude reaction mixture was quenched with water (30 mL) and extracted with chloroform (30 mL). The organic layer was separated, washed with water (3 × 20 mL), dried over magnesium sulfate, filtered and reduced to dryness. Purification by column chromatography on alumina with dichloromethane–hexane 3 : 1 as the eluant afforded a white solid (0.473 g, 92%). Mp 203–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.07 (d, $J =$ 8.0 Hz, 1H), 9.08 (d, $J = 2.0$ Hz, 1H), 8.86, (d, $J = 8.0$ Hz, 1H), 8.56 (d, $J = 2.0$ Hz, 1H), 8.42 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 2.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J =$ 8.0 Hz, 1H), 7.75 (dd, $J = 2.0$, 8.0 Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 4H), 7.47 (d, $J = 8.0$ Hz, 4H), 7.02 (d, $J = 8.0$ Hz, 4H), 6.97 (d, $J = 8.0$ Hz, 4H), 6.82 (s, 2H), 6.79 (s, 2H), 6.06 (m, 2H), 5.43 (dd, $J = 2.0$, 18.0 Hz, 2H), 5.28, (dd, $J = 2.0$, 12.0 Hz, 2H), 4.55 (d, $J = 6.0$ Hz, 4H), 4.38 (s, 4H), 4.37 (s, 4H), 2.10 (s, 6H), 2.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 158.18*, 158.00*, 157.75*, 156.39, 154.67, 151.99, 149.83, 145.74, 144.93, 138.50, 138.06, 137.91, 137.06, 137.01, 136.53, 135.93, 133.81, 133.78, 133.47, 133.45, 133.28*, 130.84, 130.61, 128.81, 128.66, 127.71*, 127.65*, 126.78, 126.74, 122.54, 120.70, 117.62*, 114.97*, 114.94*, 113.79, 113.73, 68.78*, 66.54*, 66.38, 66.35, 21.20, 21.12. MALDI HRMS *m/z*: found 1002.4458 (M^+); calcd ($C_{67}H_{60}N_3O_6$) 1002.4477.

Fe(5–5″-bis{4-[2-(4′-Allyloxybiphenyl-4-yloxy)ethoxy]-2,6-dimethylphenyl}-[2,2′:6′2″]-terpyridine)$_2$·2PF$_6$ (16). To a suspension of **15** (0.174 g, 0.18 mmol) in acetone (20 mL), at 55 °C, was added a solution of $FeSO_4 \cdot 7H_2O$ (0.049 g, 0.18 mmol) in water (12 mL) dropwise to generate an intense purple solution, which was heated at reflux for 1 h. The crude reaction was quenched with aqueous KPF_6 to generate a purple precipitate, which was filtered and washed with water. The precipitate was dissolved in dichloromethane, dried over magnesium sulfate, filtered, and reduced to dryness to yield a purple solid (0.203 g, 99%). Mp 158–159 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 9.14 (d, $J = 8.0$ Hz, 4H), 8.87 (d, $J = 8.0$ Hz, 4H), 8.67 (t, $J =$ 8.0 Hz, 2H), 7.97 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.56 (d, $J = 8.0$ Hz, 8H), 7.54 (d, $J = 8.0$ Hz, 8H), 7.35 (d, $J = 2.0$ Hz, 4H), 7.04 (d, $J = 8.0$ Hz, 8H), 7.03 (d, $J = 8.0$ Hz, 8H), 6.83 (s, 8H), 6.10 (m, 4H), 5.43 (dd, $J = 2.0$, 17.0 Hz, 4H), 5.27 (dd, $J =$ 2.0, 11.0 Hz, 4H), 4.62 (bd, $J = 5.0$ Hz, 8H), 4.37 (bd, $J =$ 8.0 Hz, 16H), 1.56 (s, 24H). ^{13}C NMR (125 MHz, CD_2Cl_2, δ): 160.42, 159.43, 158.40, 158.29, 156.20, 153.91, 1491.78, 139.90, 137.52, 134.16, 134.14, 134.13, 134.01, 133.72, 128.10, 128.03, 127.56, 124.08, 117.67, 115.50, 115.38, 114.75, 69.28, 67.14, 67.08, 20.74. MALDI HRMS *m/z*: found 2010.8226 (M^+); calcd ($C_{130}H_{118}N_6O_{12}Fe$) 2010.8152. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 202 (5.6), 269 (5.1), 333 (4.7), 556 (3.9).

Fe(8-{4-[2-(4′-allyloxybiphenyl-4-yloxy)ethoxy]-2,6-dimethylphenyl}-2-(5-{4-[2-(4′-allyloxybiphenyl-4-yloxy)ethoxy]-2,6-dimethyl-phenyl}pyridin-2-yl)-[1,10]-phenanthroline)$_2$·2PF$_6$ (19). To a suspension of **18** (0.218 g, 0.22 mmol) in acetone (20 mL), at 55 °C, was added a solution of $FeSO_4 \cdot 7H_2O$ (0.060 g, 0.22 mmol) in water (15 mL) dropwise to generate an intense purple solution, which was heated at reflux for 1 h. The crude reaction was quenched with aqueous KPF_6 to generate a purple precipitate, which was filtered and washed with water. The precipitate was dissolved in dichloromethane, dried over magnesium sulfate, filtered, and reduced to dryness to yield a purple solid (0.233 g, 91%). Mp 160–163 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 9.45 (d, $J = 8.8$ Hz, 2H), 9.23 (d, $J =$ 8.8 Hz, 2H), 9.03 (d, $J = 8.4$ Hz, 2H), 8.64 (d, $J = 8.8$ Hz, 2H), 8.44 (d, $J = 2.0$ Hz, 2H), 8.41 (d, $J = 8.8$ Hz, 2H), 7.97 (dd, $J =$ 2.0, 8.4 Hz, 2H), 7.56 (d, $J = 10.0$ Hz, 8H), 7.55 (d, $J = 2.0$ Hz, 2H), 7.54 (d, $J = 10.0$ Hz, 8H), 7.45 (d, $J = 2.0$ Hz, 2H), 7.03 (d, $J = 10.0$ Hz, 8H), 7.01 (d, $J = 10.0$ Hz, 8H), 6.66 (s, 2H), 6.64 (s, 2H), 6.58 (s, 2H), 6.56 (s, 2H), 6.09 (m, 4H), 5.45 (d, $J = 17.2$ Hz, 4H), 5.27 (d, $J = 10.8$ Hz, 4H), 4.62 (m, 8H), 4.35 (bs, 8H), 4.32 (bs, 8H), 1.56 (s, 6H), 1.54 (s, 6H), 1.26 (s, 12H). ^{13}C NMR (125 MHz, CD_2Cl_2, δ): 161.92*, 159.70*, 158.89*, 158.84, 158.06, 158.00, 156.41, 151.79, 148.68, 141.76, 141.29, 140.41, 138.80, 138.04, 137.91, 137.87, 137.73, 137.12, 134.80*, 134.32*, 134.06*, 130.80, 130.67, 130.03, 129.02, 128.56, 128.36*, 128.33, 128.31*, 125.22, 123.68, 117.41*, 115.93*, 115.80*, 114.70*, 114.63*, 69.32*, 67.43*, 67.36*, 20.66, 20.59, 20.31, 20.19. MALDI HRMS *m/z*: found 2058.8076 (M^+); calcd ($C_{134}H_{118}N_6O_{12}Fe$) 2058.8152. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 203(5.7), 267 (5.2), 357 (4.7), 579 (4.0).

Fe(terpycat)·2PF$_6$ (17). To a solution of $RuCl_2(PCy_3)_2CH_2Ph$ (8 mg, 0.20 mmol) in dichloromethane (20 mL) was added a solution of **16** (0.115 g, 0.05 mol) in dichloromethane (20 mL) *via* syringe pump over 12 h. The resulting purple solution was stirred for an additional 60 h. The crude reaction mixture was reduced to dryness and purified by column chromatography on silica gel with CH_3CN–H_2O–aqueous KPF_6 96 : 4 : 0.04 as the eluant. Subsequent centrifugal chromatography with dichloromethane–methanol 100 : 3 as the eluant afforded a purple solid (0.033 g, 30%) as a mixture of *cis*/*trans* isomers. This mixture (0.022 g, 0.010 mmol) was dissolved in dichloromethane–ethanol 1 : 1 (6 mL), and to it was added Pt/alumina (5 mol%). The resulting solution was stirred under a hydrogen atmosphere for 36 h. The crude mixture was filtered, and the solution reduced to dryness to afford a purple solid (0.020 g, 91%). Mp 218–223 °C. ^{1}H NMR (500 MHz, acetone-d_6, δ): 8.91 (d, $J = 8.0$ Hz, 4H), 8.73 (d, $J = 8.0$ Hz, 4H), 8.42 (t, $J = 8.0$ Hz, 2H), 7.87 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.56 (d, $J = 8.8$ Hz, 8H), 7.55 (d, $J = 8.8$ Hz, 8H), 7.24 (d, $J =$ 2.0 Hz, 4H), 7.06 (d, $J = 8.8$ Hz, 8H), 7.03 (d, $J = 8.8$ Hz, 8H), 6.61 (s, 8H), 4.44 (d, $J = 2.8$ Hz, 8H), 4.37 (d, $J = 2.8$ Hz, 8H), 4.21 (bs, 8H), 3.06 (bs, 8H), 1.46 (s, 24H). ^{13}C NMR (125 MHz, acetone-d_6, δ): 161.11, 159.26, 159.22, 158.28, 157.54, 154.59, 141.47, 141.35, 139.33, 137.87, 134.40, 133.83, 128.62, 128.34, 128.31, 124.58, 124.30, 116.24, 115.87, 114.67, 67.99, 66.67, 66.34, 26.26, 20.45. MALDI HRMS *m/z*: found 1958.7705 (M^+); calcd ($C_{126}H_{114}N_6O_{12}Fe$) 1958.7839. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 201 (5.5), 272 (5.0), 334 (4.5), 554 (3.8).

Terpy catenane (1). To a solution of **17** (0.020 g, 0.009 mmol) in acetonitrile–water 1 : 1 (12 mL) was added 10% sodium hydroxide (1 mL) followed by a slow addition of hydrogen peroxide (35% in water) until no purple color remained. The resulting solution was extracted with chloroform (20 mL). The organic layer was removed, washed with water (3 × 15 mL), dried over magnesium sulfate, filtered and reduced to dryness. Purification by column chromatography on alumina with chloroform–hexane 3 : 1 as the eluant afforded a white solid (0.010 g, 59%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.60 (d, $J = 8.0$ Hz, 4H), 8.50 (d, $J = 2.0$ Hz, 4H), 8.39 (d, $J =$ 8.0 Hz, 4H), 7.93, (t, $J = 8.0$ Hz, 2H), 7.32 (dd, $J = 2.0$, 8.0 Hz, 4H), 7.28 (d, $J = 9.0$ Hz, 8H), 7.27 (d, $J = 9.0$ Hz, 8H), 6.82 (d, $J = 9.0$ Hz, 8H), 6.80 (d, $J = 9.0$ Hz, 8H), 6.74 (s, 8H), 4.43 (t, $J = 4.0$ Hz, 8H), 4.27 (t, $J = 4.0$ Hz, 8H), 3.90 (t, $J = 6.0$ Hz, 8H), 1.95 (s, 24H), 1.87 (t, $J = 6.0$ Hz, 8H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 157.94, 157.23, 157.21, 155.07, 154.67, 149.46, 138.57, 138.14, 137.83, 136.67, 133.81, 133.10, 131.01, 127.59, 127.57, 121.27, 120.37, 115.32, 114.73, 114.57,

66.82, 66.23, 65.63, 25.23, 21.12. MALDI HRMS *m/z*: found 1903.8420 (M^+); calcd ($C_{126}H_{114}N_6O_{12}$) 1903.8568.

Fe(pherpycat)·2PF$_6$ (20). To a solution of **19** (0.33 g, 0.14 mmol) in dichloromethane (200 mL) was added a solution of $RuCl_2(PCy_3)_2CH_2Ph$ (12 mg, 0.01 mmol) in dichloromethane (20 mL) *via* cannula. The purple solution was stirred for 72 h. The crude reaction mixture was reduced to dryness and purified by column chromatography on silica gel with CH_3CN–H_2O–aqueous KPF_6 97 : 3 : 0.03 as the eluant. Subsequent centrifugal chromatography with dichloromethane–methanol 100 : 3 as the eluant afforded a purple solid (0.063 g, 20%) as a mixture of *cis*/*trans* isomers. This mixture (0.023 g, 0.010 mmol) was dissolved in a solution of dichloromethane–ethanol 1 : 1 (6 mL) and to it was added Pt/alumina (5 mol%). The resulting solution was stirred under a hydrogen atmosphere for 12 h. The crude mixture was filtered and the solution reduced to dryness to afford a purple solid (0.022 g, 96%). Mp 224–230 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.20 (d, $J = 9.0$ Hz, 2H), 8.98 (d, $J = 9.0$ Hz, 2H), 8.88 (d, $J = 8.5$ Hz, 2H), 8.45 (d, $J = 9.5$ Hz, 2H), 8.35 (d, $J = 2$ Hz, 2H), 8.29 (d, $J = 9.5$ Hz, 2H), 7.88 (dd, $J = 2.0$, 8.5 Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 8H), 7.58 (d, $J = 8.5$ Hz, 8H), 7.44 (d, $J = 2.0$ Hz, 2H), 7.36 (d, $J = 2.0$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 8H), 7.01 (d, $J = 8.5$ Hz, 8H), 6.59 (s, 2H), 6.57 (s, 2H), 6.51 (s, 2H), 6.49 (s, 2H), 4.4 (bt, $J = 4.0$ Hz, 8H), 4.44 (bt, $J = 4.0$ Hz, 8H), 4.23 (bt, $J = 4.0$ Hz, 8H), 2.09 (bt, $J = 4.0$ Hz, 8H), 1.45 (s, 6H), 1.44 (s, 6H), 1.15 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 161.83*, 159.32*, 159.14, 158.26*, 158.04, 157.94, 156.36, 151.67, 148.68, 141.59, 141.25, 140.33, 138.67, 137.98, 137.86, 137.81, 137.68, 136.96, 134.38*, 13384*, 130.64, 129.81,128.94, 128.50, 128.36*, 128.30, 128.28*, 126.36, 125.09, 123.60, 116.22*, 115.91*, 114.61*, 114.58*, 67.95*, 66.63*, 66.24*, 26.24*, 20.57, 20.50, 20.23, 20.12. MALDI HRMS *m/z*: found 2006.7866 (M^+); calcd ($C_{130}H_{114}N_6O_{12}Fe$) 2006.7839. UV–Vis ($CH_3CN$), λ_{max}/nm (log ε): 202 (5.6), 260 (5.2), 356 (4.5), 579 (3.9).

Pherpy catenane (2). To a solution of **20** (0.022 g, 10 μmol) in acetonitrile–water 1 : 1 (6 mL) was added 10% sodium hydroxide (1 mL) followed by a slow addition of hydrogen peroxide (35% in water) until no purple color remained. The resulting solution was extracted with dichloromethane (15 mL). The organic layer was removed, washed with water (3 × 15 mL), dried over magnesium sulfate, filtered and reduced to dryness. Purification by column chromatography on silica with 2–3% MeOH in chloroform as the eluant afforded a white solid (5 mg, 27%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.98 (d, $J = 8.0$ Hz, 2H), 8.83 (d, $J = 2.0$ Hz, 2H), 8.77 (d, $J = 8.5$ Hz, 2H), 8.54 (d, $J = 2.0$ Hz, 2H), 8.40 (d, $J = 8.0$ Hz, 2H), 8.07 (d, $J = 2.0$ Hz, 2H), 7.86 (d, $J = 9.0$ Hz, 2H), 7.80 (d, $J = 9.0$ Hz, 2H), 7.41 (dd, $J = 2.0$, 8.5 Hz, 2H), 7.30–7.25 (m, 8H), 8.86 (d, $J = 8.5$ Hz, 4H), 6.79 (d, $J = 8.5$ Hz, 4H), 6.77 (s, 4H), 6.73 (s, 4H), 4.44 (bt, $J = 5.0$ Hz, 8H), 4.31 (bs, 8H), 3.88 (bt, $J = 5.0$ Hz, 8H), 1.97 (s, 6H), 1.97 (s, 6H), 1.96 (s, 6H), 1.94 (s, 6H), 1.85 (bs, 8H). MALDI HRMS *m/z*: found 1951.8663 (MH^+); calcd ($C_{130}H_{115}N_6O_{12}$) 1951.8568.

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31 Crystal structure analysis of **11a**: crystal from dichloromethane–benzene; empirical formula including solvent molecules $C_{172.23}H_{106}Cl_{3.11}F_{12}N_6O_{15}P_2Ru$, $M_r = 3000.6$; crystal system triclinic, space group $P\bar{1}$, $a = 16.1362(14)$, $b = 17.4816(16)$, $c = 30.711(3)$ Å, $\alpha = 77.635(2)$, $\beta = 75.632(2)$, $\gamma = 65.267(2)^\circ$, $V = 7562.3(12)$ Å^3, $Z = 2$, $D_x = 1.318$ g cm^{-3}, $T = -173$ °C; crystal dimensions: 0.19 × 0.17 × 0.16 mm, Bruker SMART area-detector diffractometer, MoKα radiation $\lambda = 0.71073$ Å, $\mu = 0.260$ mm^{-1}, $\theta_{max} = 22.57^\circ$, 41159 measured reflections, 19541 independent reflections, $R_{int} = 0.044$, 12817 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL-97, 1116 parameters, $R(F)[I > 2\sigma(I)$ reflections$] = 0.098$, $wR(F^2)$ [all reflections] $= 0.307$, $S(F^2) = 1.088$, $\Delta\rho_{max} = 1.31$ e Å^{-3}. CCDC reference number 270917. See http://dx.doi.org/10.1039/b506101f for crystallographic data in CIF or other electronic format.
32 (*a*) Crystal structure analysis of the Fe(II) complex with **3a**: crystal obtained from dichloromethane–benzene; empirical formula including solvent molecules $C_{66}H_{64}F_{12}FeN_6O_5P_2$, $M_r = 1367.0$, orthorhombic, space group *Pbcn*, $a = 23.3906(5)$, $b = 11.4829(2)$, $c = 23.2945(6)$ Å, $V = 6256.7(2)$ Å^3, $Z = 4$, $D_x = 1.451$ g cm^{-3}, $T = -113$ °C, crystal dimensions: 0.20 × 0.10 × 0.07 mm, Nonius KappaCCD area-detector diffractometer, MoKα radiation, $\lambda = 0.71073$ Å, $\mu = 0.384$ mm^{-1}, $\theta_{max} = 25^\circ$, 75497 measured reflections, 5489 independent reflections, 3041 reflections with $I > 2\sigma(I)$, absorption correction based on analysis of equivalent reflections (SORTAV), refinement on F^2 with SHELXL-97,[33] 481 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] $= 0.075$, $wR(F^2)$ [all reflections] $= 0.234$, $S(F^2) = 1.021$, $\Delta\rho_{max} = 1.25$ e Å^{-3}. The hexafluorophosphate anion is highly disordered; the asymmetric unit includes one 50%-occupied site for a water molecule. CCDC reference number 274362. See http://dx.doi.org/10.1039/b506101f for crystallographic data in CIF or other electronic format; (*b*) Crystal structure analysis of the Ru(II) complex with **3a**: crystal obtained from dichloromethane–benzene; empirical formula including solvent molecules $C_{66}H_{64}F_{12}N_6O_5P_2Ru$, $M_r = 1412.2$, orthorhombic, space group *Pbcn*, $a = 23.1733(3)$, $b = 11.9603(1)$, $c = 22.8083(3)$ Å, $V = 6321.5(1)$ Å^3, $Z = 4$, $D_x = 1.484$ g cm^{-3}, $T = -113$ °C, crystal dimensions: 0.20 × 0.18 × 0.07 mm, Nonius KappaCCD area-detector diffractometer, MoKα radiation, $\lambda = 0.71073$ Å, $\mu = 0.390$ mm^{-1}, $\theta_{max} = 25^\circ$, 101070 measured reflections, 5577 independent reflections, 3965 reflections with $I > 2\sigma(I)$, absorption correction based on analysis of equivalent reflections (SORTAV), refinement on F^2 with SHELXL-97,[33] 481 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] $= 0.061$, $wR(F^2)$ [all reflections] $= 0.189$, $S(F^2) = 1.044$, $\Delta\rho_{max} = 1.31$ e Å^{-3}. The hexafluorophosphate anion is highly disordered; the asymmetric unit includes one 50%-occupied site for a water molecule. CCDC reference number 274363. See http://dx.doi.org/10.1039/b506101f for crystallographic data in CIF or other electronic format.
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