

Synthesis of Catenane Structures via Ring-Closing Metathesis

Marcus Weck,[†] Bernhard Mohr,[‡] Jean-Pierre Sauvage,^{*,‡} and Robert H. Grubbs^{*,†}

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and Laboratoire de Chimie Organo-Minérale, UMR 7513 au CNRS, Faculté de Chimie, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg

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This study presents a detailed description of a synthetic strategy to obtain catenane architectures through ring-closing metathesis. The approach is based on phenanthroline-based ligands containing terminal olefinic units that were designed to coordinate in a tetrahedral arrangement around a copper atom. Treatment of the assembled copper complexes with ruthenium catalyst **1** resulted in [2]catenates in high yields of 88–92%. Demetalation produced the corresponding [2]catenand in nearly quantitative yields. Hydrogenation of the catenates with Crabtree's catalyst and subsequent demetalation yielded fully saturated catenands. The presently described procedure makes [2]catenanes very accessible since the synthetic route consists of six steps (Schemes 2 and 4) from commercially available 1,10-phenanthroline, the overall yield being 51%.

Introduction

Mechanically linked molecules, rotaxanes, pseudorotaxanes, and catenanes¹ constitute a major research field in supramolecular chemistry.² Catenanes, from the Latin *catena* meaning chain, are molecules that contain two or more interlocked ring systems.³ These rings are inseparable without breaking a covalent bond.

Catenanes and rotaxanes started to attract considerable attention in the late 1960s because they presented a unique synthetic challenge.⁴ Also, they appeared to be promising chemical objects with novel physical properties and precursors to new materials. After the pioneering work of Schill⁴ and Wasserman,⁵ only a few research groups continued working on these kinds of systems. However, over the last 15 years the field has experienced a renaissance in response to the introduction of template

strategies, thus making the preparation of threaded and interlocked systems more accessible. Specifically, a significant number of catenane systems have been reported. Since 1983, a copper-metal template based strategy has allowed catenanes,⁶ knots,⁷ and rotaxanes⁸ to be obtained. In the last 10 years, Stoddart and his group have worked on the synthesis of interlocked systems based on secondary dialkylammonium salts and crown ethers⁹ and on systems based on π -electron-rich/ π -electron-deficient aromatic systems.¹⁰ Catenane systems based on hydrogen bonds, as reported by Hunter,¹¹ Vögtle,¹¹ and Leigh,¹² cyclodextrins as introduced by Ogino, Wenz, and Harada,¹³ and rotaxanes based on crown ether frameworks presented by Gibson¹⁴ have also been reported.^{1,15–28}

[†] California Institute of Technology.

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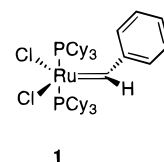
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Additionally, they display interesting physical properties, such as photoinduced intramolecular electron transfer,²⁹ electrochemically triggered molecular motions, and photochemical dethreading processes. A number of these multicomponent systems have been named "molecular machines".¹⁰ In addition, a few groups have recently described transition-metal-incorporating catenanes and rotaxanes, these compounds being most of the time obtained in good yields, under very mild conditions.^{1f,30}

For all more recent supramolecular systems, the use of a template, or auxiliary linkage, is essential for an efficient synthesis. The components of the rings that are to be incorporated into the architecture are brought together in a specific orientation so that the most favorable outcomes are interlocked rings.

Therefore, the synthesis relies on a quantitative assembly step followed by ring closure. In most cases, the cyclization reaction is restricted to the formation of ethers and amide bonds or quarternary ammonium salts by an intramolecular pathway.¹ However, this cyclization reaction also constitutes the biggest challenge in the synthesis of catenanes and rotaxanes because the yield of the product is oftentimes quite low.

Ring-closing metathesis (RCM) has been established as an efficient approach to macrocyclic systems via intramolecular formation of carbon-carbon double bonds.^{5,31,32} Ruthenium benzylidene catalyst **1** has been shown to be highly effective in these reactions mostly because of its high activity and tolerance to a wide array of functional groups.³³



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While RCM was initially applied to the synthesis of small—five to eight-membered rings^{32,34}—this methodol-

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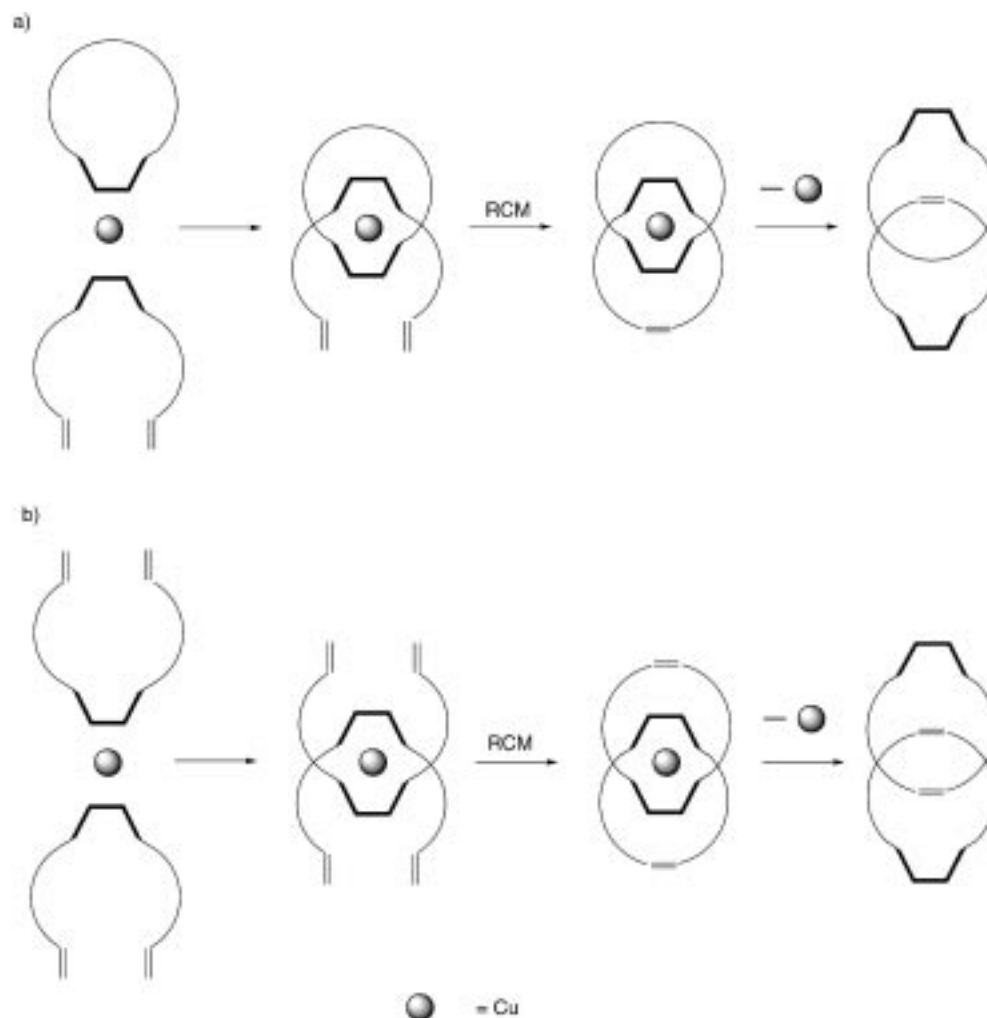
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Scheme 1. Schematic Drawing of the Approach Utilizing a Combination of a Transition-Metal-Based Template Strategy and RCM To Provide Access to [2]Catenanes^a

^a Key: (A) formation of a threaded complex followed by RCM and decomplexation; (B) formation of an intertwined complex followed by 2-fold RCM, decomplexation, and hydrogenation. The circle represents the transition ion.

ogy has recently been extended to larger ring systems incorporating up to 38 atoms.³⁵ Recently, we reported in a preliminary communication a combination of a supramolecular template strategy and RCM to provide ready access to [2]catenanes with different ring sizes in high yields.^{36–38} Herein, we report the full synthetic strategy to obtain [2]catenanes using RCM.

Results and Discussion

One of the most efficient syntheses of interlocked molecules relies on the use of a transition-metal ion as a template.^{6–8} This approach takes advantage of the preferred tetrahedral geometry of certain low-valent transition metals such as copper(I), in particular, once coordinated to two 2,9-disubstituted 1,10-phenanthroline units. In this general strategy, a complex formed between 2,9-dianisyl-1,10-phenanthroline and copper(I) initiates the construction of the catenane. Reaction of this complex with a diiodide derived from pentaethylene glycol in the presence of cesium carbonate as base resulted in the [2]-catenane in 27% yield, after difficult and time-consuming chromatographic separation.^{6c} In this study, a general strategy for the synthesis of catenanes utilizing a combination of transition metal (copper)-based preorganization and RCM will be described. Scheme 1 presents a schematic presentation of the general approach.

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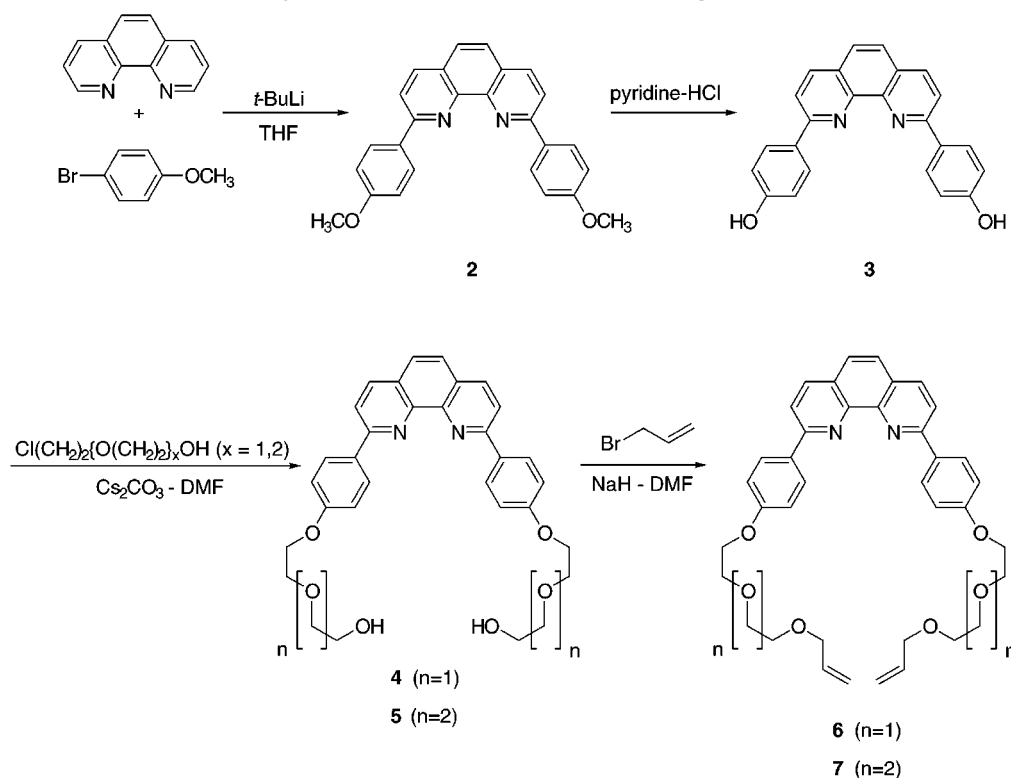
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Scheme 2. Synthesis of the Catenane Building Blocks 6 and 7



The building blocks for this system are the 30-membered macrocycle **8**, bearing a 2,9-diphenyl-1,10-phenanthroline (dpp) bidentate in its backbone, and the acyclic ligands **6** and **7**, in which the dpp moiety was symmetrically substituted with ethylene oxide groups terminated with olefins. Compound **8** was synthesized in analogy to literature.^{6c} Ligands **6** and **7** were synthesized by coupling 4-lithioanisole with 1,10-phenanthroline, followed by hydrolysis and oxidation to produce dianisyl phenanthroline (dap, **2**) in high yield. Deprotection yielded dpp **3**, which was reacted with chlorodiethyleneglycol or chlorotriethyleneglycol to give compounds **4** and **5**. Subsequent alkylation using allyl bromide resulted in ligands **6** and **7** in high yields (Scheme 2).

To ensure the compatibility of these building blocks with the ruthenium catalyst **1**, several NMR experiments were carried out in which building blocks **2** and **3**, both with and without copper, were added to a dichloromethane solution of **1** at room temperature under argon. No decomposition of the catalyst over a period of several hours was detected, which indicated the compatibility of these compounds with **1**.

Threaded complexes **9** and **10** assembled instantly and quantitatively by the reaction of **8** with a stoichiometric amount of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in dichloromethane/acetonitrile followed by the addition of diolefins **6** and **7** (Scheme 3).⁶ In a similar manner, the intertwined complex **15** was obtained in quantitative yields by complexation of 2 equiv of **6** with $[\text{Cu}(\text{MeCN})_4]$ (Scheme 4). The full complexation of these compounds could be easily monitored by NMR spectroscopy since specific aromatic proton resonances were characteristically shifted upon complexation.⁶

After complexation, complexes **9**, **10**, and **15** were subjected to intramolecular RCM with catalyst **1** to yield the corresponding [2]catenates **11**, **12**, and **16** through the formation of 32- (**11**, **16**) and 38-membered (**12**) rings (Schemes 3 and 4). All reactions were carried out at room

temperature under argon for several hours. A total of 10 mol % catalyst was used, which was added to the reaction in 5 mol % portions, once at the beginning of the reaction and again after 6 h. To drive this RCM reaction closer to completion, ethylene, a product of the RCM, was removed from the reaction by opening the reaction vessel for a short period of time every 2 h to a weak vacuum.

Two-fold RCM of **15** led exclusively to systems with two interlocked rings. The twisted product, formed by the intramolecular reaction between the olefins of different ligands, was not detected. The formation of catenates **11**, **12**, and **16** could be unequivocally shown by ¹H NMR spectroscopy and fast atom bombardment (FAB-MS) mass spectroscopy.^{39,6h} Figure 1 presents the FAB-MS spectra of catenates **11** and **16**.

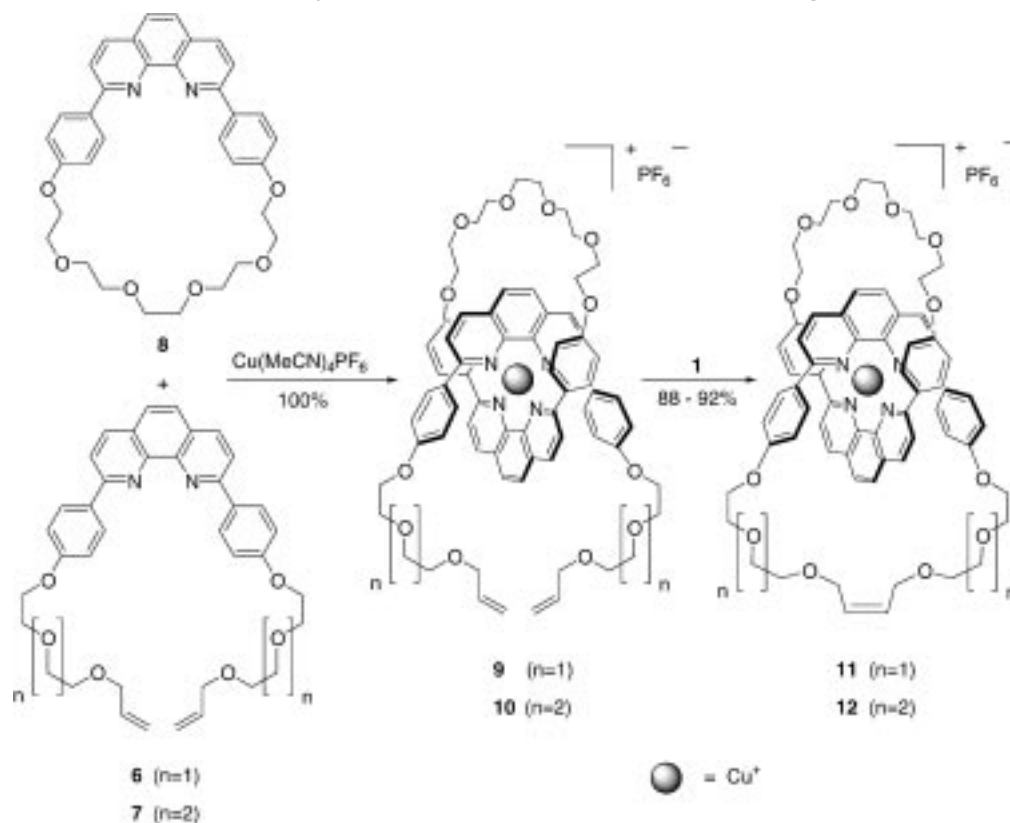
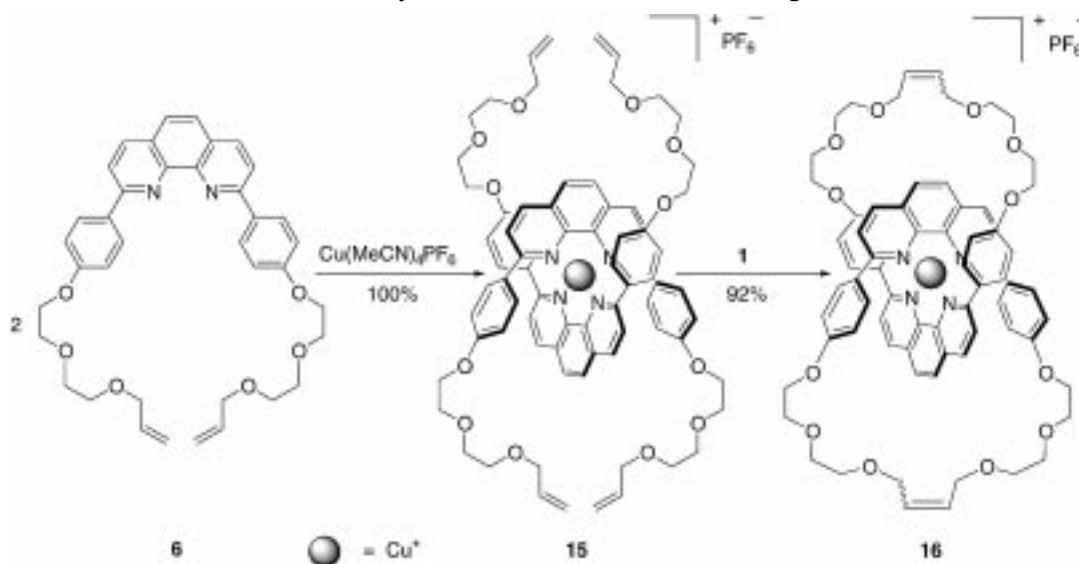
Yields of these cyclization reactions ranged from 88 to 92% as summarized in Table 1. The cyclization yields for these systems exceeded those for most other medium- or large-ring systems, where hydrogen bonding,^{32,35} conformational constraints,³⁵ or template effects⁴⁰ are present to facilitate the reaction. It is believed that the remarkable efficiency of these RCM reactions stemmed, at least in part, from a preorganization of the olefins due to electrostatic interactions between the oxygen atoms and the phenanthroline systems,⁴¹ in combination with a locked conformation of the phenyl rings (π -donors) and phenanthroline systems (π -acceptor).⁴² This assumption is supported by the exclusive formation of the interlocked species in the RCM of **15** and the observation that RCM of the free ligands **6** and **7** proceeds in lower yields between 70 and 75%.

(39) Vetter, W.; Logemann, E.; Schill, G. *Org. Mass. Spectrom.* **1977**, *12*, 351.

(40) Marsella, M. J.; Maynard, H. D.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1101.

(41) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

(42) These interactions have been observed in the solid state for structurally related [2]catenates (see ref 6j,m).

Scheme 3. Synthesis of [2]Catenates 11 and 12 Using RCM**Scheme 4. Synthesis of [2]Catenate 16 Using RCM**

For all catenates, the energetically favored *trans* configuration at the double bond prevailed, which is commonly reported for macrocycles made via RCM.^{32,35,40} The olefin *E/Z* ratio could be determined by the integration of the ^1H NMR signals of the isomeric olefin protons (*cis* multiplet around 5.80 ppm, *trans* multiplet around 5.95 ppm).

Demetalation of catenates **11**, **12**, and **16** with potassium cyanide in aqueous acetonitrile in analogy to literature procedures^{6–8} afforded [2]catenands **13**, **14**, and **17** in high yields. Scheme 5 shows the demetalation of catenates **11** and **12**.

In analogy to the catenates, the composition of catenands **13**, **14**, and **17** was confirmed by ^1H NMR and

FAB-MS. Figure 2 shows the FAB-MS spectra of catenands **13** and **17**. Both spectra display the characteristic pattern for catenated species, the absence of peaks between the molecular ion peaks and the peaks corresponding to the individual macrocycles.⁶ When an intramolecular RCM reaction between the olefins of different ligands had occurred, peaks in the region between the molecular ion peak and the peaks corresponding to the individual macrocycles would be expected. Therefore, these FAB-MS provide further proof for the exclusive formation of catenates **11**, **12**, and **16** in the RCM steps.

Upon standing at room temperature under argon for 4–5 months, catenands **13**, **14**, and **17** changed in color from white to yellow, indicating decomposition. This

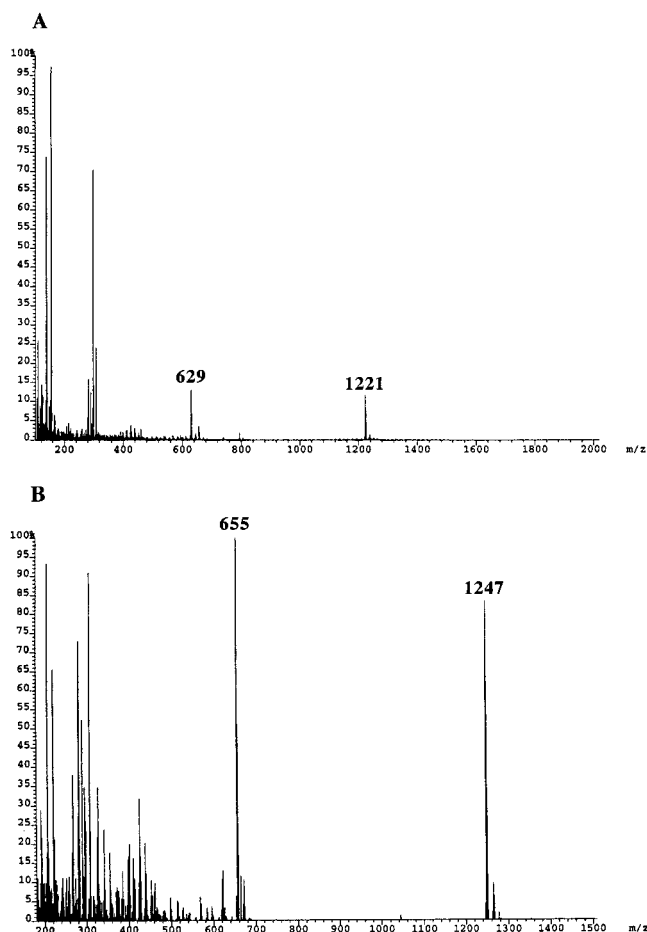


Figure 1. Positive FAB-MS spectra of (a) catenane **11** and (b) catenane **16** in a *p*-nitrobenzyl alcohol matrix. The peaks at $m/z = 1221$ and 1247 correspond to catenanes **11** and **16**, respectively. The absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic of catenane species.^{6m}

Table 1. Results of the Ring-Closing Metathesis and Demetalation Reactions

catenane	yield ^a (%)	trans/cis ^b	catenand	yield ^a (%)
11	92	97/3	13	92
12	88	95/5	14	93
16	92	98/2	17	90
			19	96

^a Yield of isolated product. ^b Determined by integration of the ¹H NMR signals of the isomeric olefin protons.

decomposition seems to occur at least partially at the carbon–carbon double bonds that were formed during the RCM. Therefore, a selective hydrogenation of these double bonds has been carried out using Crabtree's iridium-based catalyst as outlined in Scheme 6. In a general procedure, the catenane was dissolved in dichloromethane, a catalytic amount of the iridium catalyst was added, and the reaction was stirred overnight under 200 psi hydrogen pressure. Using this procedure, the hydrogenated catenane **18** was obtained in quantitative yield. As described above, demetalation was carried out using potassium cyanide to yield the free catenands in 96% yield (Scheme 6).

Catenand **19** was characterized by ¹H NMR and FAB-MS. Figure 3 shows the positive FAB-MS of **19**. As expected, no decomposition occurred after hydrogenation of the double bond over a period of several months.

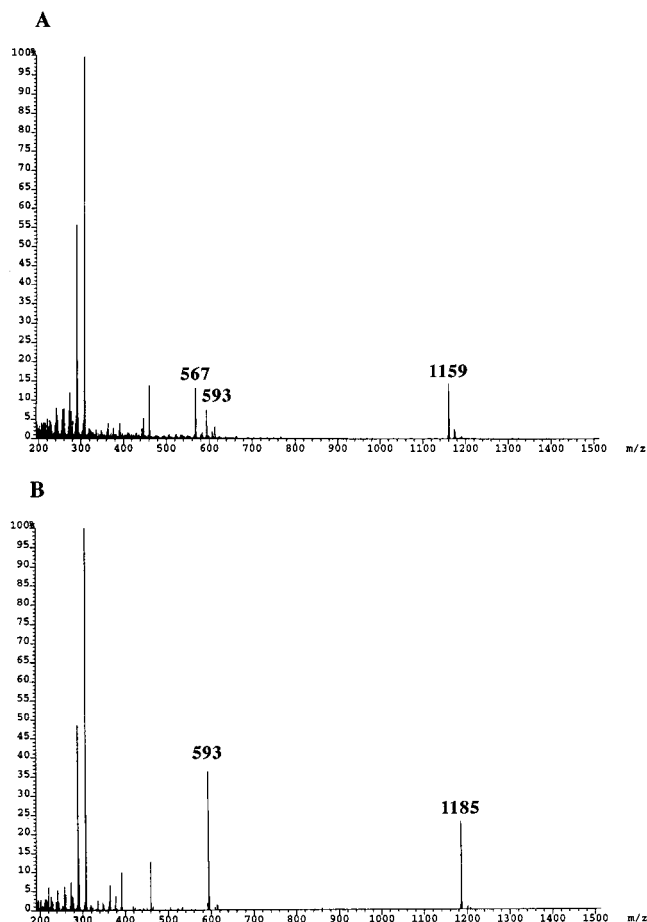


Figure 2. Positive FAB-MS spectra of catenands **13** (a) and **17** (b) in a *p*-nitrobenzyl alcohol matrix. The peaks at $m/z = 1159$ and $m/z = 1185$ correspond to catenanes **13** and **17**. The absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic for catenane species.^{6m}

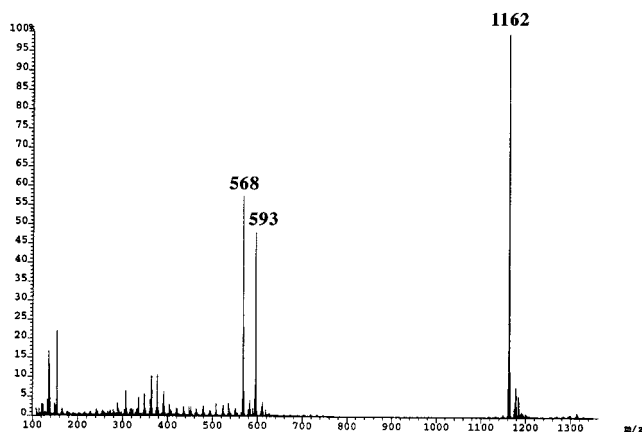
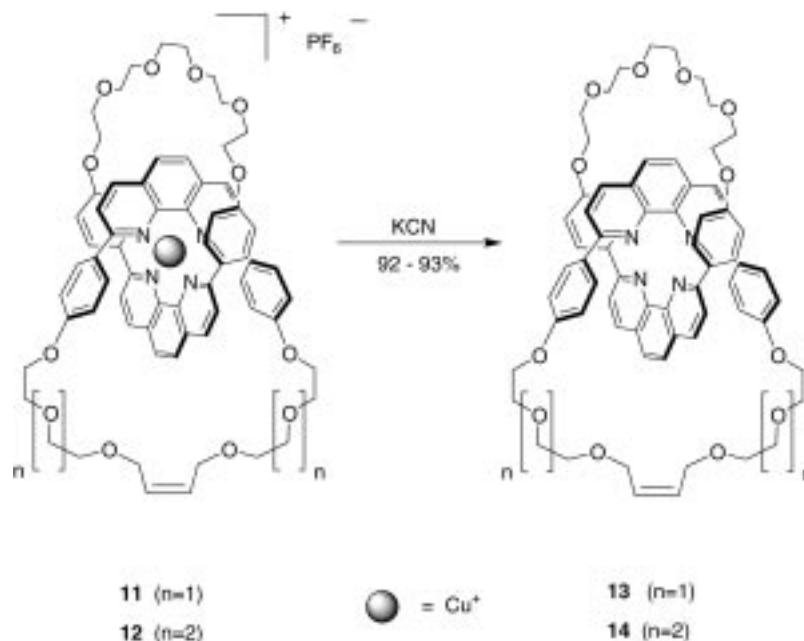
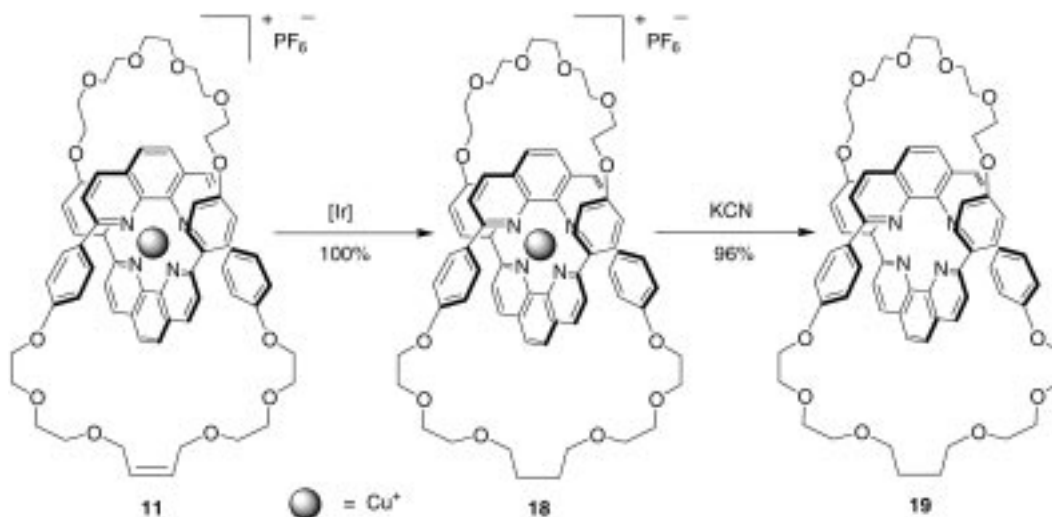


Figure 3. Positive FAB-MS spectra of catenand **19** in a *p*-nitrobenzyl alcohol matrix. The peak at $m/z = 1162$ corresponds to catenand **19**. The absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic for catenane species.^{6m}

Conclusion

Herein, we present a new approach to obtain interlocked architectures through RCM. Two new phenanthroline-based ligands that contain terminal olefinic groups were synthesized. These ligands were cyclized

Scheme 5. Demetalation of [2]Catenates 11 and 12 To Yield [2]Catenands 13 and 14**Scheme 6. Hydrogenation of [2]Catenate 9 Using Crabtree's Iridium-based Catalyst To Yield the Double-Bond-Free [2]Catenate 18 Followed by Demetalation To Yield [2]Catenand 19**

after complexation around copper using a ruthenium catalyst in nearly quantitative yield to obtain catenane precursors with different ring sizes. Demetalation of the complexes using potassium cyanide produced the corresponding [2]catenands in high yields. To prevent decomposition at the olefinic group, hydrogenation of the carbon-carbon double bonds was carried out using Crabtree's catalyst. After demetalation, the fully saturated catenand did not show any decomposition over a period of several months. The strategy presented herein establishes a highly efficient approach to interlocked structures and can be used for a large variety of interlocked structures including rotaxanes and knot structures.³⁷

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Elemental analyses were performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

Materials. Dichloromethane used in the RCM reactions was distilled from calcium hydride and degassed by repeated freeze-pump-thaw cycles. All other solvents were used without further purification unless otherwise noted. All chemicals were purchased from the Aldrich Chemical Co. and used without further purification. The ruthenium complex **1** was graciously provided by Dr. Peter Schwab. Compounds **2**, **3**, and **8** were synthesized as reported in the literature.^{6c}

Synthesis of Compound 4. A mixture of **3** (2.0 g, 5.50 mmol), chlorodiethyleneglycol (1.5 g, 12.0 mmol), and Cs_2CO_3 (4.9 g, 15.0 mmol) in 150 mL of DMF was heated for 12 h at 80 °C under argon. The solvent was removed in vacuo, and the residue was extracted with 250 mL of dichloromethane. The dichloromethane extract was washed three times with water and subsequently dried over magnesium sulfate. Final purification was achieved by silica gel column chromatography using dichloromethane/methanol (99:1) as eluent to yield 2.46 g of an amorphous white solid: yield 83%; ^1H NMR (CDCl_3) δ 8.43 (d, 4H, $J = 8.8$ Hz), 8.26 (d, 2H, $J = 8.5$ Hz), 8.08 (d, 2H, $J = 8.5$ Hz), 7.74 (s, 2H), 7.13 (d, 4H, $J = 8.8$ Hz), 4.27 (t, 4H, $J = 4.7$ Hz), 3.94 (t, 4H, $J = 4.7$ Hz), 3.79–3.69 (m, 8H); ^{13}C NMR (CDCl_3) δ 160.0, 156.3, 146.1, 136.8, 132.6, 129.1, 127.6,

125.7, 119.4, 114.9, 72.7, 69.7, 67.6, 61.8, 50.8; HRMS (FAB) calcd for $C_{32}H_{32}N_2O_6$ (MH)⁺ 541.2353, found 541.2347.

Synthesis of Compound 5. 5 was synthesized in a manner analogous to that of 4 by reacting 3 with chlorotriethyleneglycol: yield 86%; ¹H NMR (CDCl₃) δ 8.43 (d, 4H, *J* = 8.8 Hz), 8.26 (d, 2H, *J* = 8.5 Hz), 8.08 (d, 2H, *J* = 8.5 Hz), 7.74 (s, 2H), 7.13 (d, 4H, *J* = 8.8 Hz), 4.28 (t, 4H, *J* = 4.8 Hz), 3.93 (t, 4H, *J* = 4.8 Hz), 3.81–3.61 (m, 12H); ¹³C NMR (CDCl₃) δ 160.0, 156.4, 146.0, 136.8, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8, 72.7, 69.7, 69.5, 67.6, 61.6; HRMS (FAB) calcd for $C_{36}H_{40}N_2O_8$ (MH)⁺ 629.2874, found 629.2875.

Synthesis of Ligand 6. To a mixture of 4 (2.0 g, 3.7 mmol) and allyl bromide (1.0 g, 8.2 mmol) in 150 mL of DMF under argon atmosphere was added NaH (0.2 g, 8.3 mmol). The reaction mixture was heated to 80 °C, and after 2 h another portion of NaH (0.1 g, 4.2 mmol) was added. After the mixture was stirred for 8 h at 80 °C, the solvent was removed in vacuo and the residue was extracted with 250 mL of dichloromethane. The dichloromethane extract was washed three times with water and subsequently dried over magnesium sulfate. Final purification was achieved by silica gel column chromatography using dichloromethane/methanol (99:1) as eluent to yield 1.97 g of an amorphous white solid: yield 86%; ¹H NMR (CDCl₃) δ 8.43 (d, 4H, *J* = 8.8 Hz), 8.26 (d, 2H, *J* = 8.5 Hz), 8.08 (d, 2H, *J* = 8.5 Hz), 7.74 (s, 2H), 7.13 (d, 4H, *J* = 8.8 Hz), 6.05–5.85 (m, 2H), 5.35–5.18 (m, 4H), 4.27 (t, 4H, *J* = 4.9 Hz), 4.04–4.08 (m, 4H), 3.94 (t, 4H, *J* = 4.9 Hz), 3.78 (m, 4H), 3.67 (m, 4H); ¹³C NMR (CDCl₃) δ 160.2, 156.4, 146.1, 136.8, 134.8, 132.4, 129.0, 127.6, 125.7, 119.3, 117.2, 114.9, 72.4, 71.0, 69.9, 69.6, 67.6; HRMS (FAB) calcd for $C_{38}H_{40}N_2O_6$ (MH)⁺ 621.2977, found 621.2982.

Synthesis of Ligand 7. 7 was synthesized in analogy to 6 by reacting 5 with allyl bromide: yield 89%; ¹H NMR (CDCl₃) δ 8.42 (d, 4H, *J* = 8.9 Hz), 8.26 (d, 2H, *J* = 8.5 Hz), 8.08 (d, 2H, *J* = 8.5 Hz), 7.74 (s, 2H), 7.12 (d, 4H, *J* = 8.9 Hz), 6.03–5.83 (m, 2H), 5.33–5.14 (m, 4H), 4.26 (t, 4H, *J* = 4.9 Hz), 4.03 (m, 4H), 3.93 (t, 4H, *J* = 4.9 Hz), 3.81–3.60 (m, 12H); ¹³C NMR (CDCl₃) δ 160.2, 156.4, 146.1, 136.8, 134.8, 132.4, 129.0, 127.6, 125.7, 119.4, 117.1, 114.9, 72.3, 71.0, 70.8, 69.8, 69.5, 67.6; HRMS (FAB) calcd for $C_{42}H_{48}N_2O_8$ (MH)⁺ 709.3489, found 709.3486.

General Procedure for the Metal Complexation To Form the Precatenates 9, 10, and 15. In a Schlenk flask, 1 equiv of 2 (for the synthesis of 9 or 10) or 6 (for the synthesis of 15) was dissolved under argon in a 1:1 mixture of dichloromethane and acetonitrile. After addition of 1 equiv of Cu(MeCN)₄, the reaction was stirred at room temperature under argon for 15 min. In a second Schlenk flask, 1 equiv of 6 (for the synthesis of 9 and 15) or 7 (for the synthesis of 10) was dissolved in dichloromethane and cannula filtered into the first solution. The solution was stirred under argon at room temperature for an additional 30 min, followed by removal of the solvent in vacuo. Final purification was achieved by precipitation with dichloromethane/pentane and silica gel column chromatography using dichloromethane/methanol (96:4) to yield a dark red, crystalline solid in quantitative yield.

Precatenate 9: ¹H NMR (CD₂Cl₂) δ 8.63 (d, 2H, *J* = 8.4 Hz), 8.50 (d, 2H, *J* = 8.4 Hz), 8.24 (s, 2H), 8.05 (s, 2H), 7.88 (d, 2H, *J* = 8.4 Hz), 7.84 (d, 2H, *J* = 8.8 Hz), 7.48 (d, 4H, *J* = 8.6 Hz), 7.31 (d, 4H, *J* = 8.6 Hz), 6.09 (d, 4H, *J* = 8.6 Hz), 5.99 (d, 4H, *J* = 8.6 Hz), 6.05–5.87 (m, 2H), 5.36–5.15 (m, 4H), 4.03–4.07 (m, 4H), 3.73–3.48 (m, 36H); ¹³C NMR (CD₂Cl₂) δ 159.8, 159.4, 157.0, 156.3, 143.7, 138.3, 137.4, 135.5, 132.8, 131.9, 129.8, 129.6, 128.7, 128.4, 127.6, 126.6, 124.4, 117.0, 113.4, 72.5, 71.6, 71.2, 70.1, 69.8, 69.3, 67.9, 67.5; HRMS (FAB) calcd for $C_{72}H_{74}N_4O_{12}Cu$ (MH)⁺ 1249.5, found 1249.3.

Precatenate 10: ¹H NMR (CD₂Cl₂) δ 8.63 (d, 2H, *J* = 8.4 Hz), 8.50 (d, 2H, *J* = 8.4 Hz), 8.23 (s, 2H), 8.05 (s, 2H), 7.88 (d, 2H, *J* = 8.4 Hz), 7.84 (d, 2H, *J* = 8.8 Hz), 7.48 (d, 4H, *J* = 8.6 Hz), 7.30 (d, 4H, *J* = 8.6 Hz), 6.09 (d, 4H, *J* = 8.6 Hz), 5.99 (d, 4H, *J* = 8.6 Hz), 6.05–5.81 (m, 2H), 5.31–5.10 (m, 4H), 4.01–3.97 (m, 4H), 3.73–3.48 (m, 44H); ¹³C NMR (CD₂Cl₂) δ 159.8, 159.4, 157.0, 156.3, 143.8, 138.3, 137.4, 135.5, 132.8, 131.9, 129.8, 129.6, 128.7, 128.4, 127.6, 126.6, 124.4,

117.0, 113.4, 72.5, 71.6, 71.2, 70.1, 69.8, 69.3, 67.9, 67.5; HRMS (FAB) calcd for $C_{76}H_{82}N_4O_{14}Cu$ (MH)⁺ 1337.5, found 1337.5.

Precatenate 15: ¹H NMR (CD₂Cl₂) δ 8.49 (d, 2H, *J* = 8.4 Hz), 8.03 (s, 2H), 7.84 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 4H, *J* = 8.6 Hz), 6.08 (d, 4H, *J* = 8.6 Hz), 6.05–5.87 (m, 2H), 5.36–5.16 (m, 4H), 4.07–4.04 (m, 4H), 3.72–3.63 (m, 32H); ¹³C NMR (CD₂Cl₂) δ 159.8, 156.8, 143.9, 137.6, 135.5, 131.9, 129.7, 128.5, 126.7, 124.8, 117.0, 113.4, 72.5, 71.2, 70.1, 69.8, 67.9; HRMS (FAB) calcd for $C_{76}H_{80}N_4O_{12}Cu$ (MH)⁺ 1303.5, found 1303.2.

General Procedure for the Ring-Closing Metathesis of the Copper-Based Catenates 11, 12, and 16. Under exclusion of air and moisture, 1 (5 mol %) was added in dichloromethane to a 0.01 M solution of the diolefin (typically 200–900 mg) in dichloromethane. After the mixture was stirred for 6 h at room temperature, additional catalyst (5 mol %) was added, and stirring was continued for an additional 6 h. The solvent was then removed in vacuo, and the crude reaction mixture was purified by repeated silica gel column chromatography using dichloromethane/methanol (96:4) to yield the [2]catenates as burgundy solids.

Catenate 11: yield 92%; ¹H NMR (CDCl₃) δ 8.62 (d, 2H, *J* = 8.4 Hz), 8.52 (d, 2H, *J* = 8.4 Hz), 8.23 (s, 2H), 8.14 (s, 2H), 7.80 (m, 4H), 7.32 (m, 8H), 6.09 (m, 2H), 6.00 (m, 8H), 4.16 (m, 4H), 3.80–3.48 (m, 36H); ¹³C NMR (acetone-*d*₆) δ 159.0, 158.9, 155.9, 143.3, 143.2, 137.7, 137.3, 132.1, 131.7, 129.5, 129.4, 129.3, 128.1, 127.1, 126.8, 123.7, 123.6, 112.7, 112.6, 71.5, 71.1, 70.8, 70.7, 70.5, 69.1, 68.8, 67.4, 66.9; HRMS (FAB) calcd for $C_{70}H_{70}N_4O_{12}Cu$ (MH)⁺ 1221.4, found 1221.4. Anal. Calcd for $C_{70}H_{70}N_4O_{12}CuPF_6$: C, 61.41; H, 5.16; N, 4.09. Found: C, 60.92; H, 5.05; N, 3.96.

Catenate 12: yield 88%; ¹H NMR (CDCl₃) δ 8.62 (d, 2H, *J* = 8.4 Hz), 8.55 (d, 2H, *J* = 8.4 Hz), 8.22 (s, 2H), 8.12 (s, 2H), 7.84 (m, 4H), 7.47 (d, 4H, *J* = 8.7 Hz), 7.30 (d, 4H, *J* = 8.7 Hz), 6.09 (d, 8H, *J* = 8.7 Hz), 5.98 (d, 2H, *J* = 8.7 Hz), 5.83 (m, 2H), 4.16 (m, 4H), 3.80–3.48 (m, 44H); ¹³C NMR (acetone-*d*₆) δ 159.2, 158.9, 156.3, 155.9, 143.4, 143.3, 137.7, 137.3, 132.4, 132.1, 131.4, 129.5, 129.4, 129.3, 129.2, 128.2, 128.1, 127.3, 126.8, 126.4, 124.4, 123.7, 123.6, 113.0, 112.8, 112.6, 71.1, 71.0, 70.9, 70.8, 70.7, 70.5, 70.3, 69.7, 69.4, 68.8, 67.6, 66.9; HRMS (FAB) calcd for $C_{74}H_{78}N_4O_{14}Cu$ (MH)⁺ 1309.1, found 1309.3. Anal. Calcd for $C_{74}H_{78}N_4O_{14}CuPF_6$: C, 61.05; H, 5.40; N, 3.85. Found: C, 61.05; H, 5.28; N, 3.95.

Catenate 16: yield 92%; ¹H NMR (CDCl₃) δ 8.51 (d, 4H, *J* = 8.4 Hz), 8.13 (s, 4H), 7.81 (d, 4H, *J* = 8.4 Hz), 7.41 (d, 8H, *J* = 8.7 Hz), 6.11 (m, 4H), 6.02 (d, 8H, *J* = 8.7 Hz), 4.18 (m, 8H), 3.80–3.67 (m, 32H); ¹³C NMR (acetone-*d*₆) δ 159.0, 155.9, 143.3, 137.5, 131.7, 129.5, 129.3, 128.1, 126.8, 123.7, 112.7, 71.5, 70.8, 70.6, 69.1, 67.5; HRMS (FAB) calcd for $C_{72}H_{72}N_4O_{12}Cu$ (MH)⁺ 1247.2, found 1247.1. Anal. Calcd for $C_{72}H_{72}N_4O_{12}CuPF_6$: C, 61.83; H, 5.48; N, 3.88. Found: C, 62.04; H, 5.31; N, 4.00.

General Procedure for the Demetalation of the Copper-Based Catenates 11, 12, and 16. The catenate was dissolved in acetonitrile followed by addition of an excess of potassium cyanide in water. The mixture was stirred for 30 min at room temperature, during which time the dark burgundy color vanished and a brown solid precipitated. The solution was decanted and the precipitate dissolved in dichloromethane. The dichloromethane phase was washed several times with water and dried over magnesium sulfate. The solvent was removed in vacuo to yield a slightly milky solid. Final purification was achieved by silica gel column chromatography to yield a white solid.

Catenand 13: yield 92%; ¹H NMR (CDCl₃) δ 8.48 (m, 8H), 8.19 (d, 2H, *J* = 2.7 Hz), 8.17 (d, 2H, *J* = 2.7 Hz), 8.05 (s, 2H), 8.02 (s, 2H), 7.67 (m, 4H), 7.16 (t, 8H, *J* = 8.7 Hz), 5.96 (m, 2H), 4.19–3.56 (m, 42H); ¹³C NMR (CDCl₃) δ 161.5, 160.0, 156.3, 156.2, 146.1, 146.0, 136.7, 132.5, 132.4, 129.7, 129.3, 129.2, 127.4, 125.5, 119.2, 115.3, 115.2, 71.6, 71.1, 70.9, 70.7, 70.1, 68.8, 68.4, 66.8, 66.5; HRMS (FAB) calcd for $C_{70}H_{70}N_4O_{12}$ (MH)⁺ 1159.5, found 1159.5. Anal. Calcd for $C_{70}H_{70}N_4O_{12}$: C, 72.52; H, 6.09; N, 4.83. Found: C, 72.43; H, 5.95; N, 4.69.

Catenand 14: yield 93%; ¹H NMR (CDCl₃) δ 8.48 (m, 8H), 8.18 (m, 2H), 8.17 (m, 2H), 8.07 (s, 2H), 8.03 (s, 2H), 7.67 (m, 4H), 7.16 (t, 8H, *J* = 8.7 Hz), 5.99 (m, 2H), 4.17–3.54 (m, 48H);

^{13}C NMR (CDCl_3) δ 160.0, 159.8, 156.4, 156.2, 146.2, 146.0, 136.8, 132.5, 132.4, 129.7, 129.2, 129.1, 127.4, 125.6, 119.2, 114.9, 114.8, 71.3, 70.9, 70.8, 70.7, 69.8, 69.6, 68.4, 67.4, 66.8, 66.4; HRMS (FAB) calcd for $\text{C}_{74}\text{H}_{78}\text{N}_4\text{O}_{14}$ (MH) $^+$ 1242.5, found 1242.5. Anal. Calcd for $\text{C}_{74}\text{H}_{78}\text{N}_4\text{O}_{14}$: C, 71.47; H, 6.00; N, 4.51. Found: C, 71.22; H, 5.96; N, 4.41.

Catenand 17: yield 90%; ^1H NMR (CDCl_3) δ 8.47 (d, 8H, J = 2.7 Hz), 8.21 (d, 4H, J = 8.4 Hz), 8.05 (d, 4H, J = 8.4 Hz), 7.70 (s, 4H), 7.16 (d, 8H, J = 9.6 Hz), 5.93 (m, 4H), 4.18–3.56 (m, 40H); ^{13}C NMR (CDCl_3) δ 160.0, 155.9, 146.0, 136.6, 132.4, 129.5, 129.1, 127.5, 125.6, 119.1, 115.1, 71.5, 70.9, 70.1, 68.8, 66.9; HRMS (FAB) calcd for $\text{C}_{72}\text{H}_{72}\text{N}_4\text{O}_{12}$ (MH) $^+$ 1185.5, found 1185.5. Anal. Calcd for $\text{C}_{72}\text{H}_{72}\text{N}_4\text{O}_{12}$: C, 72.94; H, 6.13; N, 4.73. Found: C, 72.51; H, 6.12; N, 4.69;

Synthesis of Catenate 18. In a Schlenk flask, **11** was dissolved under argon in dichloromethane and cannula-filtered into a Schlenk flask containing Crabtree's iridium catalyst dissolved in dichloromethane. The reaction was stirred at room temperature under argon under 200 psi hydrogen pressure for 2 h. After filtration of the reaction over a plug containing Celite, the solvent was removed in vacuo to yield a dark burgundy solid. Final purification was achieved by silica gel column chromatography (dichloromethane/methanol (95:5)) to afford a burgundy solid in quantitative yield: ^1H NMR (CDCl_3) δ 8.68 (d, 2H, J = 8.4 Hz), 8.59 (d, 2H, J = 8.4 Hz), 8.27 (s,

2H), 8.21 (s, 2H), 7.85 (t, 4H, J = 7.5 Hz), 7.35 (m, 8H), 6.04 (t, 8H, J = 8.1 Hz), 3.86–3.48 (m, 44H); ^{13}C NMR (CDCl_3) δ 158.8, 158.7, 155.8, 155.7, 143.0, 142.9, 137.6, 137.1, 131.8, 131.0, 128.9, 128.8, 127.9, 127.8, 126.8, 126.5, 123.6, 123.5, 112.7, 71.3, 70.8, 70.7, 70.4, 70.3, 68.8, 68.7, 67.4; HRMS (FAB) calcd for $\text{C}_{70}\text{H}_{72}\text{N}_4\text{O}_{12}\text{Cu}$ (MH) $^+$ 1223.4, found 1223.4. Anal. Calcd for $\text{C}_{70}\text{H}_{72}\text{N}_4\text{O}_{12}\text{CuPF}_6$: C, 61.39; H, 5.30; N, 4.09. Found: C, 61.52; H, 5.11; N, 4.05.

Synthesis of Catenand 19. **19** was synthesized in analogy to **13** in 96% yield: ^1H NMR (CD_2Cl_2) δ 8.53 (d of d, 8H, J = 9 Hz), 8.24 (d, 2H, J = 12.6 Hz), 8.21 (d, 2H, J = 12.6 Hz), 8.09 (s, 2H), 8.07 (s, 2H), 7.71 (d, 4H, J = 10.5 Hz), 7.27 (d, 4H, J = 8.7 Hz), 7.16 (d, 4H, J = 9 Hz), 4.36–3.48 (m, 44H); ^{13}C NMR (CD_2Cl_2) δ 158.8, 158.7, 155.8, 155.7, 143.0, 142.9, 137.6, 137.1, 131.8, 131.0, 128.9, 128.8, 127.9, 127.8, 126.8, 126.5, 123.6, 123.5, 112.7, 71.3, 70.8, 70.7, 70.4, 70.3, 68.8, 68.7, 67.4; HRMS (FAB) calcd for $\text{C}_{70}\text{H}_{72}\text{N}_4\text{O}_{12}$ (MH) $^+$ 1161.5, found 1161.5. Anal. Calcd for $\text{C}_{70}\text{H}_{72}\text{N}_4\text{O}_{12}$: C, 72.38; H, 6.25; N, 4.83. Found: C, 72.22; H, 6.17; N, 4.62.

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