Porphyrin-Stoppered [3]- and [5]-Rotaxanes

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Abstract: A dicopper(I)-complexed [3]-rotaxane was prepared in 34% yield by a transition-metal-templated strategy involving a bis-chelating molecular thread, macrocycles incorporating the complementary chelating unit, and porphyrin stoppers as key components. A tetracopper(I)-complexed [5]-rotaxane was obtained as a byproduct in 8% yield. Coordination chemistry was performed either at the 2,9-diphenyl-1,10-phenanthroline (dpp) chelates or at the porphyrin stoppers. The latter were metalated by either Zn(II), Au(III), or Zn(II) and Au(III). Both Cu(I) template cations could be removed by competitive complexation with CN^- when at least one porphyrin stopper was complexed with Au(III), the other one being metalated with either Au(III) or Zn(II). This provided two strictly defined [3]-rotaxanes, in which the macrocycle and the molecular thread are not held together by metal coordination. Rather, dethreading is prevented by the bulky metalloporphyrin stoppers. Unexpectedly, when both stoppers were complexed with Zn(II), removal of the metal template in the same conditions as above yielded, very selectively, a copper(I)-complexed [3]-rotaxane containing only one metal-free macrocycle. The demetalated bis-dpp site could be remetalated with Ag(I), affording, in good yield, a dinuclear (Ag(I), Cu(I))-complexed [3]-rotaxane, ended by Zn(II)−porphyrin blocking groups.

Introduction

Threading macrocycles onto molecular threads is a modular, highly convergent process for assembling molecules. Once threaded, the macrocyclic rings must be held on the molecular thread to avoid disassembly of the system. This is performed by anchoring bulky stoppers at the extremities of the thread. Figure 1 shows schematically how these different components assemble to form a molecular system called an [*n*]-rotaxane, the number of macrocycles being $n - 1$.

The idea of making threaded complexes between a chain and a macrocyclic ring, stoppered by bulky end groups was stated in 1961 by Frisch and Wasserman.[1] Since then, a great variety of rotaxanes have been synthesized, initially by statistical[2] or directed[3] methods and, more recently, by template techniques, involving either hydrophobic,[4] aromatic donor−acceptor[5] interactions, hydrogen bonds,[6] or transition metals as assembling species.[7,8]

Quite common now are the [2]-rotaxanes. Molecular rotaxanes containing up to three threaded macrocycles ([4]-rotaxanes) have been described so far.[5k,l,n,o] However, of the higher order molecular rotaxanes, [3]-rotaxanes, i.e. rotaxanes involving two threaded macrocycles, form the most important class of molecules.[4p,5k,l,n−q,6c] [3]-Rotaxanes were prepared by various methods, including template and directed syntheses, with the exception of the statistical route, for obvious reasons.

The transition-metal-templated synthesis of the simplest rotaxanes, the [2]-rotaxanes, developed in our laboratory, relies on the copper(I)-directed threading of a 2,9-diphenyl-1,10-phenanthroline (dpp) ligand (the thread) into a macrocycle bearing the same chelating unit in endo fashion (the ring).[7,8] It was shown that porphyrins could be used as stoppers, by direct construction of the tetrapyrrolic macrocycles at the extremities of the thread, the latter bearing precursor aldehyde functions.[8]

A step toward the controlled, transition-metal-templated synthesis of [*n*]-rotaxanes ($n > 2$) was the threading of *two* macrocycles onto a bis-chelating molecular thread: it was shown that the equilibrium reaction of Figure 2 was shifted quantitatively to the formation of the threaded product.[9] In particular, Cu(I) complexes of the bis-chelating molecular thread, like a binuclear double helix complex, or a mononuclear complex, resulting from ligand folding, were not observed. In other words, the threaded product is formed according to the principle of maximal chelation of the Cu(I) atoms.[9]

This multithreading reaction was subsequently used as a modular "string-and-ring" approach to build multiporphyrin assemblies.[10]

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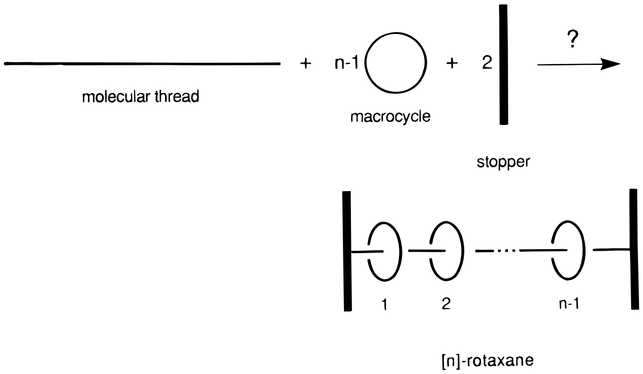

Figure 1. An [*n*]-rotaxane is made from a dumbbell component and $n - 1$ threaded rings.

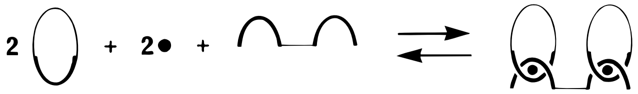

Figure 2. Principle of transition-metal-templated threading of two macrocyclic rings onto a molecular thread. The black circle is a transition metal cation, and the thick lines represent coordinating units.

The copper(I)-templated synthesis of dicopper(I)-complexed [3]-rotaxanes stoppered by porphyrin subunits was presented in a preliminary communication, together with the unexpected, but delightful formation of a compartmental tetracopper(I)-complexed [5]-rotaxane.[11] In this full paper, in addition to a detailed account of the template syntheses, we report on the coordination chemistry of the [3]-rotaxanes. This is of particular interest as far as the preparation of free rotaxanes, i.e. rotaxanes lacking the template Cu(I) atoms, is concerned.

Results and Discussion

1. Copper(I)-Templated Synthesis of Copper(I)-Complexed [3]- and [5]-Rotaxanes. Two strategies are possible for anchoring porphyrins to prerotaxane species: (i) perform a coupling reaction between the prerotaxane and a preformed porphyrin, both species being suitably functionalized, or (ii) build the porphyrin directly at the prerotaxane. We chose the latter strategy as used earlier for the preparation of [2]-rotaxanes[8] and as represented schematically in Figure 3. The chemical structures of the real precursors are given in Figure 4. The molecular thread component **1** is a $-(CH_2)_4-$ bridged bisphenanthroline molecule which proved quite efficient for the threading reaction shown in Figure 2.[9]

It was synthesized in two steps as follows: at first, 1,10-phenanthroline was reacted with 4-lithiobenzaldehyde neopentylacetal (prepared by reaction of *tert*-butyllithium with 4-bromobenzaldehyde neopentylacetal[12]). After hydrolysis and oxidation of the addition product with MnO_2, monosubstituted phenanthroline **3** was obtained in 71% yield. It was subsequently reacted with 1,4-dilithiobutane (obtained by reaction of 1,4-dichlorobutane with lithium sand[13]). After hydrolysis and rearomatization with MnO_2, the yield of pure bisphenanthroline **2** was 86%. The target bisphenanthroline **1** was obtained in 79% yield by hydrolysis of **2** with hydrochloric acid. Threading was performed as follows: at first, a 1:1 complex between macrocycle **4**[7b] and Cu(I) was formed, according to the equilibrium of Figure 2. It was then reacted with 0.5 equiv of bisphenanthroline thread **1**. As represented in Figure 5, the resulting deep red binuclear complex, prerotaxane $\mathbf{7}^{2+}$, was subsequently reacted with a mixture of 3,5-di-*tert*-butylbenzaldehyde[14] (**5**, 8 equiv) and (3,3′-dihexyl-4,4′-dimethyl-2,2′-dipyrryl)methane[15] (**6**, 10 equiv) in the presence of CF_3CO_2H, used as acid catalyst.[16,8b,c] The porphyrinogen species formed were then oxidized to the corresponding porphyrins with chloranil (31 equiv).

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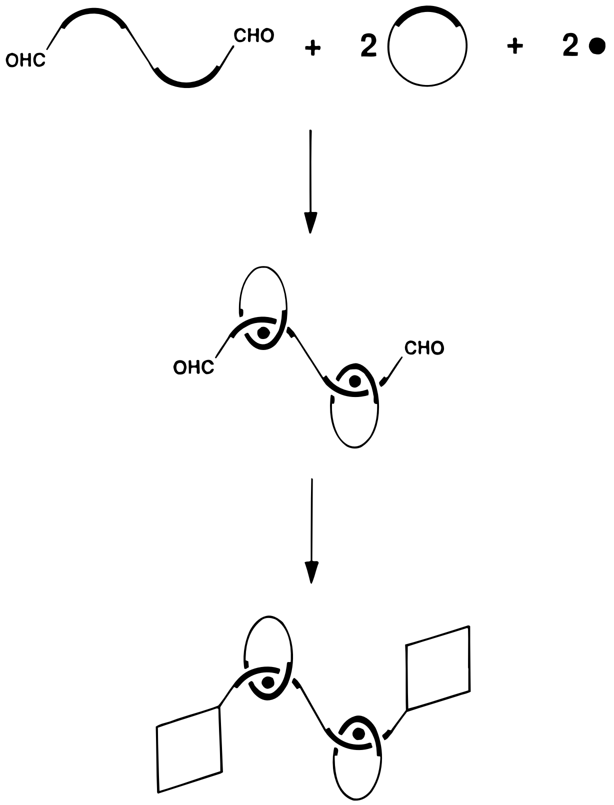

Figure 3. Principle of copper(I)-templated synthesis of a (Cu_2)-[3]-rotaxane. The black circle is Cu(I), the thick lines represent 2,9-diphenyl-1,10-phenanthroline coordinating units, and the diamonds are porphyrin stoppers.

After purification by repeated chromatography, three porphyrin-containing compounds could be isolated from the reaction mixture (Figure 5): 5,15-bis(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (**8**) in 32% yield from **5**, (Cu_2)-[3]-rotaxane $\mathbf{9}^{2+}$ in 34% yield, and (Cu_4)-[5]-rotaxane $\mathbf{10}^{4+}$ in 8% yield, the copper complexes being isolated as PF_6^- salts. Noteworthy is the high yield of (Cu_2)-[3]-rotaxane $\mathbf{9}^{2+}$. Since two porphyrins are created simultaneously, the yield of individual porphyrin formation is ca. 60%. (Cu_4)-[5]-rotaxane $\mathbf{10}^{4+}$ deserves some comment. First of all, it is a molecule with four threaded macrocycles, that is, it has a [5]-rotaxane structure; second, it results from the simultaneous formation of three porphyrins, the central one resulting from the condensation of two prerotaxane-like units. The yield of individual porphyrin formation is ca. 45% in this case. This copper(I)-complexed [5]-rotaxane may be considered as what we could call a compartmental [5]-rotaxane, since two groups of two macrocycles each are separated by an inner porphyrin blocking group. The compounds of Figure 5 (prerotaxane and rotaxanes), as well as all the other [3]-rotaxanes of this study, were characterized by fast atom bombardment (FAB) or electrospray (ES) mass spectrometry and ^{1}H NMR spectroscopy.

2. Coordination Chemistry of the Copper(I)-Complexed [3]-Rotaxanes. The various coordination chemistry studies performed starting from the free-base dicopper(I)-complexed [3]-rotaxane $\mathbf{9}^{2+}$ are summarized schematically in Figure 6. The [3]-rotaxane framework of this study contains two quite different coordinating sites: (i) the combination of two dpp chelates, one from the dumbbell and the other from a threaded macrocycle, which enforce a tetrahedral geometry around the complexed metal cation, and (ii) the porphyrinic stoppers, which bind cations with square planar, and derived geometries such as square pyramidal, or octahedral, the two latter cases involving additional, apical ligands in the complexation processes.

3. Coordination Chemistry of the Rotaxanes at the Porphyrin Stoppers: Preparation of (Cu_4)-[5]-Rotaxane $\mathbf{13}^{4+}$ and (Cu_2)-[3]-Rotaxanes $\mathbf{12}^{2+}$ and $\mathbf{14}^{3+}-\mathbf{16}^{3+}$. Reaction of (Cu_2)-[3]-rotaxane $\mathbf{9}^{2+}$ with zinc acetate in a refluxing mixture of chloroform and methanol afforded, after chromatography, (Cu_2)-[3]-rotaxane $\mathbf{12}^{2+}$ in 83% yield. Porphyrin **8** and (Cu_4)-[5]-rotaxane $\mathbf{10}^{4+}$ were treated similarly, affording, respectively, Zn(II)−porphyrin **11** and (Cu_4)-[5]-rotaxane $\mathbf{13}^{4+}$ (Figure 5) in 79% and 85% isolated yields, respectively.

Since Au(III)−porphyrins belong to stability class I (i.e., not completely demetalated by 100% sulfuric acid) and Zn(II)−porphyrins belong to stability class III (demetalated in very mild conditions, i.e., by a mixture of aqueous HCl and dichloromethane),[17] it seemed quite obvious that it was necessary to start the metalation with Au(III) to avoid transmetalation problems. At first, reaction of $Au(tht)_2(PF_6)$ (3 equiv; tht is tetrahydrothiophene) with $\mathbf{9}^{2+}$ (1 equiv) in refluxing chloroform in the presence of 2,6-lutidine produced the desired monometalated (Cu_2)-[3]-rotaxane $\mathbf{14}^{3+}$ in 38% yield, after repeated column chromatography.[18] The dimetalated (Cu_2)-[3]-rotaxane $\mathbf{15}^{4+}$ was isolated in 13% yield as a byproduct, and 28% of starting material was recovered. Therefore, the distribution of products is not very far from statistics, given that this method of metalation generally proceeds in 60−70% yields.[18] Incidentally, (Cu_2)-[3]-rotaxane $\mathbf{15}^{4+}$ was obtained directly by reaction of (Cu_2)-[3]-rotaxane $\mathbf{9}^{2+}$ with 6 equiv of $Au(tht)_2(PF_6)$ in the presence of 2,6-lutidine, in 42% yield after chromatographic purification. Next, $\mathbf{14}^{3+}$ was reacted with $Zn(OAc)_2{\cdot}2H_2O$ in a refluxing mixture of chloroform and methanol to afford the target (Cu_2)-[3]-rotaxane $\mathbf{16}^{3+}$ quantitatively.

4. Coordination Chemistry of the [3]-Rotaxanes at the Bis-dpp Subsites. 4.1. Selective Monodemetalation Reaction of (Cu_2)-[3]-Rotaxane $\mathbf{12}^{2+}$ Leading to Cu-[3]-Rotaxane $\mathbf{17}^{+}$. The rotaxanes we were dealing with until now are copper(I)-complexed rotaxanes, and chemical evidence of their very rotaxane nature has not been given yet, i.e. demetalation should afford a single molecular species and not a mixture of separated thread and macrocycles, provided that the relative dimensions of the macrocycle and the stoppers were well chosen. Demetalation of copper(I)-complexed catenates and rotaxanes is routinely performed by competitive complexation with cyanide, using a large excess of KCN (typically 20−25 mol/mol of Cu(I)) in $CH_3CN/CH_2Cl_2/H_2O$ mixtures.[7b,19] This reaction performed in similar conditions starting from $\mathbf{12}^{2+}$ (68 mol of KCN/mol of $\mathbf{12}^{2+}$, i.e. 34 mol/mol of Cu(I)) afforded cleanly and almost quantitatively the monodemetalated species ($\mathbf{17}^{+}$), to our great surprise. Prolongated reaction times or heating to 64 °C did not improve the extent of demetalation.

It was shown earlier that the CN^--triggered dissociation of a copper(I)-complexed threaded species such as $\mathbf{7}^{2+}$ took place in two consecutive bimolecular steps.[9b] The first step corresponded to the dethreading of one macrocycle, leaving an intermediate containing a single threaded macrocycle. It took place at a rate of 1120 M^{-1} s^{-1}. The second Cu(I) atom dissociated from the threaded complex at a rate of 354 M^{-1} s^{-1}. The ratio of these rate constants is 3, which is of the same order of magnitude as the statistical value (2). This indicates

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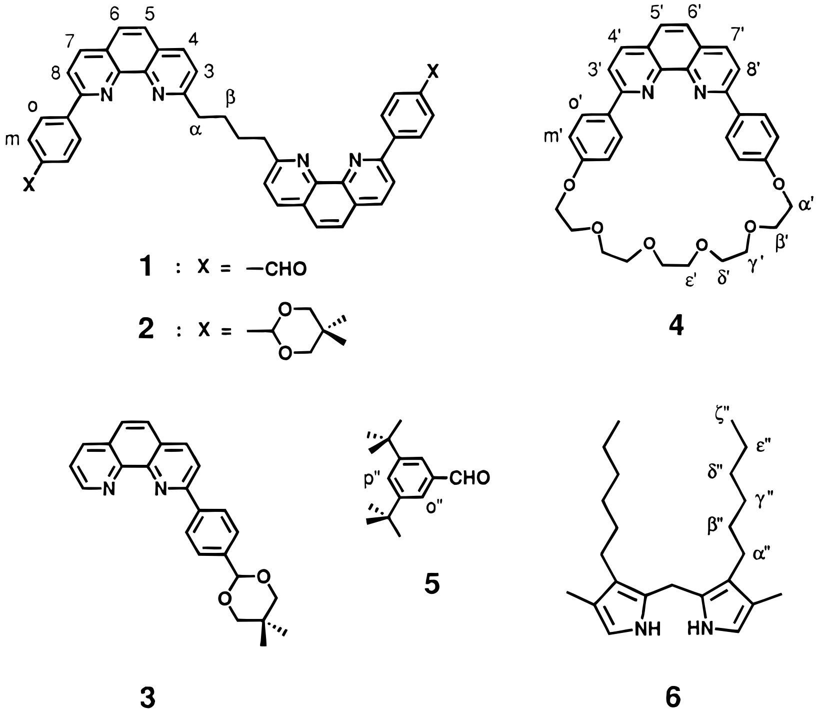

Figure 4. Chemical structures of the precursors to the [3]- and [5]-rotaxanes described in this study, with atom numbering.

that the probability that CN^- effectively finds Cu(I) is twice in the case of the binuclear complex than in the case of the mononuclear complex. Therefore, in the case of the prerotaxane, there is no particular hamper to demetalation. The outcome of the demetalation reaction of (Cu_2)-[3]-rotaxane $\mathbf{12}^{2+}$ is linked to its rotaxane nature. This phenomenon can be related to allosteric effects,[20] in the sense that the reactivity of a given site of the molecule is governed by another fragment, both units being apparently relatively remote from one another. The simplest explanation is that, after removal of the first copper(I), which proceeds with a normal rate (i.e., similar to other analogous complexes), the molecule undergoes some profound rearrangement. The new conformation obtained is such that the second coordination site has now become fully protected from attack by CN^- and is thus totally inert toward decomplexation.

4.2. Metalation of (Cu)-[3]-Rotaxane $\mathbf{17}^{+}$ with Silver(I), Affording (Ag,Cu)-[3]-Rotaxane $\mathbf{18}^{2+}$. The 2,9-diphenyl-1,10-phenanthroline chelates embedded respectively in the macrocyclic and the dumbbell-shaped components of Cu-[3]-rotaxane $\mathbf{17}^{+}$ are in fact imprints of the metal template which has been partially removed. The tetradentate cavity initially formed around Cu(I) could be restored, by reacting (Cu)-[3]-rotaxane $\mathbf{17}^{+}$ with $AgBF_4$ in a CH_2Cl_2/CH_3CN mixture. (Ag,Cu)-[3]-rotaxane $\mathbf{18}^{2+}$ was isolated in 51% yield after chromatographic purification.

5. Preparation of Free [3]-Rotaxanes $\mathbf{19}^{2+}$ and $\mathbf{20}^{+}$. To test the influence of the metal cation incorporated in the porphyrinic stoppers on the outcome of the demetalation reaction, (Cu_2)-[3]-rotaxane $\mathbf{15}^{4+}$, containing Au(III)−porphyrins as stoppers, was treated similarly with potassium cyanide in a CH_2Cl_2/H_2O heterogeneous mixture. Unlike (Cu_2)-[3]-rotaxane $\mathbf{12}^{2+}$, which contained Zn(II)−porphyrin stoppers, complete removal of the Cu(I) atoms took place, affording the first free [3]-rotaxane of this series, $\mathbf{19}^{2+}$, in 62% yield after chromatography. The demetalation reaction is depicted in Figure 7.

As seen above, template removal was complete when both porphyrinic stoppers were metalated with Au(III). When the stoppers were metalated with Zn(II), only one Cu(I) atom of two could be extracted using CN^- as a competitive ligand. The last issue to remain was the case of the (Cu_2)-[3]-rotaxane bearing a Zn(II)- *and* a Au(III)−porphyrin as stoppers. Therefore, (Cu_2)-[3]-rotaxane $\mathbf{16}^{3+}$ was reacted with a slight excess of KCN in a CH_2Cl_2/H_2O mixture. Unexpectedly, total removal of the Cu(I) template atoms took place, leaving the free [3]-rotaxane $\mathbf{20}^{+}$ as product. It was isolated in 59% yield after chromatography.

6. Mass Spectrometry Study of the Copper(I)-Complexed and Free [3]-Rotaxanes. With the exception of (Cu_2)-[3]-rotaxane $\mathbf{16}^{3+}$, which was characterized by electrospray ionization mass spectrometry, all the other [3]-rotaxanes were examined by FAB mass spectrometry. The data are collected in Table 1.

Peaks due to fragments of various charge, corresponding to (i) intact [3]-rotaxane structures, (ii) [2]-rotaxane structures resulting from the [3]-rotaxanes by dethreading of one macrocycle, and (iii) bisporphyrin dumbbells, resulting from the [3]-rotaxanes by the loss of both macrocycles, are observed in the FAB mass spectra of all copper(I)-complexed and free [3]-rotaxanes studied. What is essentially differing from one molecule to the other is the ionization process, that is how the molecular fragments have “managed” to acquire or keep their positive charges. The charges are provided either by the metal cations complexed by the dpp sites (Cu^+ or Ag^+) or by the metal complexed by the porphyrinic stoppers (Au^{3+}). It can also be provided by protonation. This is observed for the cases of the free [3]-rotaxanes $\mathbf{17}^{+}$, $\mathbf{19}^{2+}$, and $\mathbf{20}^{+}$, where free bis-dpp sites are available. This is consistent with the fact that these

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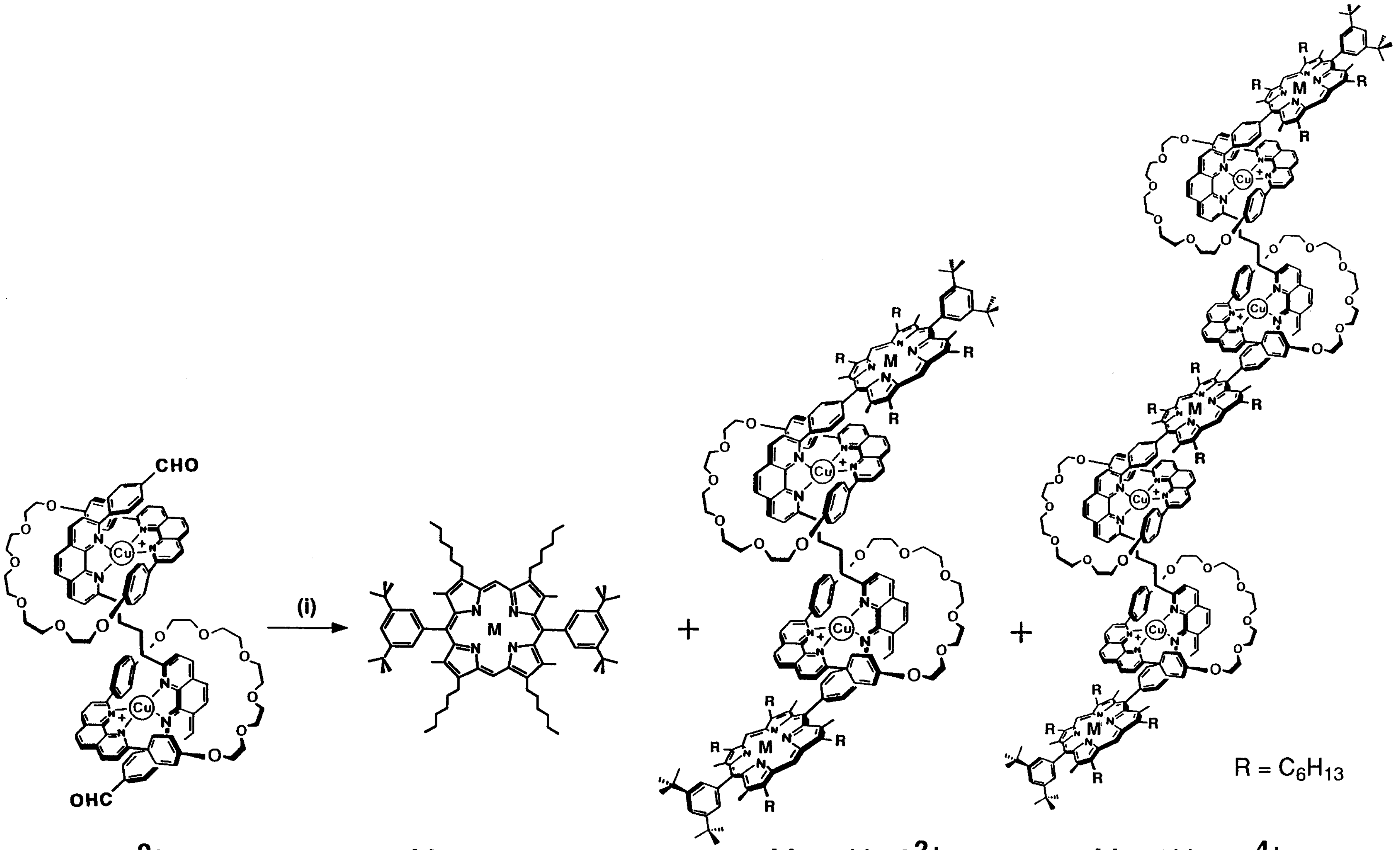
[20] (a) Rebek, J., Jr.; Marshall, L. *J. Am. Chem. Soc.* **1983**, *105*, 6668. (b) Rebek, J., Jr.; Costello, T.; Marshall, L.; Wattley, R.; Gadwood, R. C.; Onan, K. *J. Am. Chem. Soc.* **1985**, *107*, 7481. (c) Gaviña, F.; Luis, S. V.; Costero, A. M.; Burguete, M. I.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 7140. (d) Gagnaire, G.; Gellon, G.; Pierre, J.-L. *Tetrahedron Lett.* **1988**, *29*, 933. (e) Schneider, H.-J.; Ruf, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1159.



7^{2+}

M = 2H : **8**
M = Zn : **11**

M = 2H : **9^{2+}**
M = Zn : **12^{2+}**

M = 2H : **10^{4+}**
M = Zn : **13^{4+}**

Figure 5. One-pot preparation of copper(I)-complexed [3]- and [5]-rotaxanes: (i) **5** (8 equiv), **6** (10 equiv) cat. CF_3CO_2H, CH_2Cl_2, room temperature, then chloranil (35 equiv), CH_2Cl_2, reflux.

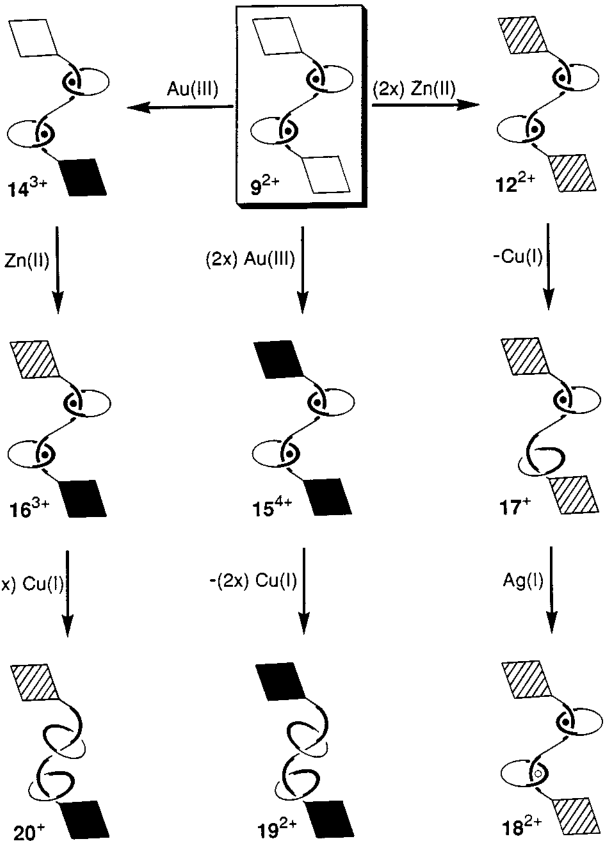


Figure 6. Coordination chemistry of (Cu_2)-[3]-rotaxane $\mathbf{9}^{2+}$. The diamonds are the porphyrin stoppers: empty = free-base, hatched = Zn(II)-complexed, black = Au(III)-complexed. The black circles are Cu(I), and the white circle is Ag(I).

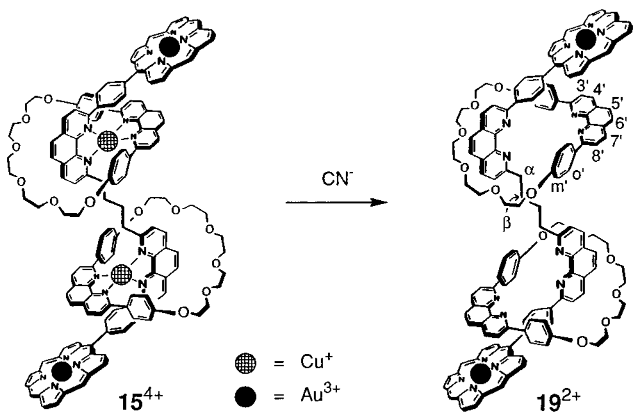


Figure 7. Removal of the metal template of (Cu_2)-[3]-rotaxane $\mathbf{15}^{4+}$, affording [3]-rotaxane $\mathbf{19}^{2+}$. The porphyrin substituents have been omitted for clarity.

sites are expected to be more basic than isolated dpp.[21] Singly charged species are usually formed by loss of one PF_6^- anion. However, if more PF_6^- anions are lost, charge compensation is provided by electronic reduction.

Multiply charged species also contribute significantly to the mass spectra. Of course the more charged the molecule, the more multiply charged species are observed. For example, in the case of (Cu_2)-[3]-rotaxane $\mathbf{15}^{4+}$, which bears the highest charge and whose tetrapositive charge is due to the two Cu(I) cations and the two Au(III)−porphyrinic stoppers, in addition to the singly charged species, doubly charged species such as $[M^{4+} + 2PF_6^-]^{2+}/2$ and a triply charged species ($[M^{4+} + PF_6^-]^{3+}/3$) are observed. The same observations hold true for [2]-rotaxane-like fragments. In addition, a feature particular to these fragments is that macrocycle dethreading is not necessarily accompanied by the loss of the complexed Cu^+ cation, when the molecule under investigation is a (Cu_2)-[3]-rotaxane. The dumbbell fragments, except for those stoppered by Au(III)−porphyrins, are not naturally charged. Therefore, the positive charge is provided by coordination of metal cations such as Cu^+ or Ag^+, or protons (in the case of $\mathbf{17}^{+}$ and $\mathbf{20}^{+}$).

7. Proton NMR Spectroscopy Study of the Complexed and Free [3]-Rotaxanes. 7.1. Effect of the Metal Complexing the Porphyrin Stoppers or the dpp Sites. Whereas incorporation of Zn(II) has little effect on the chemical shifts by comparison with the free-base porphyrin, this is not the case of Au(III). The electron-withdrawing effect of cationic Au(III) is expressed into deshielding effects only for protons either directly connected or one C−C bond away from the porphyrin macrocycle. For example, the meso protons of (Cu_2)-[3]-rotaxane $\mathbf{12}^{2+}$ (Zn(II)−porphyrin stoppers) show up at 10.12 ppm, whereas the same protons of $\mathbf{15}^{4+}$ (Au(III)−porphyrin stoppers) show up at 10.56 ppm ($\Delta\delta = +0.44$ ppm). Similar observations can be made by examining the spectrum of $\mathbf{16}^{3+}$, a (Cu_2)-[3]-rotaxane containing both Zn(II)− and Au(III)−porphyrins as stoppers: it is a superimposition of the spectra of $\mathbf{12}^{2+}$ and $\mathbf{15}^{4+}$.

(Cu,Ag)-[3]-rotaxane $\mathbf{18}^{2+}$ allows the study of the effect of complexation of one bis-dpp site of (Cu_2)-[3]-rotaxane $\mathbf{12}^{2+}$ with Ag(I), which has roughly the same stereoelectronic requirements as Cu(I). The spectra of $\mathbf{18}^{2+}$ and $\mathbf{12}^{2+}$ look similar, except that most of the peaks of the former are split, in agreement with the nonsymmetrical nature of the molecule.

7.2. Removal of the Metal Template. Removal of the Cu(I) metal template of (Cu_2)-[3]-rotaxanes $\mathbf{12}^{2+}$, $\mathbf{15}^{4+}$, and $\mathbf{16}^{3+}$ to afford (Cu)-[3]-rotaxane $\mathbf{17}^{+}$ and [3]-rotaxanes $\mathbf{19}^{2+}$ and $\mathbf{20}^{+}$ respectively, has dramatic effects on the ^1H NMR spectra of the molecules, suggesting that some rearrangement is taking place. Since these molecules share several common features, only a detailed comparison between the spectra of $\mathbf{15}^{4+}$ and $\mathbf{19}^{2+}$, the simplest ones, because of their symmetry properties, will be provided here. Figure 8 compares the aromatic regions of the spectra of these molecules. See also Figure 7 for highlighting of selected protons. The most prominent feature is the strong upfield shift of the singlet of the (5′,6′) protons of the phenanthroline moiety incorporated in the macrocycles: $\Delta\delta = -2.00$ ppm. The other phenanthroline protons show a similar trend: for (4′,7′), $\Delta\delta = -1.68$ ppm, and for (3′,8′), $\Delta\delta = -0.84$ ppm. Therefore, the closer the protons from the symmetry plane of the [3]-rotaxane molecule, containing the bisphenanthroline thread, the stronger their shielding. Protons o′ and m′ of the macrocycles experience the opposite effect upon demetalation, since resonance signals move downfield: $\Delta\delta = +0.90$ ppm for both of them. The same is true for protons α and β of the alkyl bridge linking the rotaxane subunits.

These results are consistent with the following picture of free rotaxane $\mathbf{19}^{2+}$ (Figure 7): the metal-free macrocycles have slipped toward the closest porphyrin stopper so that the phenanthroline moiety they incorporate is embedded in the strong shielding field of the porphyrins. Simultaneously, the o′ and m′ protons of the phenyl substituents of the macrocycles are no longer in the shielding field of the phenanthroline fragments of the molecular thread, hence the downfield shift of their signals upon demetalation. The deshielding of protons α and β is certainly due to similar reasons: in the complex these

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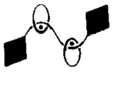
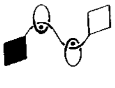
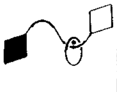
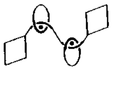
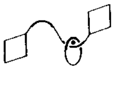
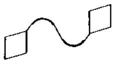
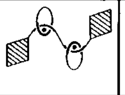
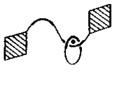
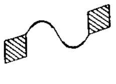
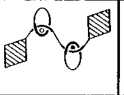
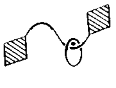
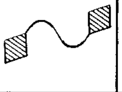
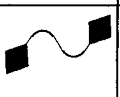
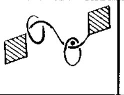
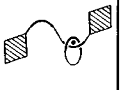
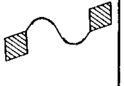
[21] Cesario, M.; Dietrich-Buchecker, C. O.; Edel, A.; Guilhem, J.; Kintzinger, J.-P.; Pascard, C.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 6250.

Table 1. FAB-MS Data for Selected Metal-Complexed and Free [3]-Rotaxanes in This Study[a]

n°	[3]-rotaxane M^{n+} fragment	Ionization process	Theory	Obsvd	%	[2]-rotaxane M^{n+} fragment	Ionization process	Theory	Obsvd	%	Dumbbell M^{n+} fragment	Ionization process	Theory	Obsvd	%
15^{4+}		$[M^{4+}+3PF_6^-]^+$ $[M^{4+}+2PF_6^-+e]^+$ $[M^{4+}+PF_6^-+2e]^+$ $[M^{4+}+2PF_6^-]^{2+}/2$ $[M^{4+}+PF_6^-+e]^{2+}/2$ $[M^{4+}+2e]^{2+}/2$ $[M^{4+}+PF_6^-]^{3+}/3$	4430.7 4285.7 4140.8 2142.9 2070.4 1997.9 1380.3	4432.0 4286.8 4141.1 2143.1 2070.2 1996.9 1379.7	24 37 15 71 60 14 100		$[M^{3+}+2PF_6^-]^+$ $[M^{3+}+PF_6^-+e]^+$ $[M^{3+}+2e]^+$ $[M^{3+}+PF_6^-]^{2+}/2$ $[M^{3+}+e]^{2+}/2$	3655.5 3510.6 3365.6 1755.3 1682.8	3655.9 3509.9 3364.3 1755.2 1681.9	8 10 6 16 13		$[M]^{2+}/2$	1367.7	1365.7	86
14^{3+}		$[M^{3+}+2PF_6^-]^+$ $[M^{3+}+PF_6^-+e]^+$ $[M^{3+}+2e]^+$ $[M^{3+}+PF_6^-]^{2+}/2$ $[M^{3+}+e]^{2+}/2$ $[M]^{3+}/3$	4090.8 3945.8 3800.9 1972.9 1900.4 1266.9	4088.9 3945.2 3799.5 1971.3 1899.9 1265.2	19 37 16 100 96 64		$[M^{2+}+PF_6^-]^+$ $[M^{2+}+Cu^++2e]^+$ $[M^{2+}+e]^+$ $[M^++Cu^++e]^{2+}/2$ $[M]^{2+}/2$	3315.6 3234.2 3170.6 1617.1 1585.3	 3232.0 1616.1 	11 33 20 55 42		$[M]^+$ $[M^++Cu^++e]^+$	2540.5 2603.6	2541.4 2602.5	3 7
9^{2+}		$[M^{2+}+2PF_6^-+H^+]^+$ $[M^{2+}+PF_6^-]^+$ $[M^{2+}+e]^+$ $[M]^{2+}/2$	3896.8 3750.9 3605.7 1803.0	3896.8 3750.2 3604.6 1802.3	4 75 27 31		$[M^{2+}+Cu^++e]^+$ $[M]^+$ $[M^++Cu^+]^{2+}/2$	3039.2 2975.7 1519.1	3037.4 2975.6 1519.1	100 72 23		$[M+2Cu^++e]^+$ $[M+Cu^+]^+$	2472.6 2409.1	2470.4 2409.4	72 12
12^{2+}		$[M^{2+}+2PF_6^--e]^+$ $[M^{2+}+PF_6^-]^+$ $[M^{2+}+e]^+$ $[M]^{2+}/2$	4022.6 3877.6 3732.6 1866.3	4022.4 3878.0 3731.3 1866.1	8 91 35 54		$[M]^+$ $[M^++Cu^+]^{2+}/2$	3102.4 1583.0	3101.1 1582.1	100 21		$[M+Cu^+]^+$ $[M+2Cu^+]^{2+}/2$	2535.8 1299.7	2534.8 1297.8	35 49
18^{2+}		$[M^{2+}+PF_6^-]^+$ $[M^{2+}+e]^+$ $[M^{2+}-Ag^+]^+$ $[M]^{2+}/2$	3921.9 3777.0 3669.1 1934.4	3921.3 3775.4 3668.1 1934.0	73 30 34 18		$[M]^+$ $[M]^+$	3102.5 3146.8	3101.5 3145.5	100 64		$[M+Cu^+]^+$ $[M+Ag^+]^+$	2535.8 2580.1	2534.2 2578.7	29 16
19^{2+}		$[M^{2+}+2PF_6^-+H^+]^+$ $[M^{2+}+PF_6^-]^+$ $[M^{2+}+e]^+$ $[M]^{2+}/2$	4158.7 4013.7 3868.7 1934.4	4159.8 4013.5 3867.8 1934.0	4 13 8 18		$[M^{2+}+PF_6^-]^+$ $[M^{2+}+e]^+$ $[M]^{2+}/2$	3446.9 3301.9 1650.9	3446.4 3301.0 1650.6	22 22 43		$[M^{2+}+PF_6^-]^+$ $[M^{2+}+e]^+$ $[M]^{2+}/2$	2880.4 2735.4 1367.7	2879.8 2734.3 1366.7	20 19 100
17^+		$[M]^+$ $[M^+-Cu^++H^+]^+$ $[M^++H^+]^{2+}/2$ $[M^+-Cu^++2H^+]^{2+}/2$	3669.1 3605.5 1835.0 1803.3	3668.6 3606.1 1834.5 1802.2	70 43 58 34		$[M]^+$ $[M^+-Cu^++H^+]^+$ $[M^++H^+]^{2+}/2$ $[M^+-Cu^++2H^+]^{2+}/2$	3102.4 3039.9 1551.7 1520.5	3101.5 3039.2 1551.1 1519.9	100 84 36 28		$[M+Cu^+]^+$ $[M+H^+]^+$ $[M+2H^+]^{2+}/2$	2535.8 2473.2 1237.1	2534.4 2472.3 1236.2	33 35 62
20^+		$[M^++PF_6^-+H^+]^+$ $[M]^+$ $[M^++H^+]^{2+}/2$	3883.1 3737.1 1869.1	3883.3 3737.6 1868.9	19 80 44		$[M]^+$ $[M^++H^+]^{2+}/2$	3170.5 1585.8	3170.3 1585.2	100 36		$[M]^+$	2603.8	2603.0	60

[a] The diamonds are the porphyrin stoppers: empty = free-base, hatched = Zn(II)-complexed, black = Au(III)-complexed. The black circles are Cu(I), and the white circle is Ag(I).

protons are shielded by the ring currents of the phenanthroline incorporated in the macrocycle, which are switched off once the metal is removed.

Conclusion

The preparation and characterization of various porphyrin-stoppered [3]-rotaxanes have been described in this study. Among all of the compounds prepared, of paramount importance is the [3]-rotaxane **20**$^+$ containing both a Zn(II)−porphyrin and a Au(III)−porphyrin as stoppers, with respect to electron transfer studies. This molecule is the [3]-rotaxane homologue of the [2]-rotaxane that was described a few years ago[8a,b] and showed an intramolecular photoinduced electron transfer between a Zn(II)−porphyrin stopper in its excited state and a Au(III)−porphyrin stopper in its ground state.[22] Photophysical studies on [3]-rotaxane **20**$^+$ and analogues are underway and will be reported in due course.

Experimental Section

^{1}H NMR spectra were obtained on either a Brucker WP 200 SY (200 MHz), AM 400 (400 MHz), or ARX 500 (500 MHz) spectrometer. Chemical shifts are referenced downfield from tetramethylsilane ("h" means hidden peaks). Labels of the protons of the [3]-rotaxanes are provided in Chart 1. They hold true for the [5]-rotaxane, which uses in addition, subscript *c* for protons of the central porphyrin, and superscript * for protons of the copper(I) complex fragments proximal to the central porphyrin. Mass spectral data were obtained on either Thomson THN 208 (chemical ionization), ZAB-HF (FAB), or VG BIOQ triple quadrupole (ES-MS). Melting points were determined in open capillary tubes on a Büchi SMP-20 apparatus and were uncorrected. Elemental analyses were performed by the Service de Microanalyse de l'Institut de Chimie de Strasbourg. IR spectra were recorded with a Perkin-Elmer 580 spectrophotometer.

All of the reactions were performed under an atmosphere of argon, using Schlenk techniques unless otherwise noted. *p*-Bromobenzaldehyde neopentylacetal,[12] $Cu(CH_3CN)_4PF_6$,[23] 3,5-di-*tert*-butylbenzaldehyde (**5**),[14] and (3,3′-dihexyl-4,4′-dimethyl-2,2′-dipyrryl)methane (**6**)[15] were prepared according to literature procedures. MnO_2 was purchased from Merck (ref 805958). Note that only the preparation and characterization of precursors **1**−**3**, and prerotaxane [**7**$^{2+}$]$(PF_6^-)_2$ are provided here, in addition to (Cu_2)-[3]-rotaxane [**9**$^{2+}$]$(PF_6^-)_2$ and (Cu_4)-[5]-rotaxane [**10**$^{4+}$]$(PF_6^-)_4$, as examples. The other rotaxanes are described in the Supporting Information.

2-(*p*-Benzaldehyde neopentylacetal)-1,10-phenanthroline 3. 89 mL of a 1.30 M solution of *tert*-butyllithium in pentane (116 mmol) were added at −78 °C to a solution of 15.0 g (55 mmol) of *p*-bromobenzaldehyde neopentylacetal in THF (110 mL). The solution was then stirred at −78 °C for 2 h, before allowing the temperature to rise to −5 °C three times. The end of the reaction was detected by the Gilman color test.[24] The resulting organolithium solution was added to a solution of 1,10-phenanthroline (8.97 g, 50 mmol) in dry THF (500 mL) maintained at 0 °C. The dark red solution obtained was stirred at 0 °C for 1 h and 30 min and at 5 °C for 1 h, and was thereafter hydrolyzed by 150 mL of water. The THF was evaporated and the resulting aqueous

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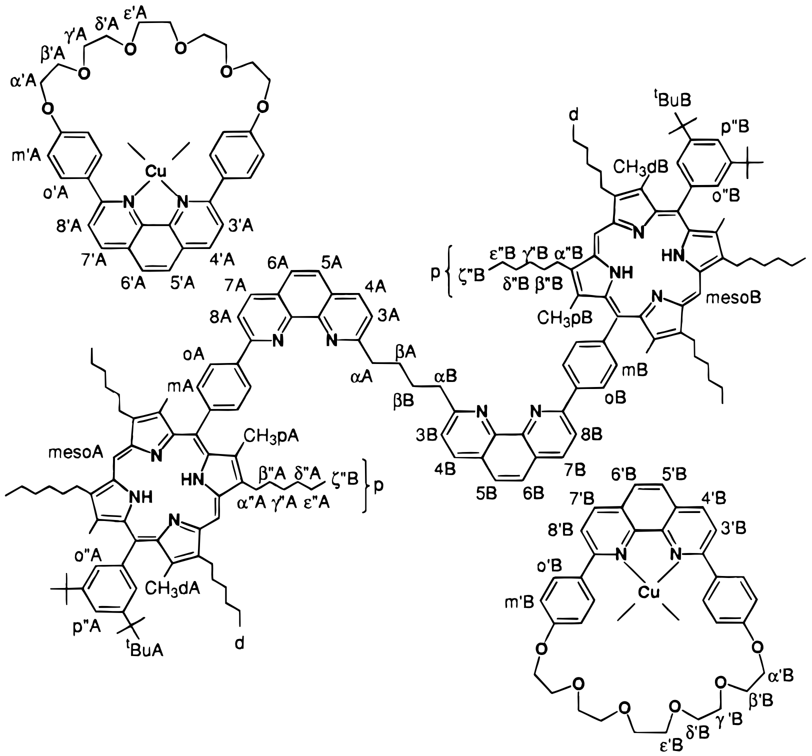
[22] (a) Chambron, J.-C.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 6109. (b) Chambron, J.-C.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 7419.

[23] Kubas, G. J.; Monzyk, B.; Crumbliss, A. L. *Inorg. Synth.* **1990**, *28*, 68.

[24] Gilman, H.; Haubein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515.

Chart 1



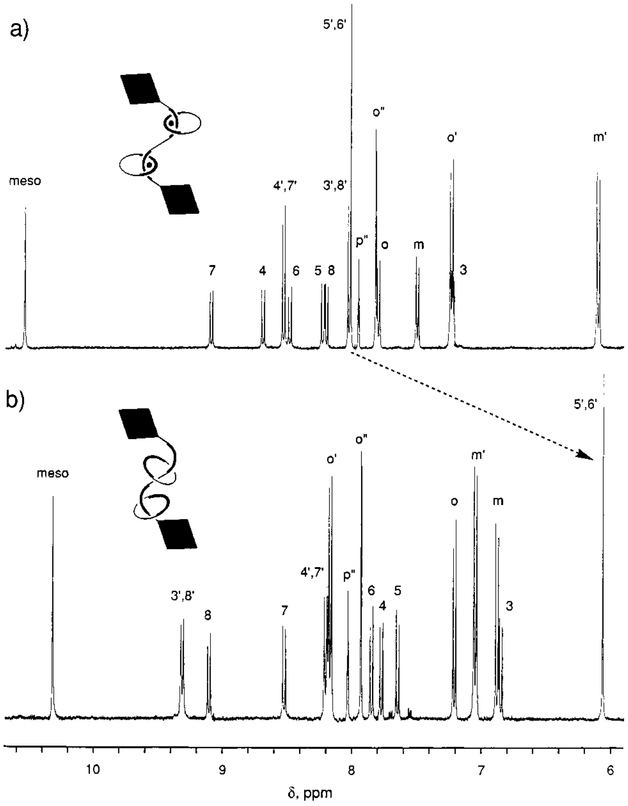


Figure 8. Comparison of the ^{1}H NMR spectra (400 MHz) of (a) (Cu$_2$)-[3]-rotaxane **15**$^{4+}$ and (b) [3]-rotaxane **19**$^{2+}$. The black diamonds are the Au(III)-complexed porphyrinic stoppers, and the black circles are Cu(I) atoms. See Figure 7 for selected atom labels and Chart 1 for complete proton labeling.

phase extracted three times with CH$_2$Cl$_2$. The combined organic layers were treated by 70 g of MnO$_2$ and dried over the same weight of MgSO$_4$. The MnO$_2$/MgSO$_4$ aggregates were filtered on a sintered glass filter and thoroughly washed with CH$_2$Cl$_2$. After evaporation of the solvent and recrystallization in benzene, 13.1 g (35.4 mmol, 71% yield) of 2-(*p*-benzaldehyde neopentylacetal)-1,10-phenanthroline (**3**) was obtained. White solid (mp = 216 °C). ^{1}H NMR (200 MHz, CDCl$_3$): δ 9.25 (dd, 1H, H$_9$, $^3J' = 4.4$ Hz, $^4J = 1.7$ Hz), 8.38 (d, 2H, H$_o$, $^3J = 8.4$ Hz), 8.33 (d, 1H, H$_4$, $^3J = 8.5$ Hz), 8.28 (dd, 1H, H$_7$, $^3J = 8.1$ Hz, $^4J = 1.8$ Hz), 8.12 (d, 1H, H$_3$, $^3J = 8.4$ Hz), 7.81 (AB, 2H, H$_{5,6}$, $^3J = 8.8$ Hz), 7.70 (d, 2H, H$_m$, $^3J = 8.3$ Hz), 7.66 (dd, 1H, H$_8$, $^3J = 8.1$ Hz, $^3J' = 4.3$ Hz), 5.51 (s, 1H, C*H*), 3.77 (AB, 4H, C*H*$_2$, $^2J = 10.9$ Hz), 1.34 (s, 3H, C*H*$_3$), 0.84 (s, 3H, C*H*$_3$). Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.8; H, 6.0; N, 7.6. Found: C, 77.6; H, 6.3; N, 7.6.

Bisphenanthroline 2. 1,4-Dilithiobutane was prepared by the direct interaction of 1,2-dichlorobutane with lithium sand[13] and titrated. A 21 mL portion of the 1.23 M solution of 1,4-dilithiobutane obtained (12.9 mmol) was added to a suspension of 2-(*p*-benzaldehyde neopentylacetal)-1,10-phenanthroline (12 g, 32.4 mmol) in dry ether (250 mL) maintained at 0 °C. The resulting dark red solution was stirred for 24 h at 0 °C and hydrolyzed with 70 mL of water. A bright orange organic phase was obtained. Ether was evaporated off and the aqueous phase extracted three times with CH$_2$Cl$_2$. The combined organic layers were washed three times with water, treated with 45 g of MnO$_2$, and dried over 45 g of MgSO$_4$. The MnO$_2$/MgSO$_4$ aggregates were filtered on a sintered glass funnel and thoroughly washed with CH$_2$Cl$_2$. After evaporation of the solvent, 16.9 g of crude beige product was obtained. After chromatography on alumina (∅ = 5 cm, *h* = 34 cm, eluent: CH$_2$Cl$_2$/MeOH 99.6/0.4) and two recrystallizations in a mixture of CH$_2$Cl$_2$/hexane, 1:2, the desired bis(1,10-phenanthroline) (**2**) was isolated pure in 86% yield (8.8 g, 11.1 mmol). White solid (mp = 219 °C). ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.42 (d, 4H, H$_o$, $^3J = 8.3$ Hz), 8.29 (d, 2H, H$_{4\text{ or }7}$, $^3J = 8.4$ Hz), 8.12 (d, 4H, H$_8$ and H$_{4\text{ or }7}$, $^3J = 7.9$ Hz), 7.73 (s, 4H, H$_{5,6}$), 7.70 (d, 4H, H$_m$, $^3J = 8.4$ Hz), 7.61 (d, 2H, H$_3$, $^3J = 8.2$ Hz), 5.49 (s, 2H, C*H*), 3.76 (AB, 8H, C*H*$_2$, $^2J = 10.8$ Hz), 3.39 (t, 4H, H$_\alpha$), 2.24 (t, 4H, H$_\beta$), 1.34 (s, 6H, C*H*$_3$), 0.83 (s, 6H, C*H*$_3$). Anal. Calcd for $C_{52}H_{50}N_4O_4 \cdot 0.25C_6H_{14}$: C, 78.7; H, 6.6; N, 6.9. Found: C, 78.8; H, 7.0; N, 7.2.

Bisphenanthroline 1. A 5% solution of hydrochloric acid (15 mL, 24.3 mmol) was added to a suspension of 1.0 g of bisphenanthroline (**2**) (1.26 mmol) in THF (80 mL). The resulting solution was stirred for 3 days at room temperature and neutralized with 50 mL of a 10% aqueous solution of sodium hydrogen carbonate. The solvent was evaporated off and the resulting aqueous phase extracted three times with CH_2Cl_2. The combined organic layers were washed three times with water and dried over $MgSO_4$. After filtration and evaporation of the solvent, 860 mg of crude beige product was obtained. Purification by recrystallization in $CHCl_3$/hexane and chromatography on silica gel (∅ = 2 cm, $h = 24$ cm, eluent: CH_2Cl_2/MeOH, 99/1) afforded the desired bisphenanthroline **1** in 79% yield (622 mg, 1.0 mmol). White solid (mp = 123 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.08 (s, 2H, C*H*O), 8.54 (d, 4H, H_o, $^3J = 8.3$ Hz), 8.34 (d, 2H, H_7, $^3J = 8.5$ Hz), 8.16 (d, 2H, H_8, $^3J = 8.5$ Hz), 8.15 (d, 2H, H_4, $^3J = 8.2$ Hz), 8.01 (d, 4H, H_m, $^3J = 8.3$ Hz), 7.77 (s, 4H, $H_{5,6}$), 7.62 (d, 2H, H_3, $^3J = 8.2$ Hz), 3.40 (t, 4H, H_α), 2.27 (t, 4H, H_β). MS (EI): 622.2 (M, calcd 622.2). IR (neat): ν (cm^{-1}) = 2821, 2738, 1695.

Prerotaxane $\mathbf{7^{2+}(PF_6^-)_2}$. By the double-ended needle technique, $[Cu(CH_3CN)_4{}^+]PF_6^-$ (0.164 g, 0.44 mmol) in acetonitrile (10 mL) was added to a solution of **4** (0.250 g, 0.44 mmol) in methylene chloride (25 mL). The mixture turned orange instantaneously, indicating the formation of $[Cu\mathbf{4}(CH_3CN)_2]^+PF_6^-$. After 20 min at room temperature, a solution of bisphenanthroline **1** (0.137 g, 0.22 mmol) in methylene chloride (15 mL) was added to the orange complex. The solution turned dark red immediately. After the mixture was stirred overnight at room temperature, the solvents were evaporated to afford crude $\mathbf{7}^{2+}(PF_6^-)_2$ in quantitative yield. Dark red solid. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 9.50 (s, 2H, C*H*O), 8.66 (d, 2H, H_7, $^3J = 8.4$ Hz), 8.46 (d, 2H, H_4, $^3J = 8.4$ Hz), 8.30 (d, 2H, $H_{5\text{ or }6}$, $^3J = 8.9$ Hz), 8.23 (d, 4H, $H_{4',7'}$, $^3J = 8.3$ Hz), 7.96 (d, 2H, $H_{5\text{ or }6}$, $^3J = 8.9$ Hz), 7.72 (s, 4H, $H_{5',6'}$), 7.72 (d, 2H, H_8, $^3J = 8.3$ Hz), 7.66 (d, 4H, $H_{3',8'}$, $^3J = 8.3$ Hz), 7.44 (d, 2H, H_3, $^3J = 8.4$ Hz), 7.10 (d, 4H, H_o, $^3J = 7.5$ Hz), 7.06 (d, 8H, $H_{o'}$, $^3J = 8.4$ Hz), 6.73 (d, 4H, H_m, $^3J = 8.1$ Hz), 5.78 (d, 8H, $H_{m'}$, $^3J = 8.6$ Hz), 3.78 (s, 8H, $H_{\epsilon'}$), 3.68−3.46 (m, 32H, $H_{\alpha',\beta',\gamma',\delta'}$), 2.27 (t, 4H, H_α), 1.13 (t, 4H, H_β). FAB-MS: $m/z = 2028.6$ ($[M - PF_6^-]^+$, calcd 2028.1, 5%), 941.3 ($[M - 2PF_6^-]^{2+}$, calcd 941.6, 84%).

(5,15-Di-*tert*-butylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (8), ($\mathbf{Cu_2}$)-[3]-Rotaxane $\mathbf{[9^{2+}](PF_6^-)_2}$, and ($\mathbf{Cu_4}$)-[5]-Rotaxane $\mathbf{[10^{4+}](PF_6^-)_4}$. $[\mathbf{7}^{2+}](PF_6^-)_2$ (0.398 g, 0.18 mmol), di-*tert*-butyl-3,5-benzaldehyde (**5**) (0.32 g, 1.47 mmol), and (dihexyl-3,3′-dimethyl-4,4′-dipyrryl-2,2′)methane (**6**) (0.627 g, 1.83 mmol) were dissolved in methylene chloride (180 mL). Trifluoroacetic acid (4 drops) was then added, and the reaction mixture was stirred overnight at room temperature. Chloranil (1.39 g, 5.65 mmol) was added and the reaction mixture refluxed for 1.5 h. After cooling, the crude reaction mixture was neutralized with 10% aqueous sodium carbonate (80 mL). The resulting organic phase (200 mL) was washed three times with water, stirred overnight with 6.5% aqueous KPF_6 (200 mL), washed again twice with water, and evaporated to dryness. The residue (1.1 g) was subjected to several column chromatographies. Elution with 2% methanol in methylene chloride on silica afforded **8** (0.255 g, 32% from **5**). Elution with 0.5% methanol in methylene chloride on alumina afforded pure [3]-rotaxane $[\mathbf{9}^{2+}](PF_6^-)_2$ (240 mg, 34%). Elution with 1.5% methanol in methylene chloride on alumina afforded pure [5]-rotaxane $[\mathbf{10}^{4+}](PF_6^-)_4$ (50 mg, 8%). **8**: Dark red solid. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 10.26 (s, 2H, H_{meso}), 7.93 (d, 4H, $H_{o''}$, $^4J = 1.7$ Hz), 7.85 (s, 2H, $H_{p''}$), 4.01 (t, 8H, $H_{\alpha''}$, $^3J = 7.6$ Hz), 2.49 (s, 12H, C*H*$_3$), 2.22 (quint, 8H, $H_{\beta''}$, $^3J = 6.7$ Hz), 1.78 (q, 8H, $H_{\gamma''}$, $^3J = 7.6$ Hz), 1.51 (s, 36H, $H_{^tBu}$), 1.51 (m, 16H, $H_{\delta'',\epsilon''}$), 0.92 (t, 12H, $H_{\zeta''}$), $^3J = 7.0$ Hz), −2.50 (br s, 2H, N*H*). $[\mathbf{9}^{2+}](PF_6^-)_2$: Dark red solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.16 (s, 4H, H_{meso}), 9.08 (d, 2H, H_7, $^3J = 8.3$ Hz), 8.67 (d, 2H, H_4, $^3J = 8.3$ Hz), 8.49 (d, 2H, H_6, $^3J = 9.0$ Hz), 8.46 (d, 4H, $H_{4',7'}$, $^3J = 8.3$ Hz), 8.23 (d, 2H, H_5, $^3J = 9.0$ Hz), 8.22 (d, 2H, H_8, $^3J = 8.2$ Hz), 8.00 (s, 4H, $H_{5',6'}$), 7.96 (d, 4H, $H_{3',8'}$, $^3J = 8.2$ Hz), 7.89 (d, 4H, $H_{o''}$, $^4J = 1.7$ Hz), 7.86 (s, 2H, $H_{p''}$), 7.71 (d, 4H, H_o, $^3J = 7.9$ Hz), 7.56 (d, 4H, H_m, $^3J = 8.0$ Hz), 7.26 (d, 8H, $H_{o'}$, $^3J = 8.6$ Hz), 7.25 (d, 2H, H_3, $^3J = 8.1$ Hz), 6.11 (d, 8H, $H_{m'}$, $^3J = 8.6$ Hz), 3.97 (t, 8H, $H_{\alpha''d}$, $^3J = 7.7$ Hz), 3.87 (s, 8H, $H_{\epsilon'}$), 3.78 (t, 8H, $H_{\alpha''p}$), 3.72 (m, 8H, $H_{\delta'}$), 3.72 (m, 8H, $H_{\alpha'}$), 3.54 (t, 8H, $H_{\gamma'}$, $^3J = 5.4$ Hz), 3.51 (br s, 8H, $H_{\beta'}$), 2.46 (s, 12H, C*H*$_{3d}$), 2.19 (quint., 8H, $H_{\beta''d}$, $^3J = 7.8$ Hz), 2.04 (quint., 8H, $H_{\beta''p}$, $^3J = 7.8$ Hz), 1.78 (s, 4H, H_α), 1.75 (m, 8H, $H_{\gamma''d}$, $^3J = 7.4$ Hz), 1.73 (m, 8H, $H_{\gamma''p}$, $^3J = 7.4$ Hz), 1.71 (s, 12H, C*H*$_{3p}$), 1.51 (s, 36H, $H_{^tBu}$), 1.51 (h, 16H, $H_{\delta''(p,d)}$), 1.40 (m, 16H, $H_{\epsilon''(p,d)}$), 0.95 (t, 12H, $H_{\zeta''d}$, $^3J = 7.3$ Hz), 0.92 (t, 12H, $H_{\zeta''p}$, $^3J = 7.3$ Hz), 0.36 (br s, 4H, H_β), −2.61 (br s, 2H, N*H*), −2.70 (br s, 2H, N*H*). FAB-MS: $m/z = 3750.2$ ($[M^{2+} + PF_6^-]^+$, calcd 3750.9, 75%). $[\mathbf{10}^{4+}]$-$(PF_6^-)_4$: Dark red solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 10.16 (s, 4H, H_{meso}), 10.06 (s, 2H, H_{meso-c}), 9.08 and 9.07 (2d, 4H, $H_{7,7*}$, $^3J = 8.2$ Hz), 8.68 and 8.67 (2d, 4H, $H_{4,4*}$, $^3J = 8.0$ Hz), 8.49 (d, 4H, $H_{6,6*}$, $^3J \sim 10.2$ Hz), 8.47 (d, 8H, $H_{4',7'}$, $^3J \sim 8.6$ Hz), 8.24 and 8.23 (2d, 4H, $H_{5,5*}$, $^3J \sim 9.3$ Hz), 8.22 and 8.21 (2d, 4H, $H_{8,8*}$, $^3J \sim 8.7$ Hz), 8.01 (s, 8H, $H_{5',6'}$), 7.97 and 7.96 (2d, 8H, $H_{3',8'}$, $^3J = 8.2$ Hz), 7.89 (d, 4H, $H_{o''}$, $^4J = 1.8$ Hz), 7.85 (t, 2H, $H_{p''}$, $^4J = 1.7$ Hz), 7.70 (d, 8H, $H_{o,o*}$, $^3J \sim 8.0$ Hz), 7.56 (d, 4H, H_m, $^3J = 7.8$ Hz), 7.51 (d, 4H, H_{m*}, $^3J = 7.8$ Hz), 7.25 and 7.24 (2d, 16H, $H_{o'}$, $^3J = 8.5$ Hz), ca. 7.24 (h, 4H, $H_{3,3*}$), 6.11 and 6.10 (2d, 16H, $H_{m'}$, $^3J = 8.5$ Hz), 3.97 (t, 8H, $H_{\alpha''d}$, $^3J = 7.8$ Hz), 3.87 (s, 16H, $H_{\epsilon'}$), ca. 3.71 (m, 48H, $H_{\gamma',\delta'}$ and $H_{\alpha''(p,c)}$), ca. 3.54 (m, 32H, $H_{\alpha',\beta'}$), 2.46 (s, 12H, C*H*$_{3d}$)), 2.19 (quint, 8H, $H_{\beta''d}$, $^3J = 7.6$ Hz), 2.02 (m, 16H, $H_{\beta''(p,c)}$), ca. 1.74 (m, 32H, $H_{\gamma''(p,c,d)}$ and $H_{\alpha,\alpha*}$), 1.71 (s, 12H, C*H*$_{3p}$), 1.68 (s, 12H, C*H*$_{3c}$), ca. 1.54 (m, 24H, $H_{\delta''(p,c,d)}$), 1.50 (s, 36H, $H_{^tBu}$), ca. 1.41 (m, 24H, $H_{\epsilon''(p,c,d)}$), ca. 0.92 (m, 36H, $H_{\zeta''}$), 0.32 (t, 8H, $H_{\beta,\beta*}$), −2.62, −2.72 and −2.84 (3 br s, 6H, N*H*). ES-MS: $m/z = 1532.51$ ($[M - 4PF_6^-]^{4+}$, calcd 1532.99, 100%).

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Supporting Information Available: Preparation and characterization of compounds **11**−**20**$^+$ and a chart describing proton labeling (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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