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# Synthesis of [5]Rotaxanes Containing Bi- and Tridentate Coordination Sites in the Axis

Jean-Paul Collin,*[a] Stéphanie Durot,*[a] Michel Keller,[a] Jean-Pierre Sauvage,*[a]
Yann Trolez,[a] Mario Cetina,[b] and Kari Rissanen[b]

**Abstract:** A new example of a linear [5]rotaxane has been synthesized by using the traditional "gathering-and-threading" approach but based on an unusual axle incorporating a symmetrical bis(bidentate) chelating fragment built on a 4,7-phenanthroline core. The stoppering reaction is particularly noteworthy since, instead of using a trivial bulky stopper as precursor to the blocking group, two semistoppered copper-complexed [2]pseudorotaxanes (namely [2]semirotaxanes) are used, which leads to the desired [5]rotaxane in good yield. The efficiency of the method relies on the use of "click" chemistry, with its very mild conditions, and on the protection by a transition-metal (copper(I)) of the various coordinating groups present in the fragments to be interconnected (terpy and bidentate chelating groups), thus inhibiting potential detrimental side reactions during the copper-catalyzed stoppering reaction. Since the external fragments and the central core of the system contain tri- and bidentate chelating units, respectively, the axle of the final [5]rotaxane incorporates two types of coordinating units: two external terpy groups (terpy: 2,2′:6′,2″-terpyridine) and two central bidentate ligands. Such a situation enables the system to tidy two different metals centers, and to localize them in a priori well-defined positions. This is what was observed when mixing the free ligand with a mixture of $Zn^{2+}$ and $Li^{+}$: the zinc(II) ions were unambiguously shown to occupy the external sites, whereas the $Li^{+}$ cations were found in the central part of the [5]rotaxane. An X-ray diffraction study carried out on a [3]pseudorotaxane, the axis of which is similar to the central part of the [5]rotaxane axle, demonstrates that $Zn^{2+}$ is clearly five-coordinate, the fifth ligand being a counterion, even when the coordination site of the pseudorotaxane is designed for four-coordinate metals, which is in marked contrast with copper(I) or $Li^{+}$.

**Keywords:** click chemistry • copper • lithium • rotaxanes • zinc

## Introduction

Although rotaxanes are not strictly speaking topologically interesting molecules (their molecular graph is planar), they have been associated with catenanes, the topological properties of which are indisputably nontrivial, from the beginning of topological chemistry.[1] The synthesis of such compounds has experienced an explosive development since the introduction of template strategies either based on transition metals or by using organic building blocks.[2–17] An efficient alternative approach was proposed long ago by Harrison. It is based on the statistical threading process at high temperature of a stringlike fragment through a ring used as the solvent, the string being end-functionalized by two bulky groups. These groups were able to act as stoppers under mild conditions but, at the same time, they could be threaded through the ring cavity at high temperature. After high temperature threading, cooling down, and then freezing, the [2]rotaxane structure was obtained.[18] A related strategy, based on crown ethers, used as rings, and poly(ethylene glycols), playing the role of threads, was also developed by Zilkha and co-workers in 1976.[19] The first templated strategy leading to [2]rotaxanes in good yields and following a simple experimental protocol was reported by Ogino in

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[a] Dr. J.-P. Collin, Dr. S. Durot, M. Keller, Prof. J.-P. Sauvage,
Dr. Y. Trolez
Laboratoire de Chimie Organo-Minérale, Institut de Chimie
LC3 UMR 7177 du CNRS, Université de Strasbourg
4 rue Blaise Pascal, 67070 Strasbourg Cedex (France)
Fax: (+33) 368851368
E-mail: jpcollin@chimie.u-strasbg.fr
sdurot@chimie.u-strasbg.fr
sauvage@chimie.u-strasbg.fr

[b] M. Cetina, Prof. K. Rissanen
Department of Chemistry, Nanoscience Center
University of Jyväskylä, P.O.Box 35
40014 Jyväskylä (Finland)

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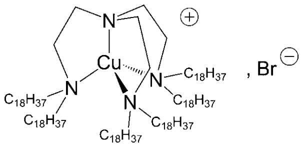
1981.[13] It consists in threading a polymethylene fragment of the α,ω-diaminoalcane type through a cyclodextrin and, subsequently, stoppering the systems by attaching cobalt(III) complexes at both ends of the thread. Since this early work, more than 1000 reports on rotaxanes have been published in the literature.[20] Poly- and multirotaxanes constitute a subclass of such compounds. These systems are important in relation to polymer chemistry[14,21–36] or for the elaboration of sophisticated molecular machines, such as molecular muscles,[22,37–47] elevators,[48] or receptors.[6,35,49–53] We would now like to report the copper(I)-templated synthesis of [5]rotaxanes consisting of four identical rings threaded by a long stringlike fragment. This thread contains two bidentate chelates and two tridentate coordinating units. The synthesis of metal-free [5]rotaxane will be described. We will also discuss some of the coordination properties of the free molecule and, in particular, its ability to sort and arrange metal ions with different coordination numbers, such as $Li^+$ and $Zn^{2+}$.

## Results and Discussion

**Strategy and design of the system**: Among the various template strategies proposed for making rotaxanes, the use of transition metals able to induce the threading process of a stringlike molecular fragment through a ring turned out to be particularly efficient. This "gathering and threading" approach has been used extensively in our group for making catenanes and rotaxanes.[54] The second step is the attachment of bulky groups at both ends of the thread, so as to "freeze" the threaded structure of the compound. This "stoppering" reaction has been performed by using a large variety of reactions.[13,15,17,55–61] Presently, the rotaxane community seems to favor[62–64] the 1,3-dipolar cycloaddition of an azide to a terminal alkyne affording a triazole (i.e., Huisgen reaction[65] for the uncatalyzed reaction and "click" chemistry for the copper-catalyzed azide–alkyne cycloaddition[66,67] (CuAAC)). Our group has also used click reactions for making various rotaxanes, often with very high yields, which is the reason why we also favored this method.[52,53,68–71] The only potential difficulty inherent to the click conditions is the presence of copper. Copper(I) will be at the same time the catalyst and the template element so that it will be important to avoid any kind of interference between the catalytic and templating functions of the metal, in spite of the presence of various coordinating groups in the molecules undergoing the click reaction. We recently attempted to prepare multirotaxanes incorporating both metal-complexed ligands and free ligands by means of click chemistry. Unfortunately, the results were very disappointing and there were clear indications that the presence of free ligands was detrimental to the formation of the desired stoppered complexes. Another series of experiments turned out to be negative but informative. When "normal" click chemistry was tried with free ligand or copper(I)-complexed coordinating fragments, "normal" meaning that the copper(I) centers supposed to act as catalysts were not coordinated to any protective ligand, the results were also disappointing. It thus appeared necessary to use an ancillary ligand, able to partially complex the catalytic copper(I) center and protect it towards potentially coordinating fragments of the compounds to be "clicked". Two remarkable examples of such protected catalysts have recently been described,[72–74] which seem to solve the interference problem between catalytic copper and functional groups belonging to the substrates, making the catalyst substantially more stable than without added ligand. We selected a modified tren, denoted tren′ ([Cu(tren′)]Br; tren: tris(2-aminoethyl)amine), as the stabilizing ligand for $Cu^I$, similar to Vincent and coworkers.[73] The efficiency of the catalyst turned out to be dramatically improved, as discussed in the following sections of the present report.

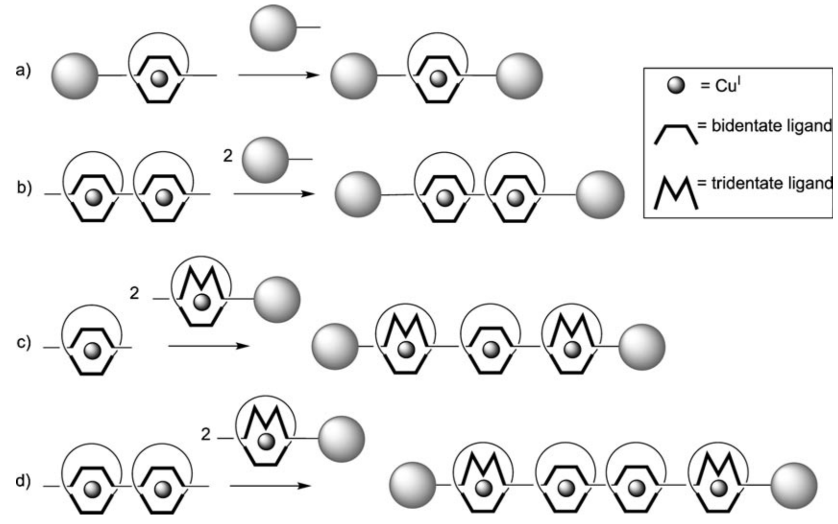


[Cu(tren′)]Br

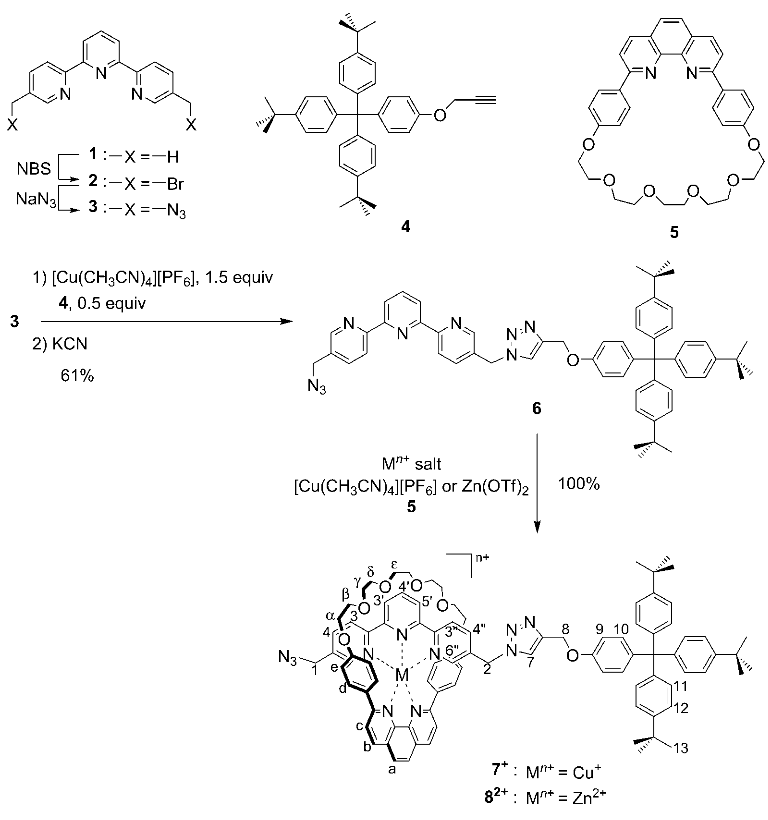
The incorporation of bidentate chelates of the 2,2′-bipyridine (bipy) family and tridentate ligands, such as 2,2′:6′,2″-terpyridine (terpy), in the same axis is related to the dynamic properties of rotaxanes behaving as molecular "shuttles".[75–92] These rotaxanes with differentiated coordination sites could also be of interest in terms of selective complexation of given ions, offering the possibility of incorporating within the same compound metal centers with different coordination numbers, these metals being located in precisely defined coordination sites. The general synthesis principle is depicted in Scheme 1.

The synthesis of copper(I)-complexed [2]rotaxanes and [3]rotaxanes by means of click chemistry has already been successfully achieved according to strategy a (Scheme 1a), in which the axis bears either a bipy[68] or a 2,9-diphenyl-1,10-phenanthroline (dpp)[69] fragment or strategy b (Scheme 1b), in which the axle is a bis[3,8-(*o*-pyridyl)-4,7-phenanthroline] bis(bidentate) unit.[71] The isolated yields for the preparation of these metallorotaxanes were good and click chemistry seemed to be well adapted to the copper(I)-template synthesis of interlocked molecules. The extension of CuAAC click chemistry to terpy-containing axle [2]semirotaxane and [5]rotaxane synthesis is reported here.

**Synthesis of [2]semirotaxanes**: A threadlike fragment **3**, consisting of a terpy, bearing azide functions at each end (Scheme 2), was prepared in two steps from the previously reported 5,5"-dimethyl-2,2′:6′,2″-terpyridine (**1**).[93] By using controlled conditions regarding the number of NBS equivalents, light, heat, and duration, the 5,5″-di(bromomethyl)-2,2′:6′,2″-terpyridine (**2**) could be isolated with an acceptable yield (48 %).[38] Easy and quantitative conversion to the diazido derivative **3** was performed by addition of a slight



Scheme 1. Construction principle of multirotaxanes by copper(I)-driven "gathering and threading" followed by stoppering; the coordinating fragments are represented by U-shaped (bidentate chelates) or M-shaped (tridentate chelates) symbols; the small sphere is a copper(I) atom and the big one represents the stopper: a) synthesis of a [2]rotaxane, b) synthesis of a [3]rotaxane, c) synthesis of a [4]rotaxane, d) synthesis of a [5]rotaxane.



Scheme 2. Precursors and synthesis of terpy-containing [2]semirotaxanes by CuAAC click chemistry. NBS = $N$-bromosuccinimide.

excess of sodium azide in a mixture of DMSO and water (2:1) at 40 °C.

A dissymmetric terpyridine **6** with one azide function and one bulky group was synthesized from compounds **3** and **4** by using a statistical "click chemistry" reaction in a yield of 61 %. This is a good yield, considering that only one azide function of the symmetric terpyridine **3** has been converted. It was achieved thanks to the use of an excess of [Cu(CH$_3$CN)$_4$][PF$_6$] on one hand, and of only 0.5 equivalent of acetylenic compound **4** on the other hand. Furthermore, non-reacted **3** could be recycled.

The "gathering and threading" reaction between the copper(I) (zinc(II), respectively) complex of the 30-membered ring **5** and the terpy string **3** led quantitatively to the expected [2]semirotaxane **7**$^+$ (**8**$^{2+}$, respectively), as confirmed by proton NMR spectroscopic studies.

The $^1$H NMR spectra were in accordance with the postulated structures of **7**$^+$ and **8**$^{2+}$. In particular, the $^1$H NMR spectrum of **7**$^+$ was significantly different from the spectra of both the copper(I)-complexed-macrocycle and the dissymmetric terpyridine **6**. This confirmed that compounds **7**$^+$ (and **8**$^{2+}$) were metalated semirotaxanes. The phenyl protons (identified as d and e, see Figure 1) of the macrocycle component **5** undergo a strong upfield shift by copper(I)-induced threading of **6**, to afford **7**$^+$. The copper(I)–[2]semirotaxane **7**$^+$ was subsequently used as a stopper for the synthesis of a new linear [5]rotaxane.

**Synthesis of [5]rotaxane**: To the best of our knowledge, very few examples of linear [5]rotaxanes were reported in the literature.[94–98] The synthesis was carried out by following the classical CuAAC strategy but an important difference with previous cases should be stressed: in the present case, the stopper precursor is a semirotaxane (copper(I)–[2]semirotaxane **7**$^+$) and not a trivial bulky compound. This semirotaxane used as a stopper precursor is, itself, half-stoppered, making the final product a complete rotaxane.

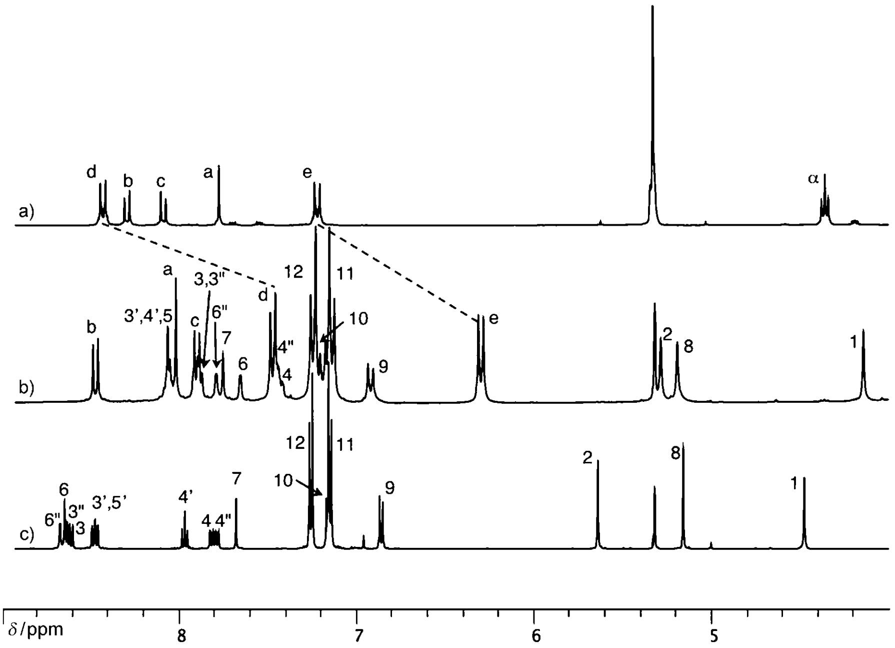


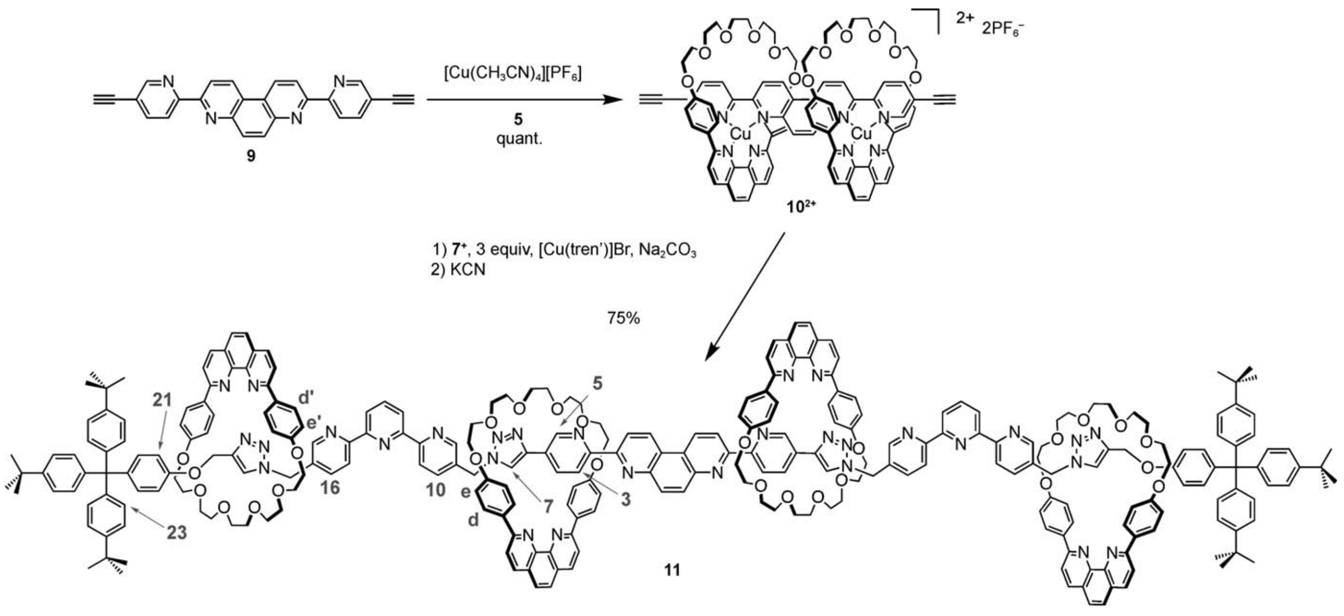
Figure 1. ${}^1$H NMR spectra of a) macrocycle **5** (300 MHz), b) copper(I) [2]semirotaxane **7**$^+$ (300 MHz), and c) dissymmetric terpyridine **6** (500 MHz) in $CD_2Cl_2$.

The central complex was the symmetrical [3]pseudorotaxane synthesized quantitatively from the bis(bidentate) chelate **9**, two macrocycles **5**, and two copper(I) ions according to a previously published procedure.[71].

Combining these two parts, **7**$^+$ and **10**$^{2+}$, allowed for the synthesis of [5]rotaxane **11** by a double click chemistry reaction with catalyst [Cu(tren′)]Br and subsequent demetalation by KCN (Scheme 3). [5]Rotaxane **11** was obtained in a yield of 75%, which is excellent considering that two CuAAC reactions are performed simultaneously by using a highly functionalized stopper precursor. Given that the demetalation process of such a rotaxane is generally quantitative, this overall yield can be considered as the yield of the stoppering reaction.

[5]rotaxane **11** was characterized by mass spectrometry (ESMS) and 1D and 2D ${}^1$H NMR spectroscopy (COSY, ROESY) experiments. Particularly noteworthy is the chemical nonequivalence of two types of macrocycles in this system: the internal and the external ones. The positions of these macrocycles were unambiguously determined by interfragment NOE interactions, for example, protons H-d′ (which belong to the external macrocycles, see Scheme 3) correlate to protons of the external part of the axle (H-16, H-21, and H-23), whereas protons H-d (which belong to the internal macrocycles) correlate to protons of the internal part of the axle (H-3, H-7, H-5, and H-10).

Even though all macrocycles are free to rotate around and to translate along the axle, the two internal macrocycles are more shielded than the external macrorings. Indeed, each one is located between two other macrocycles and is thus more exposed to the ring current effect of the various



Scheme 3. Synthesis of the [5]rotaxane **11**.

aromatic fragments belonging to the two surrounding rings. The internal rings thus undergo a more important ring-current effect than their external counterparts, the external macrocycles being located between one macrocycle and a stopper. This effect is particularly well illustrated by considering H-e and H-e′: $\delta = 6.42$ ppm for the internal macrocyclic component and $\delta = 6.64$ ppm for the external rings.

**Coordination chemistry studies**: The coordination properties of [5]rotaxane **11** were investigated. Actually, the ability of this rotaxane to complex two metal ions, $Zn^{2+}$ and $Li^{+}$, was studied. We first remetalated compound **11** with $Zn^{2+}$. Four equivalents of $Zn(OTf)_2$ in methanol were added to a solution of **11** in dichloromethane. After workup, the desired metalated compound **12**$^{8+}$ was obtained in a yield of 92%. This compound was characterized by $^{1}H$ NMR spectroscopy (1D, COSY, NOESY) as well as by mass spectrometry (ESMS). It is noteworthy that $CDCl_3$ as an NMR solvent precluded the possibility to obtain well-resolved peaks. The lithiated counterpart of this rotaxane was more difficult to obtain. Indeed, eight equivalents of $LiBF_4$ in methanol (with a few drops of $NEt_3$ to eliminate residual $HBF_4$) were necessary to obtain the desired four-lithiated rotaxane **13**$^{4+}$. No workup was possible because of the instability of the resulting complex, except for evaporation of solvents. However, this rotaxane **13**$^{4+}$ could be characterized by $^{1}H$ and $^{7}Li$ NMR spectroscopy. As expected, two signals of equal intensity were detected by $^{7}Li$ NMR spectroscopy at $\delta = 5.33$ and 4.63 ppm, which indicated that two types of magnetically nonequivalent $Li^{+}$ were present in the system: internal and external $Li^{+}$. Moreover, our attempts to completely characterize compound **13**$^{4+}$ by mass spectrometry remained unsuccessful. We detected partly or totally decomplexed species, with no, one, or two $Li^{+}$ ions incorporated in the system. Nevertheless, the NMR spectroscopic observations did not leave any doubt about the structure of compound **13**$^{4+}$. Once the ability of rotaxane **11** to complex $Zn^{2+}$ and $Li^{+}$ was demonstrated, we wondered whether this rotaxane could be able to complex two equivalents of each ion, leading to a single species with the ions located in well defined coordination sites. Each ion could be either at an internal (four-coordinate) or an external (five-coordinate) position. Adding simultaneously two equivalents of $Zn(OTf)_2$ and two equivalents of $LiBF_4$ led to a well-resolved $^{1}H$ NMR spectrum with the same number of signals as rotaxanes **12**$^{8+}$ and **13**$^{4+}$. The resulting product, **14**$^{6+}$, thus has the same symmetry as **12**$^{8+}$ and **13**$^{4+}$ and, therefore, the four ions are coordinated in precisely defined and symmetrical positions. A $^{7}Li$ NMR spectroscopic analysis showed just one peak at $\delta = 5.33$ ppm, confirming that there was just one type of $Li^{+}$ in the system, either at the internal or the external position. From previous work, it has been established that $Zn^{2+}$ "prefers" to be pentacoordinated and thus located in the external site (consisting of a tridentate ligand, part of the axle, and a bidentate chelating group, incorporated in the ring).[29] By contrast, $Li^{+}$ generally "prefers" to be tetracoordinated. $^{1}H$ NMR spectroscopic observations undoubtedly indicated the positions of the two $Li^{+}$ ions and of the two $Zn^{2+}$ ions (Figure 2). The most striking clue is the chemical shift of proton H-6, $\delta$(H-6) (Scheme 4). In $Zn^{2+}$-complexed [5]rotaxane **12**$^{8+}$, this proton is surprisingly shielded at $\delta(\text{H-6}) = 6.58$ ppm (relative to rotaxane **11**: $\delta(\text{H-6}) = 8.25$ ppm), whereas in $Li^{+}$-complexed [5]rotaxane **13**$^{4+}$ and in the mixed $Zn^{2+}/Li^{+}$ [5]rotaxane **14**$^{6+}$, it is much less shielded at $\delta(\text{H-6}) = 7.16$ and 7.20 ppm, respectively. This observation indicates that in **14**$^{6+}$ the $Zn^{2+}$ ions are not coordinated to bidentate units of the axle, but to the terpy fragments of the axle, satisfying a pentacoordinated geometry. The $Li^{+}$ ions are, therefore, situated in the internal positions.

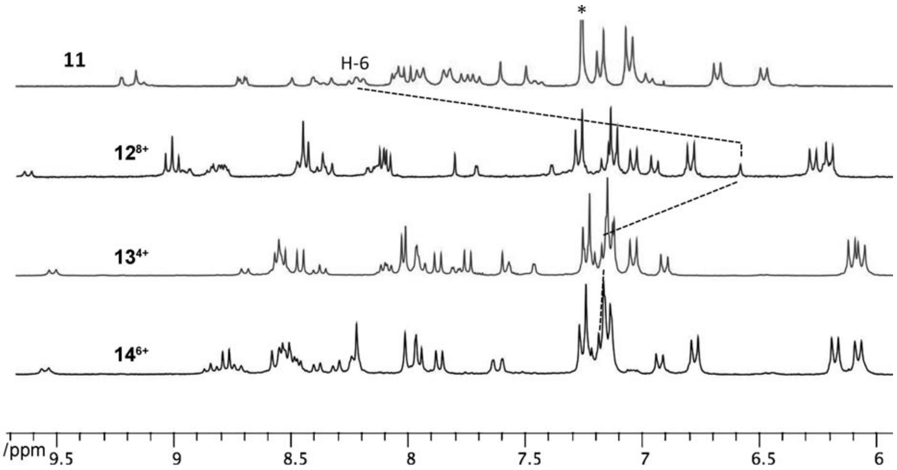
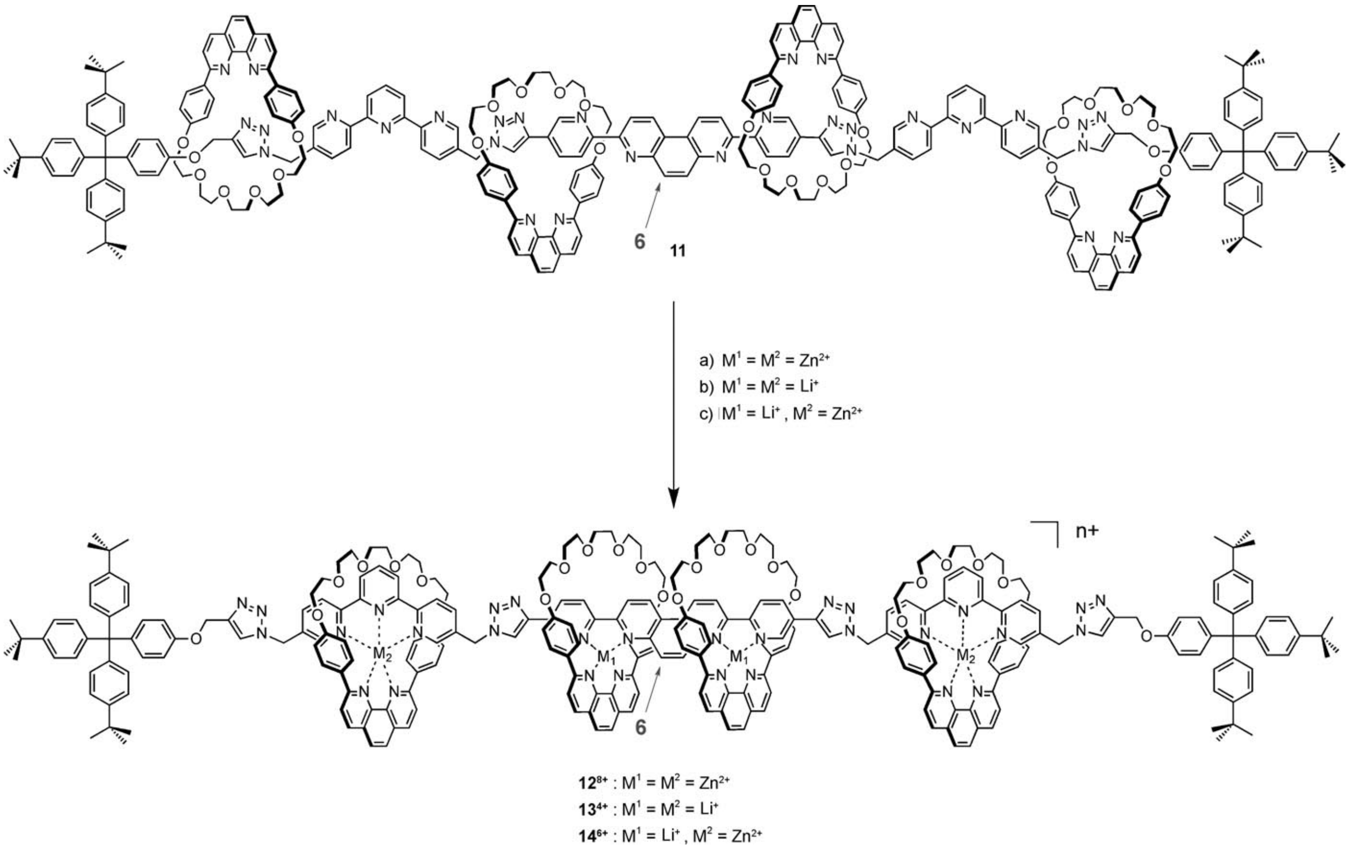
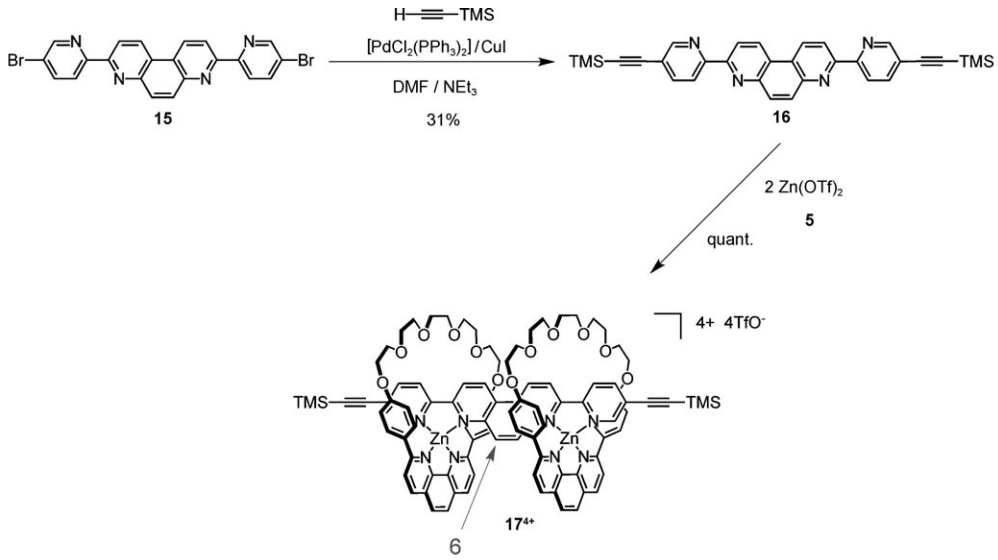


Figure 2. Aromatic part of the $^{1}H$ NMR spectra (300 MHz) of [5]rotaxanes **11**, **12**$^{8+}$, **13**$^{4+}$, and **14**$^{6+}$; the asterisk indicates residual $CHCl_3$ for **11**.

To understand the amazing chemical shift of proton H-6 in rotaxane **12**$^{8+}$, a new pseudorotaxane incorporating the central part of the axle, $Zn^{2+}$ and the same macrocycles as those of **11** was prepared. The central part of the axle was synthesized from 3,8-bis(4-bromo-2′-pyridyl)-4,7-phenanthroline (**15**), the synthesis of which has already been published.[99] Compound **15** was submitted to a double Sonogashira coupling with trimethylsilylacetylene, $[PdCl_2(PPh_3)_2]$, and CuI in a mixture of DMF and $NEt_3$ to give compound **16** (Scheme 5, yield: 31%). Compound **16** was then involved in a threading reaction with two equivalents of macrocycle **5** and two equivalents of $Zn(OTf)_2$ to afford the expected [3]pseudorotaxane **17**$^{4+}$ in a quantitative yield. This [3]pseu-



Scheme 4. Syntheses of [5]rotaxanes $\mathbf{12}^{8+}$, $\mathbf{13}^{4+}$, and $\mathbf{14}^{6+}$ by remetalation of compound **11**. The figure is dealing with three independent experiments: a) consists in adding four equivalents of $Zn^{2+}$ with formation of $\mathbf{12}^{8+}$, b) a large excess of $Li^{+}$ was added to the free ligand **11**; $\mathbf{13}^{4+}$ was obtained, and c) two equivalents of a one-to-one mixture of $Zn^{2+}$ and $Li^{+}$ was reacted with **11** to afford $\mathbf{14}^{6+}$ quantitatively.



Scheme 5. Synthesis of [3]pseudorotaxane $\mathbf{17}^{4+}$.

dorotaxane $\mathbf{17}^{4+}$ was characterized by $^{1}H$ NMR spectroscopy (1D, COSY, NOESY) and mass spectrometry (ESMS). The $^{1}H$ NMR spectrum of this species confirmed the particular chemical shift of proton H-6 at $\delta(\text{H-6}) = 6.50$ ppm. Consequently, this observation is due to an intrinsic property of the coordination of $Zn^{2+}$ to bidentate units of the axle. It confirms the conclusions of the previously discussed $^1$H NMR spectroscopic study.

X-ray quality crystals of [**17**][TfO$^-$]$_4$ were grown by slow diffusion of diisopropylether into an acetone solution. The X-ray structure (Figure 3) confirms the [3]pseudorotaxane structure of the compound. Due to the nature of the axle, the Zn atoms reside on the same side of the axle (*cis*-rotaxane). The Zn$^{II}$ ions show a distorted penta-coordination with N-Zn-N and N-Zn-O bond angles between 80–160° and the bond lengths 2.03–2.17 Å for Zn–N and 2.26–2.33 Å for the Zn–O bonds, respectively (Table 1). As in the corresponding Cu$^I$-[3]rotaxane,[71] the long (Si···Si distance of 2.4 nm) axle is not linear, but is bent by the coordination to the Zn ions so that the angle between the centroid of the axle and the terminal Si atoms is 165.4°, slightly more linear than in the Cu$^I$ rotaxane (164°).

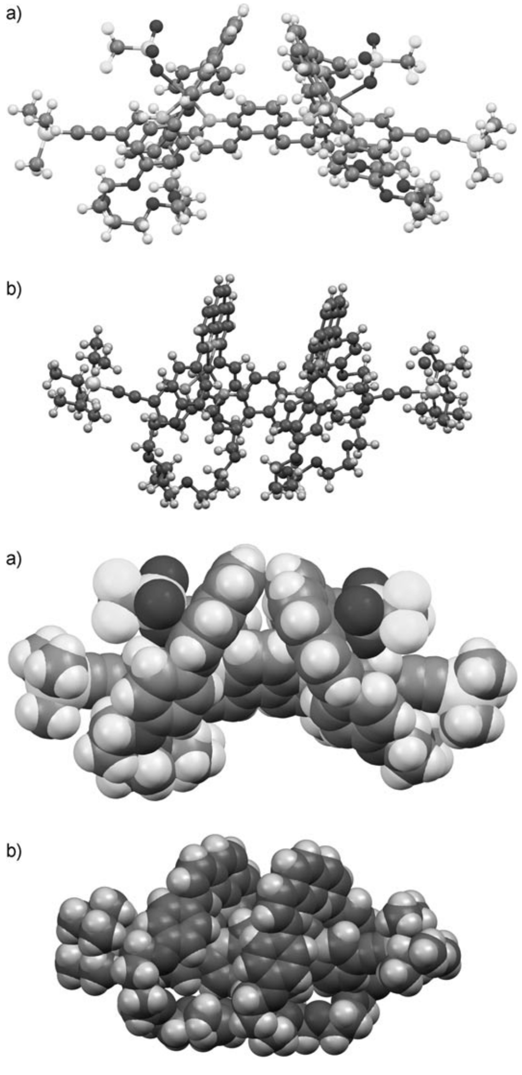


Figure 3. The ball and stick (top) and the CPK (bottom) representations of [3]pseudorotaxanes: a) **17**$^{4+}$ and b) its Cu$^I$ counterpart.[71] The non-coordinated triflate anions and solvent molecules are omitted for clarity.

Table 1. Bond lengths [Å] and angles [°] around the zinc ions.

| | | | |
|---|---|---|---|
| Zn1–N9 | 2.041(7) | N9-Zn1-N18 | 80.3(3) |
| Zn1–N18 | 2.174(7) | N9-Zn1-N49 | 146.4(3) |
| Zn1–N49 | 2.041(8) | N9-Zn1-O1A | 84.2(2) |
| Zn1–O1A | 2.334(6) | N40-Zn1-N18 | 115.0(3) |
| | | N49-Zn1-N18 | 100.6(3) |
| | | N18-Zn1-O1A | 160.1(2) |
| | | N40-Zn1-N49 | 82.9(4) |
| | | N40-Zn1-O1A | 84.4(3) |
| | | N49-Zn1-O1A | 85.6(3) |
| Zn2–N28 | 2.028(8) | N28-Zn2-N82 | 127.7(3) |
| Zn2–N26 | 2.140(7) | N28-Zn2-N91 | |
| | 146.2(3) | | |
| Zn2–N82 | 2.029(9) | N28-Zn2-O1B | 83.0(3) |
| Zn2–N91 | 2.073(9) | N26-Zn2-N28 | 79.2(3) |
| Zn2–O1B | 2.263(6) | N26-Zn2-N82 | 118.4(3) |
| | | N26-Zn2-N91 | 98.4(3) |
| | | N26-Zn2-O1B | 153.1(3) |
| | | N82-Zn2-N91 | 83.4(4) |
| | | N82-Zn2-O1B | 88.5(3) |
| | | N91-Zn2-O1B | 85.3(3) |
| | | N26-Zn2-N91 | 98.4(3) |

The change of the metal ions from tetrahedral Cu$^I$ to Zn$^{II}$ ions leads to a dramatic modification of the overall structure of the [3]rotaxane. Zn$^{II}$ usually has a significantly different chemistry than Cu$^I$ in terms of geometry and coordination number. This is well illustrated in the present study, since in **17**$^{4+}$ both Zn ions exhibit a similar penta-coordination (Table 1.), the fifth coordination sites are occupied with the triflate anions, resulting in a [Zn$_2$(**17**)(OTf)$_2$][OTf$^-$]$_2$ structure. The two remaining triflate anions and the solvent molecules (1.5 acetone and one water) are located/trapped into a V-shaped cleft induced by the penta-coordinated Zn ion and subsequent reorientation of the phenanthroline-containing macrocycles with respect to the axle. In the corresponding Cu$^I$-[3]rotaxane,[71] the wheels are perpendicular due to the tetrahedral coordination of the Cu$^I$ ions, whereas in **17**$^{4+}$ the wheels are titled towards each other, so that the phen moieties are nearly touching each other, creating a triangle between the axle and the two wheels (the angle between the phen moieties is 59° and the angle between the axle and the phen moieties 65°, resulting is a nearly perfect triangle, Figure 3). As a consequence the poly(ethyleneglycol) parts of the wheel are widely separated (the distances between the carbon atoms at the open-end of the V is $>10$ Å). Thus the overall structure of **17**$^{4+}$ can be described by a slightly modified letter A, namely, ~~A~~.

Due to the different coordination geometry around the metal ion the phen wheels in **17**$^{4+}$ are not eclipsed as they are in the corresponding Cu$^I$ analogue.[71] The torsion angle between the centroids of the phen wheels and the axle, defined as phen$_{cen}$-Zn1-Zn2-phen$_{cent}$ is 21.23°. Also the metal ion to metal ion distance is slightly different between the Zn and Cu rotaxanes. The penta-coordination of the Zn ions results in a Zn···Zn distance of 8.2 Å, whereas the Cu···Cu distance in the Cu analogue is 7.8 Å.

The overall geometry of the [3]pseudorotaxane is to a large extent dictated by the asymmetry of each bidentate chelate belonging to the axle. The presence of a central HC=CH group (H-6 positions of the central 4,7-phenanthroline nucleus) has a marked steric effect on each bidentate chelating unit. The two positions α to the nitrogen atoms are markedly different since one of them (the external one) is not substituted (position numbered 5 in Scheme 3), whereas the other bears a CH=CH substituent. Formation of five-coordinate complexes will thus imply that the fifth ligand (either solvent or counterion) be coordinated to the complexed metal on the most accessible site and thus close to the external nitrogen atoms. This is exactly what the X-ray structure shows, with coordination of two triflate ions on the nonsubstituted side of each bipylike fragment, thus forcing the two rings to be tilted, with the back portion of each ring-incorporated 1,10-phenanthroline being close to that of the other ring. As a consequence, proton H-6 is in the shielding cone of each ring-incorporated 1,10-phenanthroline, which explains the strong upfield shift observed for H-6 in the [3]pseudorotaxane $\mathbf{17}^{4+}$, and by extension, in [5]rotaxane $\mathbf{12}^{8+}$.

## Conclusion

A new linear [5]rotaxane prepared according to the traditional template effect of copper(I) shows novel coordination properties due to the presence of two types of coordinating fragments in its axis. In particular, the metal-free molecule when reacted with a 1:1 mixture of a divalent metal ($Zn^{2+}$), eager to be five-coordinate, and a monovalent cation ($Li^{+}$), which can easily be four-coordinate, affords a single species quantitatively with the four metal centers at the right places: two $Zn^{2+}$ cations at the periphery and two $Li^{+}$ ions coordinated with the central core of the [5]rotaxane. An attractive X-ray structure of a dizinc [3]pseudorotaxane confirms that $Zn^{2+}$ prefers to be five-coordinate even if the organic ligands offered to it are expected to lead to a four-coordinate complex. In this case, each zinc(II) cation is coordinated to an additional ligand ($OTf^{-}$) which satisfies its coordination requirements. The synthesis of related compounds containing a smaller number of threaded rings than coordination sites in the axle should lead to molecular systems for which it will be possible to trigger translation motions of given rings from one position to another on the axle.

## Experimental Section

**General methods**: Dry $CH_2Cl_2$ and $CHCl_3$ were distilled from $CaH_2$ as the drying agent and dry $CH_3CN$ was purchased from Aldrich. Preparative column chromatography was carried out by using silica gel (Merck Kieselgel, silica gel 60, 0.063–0.200 mm).

NMR spectra were acquired on Bruker AVANCE 300, 400, or 500 spectrometers. The spectra were referenced to residual proton-solvent references ($^{1}H$, $CD_2Cl_2$ at $\delta=5.32$ ppm, $CDCl_3$ at $\delta=7.26$ ppm, $CD_3CN$ at $\delta=1.94$ ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet), the value of the coupling constants in Hz if applicable, the number of protons implied, and finally the assignment.

Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ESMS).

**5,5″-Di(azidomethyl)-2,2′:6′,2″-terpyridine (3)**: $NaN_3$ (0.676 g, 10.4 mmol) and water (21 mL) were added to a suspension of di(bromomethyl)terpyridine (**2**) (1.44 g, 3.44 mmol) in DMSO (30 mL). The white suspension was heated at 40 °C overnight (with aluminum foil around the flask to protect the mixture from light). The aqueous layer was five times extracted with $CH_2Cl_2$ and the organic phase dried over $MgSO_4$ and then concentrated under vacuum. DMSO was removed by trap to trap distillation at 40 °C or by filtration over alumina. A white solid product was obtained quantitatively (1.19 g). M.p. 102 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=8.64$ (d, $^{4}J=2.4$ Hz, 2H; H-6,6″), 8.62 (d, $^{3}J=7.9$ Hz, 2H; H-3,3″), 8.46 (d, $^{3}J=7.9$ Hz, 2H; H-3′,5′), 7.96 (t, $^{3}J=7.9$ Hz, 1H; H-4′), 7.82 (dd, $^{3}J=7.9$, $^{4}J=2.4$ Hz, 2H; H-4,4″), 4.46 ppm (s, 4H; H-1); MS (ES): *m*/*z* (%): calcd for $[C_{17}H_{13}N_9H]^{+}$: 344.14; found: 344.11 (100) $[M+1H]^{+}$.

**Dissymmetric terpyridine (6)**: Di(azidomethyl)terpyridine (**3**) (0.440 g, 1.28 mmol) was dissolved in distilled and degassed $CH_2Cl_2$ (7.5 mL) under argon. $[Cu(CH_3CN)_4][PF_6]$ (0.692 g, 1.86 mmol) dissolved in degassed $CH_3CN$ (5 mL) was added to the above mixture under argon. The dark-red solution was agitated for 0.5 h. Then, stopper **4** (412 mg, 0.76 mmol) and $Na_2CO_3$ (62 mg, 0.58 mmol) were added under argon. The mixture was stirred for 16 h 30 min under argon. KCN (1.478 g, 22.7 mmol) diluted in the minimum amount of distilled water was then added and the mixture was stirred for 2 h 30 min. Then, distilled water (20 mL) was added and this layer was extracted with $CH_2Cl_2$. The organic layer was dried over $Na_2SO_4$, the solvent evaporated, and the resulting yellow residue was purified by alumina chromatography (elution ether) to give pure **6** (411 mg, 0.464 mmol, 61 %). $^{1}H$ NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta=8.67$ (d, $^{4}J=2.1$ Hz, 1H; H-6″), 8.65 (d, $^{3}J=2.1$ Hz, 1H; H-6), 8.64 (d, $^{3}J=8.1$ Hz, 1H; H-3″), 8.62 (d, $^{3}J=8.1$ Hz, 1H; H-3), 8.48 (2 dd, $^{3}J=7.8$, $^{4}J=0.9$ Hz, 2H; H-3′, H-5′), 7.97 (t, $^{3}J=7.8$ Hz, 1H; H-4′), 7.82 (dd, $^{3}J=8.1$, $^{4}J=2.1$ Hz, 1H; H-4), 7.79 (dd, $^{3}J=8.1$, $^{4}J=2.1$ Hz, 1H; H-4″), 7.68 (s, 1H; H-7), 7.26 (d, $^{3}J=8.8$ Hz, 6H; H-12), 7.15 (d, $^{3}J=9.0$ Hz, 2H; H-10), 7.14 (d, $^{3}J=8.8$ Hz, 6H; H-11), 6.86 (d, $^{3}J=9.0$ Hz, 2H; H-9), 5.64 (s, 2H; H-2), 5.16 (s, 2H; H-8), 4.48 (s, 2H; H-1), 1.29 ppm (s, 27H; H-13); MS (ES): *m*/*z* (%): calcd for $[C_{57}H_{59}N_9O_1H]^{+}$: 886.49; found: 886.48 (100) $[M+1H]^{+}$.

The compound decomposes as a solid above 170 °C. The melting point of **6** could thus not be measured.

**$Cu^{I}$–[2]semirotaxane ([7][PF$_6$])**: A solution of $[Cu(CH_3CN)_4][PF_6]$ (6.3 mg, 17 µmol) in dry and degassed $CH_3CN$ (0.4 mL) was added to a degassed solution of macrocycle **5** (9.6 mg, 17 µmol) in dry $CH_2Cl_2$ (0.4 mL) and it was stirred at room temperature over 15 min under an inert atmosphere. A degassed solution of dissymmetric terpyridine (15.0 mg, 17 µmol) in dry $CH_2Cl_2$ (2.1 mL) was then added to this orange solution by cannula. The mixture turned immediately intensely dark red and was left to react for 30 min. After evaporation of the solvents, $Cu^{I}$–[2]semirotaxane (29.6 mg, 17.0 µmol) was obtained quantitatively. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$, 25 °C): $\delta=8.47$ (d, $^{3}J=8.1$ Hz, 2H; H-b), 8.09–8.02 (m, 3H; H-3′, H-4′, H-5′), 8.02 (s, 2H; H-a), 7.91 (d, $^{3}J=8.1$ Hz, 2H; H-c), 7.92–7.87 (m, 2H; H-3,3″), 7.79 (d, $^{4}J=1.3$ Hz, 2H; H-6″), 7.75 (s, 1H; H-7), 7.66 (d, $^{4}J=1.3$ Hz, 2H; H-6), 7.47 (d, $^{3}J=8.6$ Hz, 4H; H-d), 7.44 (d, 1H; H-4″), 7.42 (d, 1H; H-4), 7.25 (d, $^{3}J=8.9$ Hz, 6H; H-12), 7.19 (d, $^{3}J=8.9$ Hz, 2H; H-10), 7.13 (d, $^{3}J=8.9$ Hz, 6H; H-11), 6.92 (d, $^{3}J=8.9$ Hz, 2H; H-9), 6.30 (d, $^{3}J=8.6$ Hz, 4H; H-e), 5.29 (s, 2H; H-2), 5.19 (s, 2H; H-8), 4.14 (s, 2H; H-1), 3.92–3.86 (m, 4H; H-α), 3.79 (s, 4H; H-ε), 3.81–3.70 (m, 12H; H-β, H-γ, H-δ), 1.29 ppm (s, 27H; H-13).

**$Zn^{II}$–[2]semirotaxane ([8][OTf]$_2$)**: Same procedure as for $Cu^{I}$–[2]semirotaxane $\mathbf{7}^{+}$ by using $[Zn(OTf)_2]$ (6.2 mg, 17 µmol) instead of $[Cu(CH_3CN)_4][PF_6]$. $Zn^{II}$–[2]semirotaxane (30.8 mg, 17.0 µmol) was obtained quantitatively as a yellow solid. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$, 25 °C): $\delta=8.87$ (d, $^{3}J=8.3$ Hz, 2H; H-b), 8.83 (m, 1H; H-4′), 8.60–8.50 (m, 3H; H-3, H-3′, H-5′), 8.38 (d, $^{3}J=8.2$ Hz, 1H; H-3″), 8.32 (s, 2H; H-a), 8.32 (dd, $^{3}J=8.2$, $^{4}J=1.4$ Hz, 1H; H-4″), 8.16 (dd, $^{3}J=8.2$, $^{4}J=1.4$ Hz, 1H; H-4), 8.07 (d, $^{3}J=8.3$ Hz, 2H; H-c), 8.06 (s, 1H; H-7), 7.79 (d, $^{4}J=1.4$ Hz, 1H; H-6″), 7.35 (d, $^{4}J=1.4$ Hz, 1H; H-6), 7.26 (d, $^{3}J=8.8$ Hz, 6H; H-12), 7.20

(d, $^{3}J=8.8$ Hz, 2H; H-10), 7.16 (d, $^{3}J=8.8$ Hz, 6H; H-11), 6.89 (d, $^{3}J=8.8$ Hz, 2H; H-9), 6.86 (d, $^{3}J=8.7$ Hz, 4H; H-d), 6.23 (d, $^{3}J=8.7$ Hz, 4H; H-e), 5.59 (s, 2H; H-2), 5.10 (s, 2H; H-8), 4.33 (s, 2H; H-1), 3.86–3.66 (m, 20H; H-α, H-β, H-γ, H-δ, H-ε), 1.29 ppm (s, 27H, H-13); MS (ES): $m/z$ (%): calcd for $[C_{91}H_{93}N_{11}O_7Zn]^{2+}/2$: 757.83; found: 758.75 (42) $[M-2\,OTf]^{2+}/2$.

**Demetalated [5]rotaxane (11)**: Terpyridinic [2]semirotaxane **7**$^{+}$ (198 mg, $1.19\times10^{-4}$ mol), $Na_2CO_3$ (3.9 mg, $3.7\times10^{-5}$ mol), tren′-Br Cu$^{I}$ catalyst (33.6 mg, $1.86\times10^{-5}$ mol), sodium ascorbate (14.6 mg, $7.37\times10^{-5}$ mol), and [3]pseudorotaxane **9**$^{2+}$ (76 mg, $3.9\times10^{-5}$ mol) were introduced in distilled and degassed $CH_2Cl_2$ (6 mL) and degassed anhydrous $CH_3CN$ (3 mL). The mixture was stirred for 5 days and the solvents subsequently evaporated. The resulting residue was then dissolved in a mixture of $CH_2Cl_2/CH_3CN/H_2O$ (2:1:1, 8 mL), and KCN (300 mg, $4.61\times10^{-3}$ mol) was then added. The mixture was stirred for 4 h. Then, distilled water (20 mL) was added and this layer was extracted with $CH_2Cl_2$. The solvent was then evaporated and the resulting brown residue was purified by alumina chromatography. A gradient of elution ($CH_2Cl_2$/MeOH 100:0 → 97:3) gave pure [5]rotaxane (130 mg, $2.94\times10^{-5}$ mol, 75%). $^{1}$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta=9.22$ (d, $^{4}J=1.7$ Hz, 2H; H-5), 9.20 (d, $^{3}J=9.1$ Hz, 2H; H-1), 9.04 (s, 2H; H-7), 8.76 (d, $^{3}J=8.5$ Hz, 2H; H-2), 8.74 (d, $^{3}J=8.4$ Hz, 2H; H-3), 8.41 (d, $^{4}J=1.8$ Hz, 2H; H-9), 8.35 (dd, $^{3}J=8.3$, $^{4}J=2.1$ Hz, 2H; H-4), 8.32 (s, 2H; H-19), 8.31 (t, $^{3}J=4.3$ Hz, 2H; H-13), 8.26 (d, $^{3}J=7.7$ Hz, 2H; H-11), 8.25 (s, 2H; H-6), 8.25 (s, 2H; H-17), 8.24 (d, $^{3}J=7.9$ Hz, 2H; H-15), 8.11 (d, $^{3}J=8.4$ Hz, 4H; H-b′), 8.03 (d, $^{3}J=8.4$ Hz, 4H; H-b), 7.94 (d, $^{3}J=8.8$ Hz, 8H; H-d′), 7.89 (d, $^{3}J=8.8$ Hz, 8H; H-d), 7.88–7.84 (m, 4H; H-12, H-14), 7.80 (d, $^{3}J=8.3$ Hz, 8H; H-c′), 7.74 (d, $^{3}J=8.2$ Hz, 8H; H-c), 7.66 (s, 4H; H-a′), 7.52 (s, 4H; H-a), 7.42 (dd, $^{3}J=8.4$, $^{4}J=2.1$ Hz, 2H; H-10), 7.25 (dd, $^{3}J=8.3$, $^{4}J=2.1$ Hz, 2H; H-16), 7.21 (d, $^{3}J=8.6$ Hz, 12H; H-24), 7.11 (d, $^{3}J=8.7$ Hz, 12H; H-23), 7.06 (d, $^{3}J=8.9$ Hz, 4H; H-22), 6.89 (d, $^{3}J=8.9$ Hz, 4H; H-21), 6.64 (d, $^{3}J=8.8$ Hz, 8H; H-e′), 6.42 (d, $^{3}J=8.7$ Hz, 8H; H-e), 5.29 (s, 4H; H-8), 5.20 (s, 4H; H-18), 5.06 (s, 4H; H-20), 3.90 (m, 8H; H-α′), 3.75 (t, $^{3}J=6.1$ Hz, 8H; H-α), 3.67 (s, 8H; H-ε), 3.60–3.40 (m, 56H; H-β, H-β′, H-γ, H-γ′, H-δ, H-δ′, H-ε′), 1.27 ppm (s, 56H; H-25); MS (ES): $m/z$: calcd for $[C_{276}H_{268}N_{30}O_{26}H_4]^{4+}/4$: 1106.274, $[C_{276}H_{268}N_{30}O_{26}H_3]^{3+}/3$: 1474.696, $[C_{276}H_{268}N_{30}O_{26}NaH_2]^{3+}/3$: 1482.023, $[C_{276}H_{268}N_{30}O_{26}H_2]^{2+}/2$: 2211.504; found: 1106.265 $[M+4H]^{4+}/4$, 1474.684 $[M+3H]^{3+}/3$, 1482.012 $[M+Na+2H]^{3+}/3$, 2211.541 $[M+2H]^{2+}/2$.

**Zn–[5]rotaxane (12$^{8+}$)**: Demetalated [5]rotaxane **11** (6.3 mg, $1.4\times10^{-6}$ mol) was diluted in $CH_2Cl_2$ (3 mL) and then a solution of $Zn(OTf)_2$ in MeOH (3.4 mL, $6.3\times10^{-6}$ mol; $1.86\times10^{-3}$ mol L$^{-1}$) was added. The solution was stirred for 1 h and the solvents were subsequently evaporated. The resulting precipitate was then redissolved in $CH_2Cl_2$ and filtered to get rid off the excess of inorganic salts. Metalated [5]rotaxane was thus obtained (7.7 mg, $1.32\times10^{-6}$ mol, 92%). $^{1}$H NMR (300 MHz, $CD_3CN$, 25 °C): $\delta=9.62$ (d, $^{3}J=9.0$ Hz, 2H; H-1), 9.02 (d, $^{3}J=8.4$ Hz, 4H; H-b′), 8.99 (d, $^{3}J=8.3$ Hz, 4H; H-b), 8.95 (dd, $^{3}J=8.5$, $^{4}J=2.0$ Hz, 2H; H-4), 8.88–8.78 (m, 8H; H-2, H-3, H-12, H-14), 8.48–8.42 (m, 12H; H-13, H-15, H-a, H-a′), 8.38 (d, $^{3}J=8.3$ Hz, 2H; H-16), 8.37 (s, 2H; H-7), 8.34 (d, $^{3}J=8.3$ Hz, 2H; H-11), 8.16 (dd, $^{3}J=8.3$, $^{4}J=2.0$ Hz, 2H; H-10), 8.14 (d, $^{4}J=1.7$ Hz, 2H; H-5), 8.11 (d, $^{3}J=8.5$ Hz, 4H; H-c′), 8.09 (d, $^{3}J=8.4$ Hz, 4H; H-c), 7.80 (s, 2H; H-19), 7.71 (d, $^{4}J=1.4$ Hz, 2H; H-9), 7.39 (d, $^{4}J=1.4$ Hz, 2H; H-17), 7.27 (d, $^{3}J=8.6$ Hz, 12H; H-24), 7.16 (d, $^{3}J=9.0$ Hz, 4H; H-22), 7.12 (d, $^{3}J=8.5$ Hz, 12H; H-23), 7.04 (d, $^{3}J=8.6$ Hz, 8H; H-d), 6.95 (d, $^{3}J=9.0$ Hz, 4H; H-21), 6.80 (d, $^{3}J=8.8$ Hz, 8H; H-d′), 6.58 (2H, s; H-6), 6.27 (d, $^{3}J=8.5$ Hz, 8H; H-e), 6.20 (d, $^{3}J=8.6$ Hz, 8H; H-e′), 5.53 (4H, s; H-8), 5.40 (4H, s; H-18), 5.13 (4H, s; H-20), 3.90–3.55 (80H, m; H-α, H-α′, H-β, H-β′, H-γ, H-γ′, H-δ, H-δ′, H-ε, H-ε′), 1.26 ppm (54H, s; H-25); MS (ES): $m/z$: calcd for $[C_{276}H_{268}N_{30}O_{26}Zn_4(OTf)_5]^{3+}/3$: 1809.178, $[C_{276}H_{268}N_{30}O_{26}Zn_4(OTf)_4]^{4+}/4$: 1319.146, $[C_{276}H_{268}N_{30}O_{26}Zn_4(OTf)_3]^{5+}/5$: 1025.719, $[C_{276}H_{268}N_{30}O_{26}Zn_4(OTf)_2]^{6+}/6$: 830.113; found: 1809.176 $[M-3\,OTf]^{3+}/3$, 1319.146 $[M-4\,OTf]^{4+}/4$, 1025.719 $[M-5\,OTf]^{5+}/5$, 830.106 $[M-6\,OTf]^{6+}/6$.

**Li–[5]rotaxane (13$^{4+}$)**: Demetalated [5]rotaxane **11** (6.7 mg, $1.5\times10^{-6}$ mol) was dissolved in $CH_2Cl_2$ (1 mL). A solution (1.4 mL, $1.2\times10^{-5}$ mol) containing $LiBF_4$ (8 mg) and two drops of $NEt_3$ in MeOH (10 mL) was added and the resulting solution stirred overnight. Solvents were subsequently evaporated to give a white residue. The desired compound was directly characterized by NMR spectroscopy without any further purification. The yield is quantitative according to the NMR spectrum. $^{1}$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta=9.52$ (d, $^{3}J=8.9$ Hz, 2H; H-1), 8.70 (d, $^{3}J=9.0$ Hz, 2H; H-2), 8.55 (m, 12H; H-3, H-4, H-5, H-7, H-b′), 8.46 (d, $^{3}J=8.3$ Hz, 4H; H-b), 8.38 (t, $^{3}J=8.0$ Hz, 2H; H-13), 8.10 (m, 4H; H-12, H-14), 8.03 (s, 4H; H-a′), 8.01 (s, 4H; H-a), 7.97 (m, 4H; H-9), 7.94 (d, $^{3}J=8.1$ Hz, 2H; H-15), 7.87 (d, $^{3}J=8.2$ Hz, 4H; H-c), 7.80 (dd, $^{3}J=8.3$, $^{4}J=2.1$ Hz, 2H; H-16), 7.75 (d, $^{3}J=8.2$ Hz, 4H; H-c′), 7.59 (m, 4H; H-10, H-19), 7.46 (d, $^{4}J=1.7$ Hz, 2H; H-17), 7.24 (d, $^{3}J=8.7$ Hz, 12H; H-24), 7.19 (d, $^{3}J=9.0$ Hz, 4H; H-22), 7.16 (s, 2H; H-6), 7.14 (d, $^{3}J=8.4$ Hz, 8H; H-d), 7.13 (d, $^{3}J=8.7$ Hz, 12H; H-23), 7.04 (d, $^{3}J=8.6$ Hz, 8H), 6.91 (d, $^{3}J=8.9$ Hz, 4H; H-21), 6.11 (d, $^{3}J=8.6$ Hz, 8H; H-e), 6.07 (d, $^{3}J=8.5$ Hz, 8H; H-e′), 5.38 (s, 4H; H-8), 5.25 (s, 4H; H-18), 5.16 (s, 4H; H-20), 3.95–3.60 (m, 80H; H-α, H-α′, H-β, H-β′, H-γ, H-γ′, H-δ, H-δ′, H-ε, H-ε′), 1.28 ppm (s, 54H; H-25); $^{7}$Li NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta=5.33$, 4.63 ppm.

**Li/Zn–[5]rotaxane (14$^{6+}$)**: Demetalated [5]rotaxane **11** (7.7 mg, $1.7\times10^{-6}$ mol) was diluted with $CH_2Cl_2$ (1 mL) and then a solution of $LiBF_4$ (0.45 mL, 0.36 mg, $3.8\times10^{-6}$ mol) in MeOH with few drops of $NEt_3$ ($8.53\times10^{-3}$ mol L$^{-1}$) and a solution of $Zn(OTf)_2$ (1.9 mL, 1.28 mg, $3.52\times10^{-6}$ mol) in MeOH ($c=1.9\times10^{-3}$ mol L$^{-1}$) were added. The solution was stirred overnight and the solvents were evaporated. Heterodinuclear [5]rotaxane was obtained in a quantitative yield (9.3 mg, $1.7\times10^{-6}$ mol). $^{1}$H NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta=9.55$ (d, $^{3}J=8.9$ Hz, 2H; H-1), 8.85 (t, $^{3}J=7.9$ Hz, 2H; H-13), 8.78 (d, $^{3}J=8.4$ Hz, 4H; H-b′), 8.73 (d, $^{3}J=8.9$ Hz, 2H; H-2), 8.59 (s, 2H; H-7), 8.57–8.51 (m, 10H; H-b, H-3, H-4, H-5), 8.49 (d, $^{3}J=7.6$ Hz, 2H; H-14), 8.48 (d, $^{3}J=7.7$ Hz, 2H; H-12), 8.39 (d, $^{3}J=8.5$ Hz, 2H; H-15), 8.31 (d, $^{3}J=8.4$ Hz, 2H; H-11), 8.23 (m, 4H; H-10, H-16), 8.22 (s, 4H; H-a′), 8.02 (s, 4H; H-a), 7.97 (s, 2H; H-19), 7.96 (d, $^{3}J=8.6$ Hz, 4H; H-c′), 7.87 (d, $^{3}J=8.2$ Hz, 4H; H-c), 7.64 (d, $^{4}J=1.6$ Hz, 2H; H-17), 7.60 (d, $^{4}J=1.5$ Hz, 2H; H-9), 7.25 (d, $^{3}J=8.6$ Hz, 12H; H-24), 7.20 (d, $^{3}J=8.9$ Hz, 4H; H-22), 7.20 (s, 2H; H-6), 7.15 (d, $^{3}J=8.5$ Hz, 12H; H-23), 7.15 (d, $^{3}J=8.6$ Hz, 8H; H-d), 6.93 (d, $^{3}J=8.9$ Hz, 4H; H-21), 6.78 (d, $^{3}J=8.7$ Hz, 8H; H-d′), 6.18 (d, $^{3}J=8.6$ Hz, 8H; H-e′), 6.08 (d, $^{3}J=8.5$ Hz, 8H; H-e), 5.56 (s, 4H; H-8), 5.51 (s, 4H; H-18), 5.14 (s, 4H; H-20), 3.95–3.65 (m, 80H; H-α, H-α′, H-β, H-β′, H-γ, H-γ′, H-δ, H-δ′, H-ε, H-ε′), 1.29 ppm (s, 54H; H-25); $^{7}$Li NMR (500 MHz, $CD_2Cl_2$, 25 °C): $\delta=5.33$ ppm.

**TMS axle (16)**: Anhydrous DMF (8 mL) and distilled $NEt_3$ (1 mL) were introduced into an oven-dried flask. The mixture was degassed for 25 min with argon. Trimethylsilyacetylene (0.15 mL, 104 mg, $1.1\times10^{-3}$ mol), compound **15** (99 mg, $2.0\times10^{-4}$ mol), CuI (8.5 mg, $4.5\times10^{-5}$ mol), and $[PdCl_2(PPh_3)_2]$ (20 mg, $2.8\times10^{-5}$ mol) were subsequently added. The solution was then heated up to 100 °C under an argon atmosphere and then stirred for 2 h. The reaction mixture was cooled to room temperature and the solvents evaporated. The product was purified by alumina chromatography with chloroform. The product was then washed with acetone, *n*-pentane, and diethyl ether. A beige powder was obtained (33 mg, $6.27\times10^{-5}$ mol, 31%). M.p. > 300 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=9.06$ (d, $^{3}J=8.8$ Hz, 2H; H-1), 8.81 (dd, $^{4}J=2.1$, $^{5}J=0.6$ Hz, 2H; H-5), 8.78 (d, $^{3}J=8.6$ Hz, 2H; H-2), 8.69 (dd, $^{3}J=8.3$, $^{5}J=0.6$ Hz, 2H; H-3), 8.32 (s, 2H; H-6), 7.95 (dd, $^{3}J=8.2$, $^{4}J=2.0$ Hz, 2H; H-4), 0.31 ppm (s, 18H; H-TMS); $^{13}$C NMR (300 MHz, $CDCl_3$, 25 °C): $\delta=155.62$, 154.57, 152.11, 147.59, 139.83, 132.56, 131.73, 124.81, 120.82, 120.65, 119.64, 101.80, 99.63, −0.14 ppm; MS (ES): $m/z$: calcd $[C_{32}H_{30}N_4Si_2+H]^{+}$: 527.208, $[C_{32}H_{30}N_4Si_2+Li]^{+}$: 533.217; found: 527.239 $[M+H]^{+}$, 533.248 $[M+Li]^{+}$.

**Zn–[3]pseudorotaxane (17$^{4+}$)**: $Zn(OTf)_2$ (6.9 mg, $1.9\times10^{-5}$ mol) in $CH_3OH$ (1 mL) was added to a solution of macrocycle **5** (10.9 mg, $1.92\times10^{-5}$ mol) in $CH_2Cl_2$ (2 mL). This solution was added to a solution of axle **16** (5.0 mg, $9.5\times10^{-6}$ mol) in $CH_2Cl_2$ (2 mL) and the mixture was reacted overnight. After evaporation of the solvents, the [3]pseudorotaxane **17**$^{4+}$ was obtained (22.2 mg, $9.30\times10^{-6}$ mol, 98%). $^{1}$H NMR (300 MHz, $CD_2Cl_2$, 25 °C): $\delta=9.67$ (d, $^{3}J=8.9$ Hz, 2H; H-1), 8.93 (d, $^{3}J=8.5$ Hz, 4H; H-b), 8.79 (d, $^{3}J=9.0$ Hz, 2H; H-2), 8.68 (d, $^{3}J=8.4$ Hz, 2H; H-3), 8.56 (dd, $^{3}J=8.4$, $^{4}J=1.7$ Hz; H-4), 8.36 (s, 4H; H-a), 8.25 (d, $^{4}J=1.7$ Hz, 2H; H-5), 8.05 (d, $^{3}J=8.4$ Hz, 4H; H-c), 7.07 (d, $^{3}J=8.6$ Hz, 8H; H-d), 6.51 (s, 2H; H-6), 6.34 (d, $^3J=8.8$ Hz, 8H; H-e), 4.10–3.70 (m, 40H; H-α, H-β, H-γ, H-δ, H-ε), 0.30 ppm (s, 18H; H-TMS); MS (ES): the ESMS spectrum of the complex could not be obtained; however, loss of a TMS group was observed: $m/z$ (%): calcd: $[C_{99}H_{90}N_8O_{18}SiZn_2S_2F_6]^{2+}/2$: 1008.203; found: 1008.260 (100) $[M-2\,OTf-TMS+H]^{2+}/2$; crystal data for [**17**]$[TfO^-]_4$: $M=2492.20.91$; pale-yellow plates/prisms; $0.10\times0.40\times0.40$ mm$^3$; monoclinic; space group $P2_1/c$; $a=13.8452(6)$, $b=28.0649(14)$, $c=30.6242(13)$ Å; $\beta=102.344(2)°$; $V=11624.4(9)$ Å$^3$; $Z=4$; $\rho_{calcd}=1.424$ g cm$^{-3}$; $F_{000}=5152$; $\mu=2.190$ mm$^{-1}$ ; $T=123(2)$ K; $2\theta_{max}=127.0°$; 18823 reflections used, 11156 with $I_o> 2\sigma(I_o)$, $R_{int}=0.1769$, 1402 parameters, 36 restraints, $GoF=1.451$, $R=0.1317$ $[I_o>2\sigma(I_o)]$, $wR=0.4088$ (all reflections), $1.717<\Delta\rho<-1.422$ e Å$^3$.

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