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# Adjustable Receptor Based on a [3]Rotaxane Whose Two Threaded Rings Are Rigidly Attached to Two Porphyrinic Plates: Synthesis and Complexation Studies

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***Abstract:*** The design and synthesis of a new type of receptor based on a [3]rotaxane, consisting of one thread and two threaded rings, is reported, as well as some of its complexing properties toward given guests. Two rings rigidly attached to porphyrins are threaded by a stiff rod incorporating two 2,2′-bipyridine-like chelates, the threading process being driven by two Cu(I) atoms acting as templates. A double-stoppering reaction based on click chemistry leads to the copper-complexed [3]rotaxane in which the rings are located close to the central part of the thread and the distance between the two porphyrin plates is short. Removal of the two Cu(I) cations releases the two rings which are now free to move along and around the thread. In these two states of the [3]rotaxane, free and complexed with copper, the two zinc(II) porphyrins attached to the rings can bind different ditopic guests bearing pyridyl groups or amines as terminal functions. UV−visible and NMR DOSY experiments were realized with guests of different sizes, and the association constants were determined. The free [3]rotaxane is both a strong and highly adaptable receptor with high stability constants for the host/guest complexes, log $K$ being in the range of 6.3−7.5 for guests with a length varying between 2.8 and 18 Å. The copper-complexed [3]rotaxane is still a good receptor for small guests due to an entropic gain for this preorganized molecule compared to the free [3]rotaxane, but it is a less strong receptor for guests which do not fit the short distance between the two porphyrins.

## Introduction

The field of chemical topology has undergone spectacular developments in the course of the past 20 years, mostly in relation to the introduction of efficient template synthesis.[1] Catenanes, rotaxanes, and to a lesser extent, molecular knots[2] are nowadays accessible compounds whose chemistry finds interesting applications in related fields such as that of artificial molecular machines and motors.[3] Within the past 10 years, non-interlocking systems have also led to outstanding results in this latter field.[4] Apart from the area of machines at the molecular level, catenanes and rotaxanes have been used in the field of electron and energy transfer, often as mimics of given fragments of the photosynthetic reaction center or antennas.[5] In contrast, this family of molecules has not been much used in host−guest chemistry. Rare examples are those of luminescent anion binders[6] or systems related to biomolecules.[7] The present report is dealing with the synthesis of a new type of receptors consisting of porphyrin-based [3]rotaxanes, as well as the study of their complexation properties. A brief report of this work has been published in a recent communication.[8] A related study

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(1) (a) Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795–810. (b) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725–2828. (c) Vögtle, F.; Dünnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451–460. (d) Dietrich-Buchecker, C.; Sauvage, J.-P. *Molecular Catenanes, Rotaxanes and Knots. A Journey Through the World of Molecular Topology*; Wiley-VCH: Weinheim, Germany, 1999. (e) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53–61.

(2) (a) Dietrich-Buchecker, C.; Rapenne, G.; Sauvage, J.-P. In *Molecular Catenanes, Rotaxanes and Knots. A Journey Through the World of Molecular Topology*; Dietrich-Buchecker, C., Sauvage, J.-P., Eds.; Wiley-VCH: Weinheim, Germany, 1999; Vol. 10, pp 7−142. (b) Dietrich-Buchecker, C.; Colasson, B. X.; Sauvage, J.-P. *Top. Curr. Chem.* 2005, 249. (c) Lukin, O.; Vögtle, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 1456–1477.

(3) (a) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611–619. (b) Stoddart, J. F. *Acc. Chem. Res.* **2001**, *34*, 410–411. (c) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456–464. (d) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines. A Journey into the Nano World*; Wiley-VCH: Weinheim, Germany, 2003. (e) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191.

(4) (a) Feringa, B. L. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001. and references therein. (b) Muraoka, T.; Kinbara, K.; Aida, T. *Nature (London)* **2006**, *440*, 512–515.

(5) Flamini, L.; Heitz, V.; Sauvage, J.-P. In *Non-Covalent Multiporphyrin Assemblies: Synthesis and Properties, Structure and Bonding*; Enzo, A., Ed.; Springer: Berlin; New York, 2006; Vol. 121, pp 217−261.

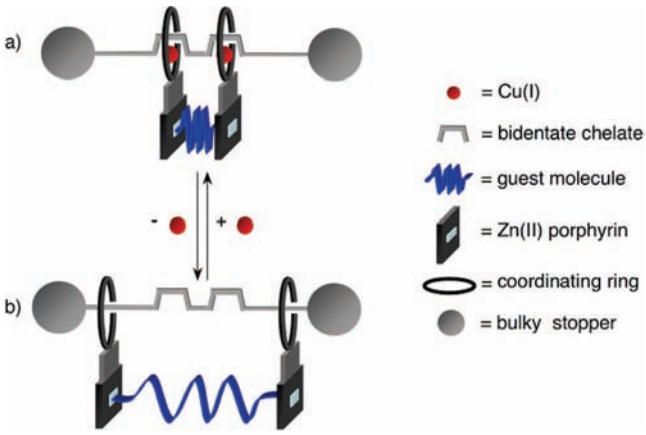
(6) Beer, P.; Sambrook, M. R.; Curiel, D. *Chem. Commun.* **2006**, 2105–2117.

(7) (a) Smukste, I.; Smithrud, D. B. *J. Org. Chem.* **2003**, *68*, 2547–2558. (b) Lam, R. T. S.; Belenguer, A.; Roberts, S. L.; Naumann, C.; Jarrosson, T.; Otto, S.; Sanders, J. K. M. *Science* **2005**, *308*, 667–669. (c) Wenz, G.; Han, B.-H.; Müller, A. *Chem. Rev.* **2006**, *106*, 782–817.

(8) Frey, J.; Tock, C.; Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2008**, *130*, 4592–4593.

***Scheme 1.*** Principle of the Adaptable [3]Rotaxane Receptor[a]




[a] The two rings threaded by the rotaxane axis (grey) are rigidly attached to Zn-porphyrins (pale blue and black moieties). The guest (blue) is an organic fragment able to coordinate the Zn atom of the porphyrins. (a) In the dicopper(I) rotaxane complex, the porphyrin−porphyrin distance is more or less determined by the geometry of the central dinucleating unit (the chelates are represented by a U-shaped form). The Cu(I) metal centers (red) occupy well-defined positions: the chelate of the ring sits on one of the bidentate ligands of the thread, thus offering a tetracoordination site to the Cu(I). The guest molecule has to adopt its conformation to the offered space and it may thus have to be folded. (b) After demetalation, the macrocycles are free to glide on the thread and the guest molecule can extend itself to its preferred conformation and will thus partly determine the position of the rings.

of a [3]rotaxane acting as a host for $C_{60}$ has also been disclosed by Canadian researchers simultaneously to our first report.[9]

The general principle of the recognition process and of the ability of the receptor to adjust its size to that of the guest is represented in Scheme 1.

The two zinc(II)-complexed porphyrins are able to interact with Lewis bases such as pyridyl groups or amines. A compound with two terminal pyridyl groups will thus be susceptible of being coordinated to the [3]rotaxane via interactions with the Zn atoms in a very classical way, similar to what has been exploited in the past for constructing large noncovalent multiporphyrin assemblies[10] or host−guest complexes incorporating two or several porphyrins and a pyridinic substrate.[11] Incidentally, it should be noted that many examples of porphyrin-incorporating catenanes or rotaxanes have been reported either by our team[12] or by others,[13] mostly in relation to electron and energy transfer.

If the rings and the threaded fragment, which must necessarily be rigid, are connected by mechanical bonds only, the rings can freely move with respect to each other: translation along the threaded rod or spinning around it in the free form of the [3]rotaxane. The distance between the two porphyrinic plates can thus vary enormously by just changing the positions of the rings on the "rail" and the angle between the two porphyrin nuclei. The compound can thus behave as an efficient receptor toward guests of the type py−Z−py (py: 4-pyridyl; Z: spacer) regardless of the shape and the length of the complexed guest provided its length stays under a certain limit fixed by the size of the bis-porphyrinic [3]rotaxane. As shown in Scheme 1, the porphyrin nuclei are rigidly attached to the mobile rings of the rotaxane receptor which is very favorable to a good control over the Zn−Zn distance. As a consequence, once the [3]rotaxane is complexed to two copper(I) ions, the rigidity of the system should be such that only certain relatively short substrates will be strongly complexed. Alternatively, the same system can be regarded as a "compressor" since the distance between the two plates, which is not controlled at all in the free [3]rotaxane, can be dramatically shortened by complexing two copper(I) atoms to the rotaxane. This may induce a compression of a substrate lying between the two porphyrinic plates and, possibly, its expulsion if the steric strain becomes too important.

## Results and Discussion

**1. Synthesis and Characterization of the Copper-Complexed [3]Rotaxane and Its Metal-Free Form. 1.1. Choice of the Molecular Fragments and Synthesis Strategy.** The chemical formula of the target free rotaxane **1** is represented in Figure 1. Each threaded ring of the [3]rotaxane contains a 2,9-diaryl-1,10-phenanthroline coordinating fragment. The back of the 1,10-phenanthroline nucleus (positions 5 and 6) has been modified in order to perform a condensation reaction leading to the attachment of a porphyrin in a rigid fashion, as already described in a previous report from our group.[14] The two-station "rail" is rigid and, thanks to the central 4,7-phenanthroline core, the coordination axes of the bidentate chelates belonging to the rod are parallel to one another. Bis-bidentate chelates containing a 4,7-phenanthroline central unit associated to two lateral 2-pyridyl groups have already been used by others in the construction of multinuclear complexes[15] or by our team in the preparation of copper-based [3]pseudorotaxanes[16] or for making dinuclear iridium complexes in relation to electronic coupling and luminescent complexes.[17]

As already mentioned, the synthesis of the ring-and-porphyrin conjugate has previously been reported[14] and will not be discussed. In contrast, the preparation of the rod will be described. Before describing the synthetic details leading to these

(9) Marois, J.-S.; Cantin, K.; Desmarais, A.; Morin, J.-F. *Org. Lett.* **2008**, *10*, 33–36.
(10) (a) Tominaga, M.; Suzuki, K.; Kawano, M.; Kusukawa, T.; Ozeki, T.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5621–5625. (b) Tsuda, A.; Nakamura, T.; Sakamoto, S.; Yamaguchi, K.; Osuka, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2817–2821. (c) Iengo, E.; Zangrando, E.; Alessio, E. *Acc. Chem. Res.* **2006**, *39*, 841–851. (d) Takahashi, R.; Kobuke, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2372–2373. (e) Akihiko Tsuda, A.; Hu, H.; Tanaka, R.; Aida, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 4884–4888. (f) Hoffmann, M.; Wilson, C. J.; Odell, B.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 3122–3125.
(11) (a) Sanders, J. K. M. In Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F. *Comprehensive Supramolecular Chemistry* Pergamon: Oxford, U.K., 1996; Vol. 9, pp 131−164. (b) Satake, A.; Kobuke, Y. *Tetrahedron* **2005**, *61*, 13–41.
(12) (a) Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 12378–12384. (b) Amabilino, D. B.; Sauvage, J.-P. *New J. Chem.* **1998**, *39*, 405–409. (c) Linke, M.; Fujita, N.; Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. *New J. Chem.* **2001**, *25*, 790–796.
(13) (a) Gunter, M. J.; Johnston, M. R. *J. Chem. Soc., Chem. Commun.* **1994**, 829–830. (b) Schuster, D. I.; Li, K.; Guldi, D. M.; Ramey, J. *Org. Lett.* **2004**, *6*, 1919–1922. (c) Ashton, P. R.; Johnston, M. R.; Stoddart, J. F.; Tolley, M. S.; Wheeler, J. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1128–1131. (d) Hunter, C. A.; Low, C. M. R.; Packer, M. J.; Spey, S. E.; Vinter, J. G.; Vysotsky, M. O.; Zonta, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2678–2682. (e) Chichak, K.; Walsh, M. C.; Branda, N. R. *Chem. Commun.* **2000**, 847–848. (f) Wu, J.; Fang, F.; Lu, W.-Y.; Hou, J.-L.; Li, C.; Wu, Z.-Q.; Jiang, X.-K.; Li, Z.-T.; Yu, Y.-H. *J. Org. Chem.* **2007**, *72*, 2897–2905.
(14) Frey, J.; Dobbs, W.; Heitz, V.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **2007**, *241*, 2416–2419.
(15) Baxter, P. N. W.; Khoury, R. G.; Lehn, J. M.; Baum, G.; Fenske, D. *Chem.—Eur. J.* **2000**, *6*, 4140–4148.
(16) Frey, J.; Tock, C.; Collin, J.-P.; Heitz, V.; Sauvage, J.-P.; Rissanen, K. *J. Am. Chem. Soc.* **2008**, *130*, 11013–11022.
(17) Auffrant, A.; Barbieri, A.; Barigelletti, F.; Lacour, J.; Mobian, P.; Collin, J.-P.; Sauvage, J.-P.; Ventura, B. *Inorg. Chem.* **2007**, *46*, 6911–6919.

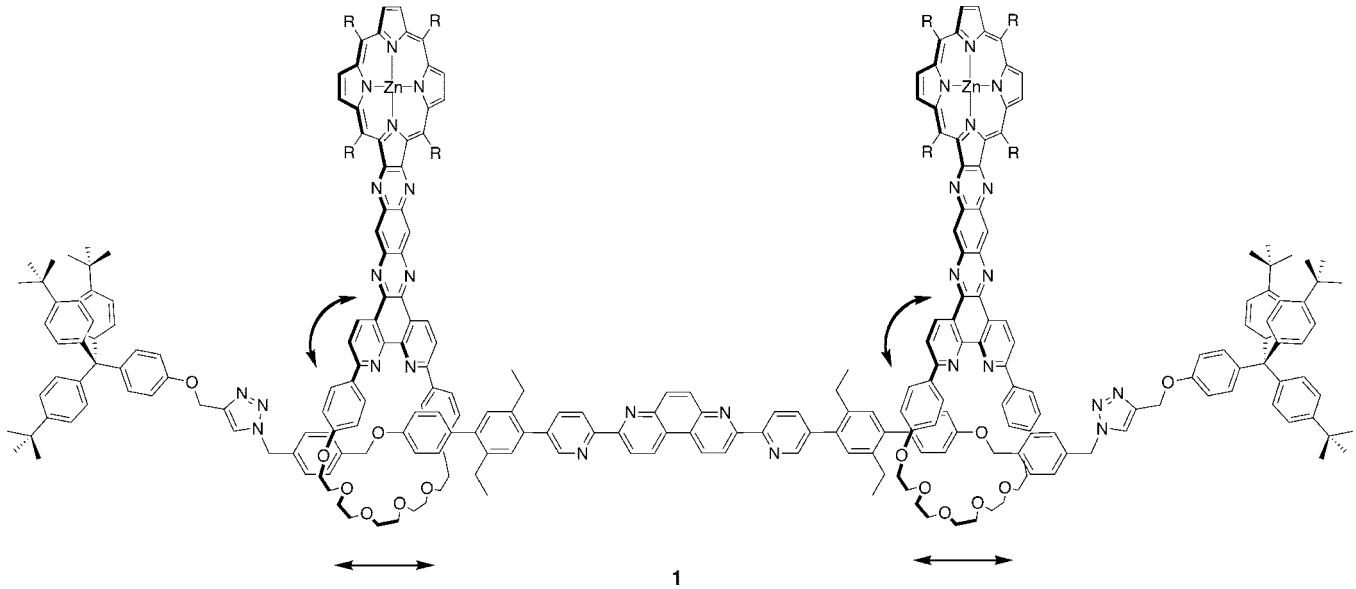


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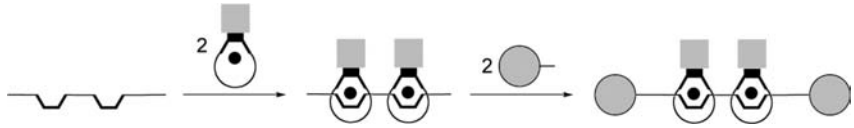
***Figure 1.*** Target free [3]rotaxane.

***Scheme 2.*** Cartoon Representation of the Strategy Used for Making the Copper-Complexed Rotaxane, Precursor to Compound **1**[a]



[a] The double-stoppering reaction is carried out in a one-pot procedure. The copper-complexed rings are prepared from copper(I) (black dot) and the metal-free ring in a quantitative reaction.

two latter species, it is useful to indicate the general synthesis strategy. As shown in Scheme 2 the two key steps are copper(I)-driven double threading process and the stoppering reaction.

**1.2. Synthesis of the Two-Station Rod and the Stopper Precursor.** The use of the recently developed "click" chemistry,[18−20] which is a catalytic version of an old procedure discovered originally by Huisgen,[21] was recently successfully exploited as the final reaction ("stoppering") for making a wide family of rotaxanes.[22−27] Since this copper-catalyzed procedure is compatible with the presence of other copper complexes used as precursors, it was selected as the final reaction in the present synthetic sequence. The azide function was introduced as terminal function of the threaded fragment (Scheme 3), whereas the stopper was attached to the terminal acetylenic function.

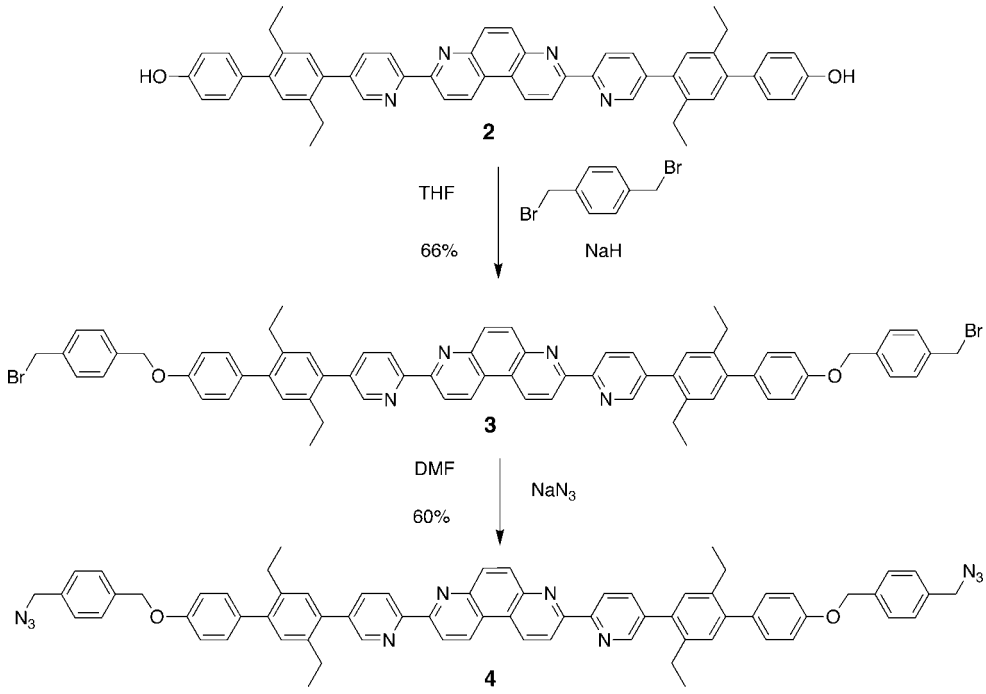
Compound **2** was prepared following a previously published procedure.[16] The presence of ethyl groups grafted on the phenyl rings is essential in order to increase the solubility of the molecule. The unsubstituted compound corresponding to **2** has been made at first in our team, and unfortunately, it turned out to be almost totally insoluble in the most common solvents. The dibromo derivative **3** was obtained in reasonably good yield from **2** via a double Williamson reaction. In order to avoid the formation of polymers, a large excess of α,α′-dibromo-*p*-xylene (15 equivalents) was used. Compound **3** can be easily obtained upon simple washings with ethanol and water. The thus-obtained bromobenzyl-thread was subsequently reacted with $NaN_3$ (2.4 equivalents) to afford the azide-thread **4** in 60% yield (see Scheme 3). The product was purified by column chromatography, which is essential toward the subsequent threading reaction (Scheme 5).

The stopper precursor **6** used to change the [3]pseudorotaxane $\mathbf{8}\cdot 2PF_6$ of Scheme 5 into a real rotaxane was synthesized according to recent literature[28,29] starting from the phenol stopper **5**[28] and propargyl bromide (Scheme 4).

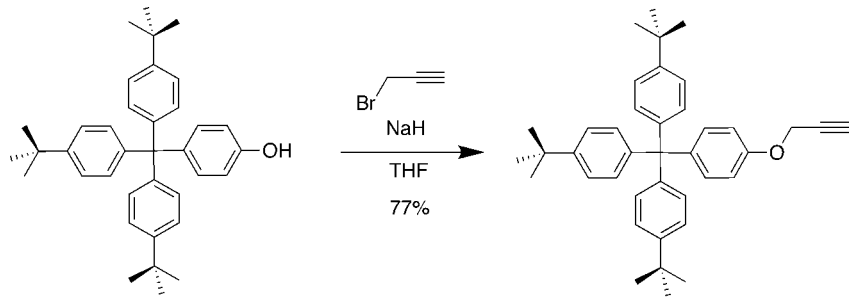
**1.3. Threading Reaction Leading to the [3]Pseudorotaxane.** The thermodynamically favored [3]pseudorotaxane can only be obtained quantitatively if no impurities are present that could interfere with the equilibrium. Indeed respecting the stoichiometry is very important for this kind of reactions, and is obviously only possible if compounds of high purity are used. The pseudorotaxane $\mathbf{8}^{2+}$ was synthesized by threading **4** into macrocycle **7**, using $[Cu(CH_3CN)_4](PF_6)$ in a degassed solvent

(18) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064.
(19) Rostovtsev, V. V.; Green, L. G.; Fokin, V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.
(20) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.
(21) Huisgen, R. *Angew. Chem.* **1963**, *75*, 565–598.
(22) Aucagne, V.; Berna, J.; Crowley, J. D.; Goldup, S. M.; Hänni, K. D.; Leigh, D. A.; Lusby, P. J.; Ronaldson, V. E.; Slawin, A. M. Z.; Viterisi, A.; Walker, D. B. *J. Am. Chem. Soc.* **2007**, *129*, 11950–11963.
(23) Aprahamian, I.; Dichtel, W. R.; Ikeda, T.; Heath, J. R.; Stoddart, J. F. *Org. Lett.* **2007**, *9*, 1287–1290.
(24) Miljanic, O. S.; Dichtel, W. R.; Mortezaei, S.; Stoddart, J. F. *Org. Lett.* **2006**, *8*, 4835–4838.
(25) Durot, S.; Mobian, P.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron* **2008**, *64*, 8496–8503.
(26) Prikhod'ko, A. I.; Durola, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2008**, *130*, 448–449.
(27) Coutrot, F.; Romuald, C.; Busseron, E. *Org. Lett.* **2008**, *10*, 3741–3744.
(28) Gibson, H. W.; Lee, S.-H.; Engen, P. T.; Lecavalier, P.; Sze, J.; Shen, Y. X.; Bheda, M. *J. Org. Chem.* **1993**, *58*, 3748–3756.
(29) (a) Aucagne, V.; Hänni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker, B. D. *J. Am. Chem. Soc.* **2006**, *128*, 2186–2187. (b) Mobian, P.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **2006**, *47*, 4907–4909.

***Scheme 3.*** Preparation of the Thread Bearing Two Terminal Azide Functions




***Scheme 4.*** Synthesis of the Acetylenic Stopper Precursor




mixture of $CH_2Cl_2$ and MeCN (2:1), as shown in Scheme 5. After 3 days at room temperature, in the absence of light and oxygen, [3]pseudorotaxane $\mathbf{8}^{2+}$ was obtained in quantitative yield and characterized by $^1$H NMR and ES-MS.

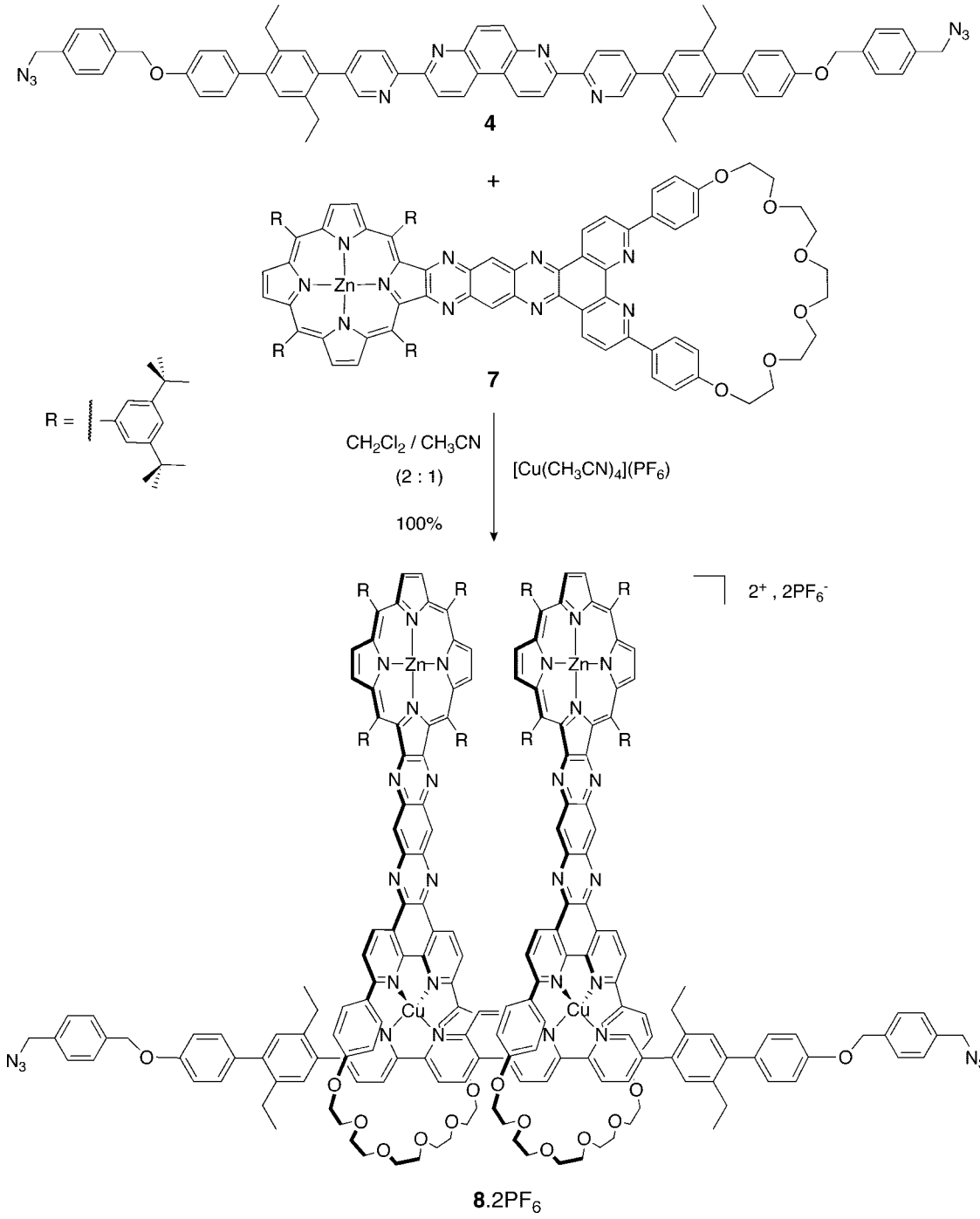
**1.4. Stoppering Reaction Yielding the Copper-Complexed [3]Rotaxane and Its Demetalation to the Free [3]Rotaxane.** The experimental conditions used for performing the click chemistry are critical, in part because copper(I) is already present in the molecule and unthreading reactions must be strictly avoided in order to favor formation of the rotaxane versus that of other compounds from the constitutive fragments of $\mathbf{8}^{2+}$. The use of copper(I) instead of classic [$Cu^{II}$−sodium ascorbate] system so as to avoid any competition or reaction with the copper(I) complexes from the [3]pseudorotaxane $\mathbf{8}\cdot 2PF_6$ was thus preferred. Copper(I) was used in excess in order to prevent the precursor complex $\mathbf{8}^{2+}$ from unthreading. A mixed solvent was used in order to ensure a good solubility of the organic molecules (in $CH_2Cl_2$) and the inorganic base and copper source (in MeCN). Finally, the concentration should be as high as possible.

Experimentally, all reagents, namely pseudorotaxane $\mathbf{8}\cdot 2PF_6$, propargylic stopper precursor **6**, copper "catalyst" $[Cu(MeCN)_4](PF_6)$, and $Na_2CO_3$ as a base were mixed. The solids were degassed and dissolved in the minimum amount of solvent (9:1 mixture of $CH_2Cl_2$ and MeCN). Protected from a light exposure, the paste was stirred under argon for 3 days, after which it was evaporated to dryness. Then the product was extracted with $CH_2Cl_2$ and water and subjected to chromatography (silica, gradient elution from $CH_2Cl_2$/MeOH 0% to 1%). Incidentally, the purification of this [3]rotaxane was extremely laborious (more than 10 column chromatographies). The copper(I)-complexed rotaxane $\mathbf{9}^{2+}$ was isolated pure in 45% yield. In terms of quantities, 54 mg was obtained per reaction.

[3]Rotaxane $\mathbf{9}^{2+}$ was fully characterized by cyclic voltammetry, UV−vis spectroscopy, mass spectrometry (ES-MS), and $^1$H NMR (1D, COSY, ROESY, DOSY). Figure 2 shows the aromatic region of the 1D $^1$H NMR spectrum of rotaxane $\mathbf{9}^{2+}$. The complete atom numbering is indicated in Figure 3.

The protons that are labeled by op1, correspond to two different signals in the $^1$H NMR spectrum of the metalated rotaxane $\mathbf{9}^{2+}$. This is due to the fact that the di-*tert*-butylphenyl units attached to the porphyrin moiety are disposed approximately orthogonally to the porphyrin itself. Free rotation is hindered by bulky $^t$Bu groups. Therefore, one op1 proton points "into" the space between the two porphyrins and one "outside" the porphyrins; hence, they correspond to two different

***Scheme 5.*** Copper(I)-Directed Gathering and Threading Reaction




**8**.$2PF_6$

peaks on the NMR spectrum. The same explanation applies to the proton groups labeled by op2, tBu1, and tBu2.

ROESY NMR coupling between $H_{12'}$ of the thread part, $H_{13'}$ of the newly formed triazole unit and $H_{14'}$ of the stopper unit is clear evidence for the success of the stoppering reaction. ROESY couplings are also observed between protons of the thread and protons of the macrocycles, thus leaving no doubt that the axle and the macrocycles are threaded (see the Supporting Information). Protons $H_o$ and $H_m$ of the macrocycles couple with $H_{6'}$, and $H_{7'}$, respectively. Therefore, we can assume that one of the phenyl groups of each macrocycle is situated next to the ethyl bridge of the central 4,7-phenanthroline unit ($H_{6'}$) of the thread, whereas the other one is in close proximity to the diethylphenyl moiety ($H_{7'}$). This is a clear indication that the dihedral distortion angle between the phenanthroline (macrocycle) and the bipyridine ligands (thread) of the Cu(I) metal center is smaller than 90° as it would be for a perfect tetrahedral geometry. The macrocycles are not orthogonal to the thread but rather, they rotate to bring their phenyl units closer to the thread, thus "flattening" the system.

The dicopper [3]rotaxane $\mathbf{9}^{2+}$ could also be characterized by electrospray mass spectrometry (ES-MS). ES-MS (Figure 4) shows two major peaks at *m*/*z* 1975.2829 and 2961.9201 corresponding to $[\mathbf{9} + H]^{3+}$ and $[\mathbf{9}]^{2+}$, respectively. All other small peaks may result from fragmentation of the molecule but could not be assigned. The molecular mass of the compound (6215.30 $g \cdot mol^{-1}$) challenges MALDI-TOF resolution, but its nature and purity could be appreciated using the ES-MS technique.

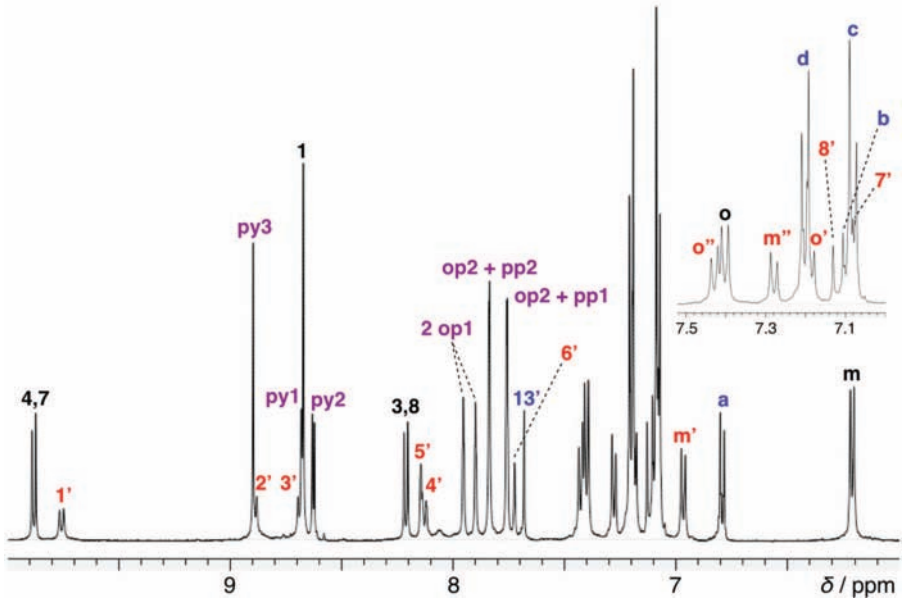



***Figure 2.*** $^1$H NMR (500 MHz, $CD_2Cl_2$, 25 °C) spectrum of rotaxane $\mathbf{9}^{2+}$ displaying the peaks in the 6−10 ppm range. (See Scheme 3 for atom labeling). Protons that are part of the thread are marked with a prime (′).

Rotaxane $\mathbf{9}^{2+}$ represents the receptor in its contracted situation. To be able to study the [3]rotaxane receptor in its extended conformation, the complex had to be demetalated so as to yield the metal-free rotaxane **1**. In the copper-free form, the macrocycles will be able to glide on the axle and rotate around it. An excess of potassium cyanide accomplishes the demetalation as shown in Scheme 6. Compound **1** was easily obtained from $\mathbf{9}\cdot 2PF_6$ by reaction with KCN in $CH_2Cl_2$/MeCN/$H_2O$. After 1 h of stirring, the compound was extracted with $CH_2Cl_2$ and water; the organic layers were separated and evaporated to dryness, yielding **1** in almost quantitative yield (95%).

The macrocycles and their attached porphyrin units can randomly glide on and spin around the thread. Unfortunately, these conformational changes, some of them being probably relatively slow on the NMR time scale, do not allow to characterize rotaxane **1** by $^1$H NMR. Even at low (−40 °C) or high (80 °C) temperatures with DMF-$d_7$ as solvent, the peaks are too broad to allow a detailed analysis. Nevertheless, the compound could unambiguously be identified by mass spectrometry (see the Supporting Information).

The copper-complexed rotaxane $\mathbf{9}^{2+}$ and its free form **1** were studied by cyclic voltammetry. As expected, the various redox couples corresponding to the different electroactive fragments could be observed. They are in agreement with the values determined for related compounds. The electrochemical data for compounds $\mathbf{9}^{2+}$ and **1** are given in the Experimental Section. They clearly show that the various components are mostly electronically decoupled. This observation is not surprising, at least for the two copper(I) complex subunits which are bridged by the 4,7-phenanthroline nucleus. Dicopper complexes have to be bridged by electronically highly coupling ligands to show any electronic coupling.[30]

**2. Host−Guest studies. 2.1. UV−Visible Absorption Spectroscopy. Stability Constants.** The stability constants between the receptor rotaxanes **1** or $\mathbf{9}^{2+}$ and various guests have been determined by UV−visible spectroscopic titrations. The guests used, **G1**−**G5**, are represented in Figure 5.

The bidentate ligand **G1** is the shortest one and the most basic guest (p$K_a$: 8.7 and 4.2) with a distance of 2.8 Å between the nitrogen atoms. It has been used previously in conjunction with various porphyrinic assemblies.[31−33] The guests **G2**−**G5** are constituted by two pyridyl units connected by rigid spacers (0, 1, or 2 phenyl groups) or by a flexible C10 aliphatic chain (**G5**). The Soret band of the Zn-porphyrins is an excellent probe to monitor the complexation reaction between host **1** or $\mathbf{9}^{2+}$ and the various guests. By adding gradual amounts of the bidentate substrate **G1**−**G5** dissolved in toluene to a toluene solution of **1** or $\mathbf{9}^{2+}$, significant bathochromic shift of the Soret band (3−5 nm) was observed, as well as a small hyperchromic effect, in accordance with previous observations.[34]

Clear isosbestic points were observed for all the performed titrations. As examples, Figure 6 and 7 show the spectra, in the range of the Soret band, obtained by titration of the rotaxane **1** and $\mathbf{9}^{2+}$ by the guest **G5**. This behavior constitutes a good indication that one equilibrium only is to be considered. In addition, the 1:1 stoichiometry is corroborated by a mathematical treatment of the spectroscopic data by Specfit 32 software since the best fit is obtained for the 1:1 model.

The stability constants for the complexes corresponding to the following equilibrium have been determined, $H + G \rightleftharpoons [H\cdot G]$, $K = [H\cdot G]/[H \times G]$ (H, **1** or $\mathbf{9}^{2+}$; G, **G1**−**G5**). Their values are reported in Table 1.

Concerning [3]rotaxane **1** the stability constants reflect the high adaptability of the rotaxane host and follow the expected order of basicity of the bis-pyridyl ligands (p$K_a$ **G5** > **G4** ≈ **G3** > **G2**). The less basic and shorter 4,4′-bipyridine **G2** leads

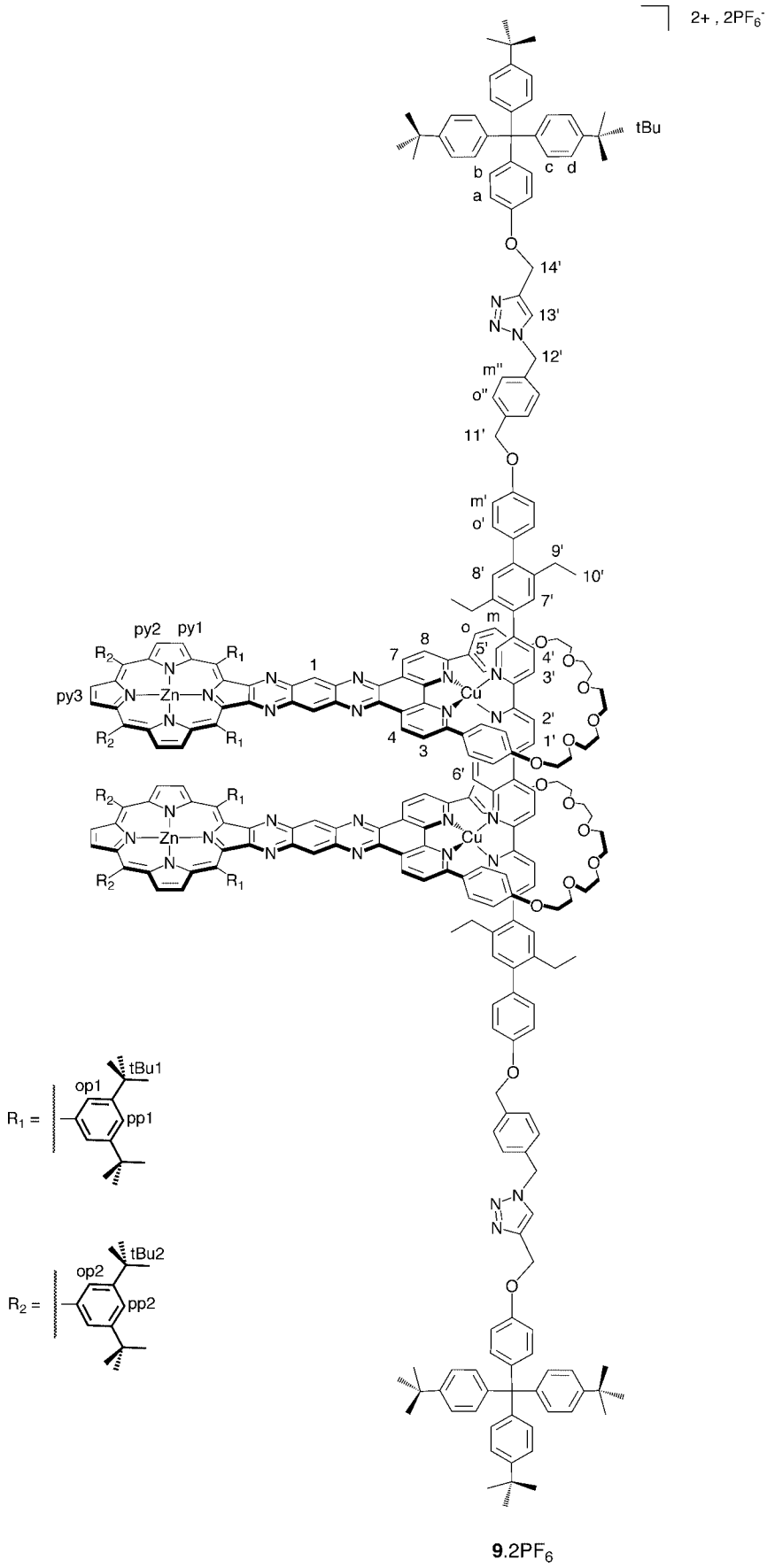
(30) Schwach, M.; Hausen, H.-D.; Kaim, W. *Inorg. Chem.* **1999**, *38*, 2242–2243.

(31) Ballester, P.; Costa, A.; Castlla, A. M.; Deyà, P. M.; Frontera, A.; Gomila, R.; Hunter, C. A. *Chem.−Eur. J.* **2005**, *11*, 2196–2206.

(32) Anderson, H. L.; Hunter, C. A.; Nafees Meah, M.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5780–5789.

(33) Hunter, C. A.; Nafees Meah, M.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5773–5780.

(34) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5075–5080.




**9**.2PF$_6$

***Figure 3.*** Atom numbering of [3]rotaxane $\mathbf{9}^{2+}$.

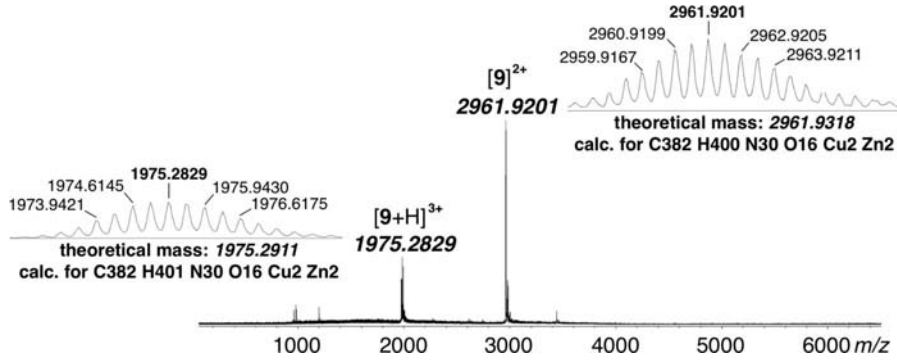
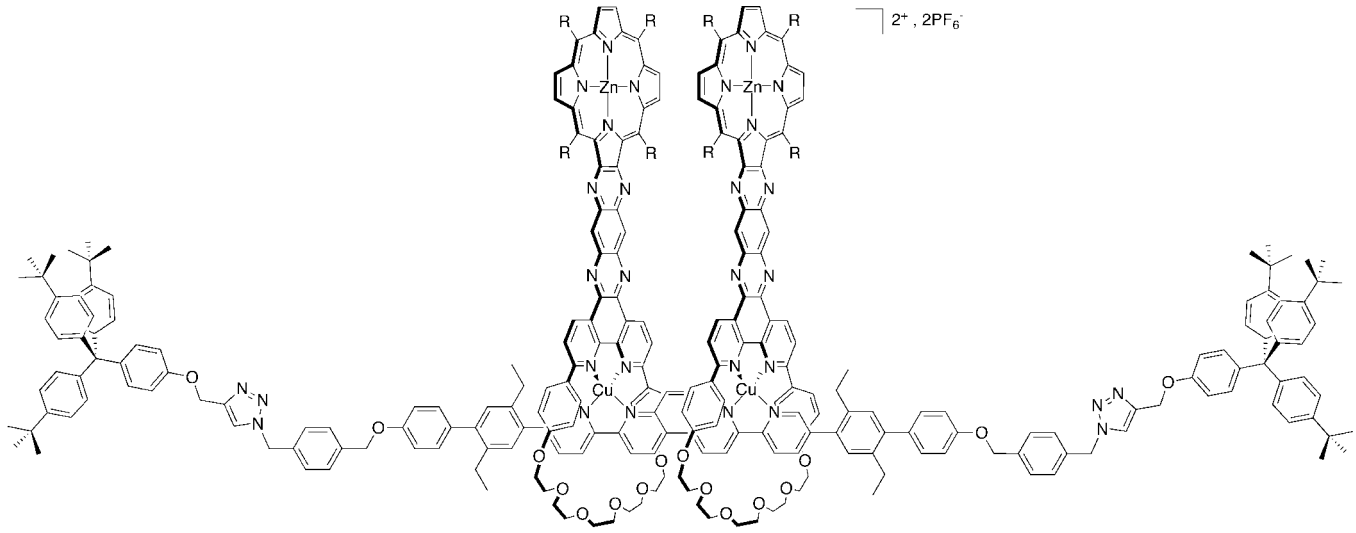


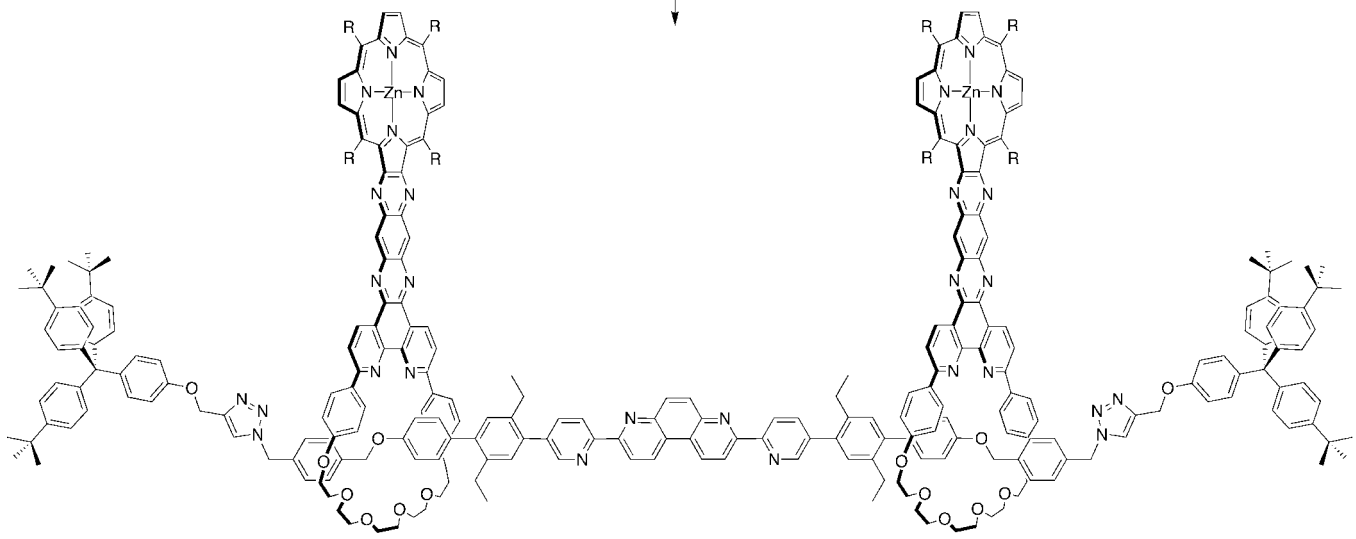

***Figure 4.*** HR ES-MS spectrum of **9**·2$PF_6$. The insets show the experimental isotope profiles observed at the corresponding mass; these were in perfect agreement with simulations.

***Scheme 6.*** Demetalation of $\mathbf{9}^{2+}$




**9**.2$PF_6$

$CH_2Cl_2$ / MeCN / $H_2O$
2:1:1
95%
KCN



**1**

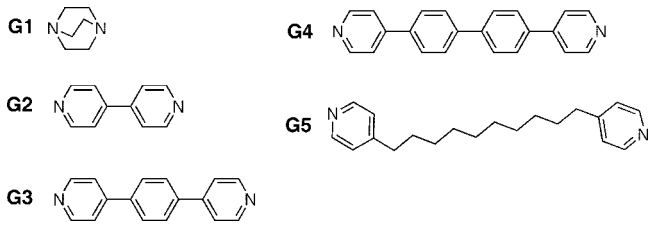



***Figure 5.*** Chemical structures of the guests **G1**−**G5**.

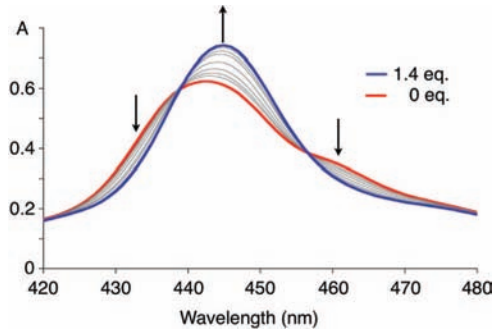



***Figure 6.*** UV−visible titration spectra in toluene (Soret band) of [3]rotaxane **1** ($1.73 \times 10^{-6}$ M) with substrate **G5** from 0 (red curve) to 1.4 equiv (blue curve). Arrows show changes of the host spectrum with increasing guest **G5** concentration.

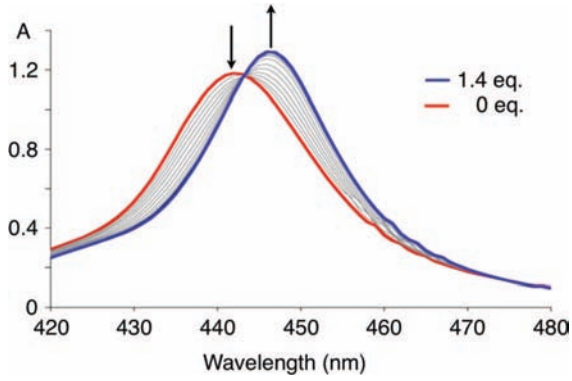



***Figure 7.*** UV−visible titration spectra in toluene (Soret band) of [3]rotaxane **9**·$2PF_6$ ($1.73 \times 10^{-6}$ M) with substrate **G5** from 0 (red curve) to 1.4 equiv (blue curve). Arrows show changes of the host spectrum with increasing guest **G5** concentration.

***Table 1.*** Stability Constants for the [H·G] Complexes Formed with [3]Rotaxane **1** and Copper−[3]Rotaxane **9**·$2PF_6$ and the Bridging Ligands **G1**−**G5**

| bridging ligand | N−N distance in Å, extended conformation (from CPK model) | rotaxane **1** log *K* | copper rotaxane $\mathbf{9}^{2+}$ log *K* |
|---|---|---|---|
| **G1** | 2.8 | 6.3 ± 0.1 | 6.3 ± 0.1 |
| **G2** | 8.2 | 6.0 ± 0.2 | 6.8 ± 0.2 |
| **G3** | 12.3 | 7.0 ± 0.3 | 7.5 ± 0.4 |
| **G4** | 16.5 | 7.0 ± 0.3 | 7.0 ± 0.2 |
| **G5** | 18.0 | 7.5 ± 0.2 | 6.8 ± 0.2 |

to the less stable assembly. The electronic coupling between the pyridyl units decreases with the distance inducing two more basic sites and as a consequence a higher stability of the corresponding complexes. The relatively low value of *K* for the strongly basic **G1** guest (DABCO) indicates probably that steric factors due to the bulky groups in meso position of the porphyrins require a longer bridge to fit the Zn−Zn distance. This hypothesis is also in accordance with the fact that the stability constants for **G1** are identical for the free **1** rotaxane and the copper-metalated [3]rotaxane $\mathbf{9}^{2+}$.

Regarding [3]rotaxane $\mathbf{9}^{2+}$ the following observations can be made (i) the guest **G3** leads to the strongest complex as compare to **1**, probably because of its basicity and of a large gain of entropy for the preorganized [3]rotaxane $\mathbf{9}^{2+}$, (ii) the entropic factor can also be invoked to explain the relative high stability constant with the **G2** guest, and (iii) for guests **G4** and **G5**, the entropic gain is not enough to compensate the deformation of the complexes formed by guests inclusion that obviously do not fit the distance between parallel porphyrinic units.

**2.2. $^1$H NMR DOSY Studies. 2.2.1. $^1$H NMR DOSY Experiment on Free [3]Rotaxane 1.** Diffusion-ordered spectroscopy enables to separate the NMR signals of different species according to their diffusion coefficient.[35] It allows therefore to determine whether different species are present in solution and provides an estimation of the hydrodynamic radius of molecules, thanks to the Stokes−Einstein equation, from the measured diffusion coefficient.[36] This experiment was particularly ingenious to characterize free [3]rotaxane **1** since slow internal motions of the molecule gave unexploited NMR spectrum. The DOSY spectra of the free [3]rotaxane **1** obtained after demetalation of $\mathbf{9}^{2+}$ is represented in Figure 8. It shows that only one species **1** is formed in solution upon demetalation, characterized by a diffusion coefficient of 130 $\mu m^2 \cdot s^{-1}$.

Knowing the experimental diffusion coefficient, we estimate the size of the molecule in solution, using the Stokes−Einstein equation applied to an ellipsoid model with *a* (2*a*, length), *b* (2*b*, height), and *c* (2*c*, width).[37] The length of the axle (2*a*) was estimated from a simulation of $\mathbf{9}^{2+}$ on Hyperchem by using MM2 energy minimization calculations (Figure 9a). The length is around 85−90 Å, taking into account the solvation sphere. Using this value in the Stokes−Einstein equation, we deduce a height and a width of $2b = 2c = 75-77$ Å, which is about twice the length of the macrocycle (lm = 35−37 Å). These values fit very well with the theoretical model if we consider that the rings are free to move along and around the axle (Figure 9b).

**2.2.2. $^1$H NMR DOSY Studies of the Host−Guest Complexes.** DOSY experiments were performed on [3]rotaxane $\mathbf{9}^{2+}$ or **1** with guests **G2** and **G5**. As an example, upon addition of 1 equiv of flexible guest **G5** in a deuterated dichloromethane solution of **1**, a new spectrum is obtained corresponding to the formation of only one species, the host−guest complex [**1**·**G5**]. This complex diffuses much faster than **1**, as attested by the higher diffusion coefficient, 240 $\mu m^2 \cdot s^{-1}$ (Figure 10). This can be understood by the lower overall volume occupied by the host−guest complex compared to the free [3]rotaxane **1**. Indeed, in **1**, the two rings are free to glide and turn around the thread, whereas in the host−guest complex, the two rings being linked together by the guest, they can only moved in a concerted way. Whereas usual proton NMR spectroscopy could not give us evidence of formation of a 1:1 host−guest complex due to the complexity of the spectrum, DOSY experiment could show it irrefutably.

(35) (a) Stejskal, O. E.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288–292. (b) Johnson, R., Jr. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203–256, and references therein. (c) Morris, G. A. *Encycl. Nucl. Magn. Reson.* **2002**, *9*, 35–44. (d) Cohen, Y.; Avram, L.; Frish, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 520–554, and references therein.
(36) (a) Waldeck, A. R.; Kuchel, P. W.; Lennon, A. J.; Chapman, B. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1997**, *30*, 39–68. (b) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351–384.
(37) Callaghan, P. T. *Aust. J. Phys.* **1984**, *37*, 359–387.

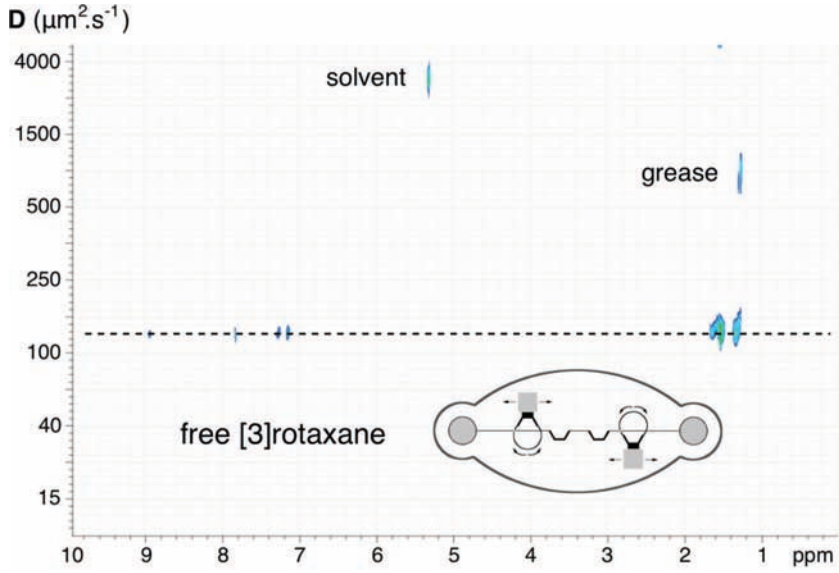



***Figure 8.*** DOSY spectrum of free [3]rotaxane **1** in $CD_2Cl_2$ and a schematic representation of the average occupied volume of the molecule.

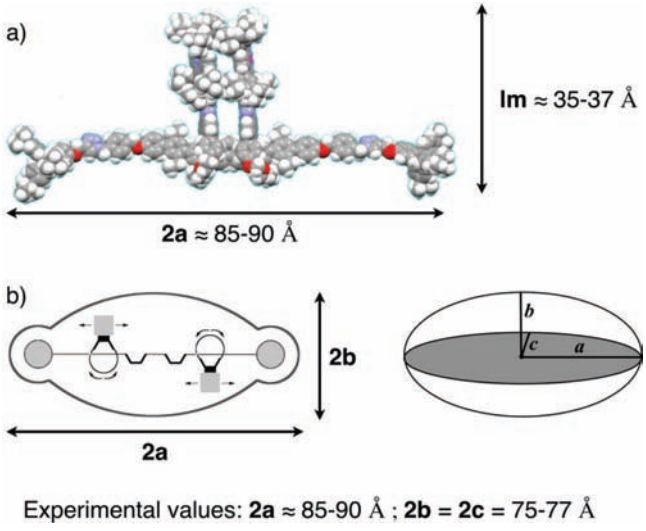



***Figure 9.*** (a) Space-filling Hyperchem model of $\mathbf{9}^{2+}$ after energy minimization by MM2 calculations. (b) Schematic representation of the average occupied volume of **1** and the experimental values found using an ellipsoid model with three parameters *a* (2*a*, length), *b* (2*b*, height), and *c* (2*c*, width).

The same DOSY experiment was done starting from a $CD_2Cl_2$ solution of [3]rotaxane $\mathbf{9}^{2+}$ to which 1 equiv of **G5** was added. Again, only one host−guest complex $[\mathbf{9}\cdot\mathbf{G5}]^{2+}$ was formed, but in this case, the diffusion coefficient is the same for [3]rotaxane $\mathbf{9}^{2+}$ and $[\mathbf{9}\cdot\mathbf{G5}]^{2+}$ (250 $\mu m^2 \cdot s^{-1}$). In fact, once the porphyrinic macrocycles are fixed to the rail by copper(I), inclusion of the guest between the porphyrins does not affect significantly the overall volume of the complex in solution.

## Experimental Section

**1. General Methods.** Dry solvents were distilled from suitable drying agents (THF from sodium/benzophenone; $CH_2Cl_2$ from $P_2O_5$). Thin layer chromatography was carried out using precoated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL G/$UV_{254}$). Preparative column chromatography was carried out using silica gel (Merck Kieselgel, silica gel 60, 0.063−0.200 mm). Flash column chromatography was carried out using silica gel (Merck Geduran, silica gel 60, 40−63 $\mu$m).

NMR spectra for $^1H$ were acquired on Bruker AVANCE 500 or 300 spectrometers. The $^{13}C$ NMR spectra were proton-decoupled. The spectra were referenced to residual proton-solvent references ($^1H$, $CD_2Cl_2$ at 5.32 ppm, $CDCl_3$ at 7.25 ppm; $^{13}C$, $CD_2Cl_2$ at 54.0 ppm and $CDCl_3$ at 77.23 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; tt, triplet of triplets; dt, doublet of triplets; m, multiplet), the value of the coupling constants in Hz if applicable, the assignment and finally the number of protons implied.

Mass spectra were obtained by using a VG ZAB-HF (FAB) spectrometer, a VG-BIOQ triple quadrupole, positive mode, a Bruker MicroTOF spectrometer (ES-MS). MALDI analysis were performed on an Autoflex II TOF/TOF Bruker Daltronics spectrometer.

**2. Starting Materials.** All chemicals were of best commercially available grade and used without further purification (unless mentioned). DABCO and 4,4′-bipyridine were purchased from Aldrich. Compounds **2**,[16] **5**,[28] **6**,[28,29] and **7**[14] were prepared according to literature procedures. The guests **G3** (1,4-bis(4-pyridyl)benzene) and **G4** (4,4′-bis(4-pyridyl)biphenyl) were prepared by Suzuki coupling reactions between pyridine-4-boronic acid and the corresponding *p*-dibromobenzene and *p*-dibromodiphenyl, respectively, according to published procedures.[38]

**3. Electrochemistry.** Electrochemical measurements were performed with a three-electrode system consisting of a platinum disk working electrode, a platinum wire counter electrode, and a silver wire as a pseudoreference electrode. All measurements were carried out at room temperature under argon, in degassed spectroscopic grade solvents, using 0.1 M $n$-$Bu_4NPF_6$ solutions in $CH_2Cl_2$ as supporting electrolyte. Ferrocene ($E°$ $Fc/Fc^+$ = 0.56 V vs SCE) was used as an internal reference, all redox potentials are given versus SCE. The scan rate is 100 $mV \cdot s^{-1}$. An EG&G Princeton Applied Research model 273A potentiostat connected to a computer was used (software from Electrochemistry Research).

**4. Spectral and Equilibrium Constant Measurements.** UV−visible spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 25 °C with 1 cm path cell. All measurements were made in toluene solutions, $1.725 \times 10^{-6}$ M in rotaxane **1** or $\mathbf{9}^{2+}$. Guests **G1**−**G5** toluene solutions ($5.18 \times 10^{-5}$ M) were added to the rotaxane sample in 10 $\mu$L aliquots via a 100-$\mu$L Hamilton syringe. UV−visible spectrophotometric titrations were analyzed by fitting the series of spectra at 1 nm intervals by

(38) Han, Y.-F.; Lin, Y.-J.; Jia, W.-G.; Jin, G.-X. *Organometallics* **2008**, *27*, 4088–4097.

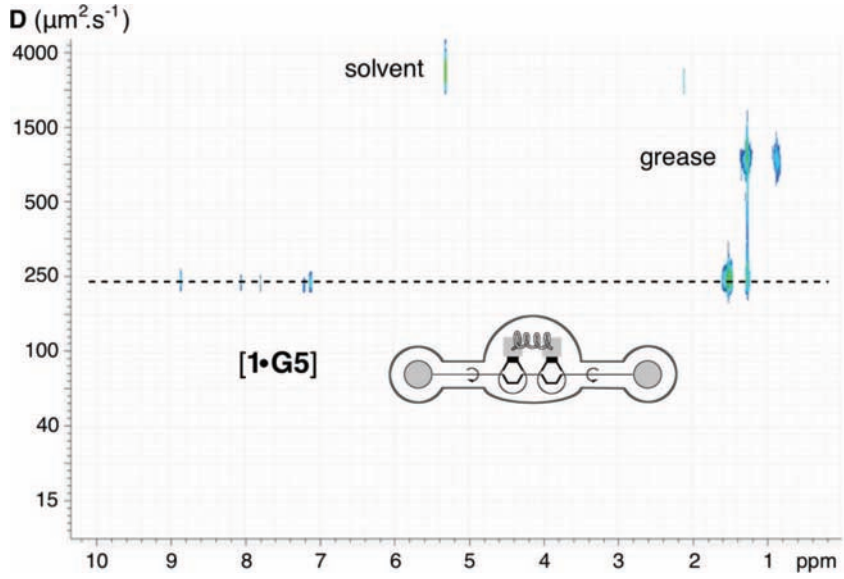



***Figure 10.*** DOSY spectra obtained upon addition of 1 equiv of guest **G5** to a $CD_2Cl_2$ solution of [3]rotaxane **1** and a schematic representation of the average occupied volume of [**1**·**G5**].

using the SPECFIT/32 3.0 (Spectrum Software Associates), which takes into account the changes in volume during the titration.[39]

**5. DOSY Experiments.** Diffusion NMR spectroscopy measurements were acquired on a Bruker Avance spectrometer, at the resonating frequency of 500.13 MHz for $^1$H, using a Bruker BBI 5 mm probe. Samples were prepared in $CD_2Cl_2$, and the temperature was regulated at 298 K. The diffusion NMR experiments were performed with a pulsed-field gradient stimulated echo sequence (PFGSTE),[40] using bipolar gradients of 1200 $\mu$s each. Diffusion time was optimized to 150 ms for [3]rotaxane **1** and 250 ms for [3]rotaxane $\mathbf{9}^{2+}$ and [$\mathbf{9}^{2+}$·**G5**]. To build the diffusion dimension, the pulsed-field gradient was linearly incremented from 0.5 to 47 Gauss·cm$^{-1}$, in 30 steps. The NMR diffusion experiment was adjusted to finally obtain a signal-to-noise ratio of 60. DOSY spectra were generated by the program NMRNotebook 2.5 (DOSY module), developed by the NMRTec company (http://www.nmrtec.com), using adapted algorithms, such as inverse Laplace transform and maximum entropy,[41] to calculate diffusion dimension.

**6. Bromo-*p*-xylene Thread (3).** A 250 mL round-bottom flask was loaded under argon atmosphere with the phenol thread **2** (200 mg, $2.55 \times 10^{-4}$ mol) and NaH (51 mg in oil suspension (60%), 1.28 mmol) in 80 mL freshly distilled THF. After 20 min of stirring at room temperature a solution of α,α′-dibromo-*p*-xylene (1.01 g, 3.82 mmol) in 80 mL of freshly distilled THF was added. The reaction mixture was then heated to 60 °C under argon for 17 h. NaH (20 mg) was added, and the solution was stirred at 60 °C under argon for another 2 days. The solvent was then evaporated and the remaining solid dissolved in $CH_2Cl_2$. The organic layer was washed with $H_2O$ (2 × 100 mL) then evaporated and the remaining solid washed with $Et_2O$ (3 × 100 mL). The final white compound **3** was obtained in 66% yield (193 mg). $^1$H NMR (400 MHz, $CD_2Cl_2$, COSY, ROESY, 25 °C): $\delta$ 9.13 (d, $J$ = 8.8 Hz, $H_{1'}$, 2H), 8.87 (d, $J$ = 8.8 Hz, $H_{2'}$, 2H), 8.82 (d, $J$ = 8.0 Hz, $H_{3'}$, 2H), 8.77 (d, $J$ = 2.2 Hz, $H_{5'}$, 2H), 8.35 (s, $H_{6'}$, 2H), 7.94 (dd, $J$ = 8.1 Hz, $J$ = 2.2 Hz, $H_{4'}$, 2H), 7.46 (s, $H_{o''} + H_{m''}$, 8H), 7.32 (d, $J$ = 8.6 Hz, $H_{o'}$, 4H), 7.24 (s, $H_{8'}$, 2H) 7.20 (s, $H_{7'}$, 2H), 7.06 (d, $J$ = 8.6 Hz, $H_{m'}$, 4H), 5.13 (s, $H_{11'}$, 4H), 4.55 (s, $H_{12'}$, 4H), 2.68 (m, $H_{9'}$, 8H), 1.16 ppm (m, $H_{10'}$, 12H). MS (MALDI-TOF): *m*/*z* (%) =1149.280 (100) [**3** + H]$^+$ (calcd: 1149.31).

**7. Azide Thread (4).** A Schlenk flask was loaded under argon atmosphere with **3** (72 mg, $6.27 \times 10^{-5}$ mol), $NaN_3$ (9.7 mg, $1.5 \times 10^{-4}$ mol), and 5 mL of DMF. The reaction mixture was then heated to 80 °C and stirred for 20 h. The solvent was then evaporated and the remaining solid dissolved in $CH_2Cl_2$. This organic layer was washed with $H_2O$. Alumina column chromatography ($CH_2Cl_2$/MeOH 0−4%) afforded compound **4** in 60% yield (40 mg). $^1$H NMR (400 MHz, $CD_2Cl_2$, COSY, ROESY, 25 °C): $\delta$ 9.13 (d, $J$ = 8.8 Hz, $H_{1'}$, 2H), 8.88 (d, $J$ = 8.8 Hz, $H_{2'}$, 2H), 8.83 (d, $J$ = 8.4 Hz, $H_{3'}$, 2H), 8.78 (d, $J$ = 2.2 Hz, $H_{5'}$, 2H), 8.36 (s, $H_{6'}$, 2H), 7.95 (dd, $J$ = 8.2 Hz, $J$ = 2.2 Hz, $H_{4'}$, 2H), 7.53 (d, $J$ = 8.1 Hz, $H_{o''}$, 4H), 7.39 (d, $J$ = 8.1 Hz, $H_{m''}$, 4H), 7.33 (d, $J$ = 8.7 Hz, $H_{o'}$, 4H), 7.25 (s, $H_{7'}$, 2H), 7.22 (s, $H_{8'}$, 2H), 7.08 (d, $J$ = 8.6 Hz, $H_{m'}$, 4H), 5.15 (s, $H_{11'}$, 4H), 4.39 (s, $H_{12'}$, 4H), 2.68 (m, $H_{9'}$, 8H), 1.15 ppm (m, $H_{10'}$, 12H). MS (MALDI-TOF): *m*/*z* (%) =1073.43 (100) [**4** + H]$^+$ (calcd: 1073.50).

**8. [3]Pseudorotaxane (8·2PF$_6$).** An oven-dried 100 mL two-necked round-bottom flask was loaded under argon with the Zn-porphyrin macrocycle **7** (135.6 mg, $7.45 \times 10^{-5}$ mol) in solution in 25 mL freshly distilled and degassed $CH_2Cl_2$ and $[Cu(MeCN)_4](PF_6)$ (28.90 mg, $7.75 \times 10^{-5}$ mol) in 25 mL degassed MeCN. The mixture was stirred for one hour in absence of light at room temperature. Then **4** (40 mg, $3.72 \times 10^{-5}$ mol) in 25 mL of freshly distilled and degassed $CH_2Cl_2$ was added via canula technique. After 3 days of stirring under argon and in the absence of light, the solvents were evaporated and the [3]pseudorotaxane **8**·2PF$_6$ was obtained quantitatively. $^1$H NMR (500 MHz, $CD_2Cl_2$, COSY, ROESY, 25 °C): $\delta$ 9.88 (d, $J$ = 8.0 Hz, $H_{4,7}$, 4H), 9.77 (d, $J$ = 8.8 Hz, $H_{1'}$, 2H), 8.91 (s, $H_{py3}$, 4H), 8.91 (d, $J$ = 8.8 Hz, $H_{2'}$, 4H), 8.76 (d, $J$ = 4.5 Hz, $H_{py1}$, 4H), 8.74 (s, $H_1$, 4H), 8.71 (d, $J$ = 4.5 Hz, $H_{py2}$, 4H), 8.71 (d, $J$ = 8.8 Hz, $H_{3'}$, 2H), 8.21 (d, $J$ = 8.0 Hz, $H_{3,8}$, 4H), 8.13 (d, $J$ = 8.8 Hz, $H_{4'}$, 4H), 8.08 (s, $H_{5'}$, 2H), 7.96 (bs, $H_{op1}$, 4H), 7.91 (bs, $H_{op1}$, 4H), 7.88 (bs, $H_{pp2}$, 4H), 7.83 (bs, $H_{op2}$, 4H), 7.78 (bs, $H_{pp1}$, 4H), 7.77 (bs, $H_{op2}$, 4H) 7.74 (s, $H_{6'}$, 2H), 7.45 (d, $J$ = 8.3 Hz, $H_{o''}$, 4H), 7.42 (d, $J$ = 8.3 Hz, $H_o$, 8H), 7.32 (d, $J$ = 8.3 Hz, $H_{m''}$, 4H), 7.22 (d, $J$ = 8.7 Hz, $H_{o'}$, 4H), 7.15 (s, $H_{8'}$, 2H), 7.11 (s, $H_{7'}$, 2H), 7.00 (d, $J$ = 8.7 Hz, $H_{m'}$, 4H), 6.23 (d, $J$ = 8.3 Hz, $H_m$, 8H), 5.09 (s, $H_{11'}$, 4H), 4.31 (s, $H_{12'}$, 4H), 4.02−3.75 (m, $H_\alpha + H_\beta + H_\gamma + H_\delta + H_\varepsilon$, 40H) 2.65−2.55 (2q, $J$ = 6.8 Hz, $H_{9'}$, 8H) 1.48 (s, $H_{tBu1}$, 36H) 1.44 (s, $H_{tBu1}$, 36H), 1.41 (s, $H_{tBu2}$, 36H), 1.17 (s, $H_{tBu2}$, 36H), 0.87 ppm (t, $J$ = 6.8 Hz, $H_{10'}$, 12H). MS (ES): *m*/*z* (%) = 2418.543 (100) [**8**]$^{2+}$(calcd: 2418.579). UV−vis $\lambda_{max}$ ($\varepsilon$ in L·mol$^{-1}$·cm$^{-1}$) in dichloromethane: 438 ($5.75 \times 10^5$), 535 ($6.76 \times 10^4$), 705 ($1.78 \times 10^4$).

(39) Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler, A. D. *Talanta* **1985**, *32*, 257–264.
(40) Tanner, J. E. *J. Chem. Phys.* **1970**, *52*, 2523–2526.
(41) Delsuc, M. A.; Malliavin, T. E. *Anal. Chem.* **1998**, *70*, 2146–2148.

**9. Metalated [3]Rotaxane (9·2PF$_6$). CAUTION**: *Copper acetylides, which are a potential byproduct of this reaction, are shock-sensitive when dry!*

A 5 mL Schlenk flask was loaded under argon atmosphere with **8**·2PF$_6$ (100 mg, $1.95 \times 10^{-5}$), alkyne stopper **6** (32 mg, $5.85 \times 10^{-5}$ mol), $Na_2CO_3$ (1 mg, $0.97 \times 10^{-5}$ mol), and $[Cu(MeCN)_4](PF_6)$ (14.6 mg, $3.92 \times 10^{-5}$ mol). Freshly distilled and degassed $CH_2Cl_2$ (1.8 mL) and 0.2 mL of degassed MeCN were added as solvents. The mixture was then left stirring, under argon, at room temperature and in the absence of light for 3 days. The solvents were then evaporated, and the remaining solid dissolved again in $CH_2Cl_2$ and washed with $H_2O$. After several column chromatographies on silica ($CH_2Cl_2$/MeOH 99:1), the pure rotaxane **9**·2PF$_6$ was obtained in 45% yield (54 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$, COSY, ROESY, 25 °C): $\delta$ 9.88 (d, $J$ = 8.0 Hz, $H_{4,7}$, 4H), 9.75 (d, $J$ = 9.0 Hz, $H_{1'}$, 2H), 8.90 (s, $H_{py3}$, 4H), 8.89 (d, $J$ = 9.0 Hz, $H_{2'}$, 2H), 8.69 (d, $J$ = 8.7 Hz, $H_{3'}$, 2H), 8.78 (d, $J$ = 4.4 Hz, $H_{py1}$, 4H), 8.67 (s, $H_1$, 4H), 8.63 (d, $J$ = 4.4 Hz, $H_{py2}$, 4H), 8.21 (d, $J$ = 8.0 Hz, $H_{3,8}$, 4H), 8.14 (bs, $H_{5'}$, 2H), 8.13 (d, $J$ = 8.7 Hz, $H_{4'}$, 2H), 7.95 (t, $H_{op1}$, 4H), 7.90 (t, $H_{op1}$, 4H), 7.84 (bd, $H_{pp2}$ + $H_{op2}$, 8H), 7.76 (bd, $H_{op2}$ + $H_{pp1}$, 8H), 7.72 (bs, $H_{6'}$, 2H), 7.68 (s, $H_{13'}$, 2H), 7.43 (d, $J$ = 8.3 Hz, $H_{o''}$, 4H), 7.40 (d, $J$ = 8.3 Hz, $H_o$, 8H), 7.28 (d, $J$ = 8.2 Hz, $H_{m''}$, 4H), 7.21 (d, $J$ = 8.7 Hz, $H_d$, 12H), 7.19 (d, $J$ = 8.9 Hz, $H_{o'}$, 4H), 7.13 (s, $H_{8'}$, 2H), 7.12 (d, $J$ = 8.9 Hz, $H_b$, 4H), 7.08 (d, $J$ = 8.7 Hz, $H_c$, 12H), 7.08 (s, $H_{7'}$, 2H), 6.97 (d, $J$ = 8.9 Hz, $H_{m'}$, 4H), 6.80 (d, $J$ = 8.9 Hz, $H_a$, 4H), 6.21 (d, $J$ = 8.3 Hz, $H_{m,}$ 8H), 5.51 (s, $H_{12'}$, 4H), 5.07 (s, $H_{14'}$, 4H), 5.05 (s, $H_{11'}$, 4H), 3.98−3.73 (m, $H_\alpha$ + $H_\beta$ + $H_\gamma$ + $H_\delta$ + $H_\varepsilon$, 40H), 2.62−2.53 (2q, $J$ = 7.3 Hz, $H_{9'}$, 8H), 1.46 (s, $H_{tBu1}$, 36H), 1.42 (s, $H_{tBu1}$, 36H), 1.39 (s, $H_{tBu2}$, 36H), 1.23 (s, $H_{tBu}$, 54H), 1.14 (s, $H_{tBu2}$, 36H), 1.12−1.07 ppm (2t, $J$ = 7.3 Hz, $H_{10'}$, 12H). MS (ES): $m/z$ (%) = 1975.2829 (100) [**9**$^{2+}$ + H]$^{3+}$ (calcd: 1975.2911) and 2961.9201 [**9**]$^{2+}$ (calcd: 2961.9318). UV−vis $\lambda_{max}$ ($\varepsilon$ in L·mol$^{-1}$·cm$^{-1}$) in dichloromethane: 440 ($2.39 \times 10^5$), 536 ($6.76 \times 10^4$), 703 ($1.78 \times 10^4$). Cyclic voltammetry $E°$ (V/SCE): 0.87 ($\Delta E_p$ = 98 mV; 4e$^-$); −0.64 ($\Delta E_p$ = 102 mV, 2e$^-$); −1.15 (irreversible peak).

**10. Demetalated [3]Rotaxane (1).** Metalated [3]rotaxane **9**·2PF$_6$ (50 mg, $8.05 \times 10^{-5}$ mol) was dissolved in a 2:1:1 mixture of $CH_2Cl_2$/MeCN/$H_2O$ (30 mL). Then ∼50 equiv of KCN (26.2 mg, $4.02 \times 10^{-3}$ mol) was added, and the reaction mixture was vigorously stirred during 1 h. The solution was then extracted with $CH_2Cl_2$ and water; the organic layers were separated and evaporated to dryness. The crude product is then filtered over silica ($CH_2Cl_2$/MeOH, 99:1) to give demetalated rotaxane **1** in 95% yield (44 mg). $^1$H NMR was impossible (even at low and high temperatures) due to slow conformational changes—see DOSY Experiments. MS(ES): $m/z$ = 1933.6617 [**1** + 3H]$^{3+}$ (calcd 1933.6770); 1940.9887 [**1** + 2H + Na]$^{3+}$ (calcd 1941.0043); 1948.3159 [**1** + H + 2Na]$^{3+}$ (calcd 1948.3316); 1950.5092 [**1** + 4H]$^{4+}$ (calcd 1950.5096); 1455.7549 [**1** + 3H + Na]$^{4+}$ (calcd 1455.7557); 1461.2512 [**1** + 2H + 2Na]$^{4+}$ (calcd 1461.2511). UV−vis $\lambda_{max}$ ($\varepsilon$ in L·mol$^{-1}$·cm$^{-1}$) in dichloromethane: 437 ($5.01 \times 10^5$), 518 ($6.92 \times 10^4$), 672 ($1.70 \times 10^4$). Cyclic voltammetry $E°$(V/SCE): 0.78 ($\Delta E_p$ = 118 mV; 2e$^-$); −0.75 ($\Delta E_p$ = 195 mV, 2e$^-$); −1.09 ($\Delta E_p$ = 220 mV, 2e$^-$).

**11. 1,10-Di-(4-pyridyl)decane (G5).** A 50 mL three-necked round-bottom flask was loaded with picoline (2 g, 21.4 mmol) and 10 mL of freshly distilled THF. The solution was then cooled to −78 °C (dry ice/acetone bath), and 14.6 mL of *n*-BuLi in hexane (1.6 mol·L$^{-1}$, 23.5 mmol) was slowly added, keeping the temperature below −60 °C. The orange solution was allowed to warm up to room temperature. The yellow solution formed was heated up to 40 °C for 40 min, 7 mL of distilled THF were added, and the resulting solution was cooled down to −78 °C again. 1,8-Dibromooctane was then added slowly to the solution, which was then allowed to warm up to room temperature. Water (15 mL) was added, and the organic and aqueous layers were separated. The aqueous layer was extracted with 3 × 25 mL of $Et_2O$, and all the organic layers were combined, washed with 25 mL of $H_2O$, and dried over $MgSO_4$. After evaporating the solvents, we obtained a yellow oil which solidifies once dried under vacuum. After column chromatography on silica (DCM/MeOH, 99:1) the pure compound was obtained in 43% yield (2.7 g). $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.44 (d, $J$ = 6.3 Hz, $H_A$, 4H) 7.09 (d, $J$ = 6.3 Hz, $H_B$, 4H) 2.57 (t, $J$ = 7.3 Hz, $H_C$, 4H) 1.60 (q, $J$ = 7.4 Hz, $H_D$, 4H) 1.30 ppm (m, $H_E$ + $H_F$ + $H_G$, 12H). $^{13}$C NMR (100 MHz, $CD_2Cl_2$, 25 °C): 149.46, 123.72, 35.03, 30.23, 29.35, 29.25, 29.05 ppm. MS (ES): $m/z$ (%) = 297.2470 (100) [**G5** + H]$^+$ (calcd: 297.2325). UV−vis $\lambda_{max}$ ($\varepsilon$ in L·mol$^{-1}$·cm$^{-1}$) in dichloromethane: 256 ($3.8 \times 10^4$).

## Conclusions

A new [3]rotaxane and its copper complex have been prepared in several steps from sophisticated organic fragments, namely a rigid rod incorporating two bipyridine-like chelates constructed on a 4,7-phenanthroline nucleus and two 1,10-phenanthroline-containing rings, each chelate being connected to a porphyrin by a rigid aromatic spacer. The metal-free [3]rotaxane is a new type of receptor by which guests of very different sizes can be trapped between the two mobile porphyrins since they can move over an 80 Å plate-to-plate distance on the thread. The copper-free [3]rotaxane associates very strongly (log $K$ between 6.3 and 7.5) with guests of lengths comprised between 2.8 and 18 Å and is therefore highly adaptable. In the copper-complexed [3]rotaxane, the rings are fixed by coordination bonds to the rod and the distance between the porphyrins is therefore controlled, at least to a certain extent, leading to destabilization of the host/guest complex with long guests, due to distortions on both the guest and the porphyrin rings. The design of [3]rotaxanes with mobile porphyrinic plates is therefore adapted to the construction of molecular machines behaving as "compressor" of flexible guests upon addition of a metal which blocks the positions of the rings and as an "extensor" when the metal is removed.

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**Supporting Information Available:** Specific region of the ROESY $^1$H NMR spectrum of rotaxane [**9**$^{2+}$](PF$_6^-$)$_2$ and HR ES-MS spectrum of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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