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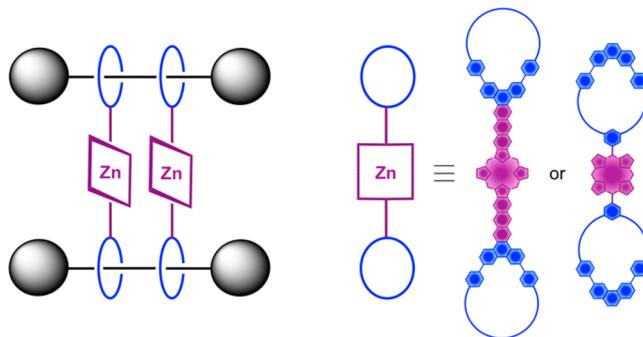
# Cyclic [4]Rotaxanes Containing Two Parallel Porphyrinic Plates: Toward Switchable Molecular Receptors and Compressors

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## CONSPECTUS



Twenty years ago, researchers considered the synthesis of simple rotaxanes a challenging task, but with the rapid development of this field, chemists now view these interlocking molecules as accessible synthetic targets. In a major advance for the field, researchers have developed transition metals or organic molecules as templating structures, making it easier to construct these molecular systems. In addition, chemists have found ways to introduce new functional groups, which have given these compounds new properties. Today researchers can also construct multirotaxanes consisting of several individual components, but the synthesis of the most complex structures remains challenging.

This Account primarily discusses the cyclic [4]rotaxanes incorporating porphyrins that the Strasbourg group has synthesized and studied during the past few years. These cyclic [4]rotaxanes consist of two rigid rods threaded through the four rings of two molecules of a bis-macrocycle, and the synthetic strategy used for making them relies on the copper(I)-driven “gathering-and-threading” reaction. The formation of the threaded precursors was mostly quantitative, and the quadruple stoppering reaction leading to the target compound produces high yields because of the efficient copper-catalyzed azide–alkyne cycloaddition (CuAAC) or click chemistry reaction.

These rotaxanes behave as receptors for various ditopic guests. We prepared and studied two types of molecules: (i) a rigid compound whose copper(I) complex has a well-defined shape, with high selectivity for the guest geometry and (ii) a much more flexible [4]rotaxane host that could act as a distensible receptor. The rigid [4]rotaxane was crystallized, affording a spectacular X-ray structure that matched the expected chemical structure. In addition, metalation or demetalation of the rigid [4]rotaxane induces a drastic geometric rearrangement. The metal-free compound is flat without a binding pocket, while the copper-complexed species forms a rectangle-like structure. The removal of copper(I) also expels any complexed guest molecule, and this process is reversible, making the rigid porphyrinic [4]rotaxane a switchable receptor. The rigid [4]rotaxane was highly selective for short, ditopic guests in its copper(I)-complexed form, but the flexible copper(I)-complexed [4]rotaxane proved to be a versatile receptor. Its conformation can adjust to the size of the guest molecule similar to the induced fit mechanism that some enzymes employ with substrates.

## 1. Introduction

The reasonably easy synthesis of catenanes, rotaxanes, and knots, based on templates of various types,<sup>1–6</sup> has

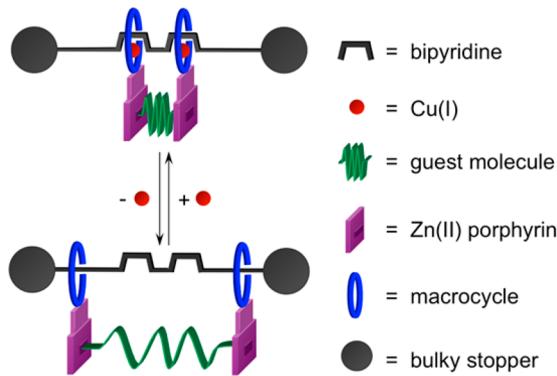
triggered much interest for these molecules. Such compounds had previously been considered as laboratory curiosities rather than as molecules that could be obtained

on a preparative scale.<sup>7–9</sup> More and more functional interlocking ring compounds have been prepared, the function being associated with novel properties in relation to electron transfer,<sup>10–12</sup> polymer science,<sup>13–17</sup> and new materials or controlled dynamic processes.<sup>18–21</sup> This latter topic, referred to as “molecular machinery”, has experienced a spectacular development in the course of the last 15 years, either with compounds of the catenane and rotaxane family or with molecules that do not contain interlocking or threaded rings.<sup>22,23</sup> Porphyrin-containing catenanes and rotaxanes are particularly promising in the context of electron transfer and molecular machines.<sup>24,25</sup> Metal-containing porphyrins such as Zn or Sn porphyrins are able to interact with various Lewis bases,<sup>26</sup> making these groups potential receptors, as amply exemplified in the literature.<sup>27,28</sup>

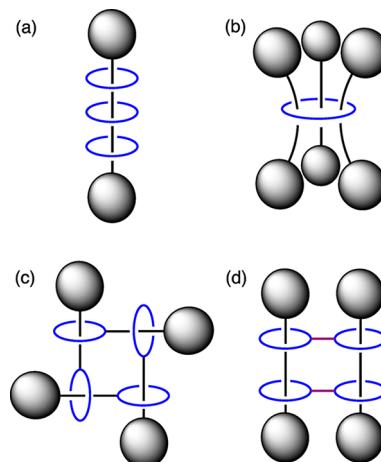
The main topic of this Account will be cyclic [4]rotaxanes containing two porphyrinic plates. These compounds are of interest for their host–guest properties and as potential molecular compressors or switchable receptors. In addition, their preparation represents a real challenge: very few cyclic multirotaxanes have been described so far, most probably due to foreseeable synthetic difficulties without an extremely efficient templated approach. Indeed, the synthesis of such compounds involves several distinct threading reactions and formation of a large cyclic structure with a controlled size instead of polymers or linear oligomers. In recent years, our group has been interested in dynamic molecular receptors containing two parallel porphyrinic plates between which guests of various lengths could be inserted and either compressed or expelled under the action of a chemical signal. A [3]rotaxane belonging to this family of compounds is represented in Figure 1.<sup>29,30</sup> The distance between the two zinc-complexed porphyrin plates can be roughly estimated (8–10 Å) when the template copper(I) centers are still present in the 1,10-phenanthroline-containing coordination sites whereas the Zn···Zn distance can vary in a substantial way when the copper(I) centers are removed, reaching a value of 50 or 60 Å for the situation in which the porphyrins are located close to the stoppers of the rotaxane axis.

## 2. Design and Synthesis Strategy

Multirotaxanes can adopt various topologies.<sup>31</sup> This Account deals with *cyclic* systems, but several types of multirotaxanes whose overall structure is *acyclic* have been described in the past.<sup>32–36</sup> A simple classification consists in distinguishing between compounds constituted by two or several rings threaded by a single thread and those containing one ring threaded by several filament-like components. These two



**FIGURE 1.** A [3]rotaxane acting as a receptor for exotoxic substrates of various lengths.<sup>29,30</sup> By adding copper(I) to the metal-free rotaxane, the complexed substrate can be compressed. The host–guest complex is thus destabilized provided that the guest is longer in its most stable conformation than the Zn···Zn distance in the copper-complexed form of the molecule.



**FIGURE 2.** Examples of [4]rotaxanes with an acyclic (a, b) or cyclic (c, d) structure. (a) Many examples of linear [n]rotaxanes consisting of one axis and  $n - 1$  rings threaded on the axis have been reported,<sup>32,33</sup> including a particularly spectacular example consisting of a [20]rotaxane.<sup>36</sup> (b) Much less common are [n]rotaxanes containing one ring and  $n - 1$  filament-like components passing through the ring.<sup>34</sup> The latter systems are reminiscent of “sheaves” as pointed out by Leigh and co-workers in a recent paper.<sup>35</sup> (c) Example of a cyclic [4]rotaxane originating from the quadruple threading of an axis through a ring using a ring-and-string conjugate as sole component.<sup>37</sup> Such species have been named “daisy-chain” by Stoddart and his group.<sup>38</sup> (d) A different type of cyclic [4]rotaxane is obtained by threading two filaments through the rings of two bis-macrocycles.

families of compounds are schematically represented in Figure 2a,b.

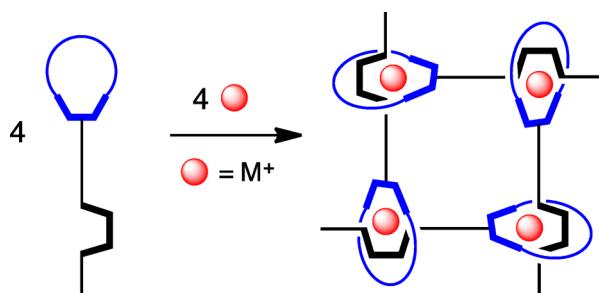
Catenanes and rotaxanes with two-dimensional structures are particularly attractive as challenging synthetic targets, as well as for the potential mechanical properties that materials built with such molecular systems would display. The X-ray structure of a bacteriophage virus, HK97,<sup>39</sup> has triggered great excitement both in molecular biology and in topological

chemistry. The membrane of this virus is an amazingly beautiful multcatenane, self-assembled using mostly hydrogen bonds. It has been very common that biology constitutes a source of inspiration for synthetic chemists. Although synthetic systems with a topology similar to that of HK97 are still out of reach today, the X-ray structure of the virus has been greeted as a particularly inspiring result. Two representative cloth-like interlocking systems are depicted in Figure 2c,d. These topologies are certainly very primitive compared with that of the multicated structure of HK97. Nevertheless, they were considered as challenging species by the catenane and rotaxane community and, at the same time, as promising targets in relation to their properties. As such, they have been prepared in recent years.<sup>37,40,41</sup> The synthesis of two-dimensional catenanes similar to cloth seems nowadays to be less realistic than that of rotaxanes.

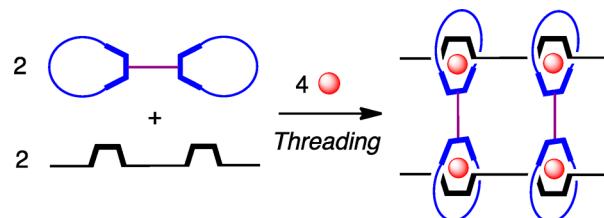
The synthesis strategy for obtaining cyclic multirotaxanes was based on the traditional approach proposed by our group long ago: the “gathering-and-threading approach” using copper(I) and 2,9-diphenyl-1,10-phenanthroline (dpp) coordinating fragments.<sup>42,43</sup> In this approach, dpp chelates are introduced in ring and rod-like molecules, and copper(I) is used to gather the building blocks together and thread the rod through the ring by formation of a tetrahedral complex with the dpp ligands. The principle was generalized to molecular components containing two or several chelating groups and thus able to coordinate two or several copper(I) centers in the course of the assembly step. By using molecular fragments consisting of rings and lateral coordinating filaments, a cyclic “daisy chain” could be obtained in high yield a few years ago as depicted in Figure 3.<sup>37</sup>

Similarly, by using different coordinating fragments such as a bis-macrocycle and a rigid rod-like unit incorporating two chelating groups, addition of copper(I) in the right stoichiometry (2:2:4, respectively) is expected to lead quantitatively to a cyclic [4]pseudorotaxane structure as represented in Figure 4.

It is important to note that both copper(I)-directed threading reactions are performed under thermodynamic control, which is the reason why, experimentally, they are virtually quantitative. Obviously, functionalization of the axis termini by bulky stoppers will lead to real rotaxanes. The main question that could be addressed about the strategy is related to the quantitative threading process. The principle has already been amply described in previous reports.<sup>42,43</sup> The threaded species of Figure 3 or Figure 4 represent the most stable situation among all the other possibilities. For instance, as far as the reaction depicted in Figure 4 is



**FIGURE 3.** Principle of the copper(II)-directed gathering-and-threading reaction leading to a cyclic daisy chain, identical to the cyclic tetramer of a simple [2]pseudorotaxane;<sup>37</sup> the red dot represents copper(II) and the U-shaped sign designates a bidentate chelate. Note that the linker between the back of the ring-included chelate and the chelate belonging to the thread has to be rigid for the four-metal assembly to be obtained.

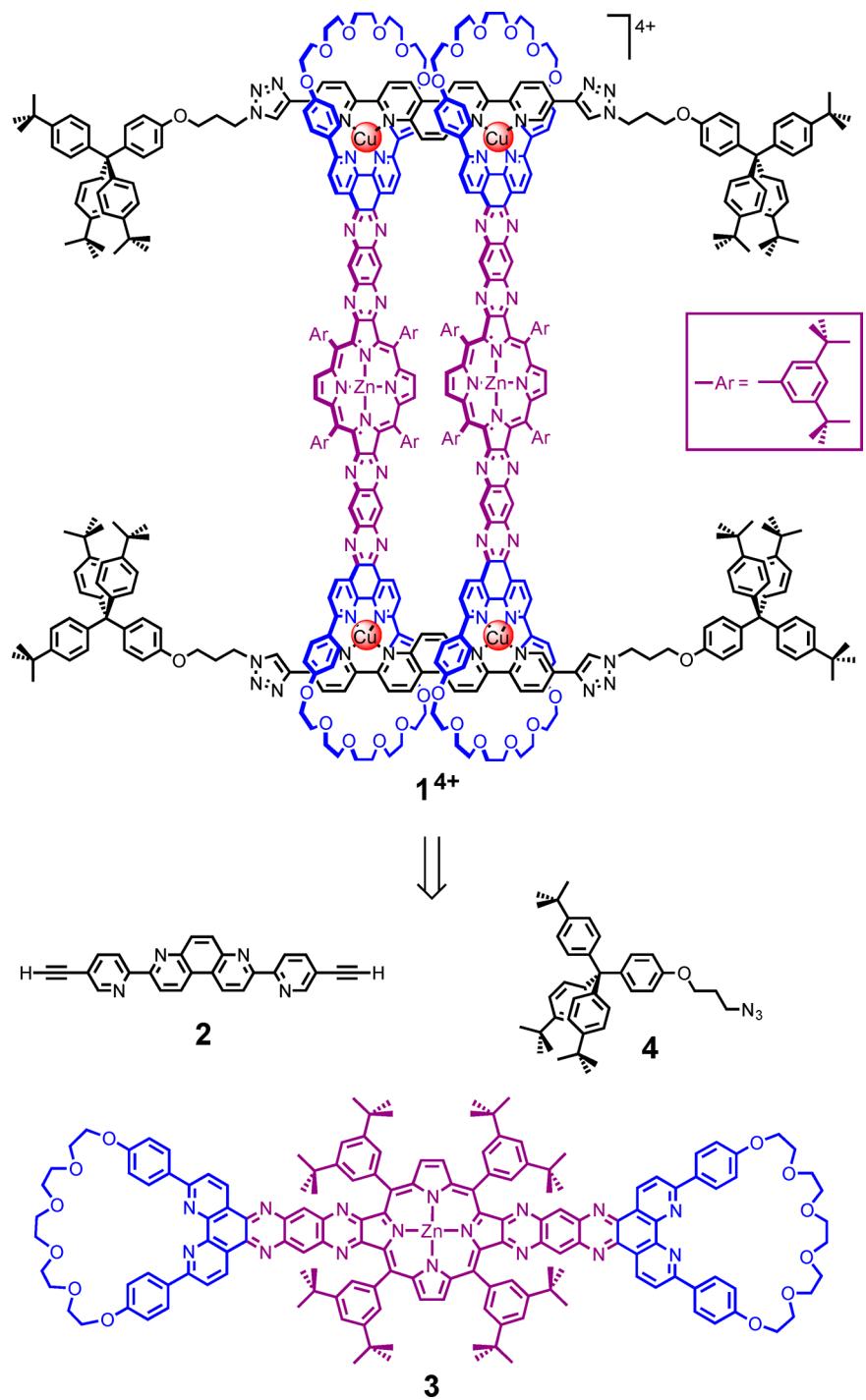


**FIGURE 4.** Copper(II)-driven formation of a cyclic [4]pseudorotaxane from a 2-chelate axis and a bis-macrocycle, each ring incorporating a chelating group. The metal center, Cu(II), is represented by a red dot, and the chelating groups are indicated by a black or blue U-shaped symbol.

concerned, mixing 2 equiv of bis-ring, 4 equiv of copper(II), and 2 equiv of an acyclic ligand will lead to multiply threaded species if the complexation reaction is done under thermodynamic control. With a 2:2:4 stoichiometry (bis-macrocycle/thread/copper(II) 2:2:4), the complex depicted in Figure 4 represents the smallest species in which neither ligands nor metal centers are “frustrated” (i.e., all the ligands are coordinated and all the metal centers are coordinatively saturated). Larger species such as a 4:4:8 grid complex would also avoid frustration; however the formation of the smaller 2:2:4 species is entropically more favorable. The formation of a 1:1:2 complex is geometrically impossible if the bis-macrocycle and thread are rigid. The multiple threading reaction of Figure 4 is thus expected to be quantitative provided the design of bis-macrocycle and thread is appropriate and the reaction stoichiometry is respected accurately.

### 3. A Rigid Copper(I)-Complexed [4]Rotaxane Containing Two Porphyrin Plates: Synthesis, Host–Guest Properties, and Demetalation

**3.1. The Target [4]Rotaxane Molecule  $\mathbf{1}^{4+}$ .** The global structure of the target molecule  $\mathbf{1}^{4+}$  depicted in Figure 5 is a copper(I)-complexed [4]rotaxane constituted by two



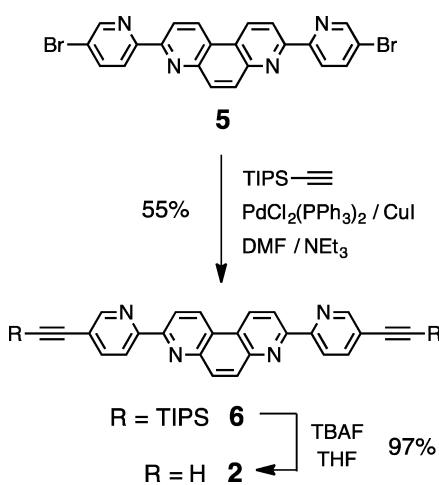
**FIGURE 5.** Target molecule **1<sup>4+</sup>**, a rigid copper(I)-complexed [4]rotaxane containing two porphyrin plates, and its precursors **2**, **3**, and **4**.<sup>41</sup>

bis-macrocycles and two rods. The success of their assembly relies not only on the reaction conditions but also on their design such as the precise position of their ligands and the rigidity of some of their elements. The central part of the rod **2** is made of two side-by-side bidentate chelating units constructed on a central rigid 4,7-phenanthroline nucleus, allowing control of the distance and orientation of the two chelates. The bis-macrocycle **3** contains zinc(II)-complexed

porphyrins rigidly connected to 2,9-diphenyl-1,10-phenanthroline (dpp)-type chelates incorporated in 30-membered rings.<sup>41</sup> Due to their free axial coordination sites, these two porphyrin plates, facing each other, should play the role of connecting places for suitable guests, like adequately oriented diamines ligands. The four blocking groups **4** at the extremities of the rods are introduced using a reaction compatible with the Cu(I)-threaded pseudorotaxane

complex, that is, a mild Cu(I)-catalyzed Huisgen reaction<sup>44,45</sup> between the two terminal acetylene functions of the rods and the azide-functionalized stoppers.

**3.2. Synthesis of the [4]Rotaxane  $\mathbf{1}^{4+}$ .** In order to build the [4]rotaxane  $\mathbf{1}^{4+}$  depicted in Figure 5, a functionalized thread had to be synthesized. This thread is constituted by two bidentate chelates and two terminal acetylenic functions for the later stoppering by “click chemistry”. Its synthesis involves a double Sonogashira coupling with triisopropylsilylacetylene and the dibromo-bisbidentate chelate



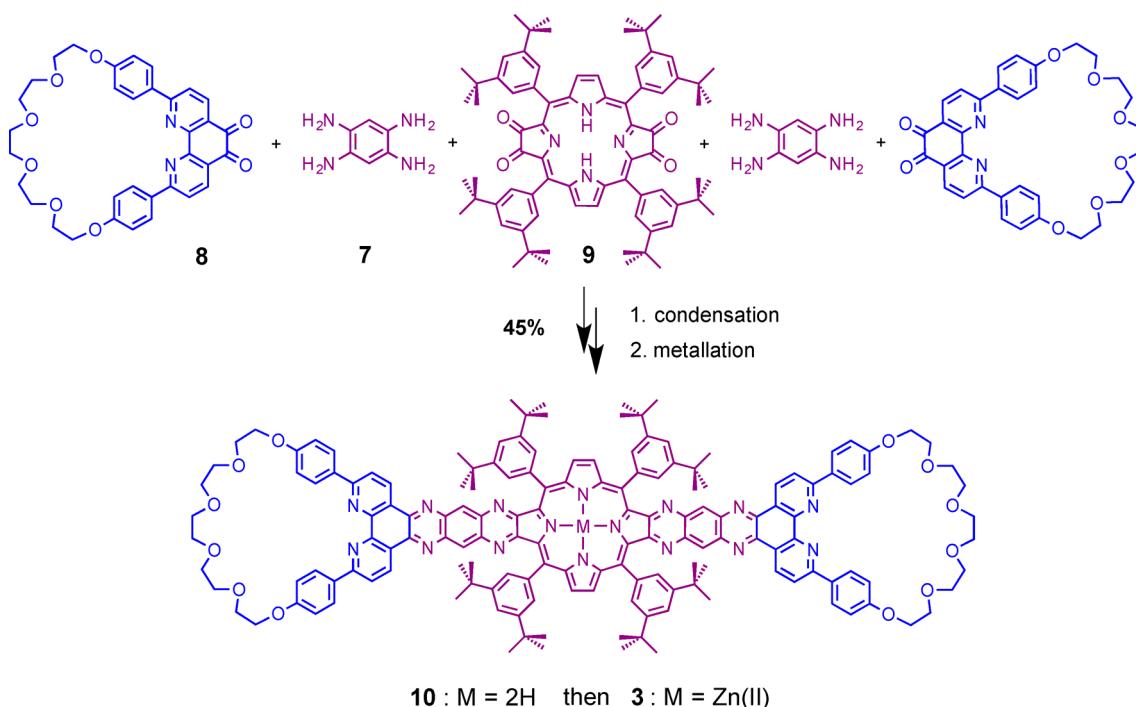
**FIGURE 6.** Synthesis of the alkyne-functionalized thread **2** (TIPS = triisopropylsilyl).<sup>46</sup>

**5** to afford the corresponding thread **6**, which was then deprotected with tetrabutylammonium fluoride (TBAF) to obtain the desired functionalized thread **2** (Figure 6).<sup>46</sup>

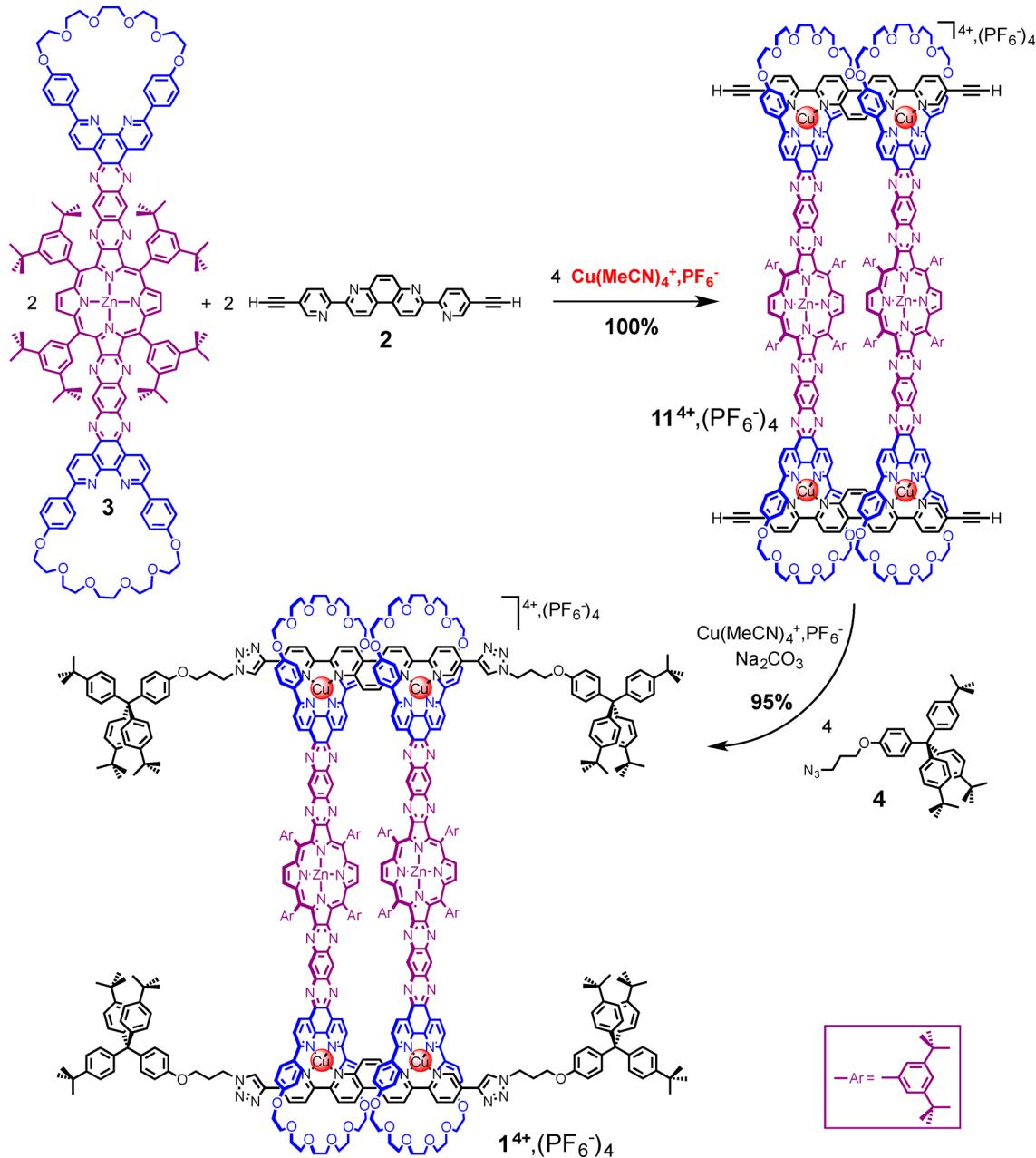
The bis-macrocycle **3**<sup>41</sup> is composed of five parts: one central Zn(II)-complexed porphyrin plate, two chelating macrocycles, and two linkers. In order to minimize the already high number of steps for the synthesis of such a molecule, the synthetic strategy for the final assembly of these components relies on the one-pot condensation of the dione-macrocycles **8**,<sup>47</sup> the tetraone-porphyrin **9**,<sup>48</sup> and the linker **7** (Figure 7). This procedure afforded nonmetalated bis-macrocycle **10** in 45% yield. Metalation of the porphyrinic site of **10** was then carried out using a large excess of Zn(OAc)<sub>2</sub>. After removal of remaining Zn(II) by a treatment with EDTA, the Zn(II)-complexed bis-macrocycle **3** was obtained quantitatively.

In a usual procedure, the copper(I) [4]pseudorotaxane **11**<sup>4+</sup> was prepared following a threading strategy (Figure 8).<sup>49</sup> Bis-macrocycle **3** and Cu(MeCN)<sub>4</sub><sup>+</sup>·PF<sub>6</sub><sup>-</sup> were mixed together in air-free conditions to afford a precursor consisting of one bis-macrocycle and two Cu(I) ions in a mixture of chloroform and acetonitrile. This complex was then added to a stoichiometric amount of thread **2**. After one week of stirring at room temperature, [4]pseudorotaxane **11**<sup>4+</sup> was obtained quantitatively.

The stoppering reaction by “click” chemistry,<sup>50</sup> leading from alkyne-functionalized [4]pseudorotaxane **11**<sup>4+</sup> to



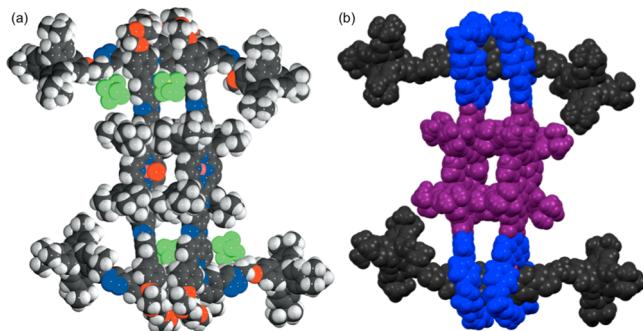
**FIGURE 7.** Synthesis of the porphyrin bis-macrocycle **3**.<sup>41</sup>



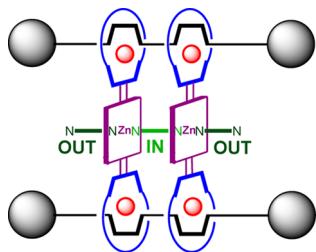
**FIGURE 8.** Quantitative formation of [4]pseudorotaxane  $11^{4+}$ <sup>49</sup> and synthesis of [4]rotaxane  $1^{4+}$  by highly efficient “click” reaction.<sup>41</sup>

[4]rotaxane  $1^{4+}$ , was performed with azide stopper **4**,<sup>46</sup> Na<sub>2</sub>CO<sub>3</sub> as a base, and again  $\text{Cu}(\text{MeCN})_4^+\cdot\text{PF}_6^-$  as a Cu(I) catalyst. The desired [4]rotaxane  $1^{4+}$  was obtained with an excellent yield of 95%.<sup>41</sup> This high yield for a tetra-stoppering reaction can be explained by the very high stability of the pseudorotaxane precursor. The fact that both bis-macrocycles are threaded twice by the same two axles implies that in order to dissociate the system, several unthreading reactions would have to be involved to separate one component from the others. This significantly stabilizes the whole architecture from complete dethreading of the axles.

Rotaxane  $1^{4+}$  was fully characterized by UV-vis spectroscopy, high resolution mass spectrometry (ES-MS) where the tetra-charged compound was clearly identified, and <sup>1</sup>H NMR (1D, COSY, ROESY, and DOSY) with complete assignment of all peaks. The whole structure of [4]rotaxane  $1^{4+}$  has finally been proven unambiguously by crystallography.<sup>41</sup> In this structure, PF<sub>6</sub><sup>-</sup> anions are close to every Cu(I) center and a water molecule is complexed to each porphyrinic Zn(II), inside the cavity between the two plates (Figure 9). The coordination geometry around Cu(I) is a distorted tetrahedron as usually observed for this kind of complex.<sup>46</sup> Particularly noteworthy



**FIGURE 9.** CPK view of the X-ray crystal structure of [4]rotaxane  $\mathbf{1}^{4+}$ . (a) Atoms colored by element: carbon atoms are depicted in gray, hydrogen atoms in white, oxygen atoms in red, nitrogen atoms in blue, zinc atoms in pink, and  $\text{PF}_6^-$  ions in green. (b) Atoms colored by building block: porphyrins and linkers are depicted in purple, coordinating macrocycles in blue, rods and stoppers in black, and  $\text{Cu}(\text{I})$  ions in red.<sup>41</sup>



**FIGURE 10.** The IN and OUT coordination modes of ditopic ligands to the two-porphyrin [4]rotaxane receptor  $\mathbf{1}^{4+}$ .<sup>41</sup>

**TABLE 1.** Stability Constants of Internal Complexes of Ditopic Ligands with Rotaxane  $\mathbf{1}^{4+}$ , Obtained from UV–Visible Titrations in Toluene<sup>a</sup>

Guest	$\log K_{\text{IN}}$	N–N distance in Å
(DABCO)	7.4	2.6
	7.2	7.2
	-	15.9
	-	18.0

<sup>a</sup>N–N distance in Å for the guests obtained from CPK models.<sup>41</sup>

is also the important bending of the two bis-macrocycles, which is due to the bulky di-*tert*-butylphenyl units. Consequently, the distance between the  $\text{Zn}(\text{II})$  ions is significantly larger than the distance between two  $\text{Cu}(\text{I})$  ions coordinated to the same thread (7.75 Å vs 8.68 Å respectively),

which would not be the case if the structure was perfectly rigid.

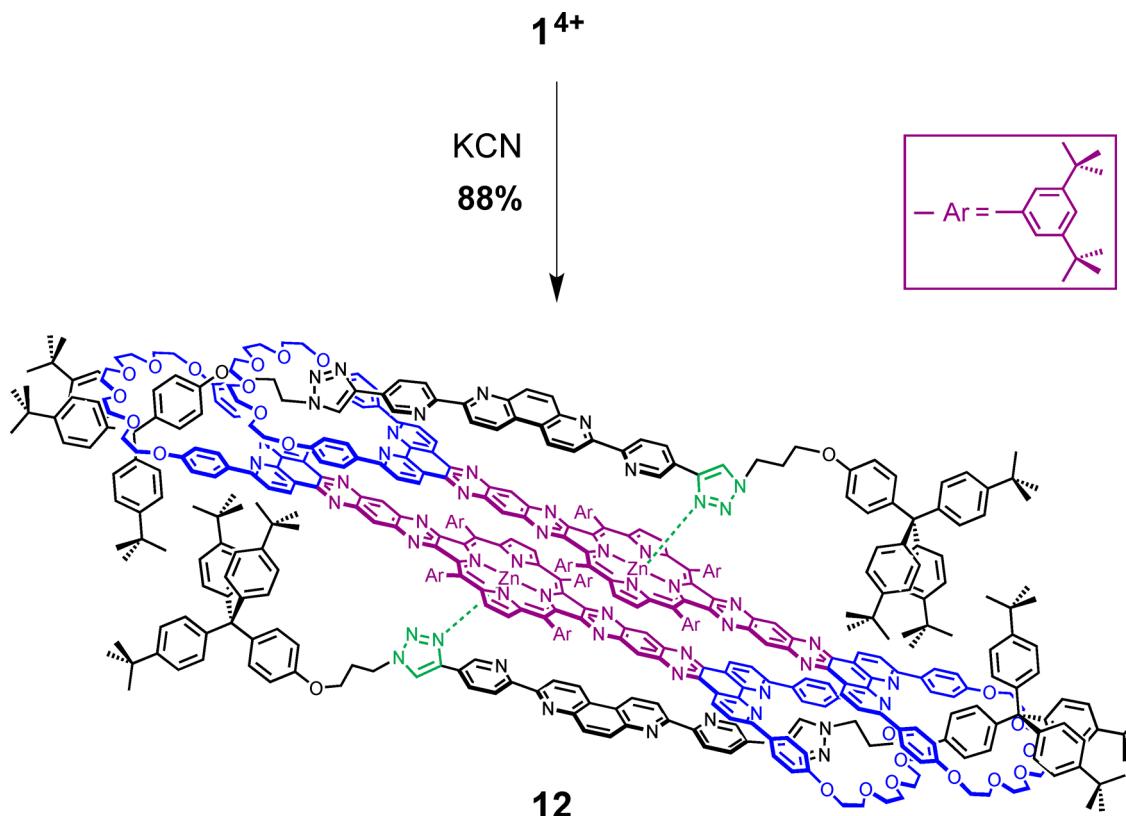
**3.3. Host–Guest Properties of the Four-Copper [4]Rotaxane.** Owing to the very good geometrical control of the distance and orientation of the two zinc(II) porphyrin plates in the [4]rotaxane, confirmed by the X-ray structure (see section 3.2), a receptor with high selectivity upon coordination of nitrogen ditopic ligands was expected. Indeed, the UV–vis titrations performed with guests of various size, flexibility, and basicity confirmed this prediction (Figure 10, Table 1).<sup>41</sup> For 1,4-diazabicyclo[2.2.2]octane (DABCO) and 4,4'-bipyridine, the N–N distance of the coordinating nitrogen atoms, 2.6 and 7.2 Å, respectively, matches the Zn–Zn porphyrin distance (8.7 Å from the X-ray structure). These ligands coordinate between the two zinc porphyrin plates with a strong stabilization of the 1:1 [4]rotaxane–guest complex, as attested by the high association constants,  $\log K_{\text{IN}}$  above 7, that were measured (IN, internal complexes). In the case of the bis 4-bipyridyl guests connected by two phenyl groups or by a flexible C<sub>10</sub> aliphatic chain, which are obviously oversized compared with the porphyrin cavity width, an external coordination mode (OUT) was observed. The rigidity of the rectangular compartment formed by the two bis-chelating units of the rods and the two face-to-face porphyrin bis-macrocycles leads to a strong size selectivity and a high stabilization of the guests that fit the receptor cavity size.

Compared with the reported porphyrin-containing [3]rotaxane,<sup>29,30</sup> which also behaves as a receptor (see Figure 1), the present system is significantly more selective in the way that long substrates, whose overall length in their extended conformation exceeds 15 Å, do not form stable 1:1 complexes with  $\mathbf{1}^{4+}$  whereas the smaller guests do form stable 1:1 complexes.

**3.4. Demetalation of the Rigid Copper-Complexed [4]Rotaxane: A Switchable Receptor.** Taking into account previous results with porphyrinic [3]rotaxanes,<sup>29,30</sup> similar complexation properties were expected for the copper-free analogue of [4]rotaxane  $\mathbf{1}^{4+}$ , which was anticipated to be a more versatile host than the corresponding copper(I) rotaxane described above.

Rotaxane  $\mathbf{1}^{4+}$  was demetalated using a large excess of KCN to yield the copper-free rotaxane  $\mathbf{12}$  in 88% yield (Figure 11). This rotaxane was fully characterized by UV/vis spectroscopy, <sup>1</sup>H NMR spectroscopy (COSY, ROESY, and DOSY), and electrospray mass spectrometry.<sup>51</sup>

Unexpectedly, the structure of the resulting demetalated rotaxane  $\mathbf{12}$  was shown to be totally collapsed and the rings



**FIGURE 11.** Demetalation of rotaxane **1<sup>4+</sup>** to yield copper-free rotaxane **12** and collapsed conformation of the demetalated species with axial coordination of two triazole units on the Zn-porphyrins.<sup>51</sup>

were not able to slide along the axes, contrary to what is generally observed for demetalated rotaxanes. This surprising structure was explained by the coordination of two triazoles of the axes out of four on Zn(II) located inside the porphyrins.<sup>52</sup> Indeed, the lengths of the various fragments fit perfectly to lock the structure as shown in Figure 11.

The flattened structure was corroborated with DOSY NMR experiments, among other techniques. Demetalated rotaxane **12** has a diffusion coefficient of  $160 \pm 3 \mu\text{m}^2 \cdot \text{s}^{-1}$  in  $\text{C}_6\text{D}_6$ .<sup>51</sup> Applying this value and the length of the rod estimated from CPK models (55 Å) to an ellipsoid model we deduced a height and a width of 19 Å for this rotaxane, in contrast with copper rotaxane **1<sup>4+</sup>** that fits a spherical radius of 23 Å. Figure 12 shows the rotaxanes with their respective spherical and ellipsoidal models.

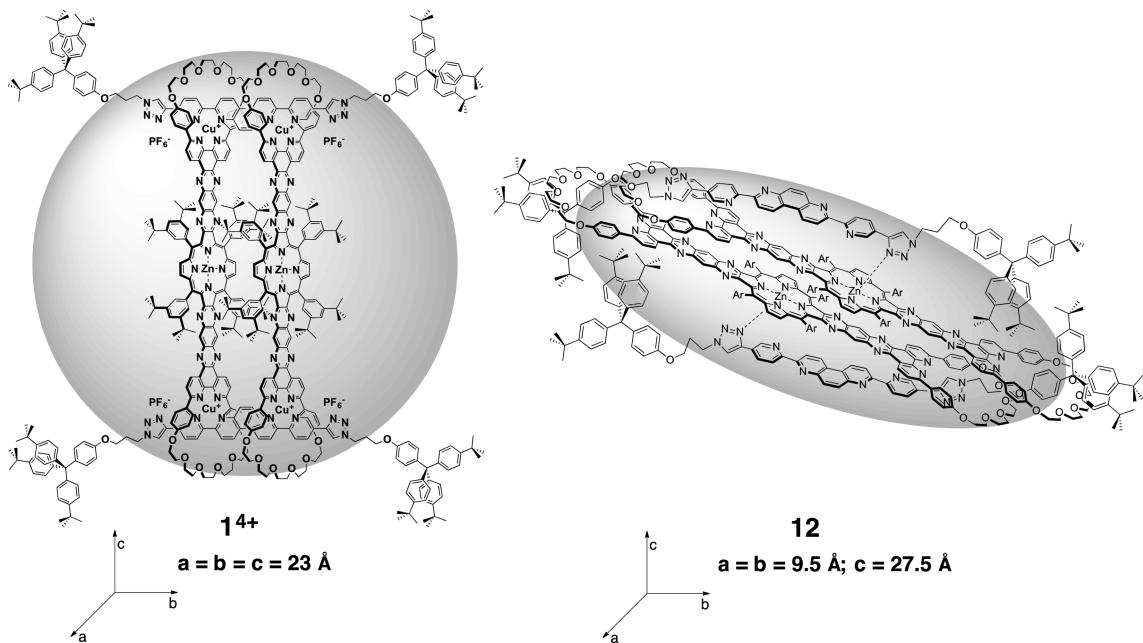
The molecular receptor properties of metal-free rotaxane **12** were investigated by UV-visible titrations and <sup>1</sup>H NMR studies with different amines, such as DABCO or 1,4-diaminobutane, but no interaction was observed.<sup>51</sup> This fact is not surprising since the coordination of the triazoles to the metalloporphyrins inhibits any possibility of interacting with amines: the external positions of the coordination sphere of Zn(II) are occupied by triazoles, whereas the internal positions are sterically hindered, due to the collapsed structure.

The system was tested for remetalation ability, and addition of Cu<sup>I</sup> ions was found to restore the initial conformation by dissociation of the Zn<sup>II</sup>-triazole complexes. This strategy was used to further investigate the complexation properties. Addition of 4 equiv of Cu<sup>I</sup> ions to 1:1 mixtures of **12** and DABCO or 1,4-diaminobutane regenerated the host-guest properties of the rotaxane and thus the complexation of the guests between the two Zn<sup>II</sup>-porphyrins of the host.<sup>51</sup>

Considering that complexation properties were fully restored, this system can be considered as a switchable host, with an active form (**1<sup>4+</sup>**, copper rotaxane) and a totally inactive form (**12**, copper-free rotaxane), both forms being interconverted by coordination or decomplexation of the four Cu(I) centers (Figure 13).

#### 4. A Flexible Copper(I)-Complexed [4]Rotaxane That Behaves as a Distensible Receptor

**4.1. Design of a Flexible Rotaxane Host.** Rigid or flexible receptors are equally interesting for different reasons. Rigidity should lead to selectivity whereas flexibility is expected to afford adaptable receptors, with analogous properties to induced-fit systems in biology.<sup>53</sup> The rotaxane **1<sup>4+</sup>** belonged to the rigid receptor family: the copper(I)-complexed



**FIGURE 12.** Chemical structure and shape of the copper(I) complex **14<sup>+</sup>** and copper-free species **12**. The spherical and ellipsoidal models (respectively) were fitted from DOSY NMR experiments; *a*, *b*, and *c* represent the dimensions of the sphere or the ellipse, respectively.<sup>51</sup>

rotaxane was a selective host for short substrates, while the demetalated species led to a totally collapsed structure, unable to accommodate any substrate between the plates. With the system presented here, flexibility will be an essential feature, which will allow for complexation of various substrates with different geometrical properties. The flexible [4]rotaxane receptor will be built from the same axle and stopper as for the rigid [4]rotaxane receptor discussed previously, but flexibility will be introduced in the bis-macrocyclic building block.<sup>54</sup>

Figure 14 highlights the common features and differences between the porphyrinic bis-macrocycle used in the present system and the previously described bis-macrocycle **3**. Flexibility is introduced in the new bis-macrocycle in two key points: (i) the macrocycles are linked to the central porphyrin via *single* C–C bonds, thereby allowing free rotation of the rings in relation to the plane of the porphyrin, and (ii) the dpp chelates are further separated from the porphyrin plate by diethylene glycol chains, which provides a greater freedom of orientation of the threaded axles compared with the porphyrin.

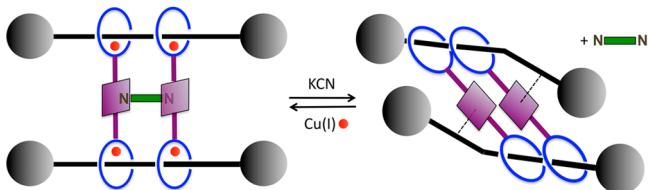
The chemical structure of the new flexible copper(I)-complexed [4]rotaxane **13<sup>4+</sup>** is depicted in Figure 15.<sup>54</sup> The rotaxane consists of two porphyrinic bis-macrocycles and two dumbbells interlocked in a cyclic structure.

**4.2. Synthesis of the [4]Rotaxane Receptor.** The [4]rotaxane **13<sup>4+</sup>** was synthesized from three different building blocks:

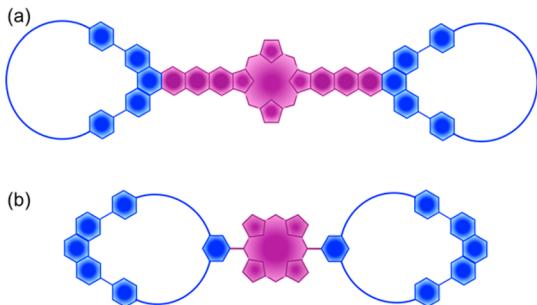
the porphyrinic bis-macrocycle **14**, acetylenic rod **2**, and azide stopper **4**. Building blocks **2** and **4** were described in sections 3.1 and 3.2; they are functionalized with terminal alkyne and azide functions, respectively, to allow introduction of the stoppers at the ends of the rod by CuAAC. The synthesis of porphyrin bis-macrocycle **14** was achieved in two steps from the functionalized 2,9-diphenyl-1,10-phenanthroline (dpp) precursor **15** (Figure 16).<sup>55</sup> The macrocyclic precursor **16** was synthesized first, followed by formation of the porphyrin core. Macrocycle **16** is a versatile building block in the design of porphyrinic multirotaxanes.<sup>56</sup> In the present case, it was reacted with 5-mesityldipyrromethane in a [2 + 2] MacDonald condensation to give the corresponding *trans*-A<sub>2</sub>B<sub>2</sub> free-base porphyrin functionalized with two lateral rings. After metalation, zinc porphyrin **14** was obtained with a global yield of 19% over two steps.<sup>55</sup>

Building blocks **14** and **2** were assembled following the copper(I)-templated threading principle described in section 2 to give the corresponding [4]pseudorotaxane. The stoppering CuAAC click reaction was carried on in the same pot, and the final copper(I)-complexed [4]rotaxane **13<sup>4+</sup>** was obtained in 50% isolated yield (threading + quadruple stoppering reaction) (Figure 17).<sup>54</sup>

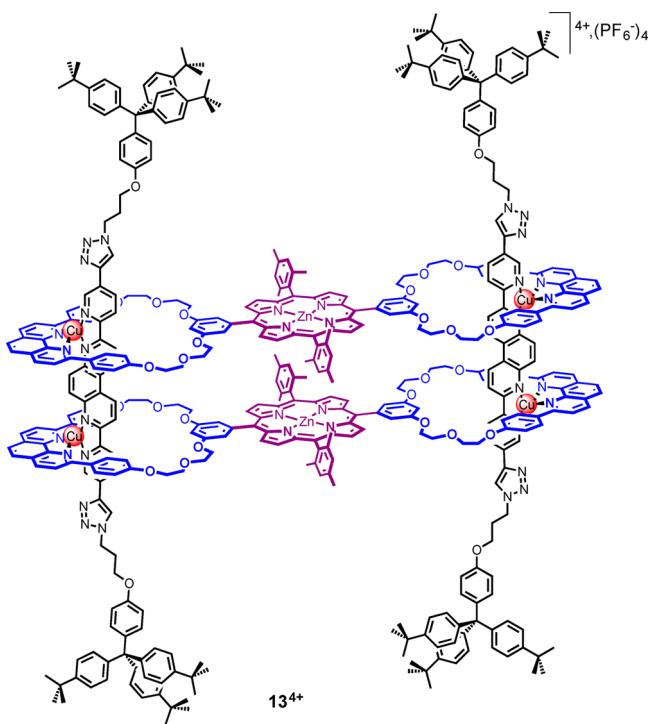
The structure of the rotaxane **13<sup>4+</sup>** was confirmed using standard characterization techniques and DOSY NMR.<sup>54</sup> The DOSY spectrum confirmed that a single product was isolated with a diffusion coefficient of  $228 \pm 5 \mu\text{m}^2 \cdot \text{s}^{-1}$  in CD<sub>2</sub>Cl<sub>2</sub> at



**FIGURE 13.** Schematic representation of the switchable rotaxane, either as its four-copper(I) complex  $\mathbf{1}^{4+}$  (scaffolding effect) or as its flattened demetalated form  $\mathbf{12}$ , with simultaneous and reversible decomplexation/recomplexation of the guest molecule (depicted in green).<sup>51</sup>

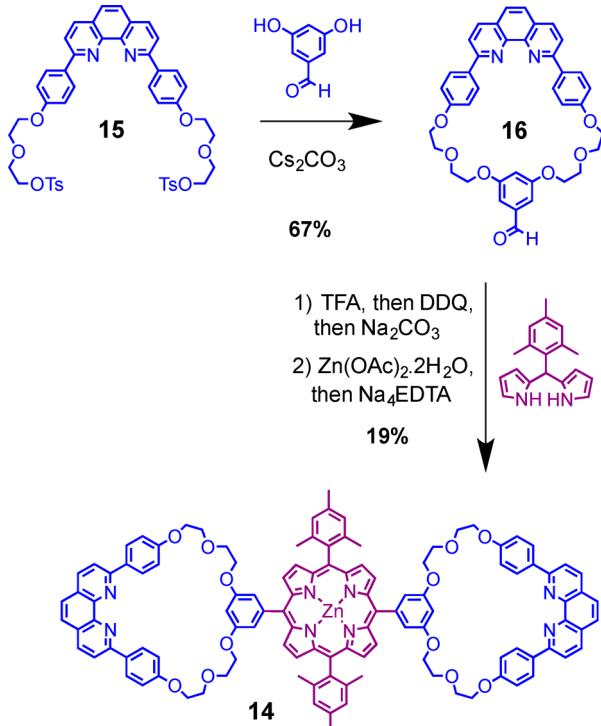


**FIGURE 14.** Schematic view of the structural difference between (a) the rigid porphyrin-incorporating bis-macrocycle  $\mathbf{3}^{41}$  and (b) the flexible bis-macrocycle used in the design of the distensible receptor.<sup>54</sup>



**FIGURE 15.** Chemical structure of the flexible [4]rotaxane  $\mathbf{13}^{4+}$ .<sup>54</sup>

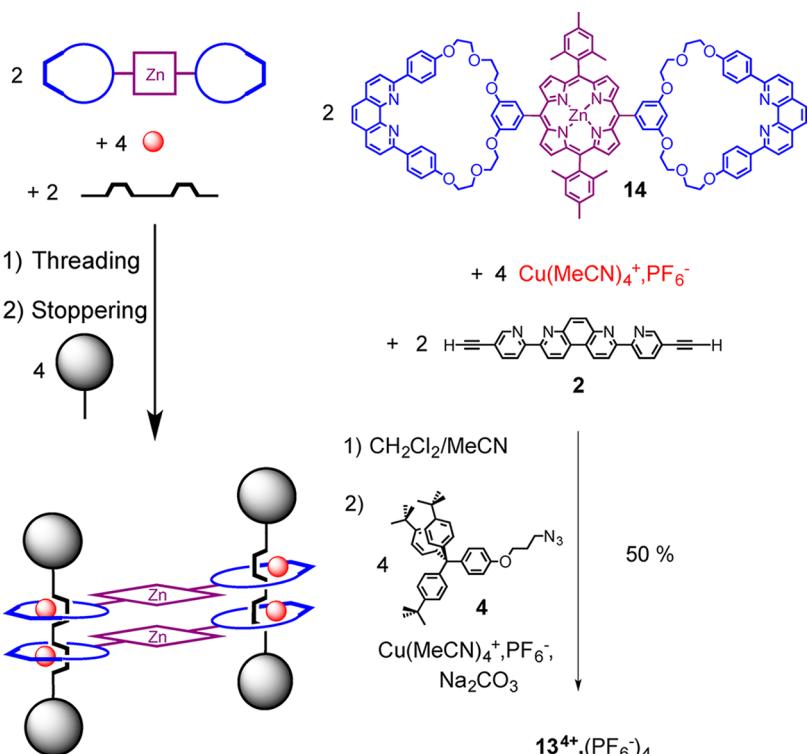
25 °C, corresponding to a 48 Å diameter sphere. This is in excellent agreement with the size estimation obtained using CPK models, which give approximate lengths of 43 and 54 Å,



**FIGURE 16.** Synthesis of porphyrinic bis-macrocycle  $\mathbf{14}$  (TFA = trifluoroacetic acid; DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone).<sup>55</sup>

respectively, for the bis-macrocycle component and the dumbbell component in fully extended conformation.

**4.3. Host–Guest Properties of the Copper(I)-Complexed [4]Rotaxane.** The molecular receptor properties of rotaxane  $\mathbf{13}^{4+}$  were investigated by UV–visible titrations with four rigid substrates of various lengths,<sup>54</sup> similarly to the host–guest studies performed with rotaxane  $\mathbf{1}^{4+}$ . (It is to be noted that formation of side products in the demetalation of rotaxane  $\mathbf{13}^{4+}$  prevented the study of the corresponding copper-free rotaxane, including potential host–guest properties.) The host–guest association constants obtained for copper(I)-complexed rotaxane  $\mathbf{13}^{4+}$  are reported in Table 2. The spectroscopic data confirmed that a single species with a 1:1 host/guest stoichiometry is formed in each case. Moreover, the high association constants obtained in all cases are consistent with an IN coordination mode (Figure 10), where the guest is bound internally in the central cavity of the rotaxane. Therefore, the receptor is able to bind guests of various sizes, including long and rigid guests like the extended bipyridines depicted in Table 2. This attests to the extreme flexibility and adaptability of the rotaxane host. The distance between the bis-macrocyclic components at the dpp coordinating sites is estimated to be 7.8 Å, but the receptor can adjust its conformation to the size of the guest. Thus, the distance between the central zinc porphyrins can vary and the



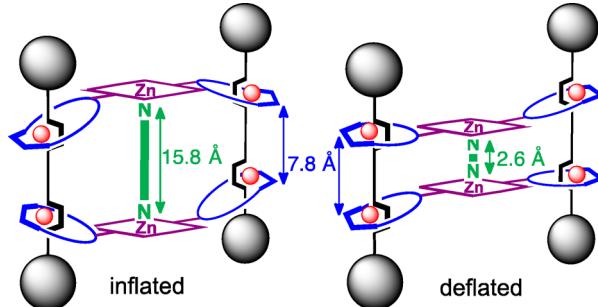
**FIGURE 17.** Schematic representation and chemical structures of the various fragments, threading, and stoppering reactions leading to copper(I)-complexed [4]rotaxane  $\mathbf{13}^{4+}$ .<sup>54</sup>

**TABLE 2.** Association Constants of Rigid Guests with Rotaxane Host  $\mathbf{13}^{4+}$  and Lengths of the Guest Molecules<sup>54</sup>

Guest	$\log K_{IN}$	N-N distance in Å
<chem>c1ccncc1</chem>	$8.1 \pm 0.5$	2.6
<chem>c1ccc(cc1)-c2cccnc2</chem>	$6.2 \pm 0.1$	7.2
<chem>c1ccc(cc1)-c2ccc(cc2)-c3cccnc3</chem>	$6.1 \pm 0.1$	11.4
<chem>c1ccc(cc1)-c2ccc(cc2)-c3ccc(cc3)-c4cccnc4</chem>	$5.6 \pm 0.1$	15.9

rotaxane host can bind short substrates (2.6 Å), as well as long substrates (15.8 Å), with high affinity. It can be described as a distensible receptor, which can adopt inflated or a deflated conformations depending on the guest molecule, as schematically depicted in Figure 18.<sup>54</sup>

Thus, [4]rotaxane  $\mathbf{13}^{4+}$  is a remarkably adaptable molecular receptor. The structural difference with rotaxane  $\mathbf{1}^{4+}$  is moderate: both systems have cyclic [4]rotaxane structures and their dumbbell components are identical. However, the flexibility introduced in the bis-macrocyclic component of rotaxane  $\mathbf{13}^{4+}$  gives rise to very different geometrical



**FIGURE 18.** Inflated and deflated structures of the host–guest complexes of [4]rotaxane  $\mathbf{13}^{4+}$  with long and short rod-like guests, respectively.<sup>54</sup>

properties and thus to dramatically different molecular receptor properties. While the previous receptor was rigid and selective, the new system is an adaptable, distensible receptor that can adjust its conformation to the size of the guest to be accommodated, in an analogous manner to the induced fit observed in some enzymatic systems.

## 5. Conclusion and Outlook

In this Account, we discuss two types of [4]rotaxanes, each of them consisting of two bis-macrocycles and two rods threading the rings. The synthesis of such compounds represents a synthetic challenge, which is part of the motivation for making such complex architectures, especially if the central

part of the compounds contains porphyrinic groups. For almost 20 years, rotaxanes and molecular machines have been closely linked. This Account is another demonstration that specific properties can be reached with interlocking ring compounds (MIMs, mechanically interlocked molecules, as coined by Stoddart and co-workers).<sup>57</sup>

Real molecular compressors represent one of the holy grails of molecular machinery, both as mimics of the extremely complex “chaperones” of the biological world and as potential activators or catalysts in synthetic chemistry. More and more sophisticated molecular machines in solution have been proposed by several groups. Host–guest chemistry with a receptor whose shape and properties can be modified at will is particularly promising in relation to mechanical activation of bound substrates and even catalysis triggered by mechanical processes at the molecular level.

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