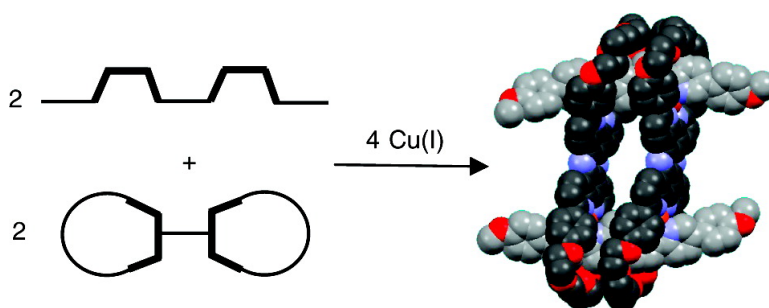


## Cyclic [2]Pseudorotaxane Tetramers Consisting of Two Rigid Rods Threaded through Two Bis-Macrocycles: Copper(I)-Templated Synthesis and X-ray Structure Studies

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## Cyclic [2]Pseudorotaxane Tetramers Consisting of Two Rigid Rods Threaded through Two Bis-Macrocycles: Copper(I)-Templated Synthesis and X-ray Structure Studies

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**Abstract:** Various substituted coordinating rigid rods have been synthesized which incorporate a central 4,7-phenanthroline nucleus attached to two 2-pyridyl groups via its 3 and 8 positions, so as to yield bis-bidentate chelates, the two-coordinating axes of the chelates being parallel to one another. Regardless of the nature of the substituents borne by the rods, the copper(I)-induced threading reaction of two such rods through the rings of two bis-macrocycles affords in a quantitative yield the 4-copper(I) threaded assembly. The [2]pseudorotaxane tetramers thus obtained have been fully characterized in solution and, for one of them, an X-ray structure could be obtained, confirming the threaded nature of the complex and providing important structural information.

### Introduction

The field of catenanes and rotaxanes<sup>1</sup> is particularly active, mostly in relation to the novel properties that these compounds may exhibit (electron transfer, controlled motions, mechanical properties, etc...). A particularly promising area is that of synthetic molecular machines and motors.<sup>2</sup> In recent years, several spectacular examples of molecular machines leading to real devices have been proposed, based either on interlocking systems or on non interlocking molecules.<sup>3</sup> In parallel, more and more sophisticated molecular machines have been reported, frequently based on multicomponent rotaxanes. Particularly

noteworthy are the muscle-like compounds reported by two groups,<sup>4,5</sup> a molecular elevator,<sup>6</sup> illustrating the complexity that dynamic threaded systems can reach, and light-driven linear motors containing an organic chromophore<sup>7</sup> or a ruthenium(II) complex acting as light-harvesting species.<sup>8</sup> Complex interlocking topologies are thus needed if one wants to increase the functionality of future molecular machines. The quest for new molecular topologies is also a challenge in itself, to demonstrate the power of modern synthetic strategies, based most of the time on organic or inorganic templates.

The synthesis of multirotaxanes incorporating several rings and several thread-like fragments is still far from being trivial.<sup>9</sup> The copper(I) templated strategy proposed long ago has been

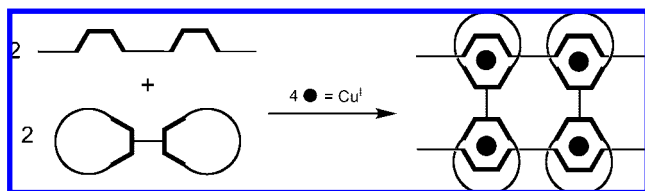
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<sup>‡</sup> Nanoscience Center, Department of Chemistry, University of Jyväskylä.

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**Scheme 1.** Principle of the Transition Metal-Directed Threading Process Leading To a Cyclic [2]Pseudo-rotaxane Tetramer<sup>a</sup>



<sup>a</sup> The black dot represents the metal center (copper(I) in the present work) and the U-shaped sign symbolizes a bidentate chelate (a diimine ligand of the 1,10-phenanthroline family).

extended to more and more complex molecules, incorporating several metal centers.<sup>10</sup> As far as Cu(I)-complexed rotaxanes are concerned, various compounds are worth noting which contain several metal centers: a [5]rotaxane with porphyrinic stoppers<sup>11</sup> and a cyclic rotaxane tetramer whose organic components consist of a coordinating “filament” appended to a ring<sup>12</sup> are particularly representative. Recently, our group has reported an unusual topology consisting of a large ring threading the two halves of a bis-macrocycle (“handcuff”).<sup>13</sup> Incidentally, such a topology had already been reported by Becher et al. containing totally different components.<sup>14</sup>

The bis-macrocycle used for the synthesis of a “handcuff” catenane can be utilized for constructing other complex systems such as, in particular, a rotaxane tetramer (stoppered or nonstoppered analogue), as depicted in Scheme 1.

The success of the strategy represented in Scheme 1 relies to a large extent on the design and synthesis of the appropriate constituents, the rod and the bis-macrocycle. In the present report, we will first describe the synthesis of the various rods used for the formation of the pseudorotaxane structures. In a

second part, we will discuss the copper(I) based threading reactions and illustrate the prototypical example by an X-ray structure. This structure will not only prove in a definitive manner the topology of the 4-copper complex but it will at the same time show that the very large molecule obtained can accommodate a certain degree of distortion. The third part will be devoted to the attempts to prepare a [3]catenane from an appropriately substituted threaded complex; as will be discussed, the compound could not be isolated pure but its formation could unambiguously be demonstrated by High Resolution Electro Spray Mass Spectrometry (HR ES–MS).

## Results and Discussion

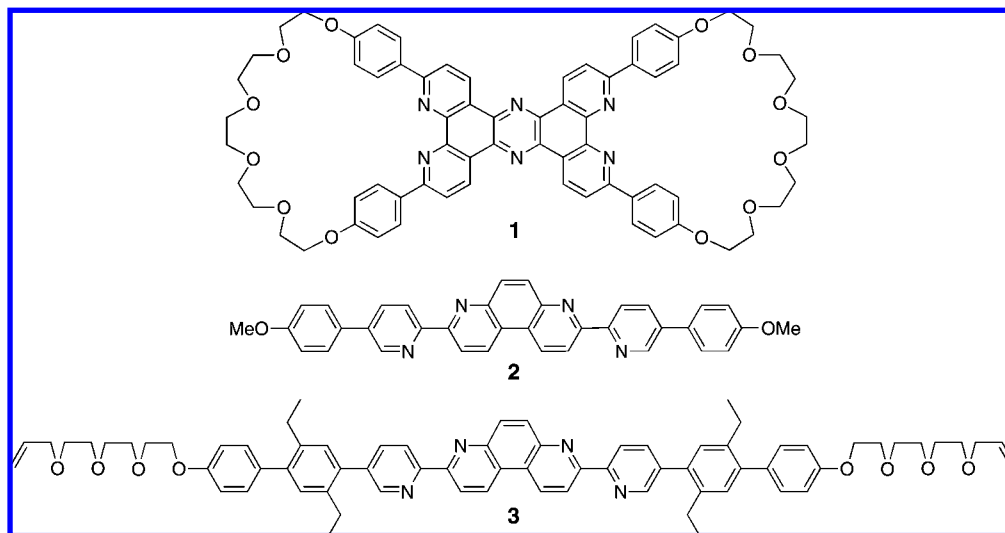
The various organic fragments leading to the formation of the threaded species described in the present report are depicted in Figure 1.

The two key components are the bis-macrocycle **1**, whose synthesis has been described not long ago,<sup>15</sup> and a two-chelating unit thread (**2** or **3**). **1** contains two back-to-back rigidly connected dpp-type chelates (dpp: 2,9-diphenyl-1,10-phenanthroline) incorporated in 30 membered-rings. The rigidity of the system is such that folding of the central aromatic part of the compound is expected to be very limited, thus allowing good control over the geometry of complexes formed by threading various fragments through the ring and, in particular, over the distance between two hypothetical metal centers coordinated in the diimine sites. Compounds **2** and **3** incorporate side-to-side bidentate chelating units, the central 4,7-phenanthroline nucleus being such that, like for **1**, the distance between the coordination sites is well-controlled. A recent X-ray structure of a di-iridium complex consisting of two iridium(III) centers coordinated to the diimine coordination sites of a ligand similar to **2** or **3** and ancillary ligands shows that the Ir–Ir distance is 8.17 Å,<sup>16</sup> whereas molecular models tend to indicate that the ideal distance, in a non-distorted ligand, should be around 8.5 Å. The 3,8-di(2'-pyridyl)-4,7-phenanthroline motif (dpyp) has already been used in a few studies, in relation to copper(I)-complexed molecular grids or pseudorotaxanes.<sup>17</sup> The use of unsubstituted ligands of the dpyp family such as **2** can be problematic in the course of synthetic work aiming at affording functionalized compounds. In fact, **2** and some of its precursors are highly insoluble, which prevents their use in further reactions except in simple coordination chemistry reactions. This is the reason why solubilizing groups have been introduced in **3** and its precursors, making the handling and the chemical modification of these molecules much easier than for **2**. Compound **3** is end-functionalized by two long fragments bearing allyl groups. These terminal olefins will be used after the threaded species has been made for preparing a cyclic structure by ring-closing metathesis (RCM), as discussed in the last section of the present report.

**1. Synthesis of the Dpyp-Type Rods.** To allow further functionalization of the dpyp ligand, compound **7**, bearing two bromine atoms at the right positions was synthesized by modification of a literature procedure developed for a slightly

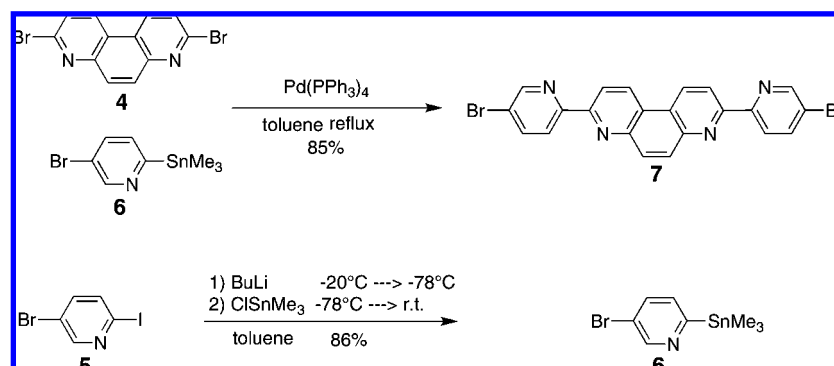
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**Figure 1.** Chemical structures of the bis-ring **1**, the short rod **2**, and the elongated rod **3**.

**Scheme 2.** Stille Coupling between **4** and **6** to Afford The Bis-bidentate Ligand **7** and Preparation of the 5-Bromo-2-trimethylstannylpyridine (**6**)

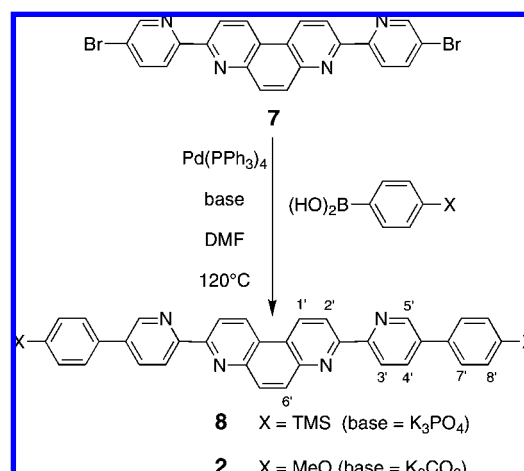


different compound.<sup>17</sup> As shown in Scheme 2, the Stille coupling between 3,8-dibromo-4,7-phenanthroline, **4**, and the trimethyl stannyl derivative **6**, prepared from **5** under classical conditions,<sup>18</sup> furnished the desired molecule **7** in good yield.

During the Stille coupling reaction between **4** and **6**,<sup>19</sup> oxidative addition to the palladium catalyst is possible on two different bromo-aryl sites. The 85% yield for compound **7** shows that it is much more likely to happen on the 1,10-phenanthroline nucleus than on the pyridine moiety. This can be explained by the electrophilic nature of the carbon ortho to the nitrogen atom in **4**. Hence, homocoupling between two pyridine heterocycles is not observed. Compound **7** is highly insoluble and could only be purified by extracting it, after sonication, from diatomaceous earth with boiling chloroform.

In subsequent reactions, the axle was elongated by Suzuki coupling<sup>20</sup> with 4-(trimethylsilyl)phenylboronic acid and 4-methoxyphenylboronic acid, which are both commercially available (Scheme 3). These boronic acids were chosen because they

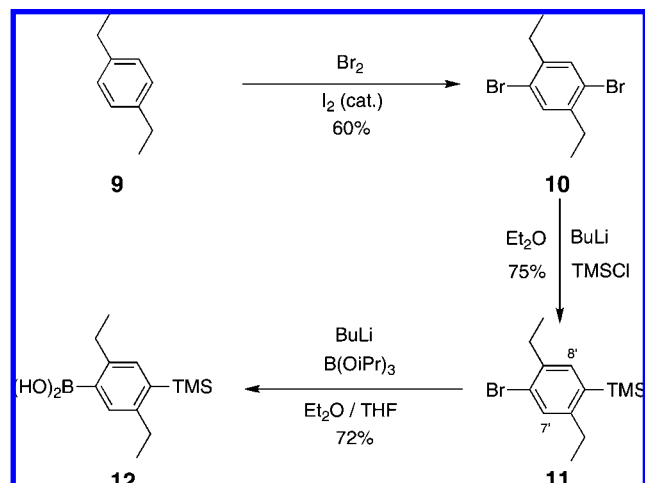
**Scheme 3.** Synthesis of the Functionalized Threads **8** and **2** by Suzuki Coupling



permit further functionalization. The trimethylsilyl group (TMS) can easily be substituted by an iodide, thus allowing further coupling reactions, whereas deprotection of the methoxyphenyl results in a phenol, able to undergo Williamson reactions.

Compounds **8** and **2**, obtained in 66% and 82% yield respectively, are the first important fragments toward the construction of a longer thread, but they are also interesting by themselves, as they can be used to drive the formation of several

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**Scheme 4.** Synthesis of 2,5-Diethyl-4-trimethylsilyl-phenylboronic Acid **12**

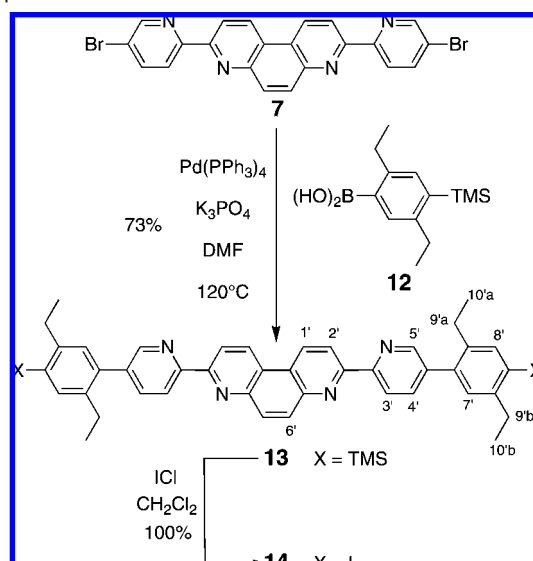
copper-complexed multicomponent systems. It is worth noticing that compound **2** is even less soluble than compound **7**, due to additional anisyl groups, elongating the delocalized system. To be able to carry out useful  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$ , we were forced to add a small amount of TFA (trifluoroacetic acid), thus protonating the diimines, and making the compound slightly more soluble. Compound **8** benefits from the presence of TMS groups as solubilizing agents and is slightly easier to handle than **7** and **2**. Nevertheless, the poor solubility of compounds **7**, **8**, and **2** prompted us to attach solubilizing groups on the dpyp-type compounds. Since, in a later stage, the rods derived from **7**, **8**, and **2** were expected to be threaded through the 30-membered rings of **1**, it was essential to avoid bulky groups as solubilizing functions. If too large, then such groups could inhibit threading of the rod through the ring. The use of ethyl groups seemed to be a good compromise between size and solubilizing effect. The precursors to compound **3** were prepared following the sequence of reactions represented in Schemes 4, 5, and 6.

Diethyl-phenyl boronic acid **12** was prepared similarly to comparable molecules of the literature<sup>21</sup> starting from the commercially available 1,4-diethylbenzene, as shown in Scheme 4.

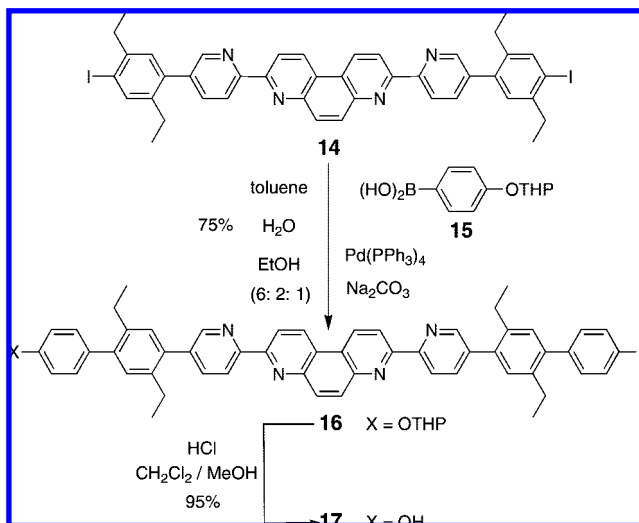
After dibromination of compound **9** to give 2,5-diethyl-1,4-dibromobenzene **10**, a first bromine atom was replaced by a TMS group upon reaction with *n*-BuLi and TMSCl to yield compound **11**. Finally, the required boronic acid is obtained by reacting **11** with first *n*-BuLi, then  $\text{B}(\text{O}^i\text{Pr})_3$  and, subsequent, hydrolysis. The TMS group is added so as to be converted later on to an iodide and hence allow further coupling reactions. Suzuki coupling between **12** and **7**, as indicated in Scheme 5, generates ligand **13**.

This new compound is now readily soluble in classical solvents, such as dichloromethane or chloroform. The short ethyl groups are thus very effective solubilizing agents. The bis-TMS compound **13** was quantitatively converted to the diiodide **14** using ICl in dichloromethane, which is also soluble in most common solvents.

In order to functionalize the rod, Williamson reaction seemed to be convenient. It was thus necessary to introduce two phenolic

**Scheme 5.** Synthesis of the Rod **13**, Containing Ethyl Solubilizing Groups and of Compound **14**, Functionalized by Two Iodide Groups<sup>a</sup>

<sup>a</sup> A numbering of the various carbon atoms is also indicated.

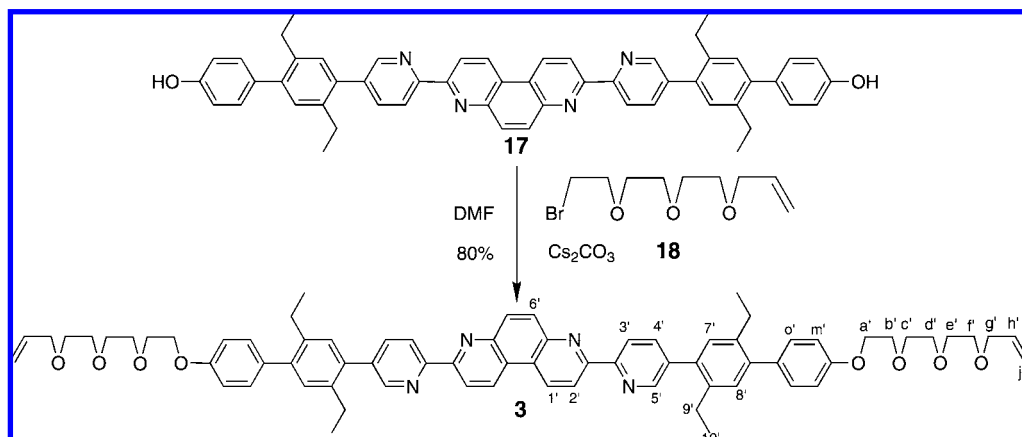
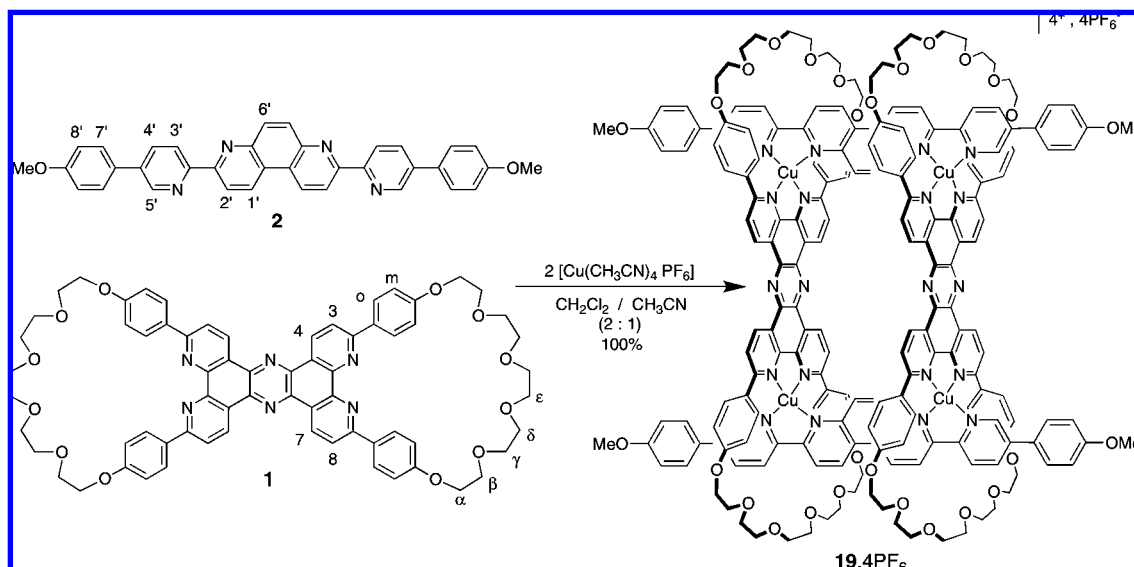
**Scheme 6.** Synthesis of the Diphenol **17**

groups at the ends of **14**. The chemical steps leading first to **16**, an elongated version of **14**, then to the corresponding diphenol (compound **17**) and subsequently to compound **3**, are represented in Schemes 6 and 7.

The THP-protected boronic acid **15**<sup>22</sup> was connected to the iodo-rod **14**, to give the elongated thread **16**. A satisfying yield of 75% for a double-Suzuki coupling reaction is an indication that the steric hindrance imposed by the ethyl groups close to the iodine atoms does not interfere with the Suzuki coupling reaction. After deprotection of the OTHP groups, the diphenol axis **17** was obtained in a nearly quantitative yield. The rod now contains eight aromatic cycles in line. Despite this structural feature and the presence of the phenol moieties at each end of molecule **17**, it can be readily manipulated and analyzed by  $^1\text{H}$  NMR. As already noted, the four ethyl groups are really powerful solubilizing

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**Scheme 7.** Synthesis of the Diolefinic Thread **3** by Williamson Reaction**Scheme 8.** Copper(I)-Directed Threading Reaction Leading to the 4-Copper [2]Pseudo-rotaxane Tetramer **19**<sup>4+a</sup>

<sup>a</sup> Due to the poor solubility of the organic fragments and to the many complexes which can potentially be formed, formation of the most stable species, namely the threaded complex **19**<sup>4+</sup>, requires a long period of time at room temperature (several days).

agents. The synthesis of **3** was then carried out using the triethylene glycol derivative **18**<sup>23</sup> and the diphenol **17**.

**2. Formation of a [2]Pseudorotaxane Tetramer from the Bismacrocyclic **1** and the Rod **2**: The Gathering and Threading Effect of Copper(I).** In recent years, transition metals have been much utilized in association with various types of ligands to generate complex architectures. Ideally, the complexation reaction should be performed under thermodynamic control. Under such conditions, the system will self-repair if unfavorable reaction pathways are taken and will finally give rise to the most stable situation. One of the main requirements to reach the thermodynamic equilibrium is certainly that the coordination and decoordination reactions must be sufficiently fast for the system to find its stable position. In spectacular studies reported by Fujita and co-workers,<sup>24</sup> the assembling metal is palladium(II) which is indeed able to undergo fast ligand substitution reactions and is thus well adapted to the formation of complexes under thermodynamic control. Many other groups have based their

studies on related principles and could demonstrate that highly complex and multicomponent species can be obtained in high yield by simply mixing appropriate multisite ligands and metals and then waiting for the equilibrium to be reached.<sup>25</sup> Along these lines, our group has used copper(I) extensively to generate a variety of threaded species.<sup>26</sup> In a preliminary communication, we recently described the copper(I)-driven threading reaction of **1** by rod **2**.<sup>27</sup> The reaction is depicted in Scheme 8. The [2]pseudorotaxane tetramer **19**<sup>4+</sup> is obtained quantitatively after

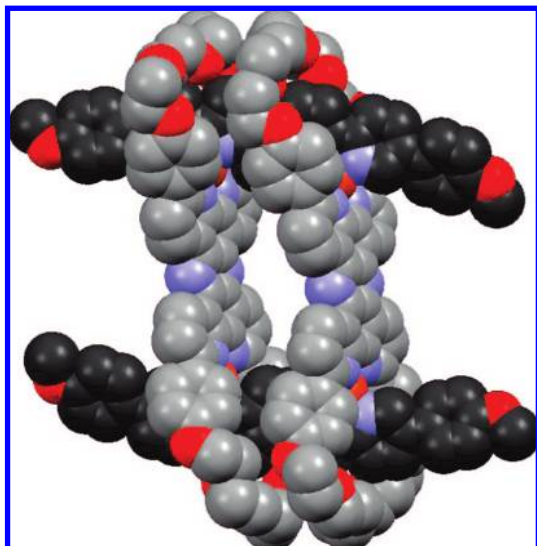
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**Figure 2.** Crystal structure of the [2]pseudorotaxane tetramer  $19^{4+}$ . Hydrogen atoms and counterions ( $\text{PF}_6^-$ ) have been omitted for the sake of clarity.

**Table 1.** Important Structural Features of  $19^{4+}$

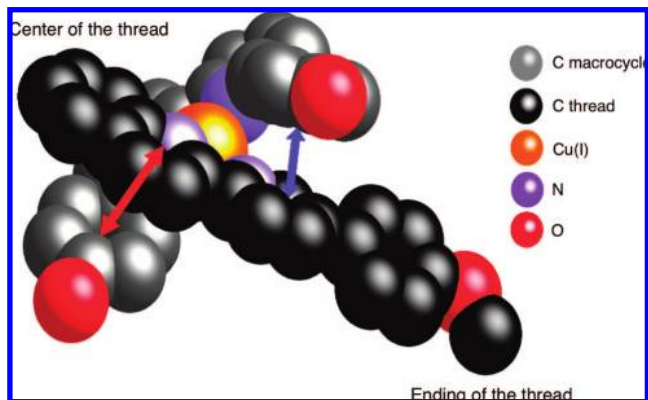
distances		
Cu—Cu	on one thread:	7.808 Å
	on one bis-macrocycle:	12.661 Å
Cu—N	Cu—N <sub>THREAD</sub> :	1.999–2.048 Å
	Cu—N <sub>MACROCYCLE</sub> :	2.030–2.052 Å
Pyrazine—Pyrazine	(centroids of the bis-macrocycles):	8.271 Å
angles		
distortion angles	Phen (macrocycle) - Bipy (thread):	53.82°
		57.74°
N—Cu—N	Phen (macrocycle) bite angles:	81.51° – 82.67°
	Bipy (thread) bite angles:	81.76° – 82.04°

7 days at room temperature. Even though the starting materials, the rod as well as the bis-macrocycle, are almost completely insoluble, the template effect of Cu(I) is strong enough to drive the reaction to completion and afford the thermodynamically favored compound  $19^{4+}$ . This, again, demonstrates the power of coordination chemistry, and in particular the efficiency of copper(I) acting as a “gathering and threading” element.

The [2]pseudorotaxane tetramer  $19^{4+}$  was obtained as its  $\text{PF}_6^-$  salt. It is well soluble and crystals of  $19.4\text{PF}_6$  could be grown from slow diffusion of THF into a  $\text{CH}_2\text{Cl}_2$  solution. The crystal structure was solved. It is represented in Figure 2. Some relevant geometrical features of  $19^{4+}$  are given in Table 1.

It is remarkable that the central aromatic groups (phenazine) of the bis-macrocycles are slightly bent away from each other, thus increasing the distance between them to 8.271 Å, compared to 7.808 Å for the copper(I)—copper(I) distances. The threads on the other hand are bent about 13° toward the copper centers, adopting some kind of curved banana shape in spite of the apparent rigidity of the rods, consisting of 6 aromatic groups in line.

The geometry of the diimine-phen environment around the metal centers is that of a distorted tetrahedron. In fact, the two chelates are not orthogonal to one another, their dihedral distortion angle being only about 54° and 58° instead of the required 90° for a perfect tetrahedron. This “flattening” of the geometry brings the phenyl groups in the 2 and 9 positions of the macrocycle phenanthrolines closer to the thread (see crystal



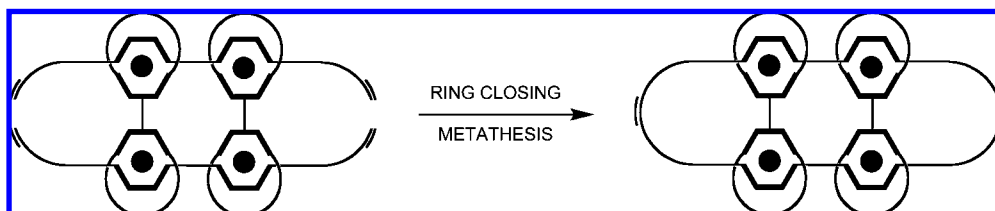
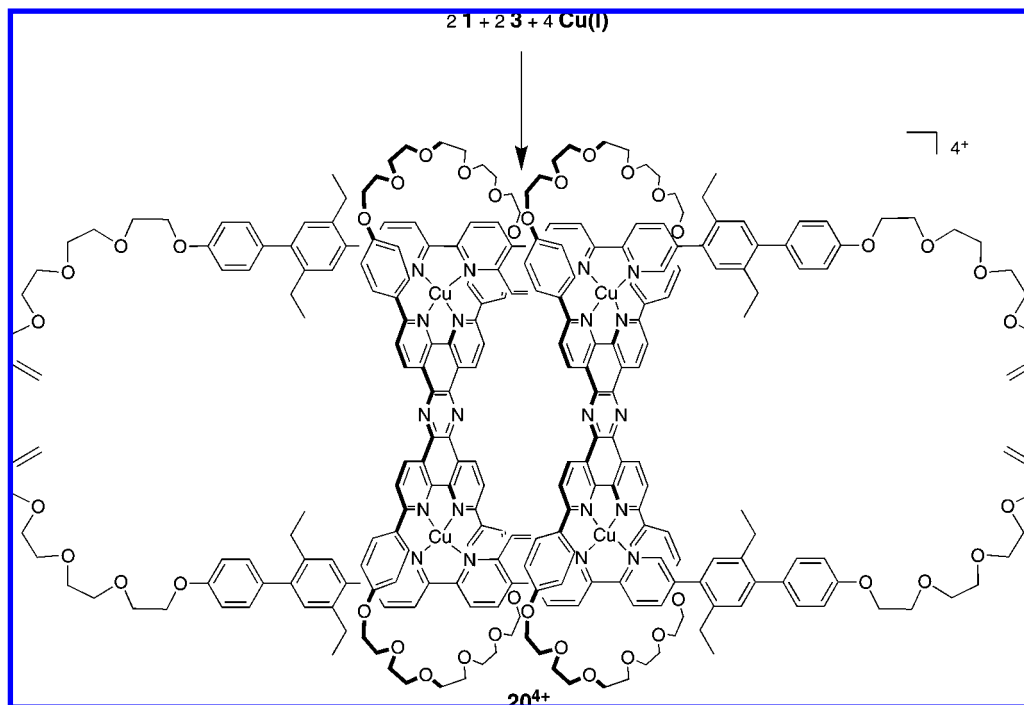
**Figure 3.** Space-filling zoom of one of the Cu(I) complex units of  $19^{4+}$ .

structure of Figure 2). The flattening of the copper complexes is not new. It has been observed in many similar copper(I) complexes including catenanes.<sup>28</sup> In the present case, the flattened situation is well-illustrated on the zoom view of the structure represented in Figure 3. For each macrocycle, one of the two phenyl rings undergoes  $\pi$ – $\pi$  interaction with an external pyridyl heterocycle of the bis-diimine ligand of the thread (blue arrow). The distance between the centroids of these two cycles is 3.865 Å, i.e., close to the expected distance between stacking aromatic nuclei. The second phenyl ring of each macrocycle moves closer to the central 4,7-phenanthroline of the rod, either toward the ethenyl-bridge or in the direction of one of the heterocycles (red arrow). These distances do allow  $\pi$ – $\pi$  interactions and also explain why the central protons of the 4,7-phenanthroline nucleus (HC=CH bridge) are dramatically upfield shifted in the  $^1\text{H}$  NMR spectrum upon coordination of the macrocycles to the rods (see experimental section). The protons of the central HC=CH bridge experience the ring current effect of the phenyl nucleus belonging to the threaded ring.

**3. Formation of a [2]Pseudorotaxane Tetramer from the Bis-macrocycle 1 and the Long Thread 3.** As already mentioned, the rod **3** was prepared in view of making a new type of catenane incorporating two units of **1** and a very large ring passing through the inner parts of the 4 rings of the two bis-macrocycles. The synthesis strategy is depicted in Scheme 9.

Since **2** and **3** display exactly the same coordination properties and considering that, in the presence of the stoichiometric amount of copper(I), the reaction between **1** and **2** results in a quantitative yield of the threaded species  $19^{4+}$ , the formation of a precursor (pseudorotaxane) adapted to the strategy of Scheme 9, consisting of 4 copper(I) atoms, two equiv of **1** and two equiv of **3**, seemed to be very likely to afford the desired threaded species. In the course of the past decade, various catenanes and knots incorporating one or several templating metal centers (copper(I) and ruthenium(II) [2]catenanes, copper(I) and iron(II) trefoil knots) have been prepared by our group.<sup>29</sup> To a large extent, such sophisticated topologies have become accessible or at least easier to obtain, thanks to the development of the powerful RCM reaction initiated by Grubbs

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**Scheme 9.** Putative Formation of a Catenane from an Appropriately Functionalized [2]Pseudo-Rotaxane Tetramer via RCM: Principle**Scheme 10.** Formation of the [2]Pseudo-rotaxane Tetramer from the Stoichiometric Amounts of Bis-macrocycle **1**, Copper(I) and Rod **3**

and co-workers.<sup>30</sup> The chemical structure of rod **3** was carefully designed: the ideal length of the allyl-bearing fragments was estimated from CPK models, allowing the two rods to be linked together once the threaded precursor was obtained but being too short to permit cyclization between two terminal allyl groups borne by the same rod.

The [2]pseudorotaxane tetramer  $20^{4+}$  was obtained following the same experimental procedure as for the [2]pseudorotaxane tetramer  $19^{4+}$ . Two equiv of the axle **3** and two equiv of bis-macrocycle **1** were reacted with four equiv of  $[\text{Cu}(\text{CH}_3\text{-CN})_4](\text{PF}_6)$  in  $\text{CH}_2\text{Cl}_2/\text{MeCN}$  at room temperature for 7 days. After filtration and removal of the solvents the [2]pseudorotaxane tetramer  $20.4\text{PF}_6$  was obtained in quantitative yield (Scheme 10).

Remarkably, as for the synthesis of  $19^{4+}$ , the 4-copper threaded assembly  $20^{4+}$  was obtained quantitatively, in spite of a much longer thread to be passed through the ring of each bis-macrocycle. This process is reminiscent of that consisting

in passing a long thread through the eye of a needle. Generally speaking, it represents a key reaction in the synthesis of catenanes and rotaxanes. In the present case, the thread to be passed through the ring is 50 atoms long. Perhaps even more striking is the fact that there are 22 noncoordinating atoms between the end of the axis and the first diimine nitrogen atom of the rod met by the copper(I) center and the ring in the course of the threading step. In terms of intimate mechanism, many factors of the reaction are still poorly understood in view of the complexity of the process. Compound  $20^{4+}$  was characterized by  $^1\text{H}$  NMR, COESY, ROESY, and mass spectrometry (see experimental section). Unfortunately, various attempts to prepare the hypothetical [3]catenane drawn in Scheme 9 using first generation Grubbs catalyst<sup>31</sup> turned out to lead to a mixture of cyclic compounds only. Although the desired catenane was clearly identified as the major components of this mixture, we have not been able to isolate it pure as yet.

## Experimental Section

**General Methods.** Dry solvents were distilled from suitable drying agents (THF from sodium/benzophenone,  $\text{CH}_2\text{Cl}_2$  from  $\text{P}_2\text{O}_5$ ). Thin-layer chromatography was carried out using precoated polymeric sheets of silica gel (Machery-Nagel, POLYGRAM, SIL G/UV<sub>254</sub>). Preparative column chromatography was carried out

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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  $\mu\text{m}$ ).

Nuclear magnetic resonance (NMR) spectra for  $^1\text{H}$  were acquired on Bruker AVANCE 500 or 300 spectrometers. The  $^{13}\text{C}$  NMR spectra were proton-decoupled. The spectra were referenced to residual proton-solvent references ( $^1\text{H}$ :  $\text{CD}_2\text{Cl}_2$  at 5.32 ppm,  $\text{CDCl}_3$  at 7.25 ppm;  $^{13}\text{C}$ :  $\text{CD}_2\text{Cl}_2$  at 54.0 ppm and  $\text{CDCl}_3$  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 Hertz 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.

**Starting Materials.** All chemicals were of the best commercially available grade and used without further purification (except when mentioned). 4-Methoxyphenylboronic acid and 5-bromo-2-iodopyridine **5** are commercially available and used without further purification. Compounds **1**,<sup>15</sup> **4**,<sup>17</sup> **6**,<sup>18</sup> **15**,<sup>22</sup> and **18**,<sup>23</sup> were prepared according to the literature procedures.

**X-ray Data Collection and Crystal Structure Determination.** X-ray data for **19**<sup>4+</sup> were collected on a Bruker Nonius Kappa APEX II diffractometer using graphite-monochromatized  $\text{Mo}_\alpha$  radiation at 173.0 K. Structure solution was performed by SIR-92<sup>32</sup> and refined on  $F^2$  by full-matrix least-squares techniques in three blocks using SHELXL-97.<sup>33</sup> Hydrogen atoms were calculated to their idealized positions and refined as riding atoms (temperature factor 1.5 times C temperature factor). No absorption correction was applied. Due to the very heavy disorder of the  $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$  moieties in the macrocycles and on the solvent THF and dichloromethane molecules as many as 1779 geometrical and/or temperature parameter restraints (DFIX, EADP, DELU, SIMU) had to be used in order to keep the model chemically acceptable.

**3,8-Bis(4-(4-methoxyphenyl)-2'-pyridyl)-4,7-phenanthroline (2).** A solution of 3,8-bis(4-bromo-2'-pyridyl)-4,7-phenanthroline **7** (200 mg, 0.4 mmol), 4-methoxyphenylboronic acid (134 mg, 0.88 mmol) and potassium carbonate (425 mg, 2 mmol) in 25 mL DMF was degassed ( $3\times$  vacuum/argon) before palladium tetrakis(triphenylphosphine) (46 mg, 0.04 mmol, 10% mol) was added. The solution was heated at 120  $^\circ\text{C}$  under argon and stirred for 3 h, then 15 mg of catalyst was added. After another 18 h of heating, the reaction mixture was cooled to room temperature and poured into 250 mL of water. The impure product that precipitated was filtered over diatomaceous earth and washed with EtOH and dichloromethane. The diatomaceous earth-product mixture was then extracted with boiling chloroform. The organic fractions were collected and washed one more time with chloroform. Compound **2** is finally obtained in 82% yield (179 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TFA 3%, 25  $^\circ\text{C}$ ):  $\delta$  = 9.42 (d,  $J$  = 8.3 Hz,  $\text{H}_{1'}$ , 2H), 9.12 (s,  $\text{H}_5$ , 2H), 8.79 (dd,  $J_1$  = 3.5 Hz,  $J_2$  = 1.3 Hz,  $\text{H}_4$ , 2H), 8.73 (d,  $J$  = 8.2 Hz,  $\text{H}_2$ , 2H), 8.57 (d,  $J_1$  = 8.8 Hz,  $\text{H}_3$ , 2H), 7.70 (d,  $J_1$  = 8.8 Hz,  $\text{H}_7$ , 4H), 7.15 (d,  $J$  = 8.9 Hz,  $\text{H}_8$ , 4H), 3.99 (s,  $\text{H}_{\text{O}-\text{CH}_3}$ , 4H) ppm.

MS (ES):  $m/z$  (%) = 547.2161 (100) [**2** +  $\text{H}$ ]<sup>+</sup> (calcd: 547.2129).

**Poly(ethylene glycol)-allyl Thread (3).** A round-bottom flask was loaded under argon atmosphere with the phenol-thread **17**, (80 mg,  $1.02 \times 10^{-4}$  mol),  $\text{Cs}_2\text{CO}_3$ , (216 mg,  $6.13 \times 10^{-4}$  mol) and

8 mL of DMF. The solution was degassed and heated to 60  $^\circ\text{C}$  before the bromo-ally poly(ethylene glycol) chain **18** (206.8 mg,  $8.17 \times 10^{-4}$  mol) in 10 mL DMF was added dropwise from a dropping funnel. After 24 h, the solvent was evaporated, and the remaining solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed twice with 100 mL  $\text{H}_2\text{O}$ . After additional washing with hexane, the pure white solid is obtained in 80% yield (90 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ ):  $\delta$  = 9.10 (d,  $J$  = 8.9 Hz,  $\text{H}_{1'}$ , 2H), 8.86 (d,  $J$  = 8.7 Hz,  $\text{H}_2$ , 2H), 8.81 (d,  $J$  = 8.3 Hz,  $\text{H}_3$ , 2H), 8.78 (dd,  $J_1$  = 2.2 Hz,  $J_2$  = 0.5 Hz,  $\text{H}_5$ , 2H), 8.34 (s,  $\text{H}_{6'}$ , 2H), 7.93 (dd,  $J_1$  = 8.2 Hz,  $J_2$  = 2.3 Hz,  $\text{H}_4$ , 2H), 7.31 (d,  $J$  = 8.7 Hz,  $\text{H}_6$ , 4H), 7.24 (s,  $\text{H}_8$ , 2H), 7.21 (s,  $\text{H}_7$ , 2H), 7.01 (d,  $J$  = 8.5 Hz,  $\text{H}_{\text{m}'}$ , 4H), 5.93 (m,  $\text{H}_b$ , 2H), 5.32–5.24 (ddt,  $J_1$  = 17.4 Hz,  $J_2$  = 1.9 Hz,  $J_3$  = 1.5 Hz,  $\text{H}_j$ , 2H), 5.19–5.14 (ddt,  $J_1$  = 10.4 Hz,  $J_2$  = 1.7 Hz,  $J_3$  = 1.5 Hz,  $\text{H}_i$ , 2H), 4.18 (m,  $\text{H}_{\text{a}'}$ , 4H), 4.00 (dt,  $J_1$  = 5.5 Hz,  $J_2$  = 1.5 Hz,  $\text{H}_g$ , 4H), 3.87 (m,  $\text{H}_b$ , 4H), 3.74–3.56 (m,  $\text{H}_c$ ,  $\text{H}_d$ ,  $\text{H}_e$ ,  $\text{H}_f$ , 16H), 2.68 (m,  $\text{H}_g$ , 8H), 1.15 (m,  $\text{H}_{10'}$ , 12H) ppm.

MS (Maldi-TOF):  $m/z$  (%) = 1127.508 (100) [**3** +  $\text{H}$ ]<sup>+</sup> (calcd: 1127.59).

**3,8-Bis(4-bromo-2'-pyridyl)-4,7-phenanthroline (7).** 5-bromo-2-trimethylstannyl pyridine **6** (1.96 g, 6.05 mmol) and 3,8-dibromo-4,7-phenanthroline **4** (1 g, 2.96 mmol) were suspended in dry toluene (130 mL) and the mixture degassed for 5 min. To this,  $\text{Pd}(\text{PPh}_3)_4$  (230 mg, 0.2 mmol) was added, and the resulting reaction mixture degassed for a further 5 min. It was then refluxed (140  $^\circ\text{C}$ ) under argon atmosphere for 18 h. A further 160 mg of  $\text{Pd}(\text{PPh}_3)_4$  was added, and the reaction stirred for 44 h under reflux. Evaporation of toluene afforded the crude product as a gray solid that was washed with MeOH ( $2 \times 150$  mL) and  $\text{Et}_2\text{O}$  ( $2 \times 150$  mL). Compound **7** was extracted from the remaining solid by washing it  $5\times$  with 150 mL of chloroform. After evaporating the chloroform, the gray solid was washed again with MeOH and  $\text{Et}_2\text{O}$ , giving 1.26 g of a grayish yellow solid (85% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):  $\delta$  = 9.05 (d,  $J$  = 8.7 Hz,  $\text{H}_{1'}$ , 2H), 8.80 (d,  $J$  = 1.6 Hz,  $\text{H}_5$ , 2H), 8.74 (d,  $J$  = 8.7 Hz,  $\text{H}_2$ , 2H), 8.64 (d,  $J$  = 9.1 Hz,  $\text{H}_3$ , 2H), 8.31 (s,  $\text{H}_{6'}$ , 2H), 8.03 (dd,  $J_1$  = 8.4 Hz,  $J_2$  = 2.3 Hz,  $\text{H}_4$ , 2H) ppm.

MS (FAB):  $m/z$  (%) = 493.0 (100) [**7** +  $\text{H}$ ]<sup>+</sup> (calcd: 492.9).

**3,8-Bis(4-(4-trimethylsilylphenyl)-2'-pyridyl)-4,7-phenanthroline (8).** The following reactants were added under argon atmosphere in DMF (total 25 mL) in the following order: compound **7** (200 mg, 0.4 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (46 mg, 0.04 mmol),  $\text{K}_3\text{PO}_4$  (255 mg, 1.2 mmol), 4-(trimethylsilyl)phenylboronic acid (171 mg, 0.88 mmol). After each addition, the reaction mixture was degassed. The mixture was then heated to 100  $^\circ\text{C}$  and stirred for 28 h. After cooling to room temperature, the solution was poured over 250 mL of water. The resulting precipitate was filtered off and washed with  $\text{Et}_2\text{O}$  ( $2 \times 250$  mL) and EtOH ( $2 \times 250$  mL). The product was extracted from the remaining solid with chloroform (350 mL). The combined organic fractions were filtered over diatomaceous earth and evaporated to dryness. After recrystallizing the yellowish-white product in chloroform, the white product **8** was obtained in 66% yield (166 mg).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):  $\delta$  = 9.10 (d,  $J$  = 8.9 Hz,  $\text{H}_{1'}$ , 2H), 9.02 (dd,  $J_1$  = 1.6 Hz,  $J_2$  = 0.8 Hz,  $\text{H}_{11'}$ , 2H), 8.83 (d,  $J$  = 8.5 Hz,  $\text{H}_2$ , 2H), 8.81 (d,  $J$  = 7.5 Hz,  $\text{H}_{13}$ ,  $\text{H}_{13'}$ , 2H), 8.37 (s,  $\text{H}_{6'}$ , 2H), 8.13 (dd,  $J_1$  = 8.0 Hz,  $J_2$  = 2.0 Hz,  $\text{H}_4$ , 2H), 7.70 (s,  $\text{H}_7$ ,  $\text{H}_8$ , 8H), 0.33 (s,  $\text{H}_{\text{Si}(\text{CH}_3)_3}$ , 9H) ppm.

MS (ES):  $m/z$  (%) = 631.3131 (100) [**8** +  $\text{H}$ ]<sup>+</sup> (calcd: 631.2713).

**1,4-Dibromo-2,5-diethylbenzene (10).** A 50-mL three-necked round-bottom flask was loaded with commercially available 1,4-diethylbenzene (5.0 g, 37.2 mmol) which was then cooled to 0  $^\circ\text{C}$ . In the absence of light,  $\text{I}_2$  (44 mg, 0.17 mmol) was added and the mixture stirred for 10 min at 0  $^\circ\text{C}$ . Then  $\text{Br}_2$  (12.19 g, 3.9 mL) was added in the dark via a dropping funnel over a period of 30 min. The ice-bath was removed and the reaction mixture left at room temperature for 24 h after which time 30 mL of KOH (20% aqueous solution) was added to neutralize the excess of bromide. After the red color had disappeared, the aqueous phase was removed and

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the crude product dissolved in 200 mL of hot EtOH. The solvents were partly removed by evaporation until crystallization occurred. The mixture was left at 4 °C overnight. After filtration the white product **10** was obtained in 60% yield (6.52 g).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.37 (s, H<sub>aromatic</sub>, 2H), 2.68 (q, *J* = 7.5 Hz, H<sub>-CH<sub>2</sub>-</sub>, 4H), 1.20 (t, *J* = 7.5 Hz, H<sub>-CH<sub>3</sub></sub>, 6H) ppm.

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 142.54, 133.04, 123.01, 28.7, 13.86 ppm.

MS (ES): *m/z* (%) = 292.0 (100) [**10**]<sup>+</sup> (calcd: 291.93).

**2,5-Diethyl-4-trimethylsilyl-bromobenzene (11).** An oven-dried three-necked round-bottom flask was loaded with 1,4-dibromo-2,5-diethylbenzene **10** (1 g, 3.42 mmol) and 20 mL of ether under argon. After cooling the solution to -78 °C, a solution of *n*-BuLi in hexane (1.34 M, 3.35 mL, 4.45 mmol) was added slowly dropwise. The mixture was then allowed to warm up to 0 °C and then cooled down again to -78 °C. Then trimethylsilylchloride (0.875 mL, 6.84 mmol) was added dropwise and mixture was allowed to warm to room temperature and stirred for another 15 h. A 10-mL portion of water was then added and stirred for 10 min. The aqueous phase was extracted twice with 10 mL of ether. The combined organic phases were washed with water (2 × 10 mL) and then dried over MgSO<sub>4</sub>. After removal of the solvents, the pure product was recovered as an oil in 75% yield (730 mg).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 7.45 (s, H<sub>7</sub>, 1H), 7.34 (s, H<sub>8</sub>, 1H), 2.77 (m, H<sub>-CH<sub>2</sub>-</sub>, 4H), 1.29 (m, H<sub>-CH<sub>3</sub></sub>, 6H), 0.38 (s, H<sub>Si(CH<sub>3</sub>)<sub>3</sub></sub>, 9H) ppm.

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 149.45, 139.46, 137.41, 135.58, 131.87, 125.64, 28.94, 28.20, 16.07, 14.37, 0.03 ppm.

MS (ES): *m/z* (%) = 287.2557 (100) [**11**]. (calcd: 287.0694).

**2,5-Diethyl-4-trimethylsilylphenylboronic Acid (12).** An oven-dried 50-mL three-necked flask was loaded with 2,5-diethyl-4-trimethylsilylbromobenzene **11** (500 mg, 1.75 mmol), 12 mL of ether and 3 mL of distilled THF under argon. After cooling down the solution to -78 °C, 3.75 mL (1.4 M solution in hexane) of *n*-BuLi (5.25 mmol) was added dropwise. The solution was then allowed to warm up to -10 °C then cooled to -78 °C again. 1.62 mL of triisopropylborate (7.02 mmol) was slowly added and the solution warmed up to room temperature and left under argon overnight. Then, 15 mL of water was added and the solution stirred for 15 min before evaporation to dryness. The crude product was dissolved in dichloromethane and washed with water. The aqueous phase was extracted 3× with 150 mL of dichloromethane. The combined organic phases were evaporated to dryness. After a rapid column chromatography on silica with pentane/ethyl acetate as eluent (100/0 to 65/35), the pure product was obtained in 72% yield as a white powder (608 mg).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C): δ = 8.10 (s, H<sub>7</sub>, 1H), 7.41 (s, H<sub>8</sub>, 1H), 3.21 (m, 2H), 2.79 (m, H<sub>-CH<sub>2</sub>-</sub>, 4H), 1.31 (m, H<sub>-CH<sub>3</sub></sub>, 6H), 0.37 (s, H<sub>Si(CH<sub>3</sub>)<sub>3</sub></sub>, 9H).

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 148.76, 146.45, 142.91, 136.65, 135.41, 28.56, 28.50, 17.73, 16.35, 0.02 ppm.

MS (ES): *m/z* (%) = 301.17 (100) dimethoxyboronic ester derivative (MeOH used as a solvent for the spectrometry) + Na<sup>+</sup> (calcd: 301.18).

**3,8-Bis(4-(2,5-diethyl-4-trimethylsilylphenyl)-2'-pyridyl)-4,7-phenanthroline (13).** A 25-mL round-bottom double-neck flask was loaded with 3,8-bis(4-bromo-2'-pyridyl)-4,7-phenanthroline **7** (99.5 mg, 0.202 mmol), 215 mg of K<sub>3</sub>PO<sub>4</sub> (1.011 mmol), and 10 mL of DMF, then degassed before 23 mg of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.202 mmol) was added under argon. After further degassing, 150 mg of 2,5-diethyl-4-trimethylsilylphenylboronic acid **12** (0.606 mmol) was added, and the solution was purged with argon once more before being heated to 120 °C. After 32 h, 23 mg of catalyst was added again and the reaction mixture left under argon at 120 °C for additional 18 h. The solution was then poured into 150 mL of water and the precipitate collected by filtration. After column chromatography

on alumina with pentane/ethyl acetate (100:0 to 70:30), the white solid **13** was obtained in 73% yield (108 mg).

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 9.11 (d, *J* = 8.8 Hz, H<sub>1'</sub>, 2H), 8.84 (d, *J* = 8.6 Hz, H<sub>2'</sub>, 2H), 8.80 (dd, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 0.6 Hz, H<sub>3'</sub>, 2H), 8.79 (dd, *J*<sub>1</sub> = 0.7 Hz, *J*<sub>2</sub> = 0.6 Hz, H<sub>5'</sub>, 2H), 8.37 (s, H<sub>6'</sub>, 2H), 7.93 (dd, *J*<sub>1</sub> = 8.3 Hz, *J*<sub>2</sub> = 2.0 Hz, H<sub>4'</sub>, 2H), 7.47 (s, H<sub>8'</sub>, 2H), 7.17 (s, H<sub>7'</sub>, 2H), 2.87 (q, *J* = 7.5 Hz, H<sub>9'a</sub>, 4H), 2.73 (q, *J* = 7.5 Hz, H<sub>9'b</sub>, 4H), 1.33 (t, *J* = 7.5 Hz, H<sub>10'a</sub>, 6H), 1.19 (t, *J* = 7.5 Hz, H<sub>10'b</sub>, 6H), 0.41 (s, H<sub>Si(CH<sub>3</sub>)<sub>3</sub></sub>, 18H) ppm.

<sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): 156.73, 154.71, 149.78, 148.11, 148.06, 138.93, 138.69, 138.64, 138.57, 137.94, 135.78, 132.93, 132.20, 129.97, 125.26, 121.23, 119.77, 28.98, 26.27, 16.75, 16.27, 0.56 ppm.

MS (ES): *m/z* (%) = 743.3961 (100) [**13** + H]<sup>+</sup> (calcd: 743.3960).

**3,8-Bis(4-(2,5-diethyl-4-iodophenyl)-2'-pyridyl)-4,7-phenanthroline (14).** A three neck round-bottom flask was loaded with the TMS-thread **13** (322 mg, 4.3 × 10<sup>-4</sup> mol) and 70 mL of freshly distilled CH<sub>2</sub>Cl<sub>2</sub>. After purging the solution with argon, it was cooled down to -10 °C. A 19-mL portion of a 0.23 M solution of ICl (4.6 × 10<sup>-3</sup> mol) in freshly distilled and degassed CH<sub>2</sub>Cl<sub>2</sub> was added slowly. The solution obtained was allowed to warm up to room temperature and left for 15 h under argon, during which time an orange precipitate formed. The reaction was then quenched with Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (stirred until the orange color had disappeared). A 50-mL portion of water was then added and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 150 mL). The combined organic layers were then washed with water (3 × 50 mL). After evaporation to dryness, the white solid product was obtained quantitatively (365 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.13 (d, *J* = 8.9 Hz, H<sub>1'</sub>, 2H), 8.85 (d, *J* = 8.6 Hz, H<sub>2'</sub>, 2H), 8.81 (dd, *J*<sub>1</sub> = 9.8 Hz, *J*<sub>2</sub> = 0.6 Hz, H<sub>3'</sub>, 2H), 8.73 (dd, *J*<sub>1</sub> = 2.2 Hz, *J*<sub>2</sub> = 0.6 Hz, H<sub>5'</sub>, 2H), 8.39 (s, H<sub>6'</sub>, 2H), 7.89 (dd, *J*<sub>1</sub> = 8.2 Hz, *J*<sub>2</sub> = 2.2 Hz, H<sub>4'</sub>, 2H), 7.82 (s, H<sub>8'</sub>, 2H), 7.12 (s, H<sub>7'</sub>, 2H), 2.81 (q, *J* = 7.5 Hz, H<sub>9'a</sub>, 4H), 2.63 (q, *J* = 7.5 Hz, H<sub>9'b</sub>, 4H), 1.27 (t, *J* = 7.5 Hz, H<sub>10'a</sub>, 6H), 1.16 (t, *J* = 7.5 Hz, H<sub>10'b</sub>, 6H) ppm.

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): 156.20, 154.73, 149.24, 147.74, 144.30, 141.53, 139.77, 138.02, 137.54, 137.29, 132.69, 131.86, 129.90, 124.88, 121.25, 119.52, 100.59, 33.68, 25.48, 15.64, 14.68 ppm.

MS (ES): *m/z* (%) = 851.1119 (100) [**14** + H]<sup>+</sup> (calcd: 851.1102).

**OTHP-Thread (16).** A two-necked round-bottom flask was loaded under argon atmosphere with 182 mg (0.214 mmol) of the iodo-thread **14**, 210 mg (0.944 mmol) of the 4-(tetrahydro-2H-pyran-2-yloxy)phenylboronic acid **15**, 226 mg (2.14 mmol) of Na<sub>2</sub>CO<sub>3</sub>, in solution in 24 mL of toluene, 8 mL of H<sub>2</sub>O, and 4 mL of EtOH. After degassing the mixture, 25 mg (2.14 × 10<sup>-5</sup> mol) of Pd(PPh<sub>3</sub>)<sub>4</sub> were added, and the mixture was heated to 90 °C. After 5 h, the reaction mixture was cooled, and the solvents evaporated. The product was purified by column chromatography on alumina with pentane/ethyl acetate (100:0 to 50:50). The white product was obtained in 75% yield (171 mg).

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 9.14 (d, *J* = 8.7 Hz, H<sub>1'</sub>, 2H), 8.88 (d, *J* = 8.7 Hz, H<sub>2'</sub>, 2H), 8.83 (d, *J* = 7.8 Hz, H<sub>3'</sub>, 2H), 8.80 (d, *J* = 2.4 Hz, H<sub>5'</sub>, 2H), 8.35 (s, H<sub>6'</sub>, 2H), 7.96 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2.4 Hz, H<sub>4'</sub>, 2H), 7.32 (d, *J* = 8.7 Hz, H<sub>6'</sub>, 4H), 7.24 (s, H<sub>8'</sub>, 2H), 7.21 (s, H<sub>7'</sub>, 2H), 7.12 (d, *J* = 8.7 Hz, H<sub>m'</sub>, 4H), 5.46 (s, H<sub>OTHP</sub>, 1H), 3.95-3.64 (m, H<sub>OTHP</sub>, 2H), 2.67 (m, H<sub>9'</sub>, 8H), 1.87 (m, H<sub>OTHP</sub>, 6H), 1.14 (m, H<sub>10'</sub>, 12H) ppm.

<sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 156.24, 154.20, 149.43, 147.57, 141.35, 139.40, 139.15, 138.04, 137.59, 136.54, 134.83, 132.46, 131.73, 130.72, 130.29, 130.12, 124.76, 120.78, 119.29, 116.07, 96.63, 62.23, 30.44, 25.71, 25.26, 19.00, 15.61, 15.51 ppm.

MS (Maldi-TOF): *m/z* (%) = 951.511 (100) [**16** + H]<sup>+</sup> (calcd: 951.483).

**Phenol-Thread (17).** A 100-mL round-bottom flask was loaded under argon atmosphere with OTHP-thread **16** (136 mg, 0.143 mmol), which was dissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub>, then 50 mL of MeOH and 3 mL of concentrated HCl (37%) were added. The mixture was heated to reflux for 4 h. The solvents were then evaporated and the remaining solid dissolved in 100 mL of CH<sub>2</sub>Cl<sub>2</sub>, before 150 mL of aqueous NaOH 1 M was added. By adding HCl (37%) the solution was brought to pH = 7, then the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 100 mL). The combined organic layers were then washed twice with 100 mL of H<sub>2</sub>O and after evaporation of the solvent the pure product was obtained in 95% yield (104 mg).

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 9.15 (d, *J* = 8.7 Hz, H<sub>1</sub>, 2H), 8.89 (d, *J* = 8.7 Hz, H<sub>2</sub>, 2H), 8.83 (dd, *J*<sub>1</sub> = 8.1 Hz, *J*<sub>2</sub> = 0.5 Hz, H<sub>3</sub>, 2H), 8.78 (dd, *J*<sub>1</sub> = 2.2 Hz, *J*<sub>2</sub> = 0.5 Hz, H<sub>5</sub>, 2H), 8.37 (s, H<sub>6</sub>, 2H), 7.96 (dd, *J*<sub>1</sub> = 8.1 Hz, *J*<sub>2</sub> = 2.2 Hz, H<sub>4</sub>, 2H), 7.27 (d, *J* = 8.6 Hz, H<sub>6</sub>, 4H), 7.23 (s, H<sub>8</sub>, 2H), 7.20 (s, H<sub>7</sub>, 2H), 6.93 (d, *J* = 8.6 Hz, H<sub>m</sub>, 4H), 2.68 (m, H<sub>9</sub>, 8H), 1.16 and 1.13 (2t, *J* = 7.6 Hz, H<sub>10</sub>, 12H) ppm.

MS (ES): *m/z*(%) = 783.3608 (100) [**17** + H]<sup>+</sup> (calcd: 783.694).

**[4]Pseudorotaxane (19.4PF<sub>6</sub>).** A solid–solid mixture of the bis-macrocycle **1** (50 mg, 4.32 × 10<sup>-5</sup> mol) and the thread **2** (23.6 mg, 4.32 × 10<sup>-5</sup> mol) was suspended in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (40 mL) under argon. A degassed solution of MeCN containing [Cu(MeCN)<sub>4</sub>](PF<sub>6</sub>) (33.3 mg, 8.94 × 10<sup>-5</sup> mol, 20 mL) was added via canula technique. The solution was stirred at room temperature avoiding light exposure. After 7 days, the mixture was homogeneous. The solvents were then evaporated and the product extracted from water with dichloromethane. After evaporation of the solvent, the tetrameric pseudorotaxane **19.4PF<sub>6</sub>** was obtained quantitatively (91 mg).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, COSY, ROESY, 25 °C): δ = 10.02 (d, *J* = 8.2 Hz, H<sub>4</sub>, H<sub>7</sub>, 8H), 9.54 (d, *J* = 8.9 Hz, H<sub>1</sub>, 4H), 8.76 (d, *J* = 9.0 Hz, H<sub>2</sub>, 4H), 8.61 (d, *J* = 8.6 Hz, H<sub>3</sub>, 4H), 8.33 (dd, *J*<sub>1</sub> = 8.6 Hz, *J*<sub>2</sub> = 2.2 Hz, H<sub>4</sub>, 4H), 8.27 (d, *J* = 1.8 Hz, H<sub>5</sub>, 4H), 8.24 (d, *J* = 8.2 Hz, H<sub>3</sub>, H<sub>8</sub>, 8H), 7.57 (m, *J* = 9.1 Hz, H<sub>7</sub>, 8H), 7.43 (s, H<sub>6</sub>, 4H), 7.34 (m, *J* = 8.4 Hz, H<sub>6</sub>, 8H), 7.06 (m, *J* = 9.1 Hz, H<sub>8</sub>, 8H), 6.10 (m, *J* = 8.5 Hz, H<sub>m</sub>, 8H), 3.95–3.78 (m, H<sub>α</sub>, H<sub>β</sub>, H<sub>γ</sub>, H<sub>δ</sub>, H<sub>ε</sub>, H<sub>OMe</sub>, 92H) ppm.

MS (ES): *m/z*(%) = 915.2614 (100) [**19**<sup>4+</sup>] (calcd: 915.2621).

**Crystallographic Details for 19<sup>4+</sup>.** Suitable crystals were obtained from slow diffusion of THF into a CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. C<sub>245</sub>H<sub>218</sub>Cl<sub>8</sub>Cu<sub>4</sub>F<sub>24</sub>N<sub>20</sub>O<sub>32</sub>P<sub>4</sub>, *M* = 5072.09 g mol<sup>-1</sup>, triclinic, *P* $\bar{1}$  (no. 2), *a* = 18.4923(2) Å, *b* = 19.6458(4) Å, *c* = 20.4339(4) Å, *a* = 86.311(1)°, *b* = 66.573(1)°, *g* = 64.109(1)°, *V* = 6074.0(2) Å<sup>3</sup>, *Z* = 1, *D*<sub>calc</sub> = 1.387 Mg m<sup>-3</sup>, *m* = 0.550 mm<sup>-1</sup>, GOF on *F*<sup>2</sup> = 1.093, *R*<sub>1</sub> = 0.1149, *wR*<sub>2</sub> = 0.3003 [*I* > 2σ(*I*)].

**[4]Pseudorotaxane (20.4PF<sub>6</sub>).** To a degassed suspension of **1** (80 mg, 6.91 × 10<sup>-5</sup> mol) and **3** (78 mg, 6.91 × 10<sup>-5</sup> mol, 1 eq.) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL), a solution of [Cu(MeCN)<sub>4</sub>](PF<sub>6</sub>) (52.0 mg, 13.95 × 10<sup>-5</sup> mol, 2.02 eq.) in dry MeCN (25 mL) was added. The mixture immediately turned red but was reacted for further 7 days to complete threading of the bis-macrocycle. The crude was then filtered and evaporated to dryness giving **20.4PF<sub>6</sub>** quantitatively (186 mg).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, COSY, ROESY, 25 °C): δ = 10.03 (d, *J* = 8.3 Hz, H<sub>4</sub>, H<sub>7</sub>, 8H), 9.67 (d, *J* = 8.3 Hz, H<sub>1</sub>, 4H), 8.88 (d, *J* = 8.3 Hz, H<sub>2</sub>, 4H), 8.71 (d, *J* = 7.5 Hz, H<sub>3</sub>, 4H), 8.27

(d, *J* = 8.6 Hz, H<sub>3</sub>, H<sub>8</sub>, 8H), 8.19 (s, H<sub>5</sub>, 4H), 8.14 (d, *J* = 7.5 Hz, H<sub>4</sub>, 4H), 7.56 (s, H<sub>6</sub>, 4H), 7.40 (d, *J* = 7.8 Hz, H<sub>6</sub>, 16H), 7.23 (d, *J* = 7.8 Hz, H<sub>6</sub>, 8H), 7.17 (s, H<sub>7</sub>, 4H), 7.13 (s, H<sub>8</sub>, 4H), 6.96 (d, *J* = 8.5 Hz, H<sub>m</sub>, 8H), 6.20 (d, *J* = 7.8 Hz, H<sub>m</sub>, 16H), 5.90 (m, *J*<sub>1</sub> = 17.0 Hz, *J*<sub>2</sub> = 10.1 Hz, *J*<sub>3</sub> = 5.4 Hz, H<sub>1</sub>, 4H), 5.25 (d, *J* = 17.0 Hz, H<sub>7</sub>, 4H), 5.13 (d, *J* = 10.1 Hz, H<sub>7</sub>, 4H), 4.18 (t, *J* = 5.1 Hz, H<sub>a</sub>, 8H), 4.09–3.89 (m, H<sub>α</sub>, H<sub>β</sub>, H<sub>γ</sub>, H<sub>δ</sub>, H<sub>ε</sub>, 80H), 3.88 (t, *J* = 5.1 Hz, H<sub>6</sub>, 8H), 3.75–3.54 (m, H<sub>c</sub>, H<sub>d</sub>, H<sub>e</sub>, H<sub>f</sub>, H<sub>g</sub>, 40H), 2.70–2.54 (2m, *J* = 7.0 Hz, H<sub>9</sub>, 16H), 1.14 (t, *J* = 7.0 Hz, H<sub>10</sub>, 24H) ppm.

MS (ES): *m/z*(%) = 1655.755 (100) [**20**.PF<sub>6</sub>]<sup>3+</sup> (calcd: 1655.590).

## Conclusions

The present report represents another illustration of the efficiency of copper(I) to act as a template in the formation of multicomponent threaded species of the rotaxane family. Under mild conditions, the copper(I)-driven formation of threaded species composed of two rods and two bis-macrocycles was shown to be quantitative. This was particularly true for a long fragment (**3**), consisting of a rigid aromatic core terminated by two long flexible chains. The driving force for making such [2]pseudorotaxane tetramers is the coordination of diimine type ligands to Cu(I). Each copper(I) center is strongly stabilized by two diimines, leading to approximately tetrahedral complexes and, in turn, each ligand “is eager” to bind avidly to a copper(I) atom. This situation, combined with the fact that the complexes are relatively labile and thus permit thermodynamic control, is very favorable to the formation of multicomponent discrete species. Another important feature of the present assembly principle is related to the translational entropy factor, which clearly favors formation of the smallest assembly as possible. This is one of the possible reasons to explain that no polymer nor uncharacterised open-chain complex is observed in the formation of the threaded compounds. Finally, an aesthetically attractive X-ray structure could be obtained which demonstrates in a nonambiguous fashion the threaded nature of the 4-copper complexes.

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**Supporting Information Available:** Crystallographic data for [4]pseudorotaxane (**19.4PF<sub>6</sub>**) in Cif format and as a checkcif file. A thermal ellipsoid figure of this compound is also included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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