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Copper(I)-Assembled [3]Rotaxane Whose Two Rings Act as Flapping Wings

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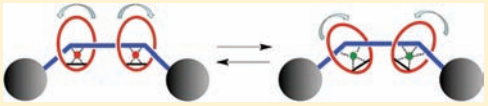
Supporting Information

ABSTRACT: A new copper-complexed [3]rotaxane consisting of two coordinating 30-membered rings threaded by a two-binding-site axis has been prepared in good yield from relatively simple organic fragments. The main specificity of the system originates from the stoppering reaction, based on "click" chemistry, and thus from the presence of two triazole groups at positions next to the bidentate chelates of the axis central part. The geometry of the coordinating atoms belonging to the axis is such that the triazole groups can either be part of the coordinating fragments when the metal center is 5-coordinate or be not at all involved in coordination to the metal when the latter is 4-coordinate. To be more specific, when the two complexed metal centers are monovalent copper(I) centers, the triazoles are not included in the metal coordination sphere, whereas when the metal centers are Cu(II) or Zn^{2+}, the triazole groups are bound to the metals. This is easily explained by the fact that Cu(I) is preferably 4-coordinate and Cu(II) and Zn^{2+} are 5-coordinate. The interconversion between both situations (4- or 5-coordinate) can be quantitatively induced by metal exchange ($Cu(I)/Zn^{2+}$) or by a redox process (Cu(II)/Cu(I)). It leads to important geometrical changes and in particular to a strong modification of the angle between the two rings. As a consequence, the two threaded rings undergo a motion which is reminiscent of a wing-flapping movement similar to that of birds. This flapping motion is fast and quantitative. It should lead to new functional molecular machines in the future.



INTRODUCTION

In the very active research area of catenanes and rotaxanes,[1] transition-metal-based systems[2] display specific features related to the electrochemical or photochemical properties associated with coordination compounds and to the topology of the systems. In addition, they are often prepared in high yield owing to the stability of the transition-metal-complexed threaded precursors, leading to the desired interlocking molecule. As far as rotaxanes are concerned, the stopper-attaching reaction has often been a limitation, leading to mediocre yields of the final product.[3] In this respect, the so-called "click" chemistry reaction[4] represents a very significant improvement, as illustrated by a few recent examples.[5] The triazole groups synthesized in the course of the stoppering click reaction have rarely been used as ligands in the field of interlocking compounds.[6] Similarly, only a very few examples exist with noninterlocking systems for which the newly synthesized triazole motif becomes a coordinating fragment of a tridentate ligand.[7] We report the copper-templated synthesis of new [3]rotaxanes via click chemistry, the two triazole groups made during the stopper-forming reaction becoming components of the coordinating fragments. In this way, the *bidentate* chelates used for assembling the various parts of the [3]rotaxane precursor ("gathering-and-threading" process) become *tridentate* ligands after the click reaction. Interestingly, the [3]rotaxane obtained can be set in motion by switching the two complexing subunits belonging to the thread from bidentate to tridentate. This simple procedure can be performed either electrochemically (Cu(I)/Cu(II)) or by metal exchange ($Cu(I)/Zn^{2+}$). It is reversible and triggers a movement of the two threaded rings which is reminiscent of the flapping wings of a bird or a butterfly.

RESULTS AND DISCUSSION

The synthesis principle relies on the ability of copper(I) to form a stable 4-coordinate complex when reacted with a bidentate-chelate-incorporating ring and a threadlike fragment incorporating another bidentate chelate, as extensively used in previous work from our group.[8] In the present case, the thread contains two bidentate chelating units, thus affording a [3]pseudorotaxane when mixed with the copper(I) complex of a macrocyclic compound whose coordinating unit is a bidentate chelate. The general synthesis principle is represented in Scheme 1. The chemical structures of the various precursors are given in Figures 1 and 2.

Synthesis of the New Thread. 2,6-Dibromopyridine (**2**) was converted to compound **4** using first a Sonogashira coupling reaction to afford **3**, followed by the substitution of bromine by a tributylstannyl group. The triisopropylsilyl (TIPS)-protected compound **4** was subsequently coupled with 3,8-dibromo-4,7-phenanthroline (**5**), which was synthesized according to a published procedure,[9] to generate the two-chelate axis precursor **7** after deprotection of the acetylenic fragments of **6** (Figure 1).

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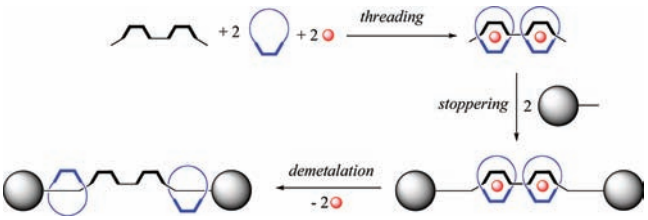
Scheme 1. Synthesis Principle: Copper(I)-Directed "Gathering-and-Threading" Reaction Performed with a Two-Chelating Group Axis and Two Rings, Followed by the Sequence of Reactions Leading to the Final [3]Rotaxane[a]



[a]The metal center is represented by a red dot, and the chelating groups are indicated by a black or blue U-shaped symbol.

Threading and Stoppering Reactions Leading to the Target [3]rotaxane $[1{\cdot}Cu_2]^{2+}$ and 1. The gathering-and-threading reaction was carried out in the usual way by first preparing a solution of the copper(I) complex of macrocycle **8** and subsequently by adding it to **7**. [3]Pseudorotaxane $\mathbf{9}^{2+}$ was obtained quantitatively from **7**, **8**, and copper(I), as indicated in Figure 2. The unstoppered species $\mathbf{9}^{2+}$ was converted into a real rotaxane using click chemistry. The double stoppering reaction was achieved by mixing the [3]pseudorotaxane $\mathbf{9}^{2+}$, the azide stopper **10**, and a catalytic amount of Cu(tren′)Br (whose chemical structure is indicated in Figure 3) in a 3/1 mixture of CH_2Cl_2/CH_3CN.

Cu(tren′)Br was proposed by Vincent and co-workers as an efficient and stable click chemistry catalyst, which turned out to be particularly useful under relatively aggressive conditions.[10] This catalyst was also shown to be particularly useful for preparing copper(I)-complexed multirotaxanes.[11] The present work confirms the efficacy of this compound for click reactions involving copper-containing precursors. To avoid any potential purification difficulty or decomplexation problem with the copper complex obtained after the click reaction, it was decided to demetalate and purify the free ligand [3]rotaxane **1**. The crude mixture obtained after the stopper-attaching reaction was thus treated by an excess of KCN in a mixture of dichloromethane, acetonitrile, and water (1/0.5/0.1), and the reaction went to completion after 4 h. After column chromatography on silica gel, the [3]rotaxane **1** was obtained in an excellent yield of 89% over two steps (stoppering and demetalation). **1** was fully characterized by 1D and 2D ^{1}H NMR spectroscopy experiments and by electrospray mass spectrometry (ES-MS). The main feature of **1** is that its axis now contains two *tridentate* chelating groups instead of bidentate ones. The triazole unit is an integral component of a terpyridine-like coordinating set consisting of two pyridinic nitrogen atoms and the N-3 atom of the triazole nucleus. In terms of coordination chemistry, the system is ideal since each hypothetical chelate ring is a five-membered ring incorporating the metal center, two nitrogen atoms, and two carbon atoms.

The coordination properties of [3]rotaxane **1** were investigated. The ability of this rotaxane to complex two metal ions, Cu(I) and Zn^{2+}, was studied. Compound **1** was first remetalated with Cu(I). A 2 equiv sample of $Cu(CH_3CN)_4PF_6$ in CH_3CN was added to a solution of **1** in dichloromethane to give quantitatively the desired [3]rotaxane $[\mathbf{1}{\cdot}Cu_2]^{2+}$. This compound was characterized by ^{1}H NMR spectroscopy (1D, correlation spectroscopy (COSY), nuclear Overhauser enhancement spectroscopy (NOESY)) as well as by ES-MS.

The zinc(II) [3]rotaxane $[\mathbf{1}{\cdot}Zn_2]^{4+}$ was also obtained quantitatively from the metal-free rotaxane **1** by reacting it in the presence of a slight excess of $Zn(OTf)_2$ in a 1/1 mixture of dichloromethane and methanol. It was fully characterized by ^{1}H NMR spectroscopy (1D, COSY, NOESY) and by ES-MS.

^{1}H NMR studies clearly demonstrated that *the copper(I) complex contains two 4-coordinate centers whereas the zinc complex consists of two 5-coordinate Zn^{2+} centers,* as depicted in Figure 4. Particularly sensitive to the coordination mode of the metal are protons H-6′ of the axis, protons H-5,6 of the 1,10-phenanthroline (phen) nucleus belonging to the threaded ring, proton H-7′ of the triazole group, and protons H-1′ and H-2′ of the central 4,7-phenanthroline nucleus. The chemical shifts (ppm) of these five protons are collected in Table 1 for various metal-free compounds and for copper(I) or zinc(II) complexes. Compound **11** and its copper(I) complex $[\mathbf{11}{\cdot}Cu_2]^{2+}$ (see Figure 5) have been included in the table since they can be considered as reference compounds. These [3]rotaxanes were recently reported by our group.[12]

From Table 1 and Figure 4, it is clear that the main difference between free rotaxanes **1** and **11** in terms of chemical shifts is the important shift of proton H-7′ ($\Delta\delta = -0.66$ ppm from **1** to **11**). This shift is very likely due to the ortho position of the triazole on the pyridine nuclei in **1**, leading to a hydrogen bond between this proton and the nitrogen atom of the vicinal pyridine, as already observed in previous work.[7c] The positions

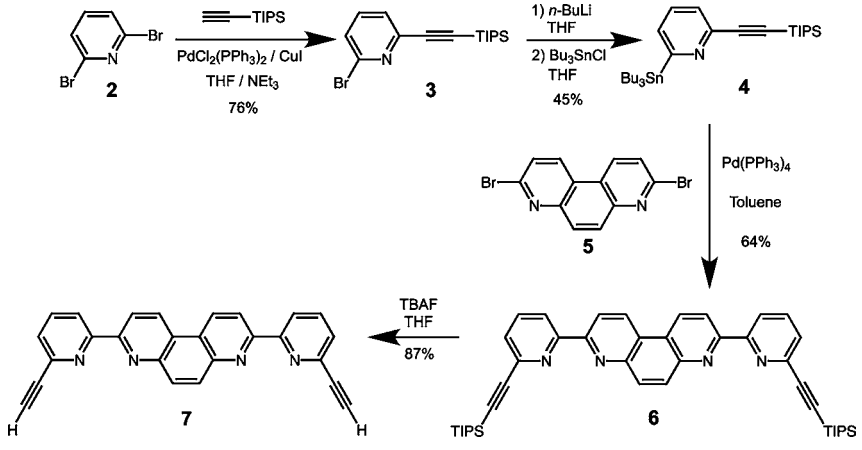


Figure 1. Preparation of the precursors of the [3]rotaxane axis.

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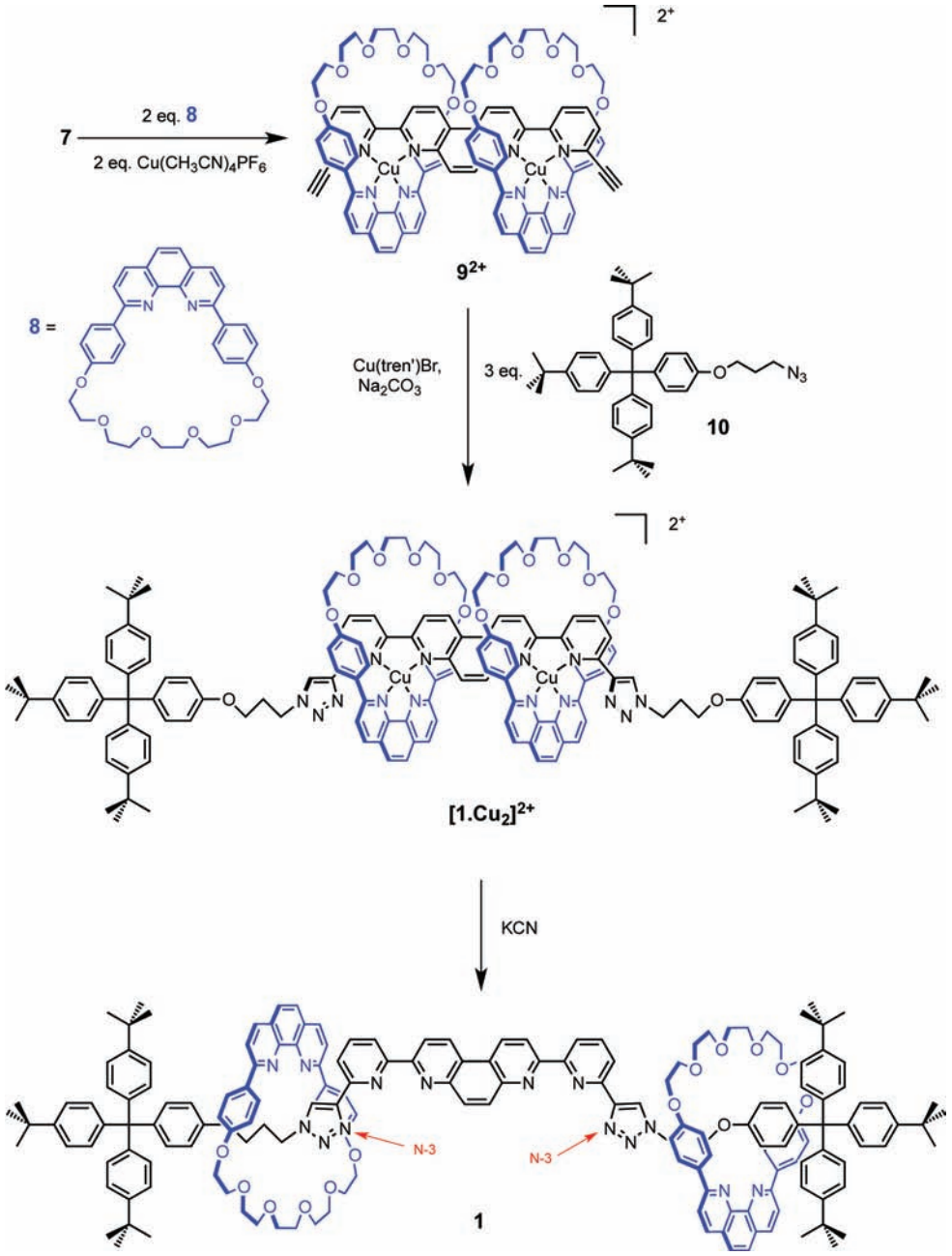

Figure 2. Synthesis of [3]rotaxane **1**.

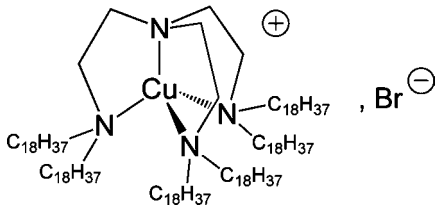

Figure 3. Chemical structure of the catalyst Cu(tren′)Br.

of the two macrocycles in the copper complexes $[\mathbf{1}\cdot Cu_2]^{2+}$ and $[\mathbf{11}\cdot Cu_2]^{2+}$ are very similar, as shown by the nearly perfect match of the chemical shifts for the protons of the 4,7-phenanthroline (9.47 vs 9.49 ppm for H-1′, 7.32 vs 7.34 ppm for H-6′, 8.71 vs 8.72 ppm for H-2′, respectively). These data clearly indicate that each copper in complex $[\mathbf{1}\cdot Cu_2]^{2+}$ is 4-coordinate, its coordination sphere consisting of the 1,10-phenanthroline unit of a ring and the nitrogen atoms of the 4,7-phenanthroline and the pyridine moieties of the axis, without any involvement of the triazole groups. Moreover, the triazole proton H-7′ is strongly upfield shifted ($\Delta\delta = -1.88$ ppm) upon copper coordination since it is in the shielding region of the 1,10-phenanthroline nuclei.

Concerning the Zn(II) rotaxane $[\mathbf{1}\cdot Zn_2]^{4+}$, the position of the rings can be deduced from the strong upfield shift of the axis protons H-6′ ($\Delta\delta = -1.92$ ppm) in comparison with those of the free rotaxane **1** (Figure 6). In fact, proton H-6′ is in the shielding cone of each ring-incorporated 1,10-phenanthroline. This is consistent with a conformation where each ring is inclined toward the axis for the triazole to be part of the coordination sphere of the zinc cation. Such a phenomenon has already been observed with related systems, and it was proven

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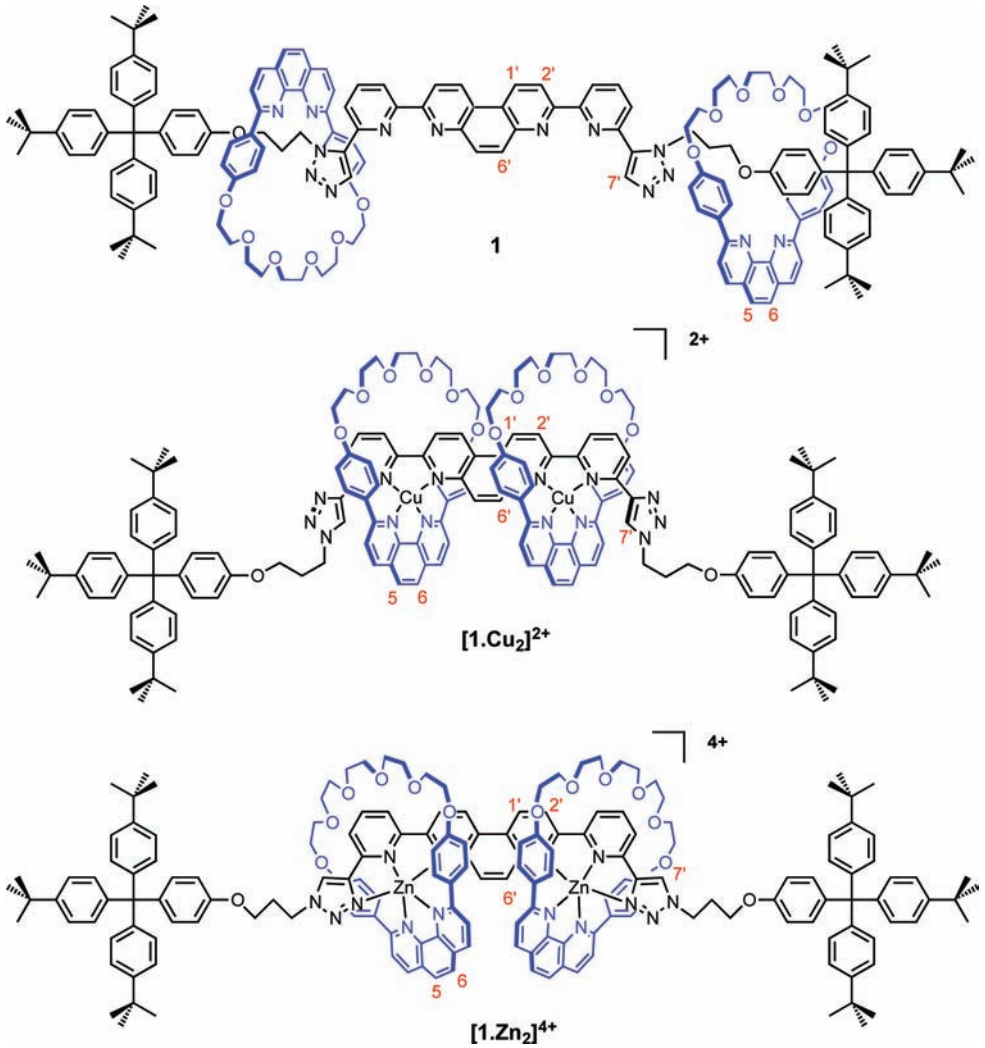

Figure 4. Chemical structures and atom numbering of [3]rotaxane **1** and its complexes $[\mathbf{1}\cdot Cu_2]^{2+}$ and $[\mathbf{1}\cdot Zn_2]^{4+}$. The protons discussed in Table 1 are in red.

Table 1

	H-6′	H-5,6	H-7′	H-1′	H-2′
11	8.31	7.77	8.81	9.16	8.77
$[\mathbf{11}\cdot Cu_2]^{2+}$	7.34	8.07	8.50	9.49	8.72
1	8.38	7.63	9.47	9.05	8.83
$[\mathbf{1}\cdot Cu_2]^{2+}$	7.32	7.95	7.59	9.47	8.71
$[\mathbf{1}\cdot Zn_2]^{4+}$	6.46	8.50	8.61	9.75	8.85

that the slanted orientation of the macrocycles toward each other induced such a shielding of the H-6′ proton.[11a] However, in the latter case, the coordination of triflates explained the conformation of the macrocycles. In the present case, the position of the triazole (in the ortho position of the pyridine nuclei) and its much stronger coordination property compared to that of the triflate are in favor of its participation in the coordination sphere of the zinc(II). Moreover, protons H-5,6 of the ring have moved downfield by 0.87 ppm since they are in the deshielding region of the other ring-incorporated 1,10-phenanthroline. Another important observation concerns proton H-7′ of the triazole. Its chemical shift is much higher in the Zn^{2+} complex $[\mathbf{1}\cdot Zn_2]^{4+}$ (8.61 ppm) than in the Cu(I) complex $[\mathbf{1}\cdot Cu_2]^{2+}$ (7.59 ppm). This downfield shift can be related to two factors: the higher electropositivity of Zn^{2+} compared to Cu(I) and the fixed position of the triazole coordinated to Zn^{2+}, driving away the proton H-7′ from the shielding cone of the ring-incorporated 1,10-phenanthroline.

Replacement of Cu(I) by Zn^{2+} and, vice versa, exchange of Zn^{2+} for Cu(I) induce a motion of the two rings which is reminiscent of a wing-flapping movement. In the copper complex the two cyclic components are approximately parallel to one another, whereas in the Zn^{2+} complex the average planes of the rings form an angle which is roughly 60° if one considers that the coordination axis of the ring-incorporated phen chelate is collinear with the N−C4 axis of the pyridine nucleus located between the triazole group and the central 4,7-phenanthroline fragment of the "thread".

Electrochemically Triggered Wing-Flapping Motion. The same motion as the one driven by metal exchange can be induced by a Cu(II)/Cu(I) redox process. This motion is illustrated in a very schematic fashion in Scheme 2.

In a preliminary study, an electrochemical analysis of the reference compound $[\mathbf{11}\cdot Cu_2]^{n+}$ (n = 2 or 4) was carried out which shows a clean two-electron redox wave at 0.65 V vs SCE in 1/1 CH_2Cl_2/CH_3CN (ΔE_p = 117 mV; see the Supporting Information). This relatively high value is in perfect agreement with a tetrahedral or distorted tetrahedral geometry for the copper center, indicating that monovalent copper is strongly

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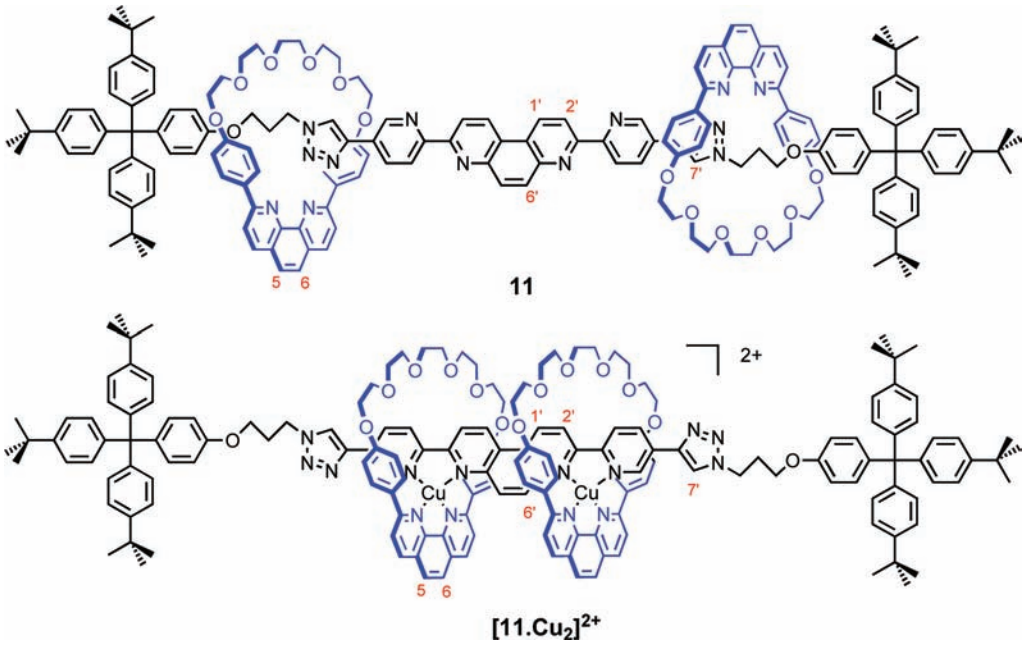


Figure 5. Chemical structures of reference compounds **11** and $[\mathbf{11}\cdot Cu_2]^{2+}$ with numbering in red of the most important protons in terms of ^1H NMR studies. Reprinted with permission from ref 12. Copyright 1999 Royal Society of Chemistry.

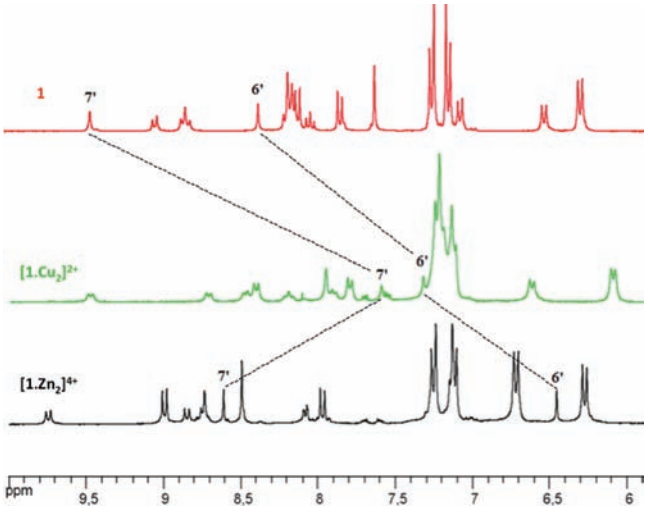
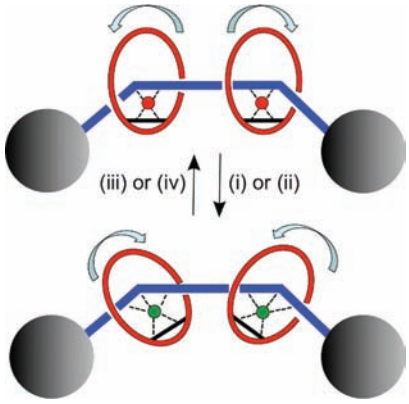


Figure 6. Partial ^1H NMR spectra of **1**, $[\mathbf{1}\cdot Cu_2]^{2+}$, and $[\mathbf{1}\cdot Zn_2]^{4+}$ in CD_2Cl_2 (except for $[\mathbf{1}\cdot Zn_2]^{4+}$ in CD_3CN).

stabilized versus copper(II). Similar redox potential values were recently reported for related 4-coordinate compounds.[9,13]

As shown in Figure 7, the cyclic voltammogram of $[\mathbf{1}\cdot Cu_2]^{n+}$ (n = 2 or 4) shows perfect chemical reversibility, with an $E_{1/2}$ value of 0.31 V vs SCE in 1/1 CH_2Cl_2/CH_3CN and a ΔE_p value of 149 mV. The comparatively low redox potential found for this complex is closer to that obtained for other related molecules with 5-coordinate copper centers.[14] Indeed, given that the redox potential of a 5-coordinate copper complex with a terpy (terpy = 2,2′:6′,2″-terpyridine) and a phen is about 0 V,[15] that found for $[\mathbf{1}\cdot Cu_2]^{n+}$ is between those of 4- and 5-coordinate copper complexes, confirming the ambivalent character of this rotaxane. The fact that only one redox wave was observed is consistent with a fast ligand exchange in the coordination sphere of the metal. The 4-coordinate species (which is likely to correspond to the most stable situation for copper(I) and which is only very minor for Cu(II) in terms of

Scheme 2. Cartoon Representing the Motions of the Two Macrocycles[a]



[a]Key: (i) oxidation of Cu(I) to Cu(II), (ii) exchange of Cu(I) for Zn^{2+}, (iii) reduction of Cu(II) to Cu(I), (iv) exchange of Zn^{2+} for Cu(I).

proportion) and the 5-coordinate compound (stable divalent copper and only small proportion for Cu(I)) undergo a fast equilibrium, regardless of the metal oxidation state, thus leading to a redox potential value for Cu(II)/Cu(I) which is intermediate between those of the 4- and 5-coordinate states. The Cu(II)/Cu(I) redox process is accompanied by a motion similar to that induced by the Zn^{2+}/Cu(I) exchange: in the divalent copper complex the rings form an angle of approximately 60°, whereas they are parallel to each other in the monovalent copper complex (Scheme 2). However, in the electrochemically triggered motion, it is clear that the movement is much faster than the chemically induced one based on metal exchange. It is particularly noteworthy that this movement is one of the fastest motions induced by a copper-centered redox process in the field of interlocking systems.[16]

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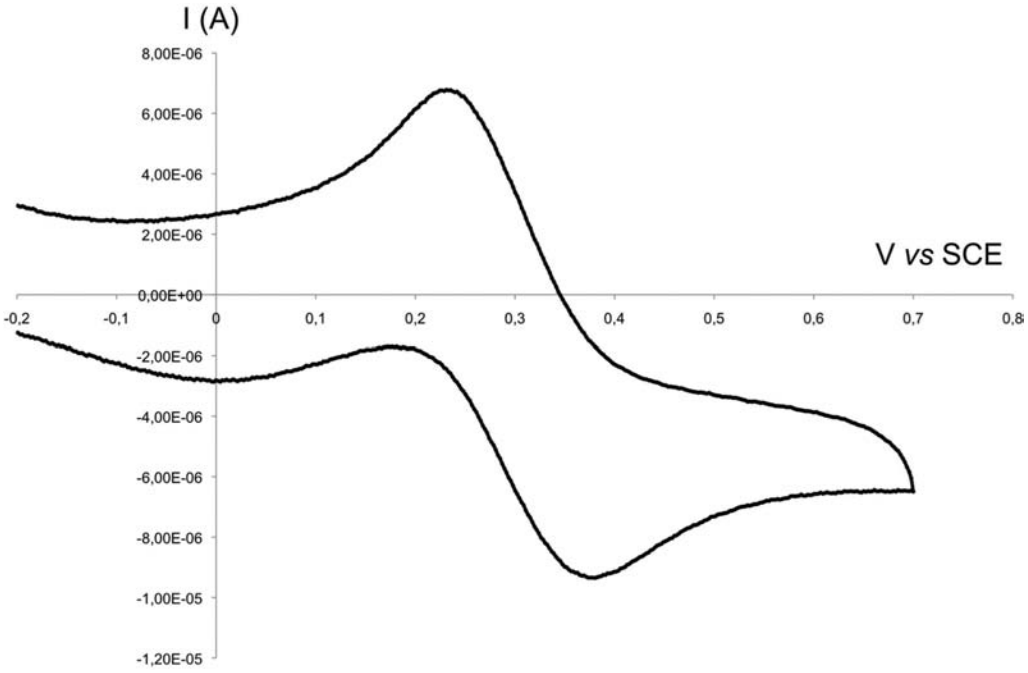

Figure 7. Cyclic voltammogram of complex $[\mathbf{1}\cdot Cu_2]^{2+}$ recorded on a Pt working electrode at 100 mV/s in CH_2Cl_2/CH_3CN (1/1) with 0.1 M Bu_4NPF_6.

CONCLUSION

In conclusion, a new copper- or zinc-complexed [3]rotaxane has been synthesized using the classical copper-templated strategy followed by click chemistry with an excellent yield. The triazole group formed by click has a dual function: (i) it serves as the attachment point of the rotaxane stopper, and (ii) it can act as the third ligand of a potential tridentate chelating group of the terpyridine family. In the dicopper(I) complex of the [3]rotaxane obtained, the two metal centers are 4-coordinate and the rings are parallel to one another, whereas in the dizinc complex obtained by metal exchange or in the dicopper(II) compound formed by oxidation of its monovalent analogue, the metal centers are 5-coordinate and the two rings form a significant angle with each other. The corresponding motion is reminiscent of that of flapping wings in birds or flying insects.

EXPERIMENTAL DETAILS

2-Bromo-6-[(triisopropylsilyl)ethynyl]pyridine (3). 2,6-Dibromopyridine (1.01 g, 4.26 mmol), (triisopropylsilyl)acetylene (0.32 mL, 1.43 mmol), $PdCl_2(PPh_3)_2$ (66 mg, 0.09 mmol), and CuI (38 mg, 0.20 mmol) were dissolved in 9 mL of degassed THF and 1 mL of degassed NEt_3. The mixture was stirred for 2 h and filtered. The solvents were then evaporated, and the residue was purified by column chromatography on silica (eluent *n*-pentane/CH_2Cl_2 from 90/10 to 70/30) to give **3** (366 mg, 1.08 mmol) as a colorless oil (76%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.51−7.39 (m, 3H, H-3, H-4, H-5), 1.13 (s, 15H, H−C$H_{3_{TIPS}}$), 1.12 (s, 3H, H−CH_{TIPS}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 143.8, 141.6, 138.1, 127.6, 126.8, 104.4, 93.9, 18.6, 11.2 ppm. HR-MS (ES): *m*/*z* (rel intens) = 340.082 (100) $[M + H]^+$ (calcd 340.092 for $[C_{16}H_{24}BrNSiH]^+$).

2-[(Triisopropylsilyl)ethynyl]-6-(tributylstannyl)pyridine (4). **3** (366 mg, 1.08 mmol) was diluted in 20 mL of distilled THF. *n*-BuLi (0.8 mL of a 1.6 M solution in hexane, 1.28 mmol) was added dropwise at −78 °C. After the addition was completed, the temperature was allowed to increase to −20 °C and then was decreased again to −78 °C. A solution of Bu_3SnCl (0.4 mL, 1.47 mmol) in 5 mL of distilled THF was then added dropwise. Once addition was completed, the solution was allowed to warm to room temperature and stirred overnight under argon. The solvents were then evaporated, and the residue was purified by column chromatography on alumina with *n*-pentane as the eluent. **4** (267 mg, 0.49 mmol) was obtained as a colorless oil (45%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.40 (dd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, 1H, H-4), 7.28 (d, *J* = 7.5 Hz, 2H, H-3), 7.27 (d, *J* = 7.6 Hz, 2H, H-5), 1.56 (m, 6H, H-a), 1.33 (s, *J* = 7.5 Hz, H-c), 1.15 (s, 18H, H−C$H_{3_{TIPS}}$), 1.14 (s, 3H, H−CH_{TIPS}), 1.10 (m, 6H, H-b), 0.88 (t, *J* = 7.4 Hz, 9H, H-d) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 174.6, 144.1, 132.6, 130.9, 126.1, 107.4, 90.51, 29.0, 27.3, 18.7, 13.7, 11.3, 10.1 ppm. HR-MS (ES): *m*/*z* (rel intens) = 550.292 (100) $[M + H]^+$ (calcd 550.289 for $[C_{28}H_{51}NSiSnH]^+$).

Ligand 6. 3,8-Dibromo-4,7-phenanthroline (**5**; 94 mg, 0.28 mmol), **4** (331 mg, 0.60 mmol), and $Pd(PPh_3)_4$ (37 mg, 0.03 mmol) were diluted in 12 mL of degassed toluene. The mixture was heated to 110 °C overnight. Toluene was then evaporated and the residue purified by column chromatography on silica (eluent CH_2Cl_2/MeOH from 100/0 to 99.7/0.3) to give 124 mg (0.18 mmol) of ligand **6** (64%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.05 (d, *J* = 8.8 Hz, 2H, H-1), 8.87 (d, *J* = 8.6 Hz, 2H, H-2), 8.68 (dd, *J* = 7.9 Hz, *J* = 1.0 Hz, 2H, H-3), 8.31 (s, 2H, H-6), 7.85 (t, *J* = 7.8 Hz, 2H, H-4), 7.56 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 2H, H-5), 1.21 (s, 18H, H−C$H_{3_{TIPS}}$), 1.20 (s, 3H, H−CH_{TIPS}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 156.0, 155.7, 147.4, 142.8, 136.9, 132.4, 131.6, 128.2, 124.9, 120.9, 119.8, 106.3, 91.4, 18.7, 11.3 ppm. HR-MS (ES): *m*/*z* (rel intens) = 348.203 (100) $[M + 2H]^{2+}$/2 (calcd 348.202 for $[C_{44}H_{54}N_4Si_2H_2]^{2+}$/2), 695.399 (10) $[M + H]^+$ (calcd 695.396 for $[C_{44}H_{54}N_4Si_2H]^+$).

Ligand 7. Ligand **6** (105 mg, 0.15 mmol) was dissolved in 7 mL of THF. A solution of TBAF (0.4 mL, 1 M solution in THF) was then added. After 30 min of stirring, the solvent was evaporated. The residual pink precipitate obtained after the evaporation of THF was washed well with water, *n*-pentane, and Et_2O and filtered over a Millipore filter. Thus, 50 mg (13 mmol, 87%) of the desired compound **7** was obtained. ^{1}H NMR (300 MHz, $CDCl_3$ + *d*-TFA, 25 °C): δ = 9.75 (d, *J* = 8.8 Hz, 2H, H-1), 8.78 (d, *J* = 8.8 Hz, 2H, H-2), 8.75 (s, 2H, H-6), 8.64 (d, *J* = 8.1 Hz, 2H, H-3), 8.46 (t, *J* = 8.1 Hz, 2H, H-4), 8.03 (d, *J* = 7.7 Hz, 2H, H-5), 3.83 (s, 2H, H-7) ppm. HR-MS (ES): *m*/*z* (rel intens) = 383.140 (100) $[M + H]^+$ (calcd 383.129 for $[C_{26}H_{14}N_4H]^+$).

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Demetalated Rotaxane 1. To a degassed solution of macrocycle **8** (29.6 mg, 52.3 μmol) in CH_2Cl_2 (2 mL) was added a solution of $Cu(CH_3CN)_4(PF_6)$ (19.5 mg, 52.3 μmol) in degassed CH_3CN (1 mL), and the resulting mixture was stirred at room temperature for 5 min under argon. This mixture was added to a suspension of the ligand **7** (10 mg, 26.1 μmol) in 2 mL of degassed CH_2Cl_2 under argon, and the resulting mixture was stirred at room temperature for 1 h. The solvents were removed in vacuum to give a red solid. A solution of this red solid, Cu(tren')Br (23.6 mg, 13.1 μmol), Na_2CO_3 (1.4 mg, 13.1 mmol), sodium ascorbate (10.4 mg, 52.3 μmmol), and azide stopper **10** (23.6 mg, 39.2 μmol) in a mixture of degassed CH_2Cl_2 (2 mL) and degassed CH_3CN (1 mL) was stirred at room temperature for 24 h. Solvents were removed under vacuum. The residue was taken up in a mixture of $CH_2Cl_2/CH_3CN/H_2O$ (1, 0.5, and 0.1 mL, respectively), KCN (34.1 mg, 104.6 μmol) was added in one portion, and the mixture was stirred for 5 h. A 5 mL volume of water was added, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic phases were combined and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel eluting with a mixture of CH_2Cl_2 and MeOH (98/2 to 85/15) to give the desired free rotaxane **1** as a pale yellow solid (62.5 mg, 23.2 μmol, 89%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.47 (s, 2H, H-7′), 9.05 (d, J = 8.6 Hz, 2H, H-1′), 8.86 (d, J = 7.8 Hz, 2H, H-5′), 8.83 (d, J = 8.6 Hz, 2H, H-2′), 8.38 (s, 2H, H-6′), 8.09−8.24 (m, 14H, H-3, H-o, H-4, H-7), 8.04 (t, J = 7.8 Hz, 2H, H-4′), 7.85 (d, J = 8.4 Hz, 4H, H-3, H-8), 7.63 (s, 4H, H-5, H-6), 7.26 (d, J = 8.5 Hz, 12H, H-14′), 7.15 (d, J = 8.5 Hz, 12H, H-13′), 7.07 (d, J = 8.6 Hz, 4H, H-12′), 6.53 (d, J = 8.6 Hz, 4H, H-11′), 6.30 (d, J = 8.5 Hz, 8H, H-m), 4.06 (d, J = 6.9 Hz, 4H, H-8′), 4.00−3.60 (t, J = 6.7 Hz, 8H, H-α), 3.69−3.33 (m, 36H, H-β, H-γ, H-δ, H-ε, H-10′), 1.82−1.96 (m, 4H, H-9′), 1.29 (s, 54H, H-15′) ppm. HR-MS (ES): m/z (rel intens) = 2691.416 (100) $[M + H]^+$ (calcd 2691.391 for $[C_{174}H_{181}N_{14}O_{14}]^+$).

Rotaxane $[1{\cdot}Cu_2]^{2+}$. To a solution of demetalated rotaxane **1** (20 mg, 7.4 μmol) in degassed CH_2Cl_2 (2 mL) was added a solution of $Cu(CH_3CN)_4(PF_6)$ (2.8 mg, 14.8 μmol) in degassed CH_3CN (1 mL) under argon, and the resulting solution was stirred for 10 min. This solution was concentrated under vacuum to give, without further purification, the desired metalated rotaxane $[1{\cdot}Cu_2]^{2+}$ as a red solid (22.8 mg, 7.4 μmol, 100%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.47 (d, J = 8.6 Hz, 2H, H-1′), 8.71 (d, J = 8.6 Hz, 8H, H-2′), 8.47 (d, J = 7.9 Hz, 2H, H-5′), 8.40 (d, J = 8.0 Hz, 4H, H-4, H-7), 8.19 (t, J = 7.9 Hz, 2H, H-4′), 7.95 (s, 4H, H-5, H-6), 7.90 (d, J = 7.9 Hz, 2H, H-3′), 7.80 (d, J = 8.0 Hz, 4H, H-3, H-8), 7.59 (s, 2H, H-7′), 7.32 (s, 2H, H-6′), 7.10−7.27 (m, 36H, H-o, H-12′, H-13′, H-14′), 6.62 (d, J = 8.5 Hz, 4H, H-11′), 6.09 (d, J = 7.9 Hz, 8H, H-m), 3.60−4.00 (m, 48H, H-α, H-β, H-γ, H-δ, H-ε, H-8′, H-10′), 1.61−1.71 (m, 4H, H-9′), 1.26 (s, 54H, H-15′) ppm. HR-MS (ES): m/z (rel intens) = 1409.15 (100) $[M - 2PF_6]^{2+}/2$ (calcd 1409.12 for $[C_{174}H_{180}N_{14}O_{14}Cu_2]^{2+}/2$).

Rotaxane $[1{\cdot}Zn_2]^{4+}$. To a solution of the demetalated rotaxane **1** (10 mg, 3.7 μmol) in CH_2Cl_2 (1 mL) was added a solution of $Zn(OTf)_2$ (4.1 mg, 11.1 μmol) in MeOH (1 mL). The solution was stirred for 1 h, and the solvents were subsequently evaporated. The resulting precipitate was then redissolved in CH_2Cl_2 and filtered to get rid of the excess inorganic salts. The solvent was removed under vacuum to give, without further purification, the desired metalated rotaxane $[1{\cdot}Zn_2]^{4+}$ as a yellow solid (9.9 mg, 3.7 μmol, 100%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.75 (d, J = 8.8 Hz, 2H, H-1′), 8.99 (d, J = 8.8 Hz, 4H, H-4, H-7), 8.85 (d, J = 8.8 Hz, 2H, H-2′), 8.70−8.80 (m, 4H, H-5′, H-4′), 8.61 (s, 2H, H-7′), 8.50 (s, 4H, H-5, H-6), 8.06−8.11 (m, H-3′), 7.97 (d, J = 8.8 Hz, 4H, H-3, H-8), 7.26 (d, J = 8.6 Hz, 12H, H-14′), 7.09−7.17 (m, 16H, H-12′, H-13′), 6.69−6.77 (m, 12H, H-o, H-11′), 6.46 (s, 2H, H-6′), 6.28 (d, J = 8.7 Hz, 8H, H-m), 4.39 (t, 6.09, J = 6.6 Hz, 4H, H-8′), 3.45−3.89 (m, 44H, H-α, H-β, H-γ, H-δ, H-ε, H-10′), 2.09−2.22 (m, 4H, H-9′), 1.23 (s, 54H, H-15′) ppm. HR-MS (ES): m/z (rel intens) = 1559.566 (100) $[M - 2OTf]^{2+}/2$ (calcd 1559.572 for $[C_{174}H_{180}N_{14}O_{14}Zn_2(CF_3SO_3)_2]^{2+}/2$), 990.387 (100) $[M - 3OTf]^{3+}/3$ (calcd 990.397 for $[C_{174}H_{180}N_{14}O_{14}Zn_2(CF_3SO_3)]^{3+}/3$), 705.551 (100) $[M - 4OTf]^{4+}/4$ (calcd 705.560 for $[C_{174}H_{180}N_{14}O_{14}Zn_2]^{4+}/4$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Labeling and ^{1}H NMR spectra of compounds **3**, **4**, **6**, **7**, **1**, $[1{\cdot}Cu_2]^{2+}$, and $[1{\cdot}Zn_2]^{4+}$, HR-MS spectra of compounds **1**, $[1{\cdot}Cu_2]^{2+}$, and $[1{\cdot}Zn_2]^{4+}$, and cyclic voltammogram of $[11{\cdot}Cu_2]^{2+}$.This material is available free of charge via the Internet at http://pubs.acs.org.

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