[3]Rotaxanes and [3]pseudorotaxanes with a rigid two-bidentate chelate axle threaded through two coordinating rings†

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New [3]rotaxanes and [3]pseudorotaxanes have been synthesised using the "gathering and threading" effect of copper(I). By using click chemistry as the "stoppering" reaction, a good yield of the [3]rotaxane was obtained, either as a dicopper complex or as a metal-free compound after demetallation. The axle contains a central rigid aromatic block incorporating two bidentate chelates, and the threaded macrocycles are 30-membered rings. A model dicopper(I) [3]pseudorotaxane whose axle was end-functionalised by triisopropylsilyl groups could be crystallised and studied by X-ray diffraction. A particularly attractive structure was obtained showing a "slanted" geometry for the two rings and the axle, the two 1,10-phenanthroline units of the rings being almost parallel to one another but their respective mean planes being more than 7 Å apart.

Introduction

Although catenanes and rotaxanes[1] are nowadays relatively accessible compounds, thanks to the template strategies introduced by various groups over the course of the last 25 years,[2,3] the synthesis of such compounds continues to benefit from more and more efficient cyclisation procedures (for catenanes) or stoppering techniques (for rotaxanes). In recent years, the Cu(I)-catalysed dipolar cycloaddition of azides and terminal alkynes, known as "click" chemistry, has been used as a mild and efficient stoppering reaction for the preparation of new rotaxanes and catenanes,[4] including copper(I)-complexed rotaxanes[5] belonging to the family of compounds prepared in Strasbourg since the 1980s. This reaction, which is an important extension of the Huisgen reaction developed by Sharpless, Meldal and their co-workers,[6] nowadays is one of the most efficient procedures for stoppering pre-rotaxanes whose axle is end-functionalised by appropriate functions, such as terminal alkynes or azides. Several years ago, a wide family of porphyrin-stoppered rotaxanes was prepared in our group using the "gathering and threading" effect of copper(I).[7,8] Unfortunately, in most cases, the limiting step of the overall synthesis was the final stopper-fixing reaction. In the present report, we describe the efficient synthesis of new [3]rotaxanes based on click chemistry. In addition, during the threading step, an interesting ring size effect was found that governs the success of pseudorotaxane formation. Using a molecular filament bearing relatively voluminous end-groups, it was shown that the copper(I)-induced threading reaction leads quantitatively to the desired [3]pseudorotaxane when the macrocycle is a 33-membered ring, whereas a 30-membered ring cannot be threaded at all under the same conditions.

Results and discussion

The general synthesis principle is shown in Scheme 1.

Several examples of [3]pseudorotaxanes with "innocent" stoppers (*i.e.* non-electro-, non-magneto- and non-photoactive) and porphyrin-stoppered rotaxanes have already been described by our group, but the axle consisted of two 1,10-phenanthroline chelates connected by a flexible linker.[9] A few years ago, Lehn and co-workers reported the synthesis of [3] and [4]pseudorotaxanes assembled *via* copper(I) coordination, whose central axle was a rigid block with no spacer between the two chelating units.[10] In the present report, the threaded fragment is a rigid rod, affording good control over the geometry of the assembly. In addition, the click-based stoppering reaction gives higher yields and is much simpler in terms of experimental procedure than the previous techniques used for making copper-complexed rotaxanes, which were generally based on Williamson reactions. The target [3]rotaxane is depicted in Fig. 1.

1. Synthesis of the organic components

The various organic precursors used are shown in Fig. 2.

Macrocyclic components **6** and **7** were synthesized according to previously published experimental procedures.[2a,11] Two-chelate rods **4** and **5** were prepared from compound **2** (Fig. 2), **4** being an intermediate in the preparation of **5**. The C≡C bonds were introduced by a Sonogashira coupling involving tri(isopropylsilyl)acetylene, NEt_3 and $PdCl_2(PPh_3)_2$ as a catalyst. The reaction was performed in hot DMF because

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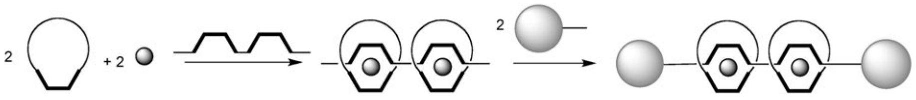
‡ X-Ray crystallography.



Scheme 1 The construction principle of a [3]rotaxane by copper(I)-driven "gathering and threading" followed by stoppering. The coordinating fragments are represented by U-shaped symbols, the small spheres are copper(I) atoms and the big spheres represent the stoppers.

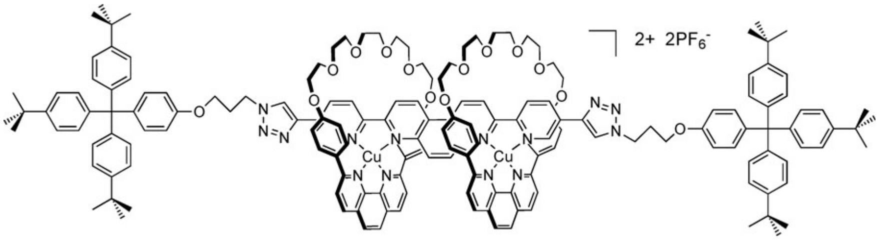


Fig. 1 The chemical structure of [3]rotaxane $\mathbf{1}^{2+}$. The central part of the axle is a rigid block consisting of two laterally-connected bidentate chelates.

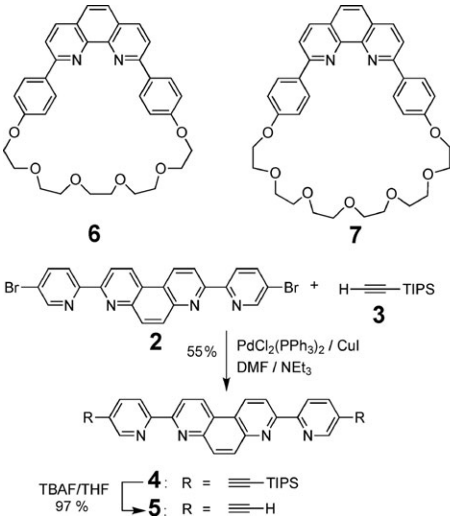


Fig. 2 The chemical structures of the organic components: axles **4** and **5**, acetylenic fragment **3**, and rings **6** and **7**; compound **2** is the precursor to both axles **4** and **5**.

of the poor solubility of precursor **2**[12] in common organic solvents. The resulting axle **4** (TIPS-ended rod; TIPS = triisopropylsilyl) was highly soluble in many common organic solvents thanks to the triisopropyl functions and could be easily purified by chromatography. Axle **4** was obtained in a moderate yield of 55%. An attempt to introduce C≡C triple bonds with trimethylsilylacetylene by following the same procedure was successful, in spite of a low yield, but the solubility of the resulting compound was too low to allow its effective purification. The acetylenic axle was obtained by the reaction of TBAF (tetra-*n*-butyl-ammonium fluoride) with **4** in THF. The poor solubility of the resulting compound meant that it quickly precipitated in the reaction flask, thus allowing purification by simple filtration and washing with water, *n*-pentane and diethyl ether. This compound was obtained with a yield of 97%. Thus, this functionalized ligand was easily synthesized in 7 steps (5 steps for precursor **2** and 2 extra steps), which is much less than the 15 steps of synthesis required for the related ligands previously used in our laboratory.[13]

2. The "gathering and threading" reaction

The first attempt to gather two macrocycles onto axle **4** were realized by using "classical" 30-membered ring **6** in the presence of two copper(I) equivalents (Fig. 3). Surprisingly, essentially no threaded species was obtained, whatever experimental conditions were employed (various solvents, temperatures and reaction times). This result indicates that the size of the triisopropyl group is too large to thread through the central cavity of precursor complex $[\mathrm{Cu}(\mathbf{6})(\mathrm{CH_3CN})_2]^+$. Interestingly, the use of a larger macrocycle, **7**, consisting of 33 bonds in its inner circumference, led almost quantitatively to the expected [3]pseudorotaxane $\mathbf{8}^{2+}$, as confirmed by a ^{1}H NMR study.

X-Ray quality crystals of $\mathbf{8}(\mathrm{PF_6})_2$ could be grown by slow diffusion of diisopropylether into an acetone solution. The X-ray study (Fig. 4) confirms the [3]pseudorotaxane structure. Due to the nature of the axle, the Cu(I) ions reside on the same side of the axle (a *cis*-rotaxane). The Cu(I) ions show a heavily distorted tetrahedral coordination, with N–Cu–N bond angles between 80–139° and bond distances between 2.03–2.08 Å (Table 1). The long (Si···Si distance of 2.4 nm) axle is not linear, but is bent by the coordination to the copper ions so that the angle between the centroid of the axle and the terminal Si atoms is 164°.

In similar rigid axle but non-acetylenic [3]- and [4]rotaxanes,[10] comparable axle length-dependent and Cu coordination-based bending is also observed. Two *cis*-[3]rotaxanes with shorter 1.1 nm axles show bending angles of 167.7 and 171.1°,[10a] while a bipy-like *cis*-4-rotaxane with a 1.48 nm axle[10b] shows curved bending of 156.7°. Contrary to the above mentioned [3]- and [4]rotaxanes and our rotaxane **8**, another bipy-like *trans*-[3]rotaxane with a 1.59 nm long axle is not bent at all (angle 180°).[10c] The phenanthroline moieties of threaded macrocycles **7** are nearly parallel to each other but form a 51.4 and 52.3° angle between the plane defined by the central part of the axle and the plane of the 5-*N*-phenanthroline part, leading to a "slanted" overall orientation of the wheels around the axle. The very strong intramolecular π–π stacking in the *cis*-[3]- and -[4]rotaxanes[10a,b] orients the wheels perpendicularly towards the axle. However, the *trans*-[3]-rotaxane[10c] shows a

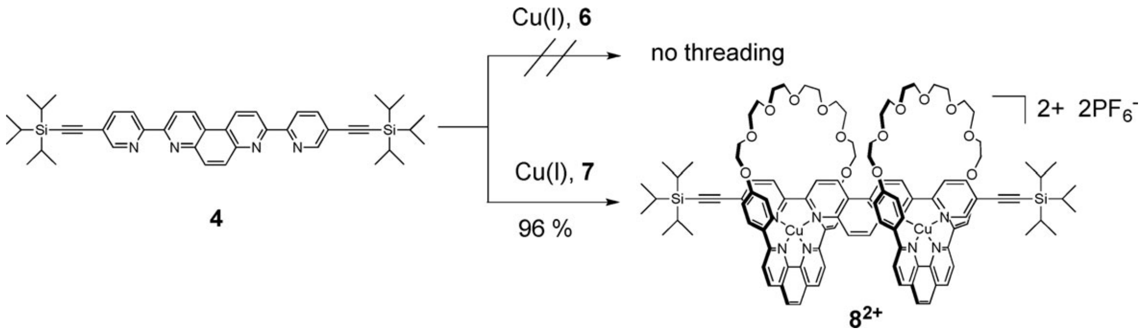


Fig. 3 Threading tests of the TIPS-bearing axle.

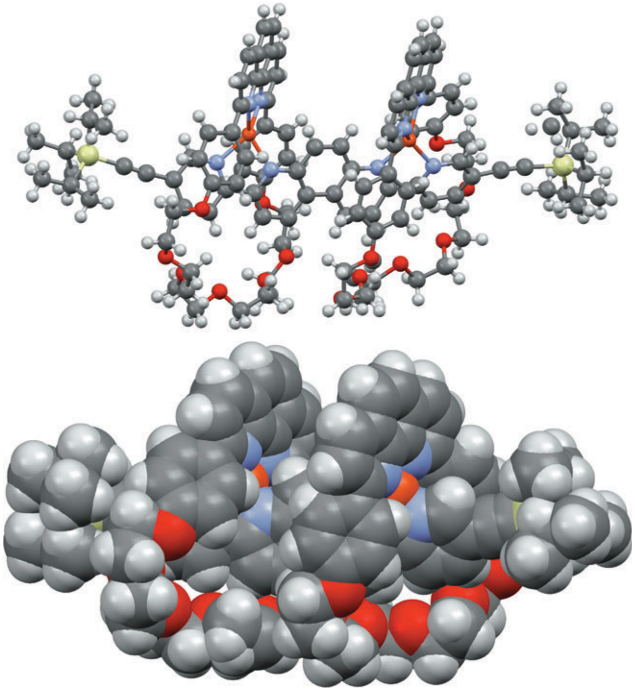


Fig. 4 Ball and stick (top) and the CPK (bottom) presentations of [3]pseudorotaxane **8**. The PF_6 anions, solvent molecules and the disorder of threaded macrocycle **7** are omitted for clarity.

Table 1 The bond distances (Å) and angles (°) around the two copper ions

Cu(1A)–N(6)	2.030(9)	N(6)–Cu(1A)–N(11)	80.7(4)
Cu(1A)–N(11A)	2.042(7)	N(1A)–Cu(1A)–N(11A)	80.3(6)
Cu(1A)–N(1A)	2.049(18)	N(6)–Cu(1A)–N(1A)	139.4(4)
Cu(1A)–N(11)	2.076(8)	N(11)–Cu(1A)–N(1A)	112.4(4)
		N(6)–Cu(1A)–N(11A)	115.9(5)
		N(11)–Cu(1A)–N(11A)	138.8(4)
Cu(1B)–N(25)	2.039(7)	N(19)–Cu(1B)–N(25)	81.1(3)
Cu(1B)–N(19)	2.045(8)	N(1B)–Cu(1B)–N(11B)	83.9(5)
Cu(1B)–N(1B)	2.053(10)	N(19)–Cu(1B)–N(1B)	137.2(3)
Cu(1B)–N(11B)	2.079(9)	N(25)–Cu(1B)–N(1B)	112.6(3)
		N(19)–Cu(1B)–N(11B)	112.7(4)
		N(25)–Cu(1B)–N(11B)	139.2(3)

slanting by 58.9°; this is due to the absence of intramolecular π–π stacking and its centrosymmetry.[10c] The Cu···Cu distance in [3]pseudorotaxane **8** is 7.8 Å, much longer that in similar *cis*-[3]- and -[4]rotaxanes,[10a,b] where the corresponding distances are 3.5 and 3.7,[10a] and 3.6 and 4.3 Å, respectively.[10b] Due to the *trans* configuration of the Cu ions in *trans*-[3]-rotaxane,[10c] the Cu···Cu distance is 9.6 Å, but the Cu ions are on the opposite sides of the axle. The large Cu···Cu separation in **8** inhibits the intramolecular π–π interactions observed in other similar rotaxanes[10a,b] and leads to relaxation of the coordination around the Cu(I) ions by the slanted orientation of the wheels around the axle. However, the intramolecular distance between the phenanthroline moieties is perfect for an insertion of the phenanthroline moiety of the adjacent pseudorotaxane molecule, and thus pseudorotaxane **8** exists in the crystal lattice as a π–π enhanced dimer (Fig. 5). It should be noted that the tilted geometry of the chelating units coordinated to Cu(I) ions has been observed both in copper(I)-complexed catenanes and knots made in our group, and studied by X-ray diffraction.[14]

In order to test the click chemistry method as a stoppering reaction, we chose to introduce two alkyne functions onto axle **5** and one azide function onto the classical tris(*p*-*tert*-butylphenyl)(phenyl)methane stopper (compound **11**). This latter reagent was obtained in good yield by the reaction of iodo derivative **10**[15] with NaN_3 (Fig. 6(a)). Compound **11** has already been synthesized by Leigh's group in a different way.[4d] The threading of two macrocycles **6** onto axle **5** in presence of two equivalents of $[Cu(CH_3CN)_4](PF_6)$ afforded quantitatively the copper [3]pseudorotaxane $\mathbf{9}^{2+}$ (Fig. 6(b)), as

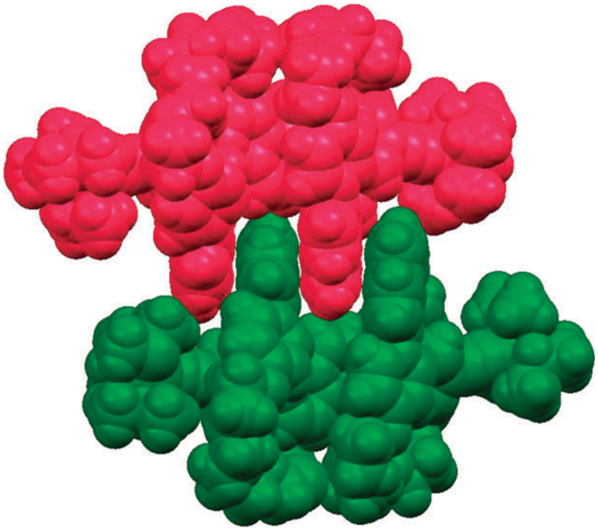


Fig. 5 π–π enhanced dimer formation of **8** in the crystal lattice.

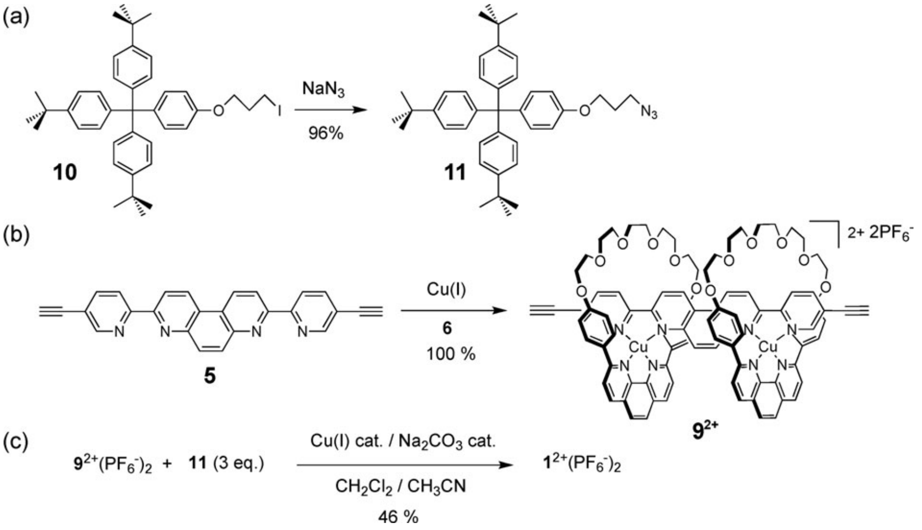


Fig. 6 (a) The synthesis of stopper **11**, (b) copper [3]pseudorotaxane $\mathbf{9}^{2+}$ and (c) the double stoppering reaction.

confirmed by a ^{1}H NMR study. This ligand has already been used for the quantitative formation of [4]pseudorotaxane-containing porphyrins.[16] The double stoppering reaction (Fig. 6(c)) was achieved in a CH_2Cl_2/CH_3CN (3 : 1) mixture with a catalytic amount of $[Cu(CH_3CN)_4](PF_6)$ and Na_2CO_3 as a base for 5 d. After work-up, the copper [3]rotaxane $\mathbf{1}^{2+}$ was obtained in 46% yield, which is very close to the yield obtained in the laboratory for the formation of a similar [3]rotaxane with other ligands but the same click reaction.[13]

3. Demetallation of copper [3]rotaxane $\mathbf{1}^{2+}$

In order to confirm the threaded nature of copper rotaxane $\mathbf{1}^{2+}$, it was demetallated and submitted to purification by silica chromatography. The treatment of $\mathbf{1}^{2+}$ with an excess of KCN in a $CH_2Cl_2/CH_3CN/H_2O$ (2 : 1 : 1) mixture at room temperature afforded free [3]rotaxane **12** in 96% yield. The ES-MS and ^{1}H NMR spectrum were in accordance with the postulated structure (Fig. 7).

We noticed large differences between the spectra of the metallated and demetallated compounds (Fig. 8). Indeed, the aromatic region of the spectrum of copper rotaxane $\mathbf{1}^{2+}$ is spread over 3.5 ppm from δ 6 to 9.5, which is characteristic of a threaded copper complex, whereas the spectrum of demetallated rotaxane **12** is spread over 2.5 ppm from δ 6.7 to 9.2. The signals of the threaded macrocycles are different from the signals of the free macrocycles, confirming that compound **12** is a real rotaxane and that the stoppers prevent the unthreading of the macrocycles.

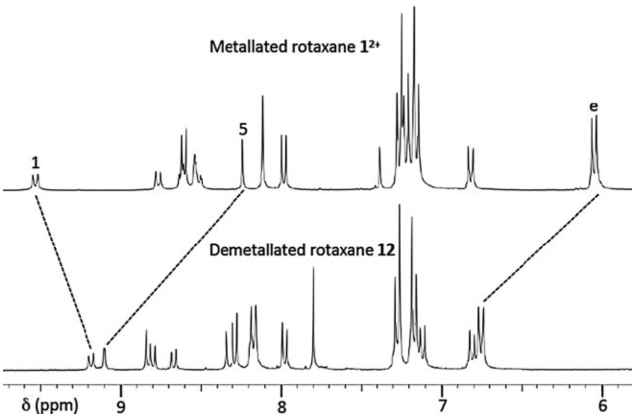


Fig. 8 ^{1}H NMR spectra of metallated rotaxane $\mathbf{1}^{2+}$ and demetallated rotaxane **12**.

Conclusion

In conclusion, the use of a bis(2-pyridyl)-4,7-phenanthroline unit as a central part of an axle, with its rigid structure and two bidentate chelating sites, allowed the preparation of a copper-complexed [3]rotaxane in good yield. The synthesis relied on a copper(I)-induced double threading reaction of two large macrocycles onto the rigid axle and, subsequently, click chemistry as the stopper-fixing reaction. Demetallation afforded quantitatively the metal-free [3]rotaxane. Dicopper [3]pseudorotaxane **8**, containing TIPS groups at the ends of

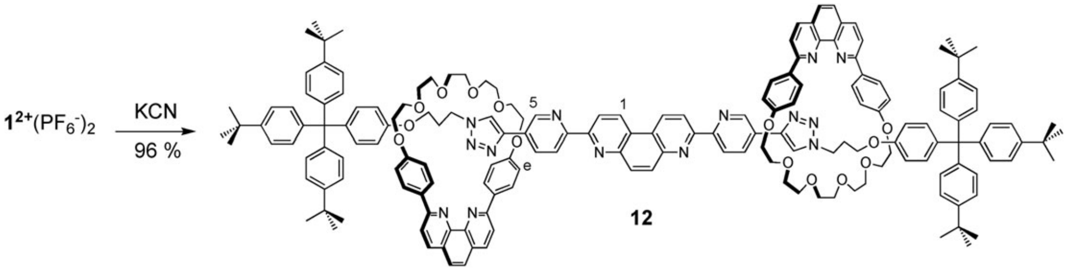


Fig. 7 The demetallation of $\mathbf{1}^{2+}$.

the threaded axle, could be crystallised and studied by X-ray crystallography. This structure is a rare example of a Cu(I) rotaxane or pseudorotaxane. It shows that the two threaded rings are coordinated to the axle and that the rings are slanted towards the axle, the planes of the ring-incorporated 1,10-phenanthroline chelates being tilted with respect to the axis and not at all perpendicular to it.

Experimental section

TIPS axle 4

12 mL of anhydrous DMF and 1 mL of distilled NEt_3 were introduced into an oven-dried flask. The mixture was de-gassed for 20 min with argon. 11.5 mg (60.4 μmol) of CuI, 31.7 mg (45.2 μmol) of $PdCl_2(PPh_3)_2$, 301 mg (612 μmol) of bromide thread **2** and 0.6 mL (2.72 mmol) of triisopropylsilylacetylene were subsequently added. The solution was then heated up to 100 °C under an argon atmosphere and stirred for 17 h. The reaction mixture was cooled down to room temperature and 13.4 mg (19.1 μmol) of $PdCl_2(PPh_3)_2$ was added. The solution was heated to 100 °C for a further 5 h and then cooled down to room temperature. The solvents were evaporated and the product purified by silica chromatography with CH_2Cl_2. The product was then washed with pentane, and was obtained in 55% yield. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.05 (d, J^3 = 8.8 Hz, 2H), 8.82 (dd, J^4 = 1.3 Hz, J^5 = 0.7 Hz, 2H), 8.78 (d, J^3 = 8.8 Hz, 2H), 8.68 (dd, J^3 = 8.2 Hz, J^5 = 0.7 Hz, 2H), 8.33 (s, 2H), 7.95 (dd, J^3 = 8.2 Hz, J^4 = 2.2 Hz, 2H) and 1.17 (s, 42H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 155.70, 154.44, 152.28, 147.61, 139.81, 132.59, 131.77, 124.81, 121.03, 120.84, 119.67, 103.80, 96.38, 18.69 and 11.30. MS (ES) : *m/z* (%) = 695.4044 (100) $[M + H]^+$ (calc. 695.3960) and 717.3862 (100) $[M + Na]^+$ (calc. 717.3779).

Acetylenic axle 5

101 mg (0.14 mmol) of TIPS axle **4** was diluted in 7 mL of THF. 0.39 mL of a 1 M solution of TBAF (0.39 mmol) in THF was then added and a fine precipitate immediately formed. After half an hour of stirring, the solvent was evaporated. The residual brown precipitate obtained after the evaporation of the THF was washed well with water, ether and n-pentane, and filtered over a Millipore filter. 54 mg (0.14 mmol) of a yellowish powder was thus obtained (97% yield). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.07 (d, J^3 = 8.8 Hz, 2H), 8.85 (dd, J^4 = 2.0 Hz, J^5 = 0.7 Hz, 2H), 8.78 (d, J^3 = 8.8 Hz, 2H), 8.72 (dd, J^3 = 8.1 Hz, J^5 = 0.6 Hz, 2H), 8.33 (s, 2H), 7.99 (dd, J^3 = 8.1 Hz, J^4 = 2.1 Hz, 2H) and 3.34 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 161.53, 160.95, 160.39, 159.81, 148.49, 146.79, 138.80, 132.22, 120.77, 119.97, 116.20, 112.43 and 108.65. MS (ES): *m/z* (%) = 383.1175 (100) $[M + H]^+$ (calc. 383.1291).

TIPS [3]pseudorotaxane $8^{2+}(PF_6^-)_2$

To a de-gassed solution of macrocycle **7** (17.5 mg, 28.7 μmol) in CH_2Cl_2 (2 mL) was added a solution of $[Cu(CH_3CN)_4](PF_6)$ (10.7 mg, 28.7 μmol) in de-gassed CH_3CN (1 mL) and stirred at room temperature for 20 min under an inert atmosphere. This solution was then added to a de-gassed solution of TIPS thread **4** (9.97 mg, 14.4 μmol) in CH_2Cl_2 (2 mL) *via* a cannula; the mixture immediately turned brown and was reacted overnight. After evaporation of the solvents, the crude product was redissolved in CH_3CN and filtered in order to eliminate the possible excess of organic ligands. The CH_3CN was evaporated to give 33 mg (14.1 μmol) of [3]pseudorotaxane (96% yield). ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 9.44 (d, J^3 = 8.8 Hz, 2H), 8.69 (d, J^3 = 8.8 Hz, 2H), 8.60 (d, J^3 = 8.3 Hz, 4H), 8.50 (d, J^3 = 8.3 Hz, 2H), 8.26 (dd, J^3 = 8.3 Hz, J^4 = 1.8 Hz, 2H), 8.08 (s, 4H), 7.98 (d, J^3 = 8.3 Hz, 4H), 7.94 (d, J^4 = 1.8 Hz, 2H), 7.30 (s, 2H), 7.24 (d, J^3 = 8.6 Hz, 8H), 6.11 (d, J^3 = 8.6 Hz, 8H), 4.00–3.70 (m, 48H) and 1.15 (s, 42H). MS (ES): *m/z* (%) = 1021.3189 (100) $[M^{2+}]/2$ (calc. 1021.3924).

Acetylenic [3]pseudorotaxane $9^{2+}(PF_6^-)_2$

To a de-gassed solution of macrocycle **6** (29.6 mg, 52.2 μmol) in dry $CHCl_3$ (5 mL) was added a solution of $[Cu(CH_3CN)_4](PF_6)$ (21 mg, 56.3 μmol) in dry and de-gassed CH_3CN (5 mL), and stirred at room temperature for 30 min under an inert atmosphere. This solution was then added to a de-gassed suspension of acetylenic axle **5** (9.8 mg, 25.6 μmol) in dry $CHCl_3$ (15 mL) *via* a cannula; the mixture turned immediately brown and homogeneous, and was reacted overnight. After evaporation of the solvents, the crude product was redissolved in CH_3CN and filtered in order to eliminate the possible excess of organic ligands. The CH_3CN was evaporated to give the [3]pseudorotaxane (49 mg, 25.4 μmol) in quantitative yield. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 9.54 (d, J^3 = 8.8 Hz, 2H), 8.77 (d, J^3 = 8.8 Hz, 2H), 8.64 (d, J^3 = 8.4 Hz, 4H), 8.57 (d, J^3 = 8.3 Hz, 2H), 8.23 (dd, J^3 = 8.2 Hz, J^4 = 1.9 Hz, 2H), 8.13 (s, 4H), 8.06 (d, J^4 = 1.6 Hz, 2H), 8.03 (d, J^3 = 8.3 Hz, 4H), 7.38 (s, 2H), 7.22 (d, J^3 = 8.7 Hz, 8H), 6.12 (d, J^3 = 8.7 Hz, 8H), 4.00–3.75 (m, 40H) and 3.53 (s, 2H). MS (ES): *m/z* (%) = 821.2281 (100) $[M^{2+}]/2$ (calc. 821.2324).

Azide stopper 11

Iodide derivative **10** (603 mg, 0.90 mmol) and NaN_3 (482 mg, 7.41 mmol) were diluted in 10 mL of DMF, 3 mL of water, 10 mL of THF and 10 mL of CH_2Cl_2. The solution was stirred for 4 d and the solvents evaporated. The crude product was then washed with 20 mL of water and the aqueous layer extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$. After evaporation of the CH_2Cl_2, 506 mg (0.86 mmol) of a white powder was obtained (96% yield). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.27 (d, J^3 = 8.8 Hz, 6H), 7.16 (d, J^3 = 8.6 Hz, 6H), 7.16 (d, J^3 = 8.6 Hz, 2H), 6.79 (d, J^3 = 8.8 Hz, 2H), 4.02 (t, J^3 = 6.0 Hz, 2H), 3.50 (t, J^3 = 6.7 Hz, 2H), 2.03 (q, J^3 = 6.3 Hz, 2H) and 1.31 (s, 27H).

[3]Rotaxane $1^{2+}(PF_6^-)_2$

[3]Pseudorotaxane $9^{2+}(PF_6^-)_2$ (49 mg, 25.5 μmol), N_3 stopper **11** (50 mg, 85.1 μmol), Na_2CO_3 (1.8 mg, 16.9 μmol) and $[Cu(CH_3CN)_4](PF_6)$ (5 mg, 13.4 μmol) were diluted in 3 mL of dry and de-gassed CH_2Cl_2 and 1 mL of dry and de-gassed CH_3CN. The solution was stirred under argon for 5 d.

The solvents were then evaporated and the resulting black residue purified by silica chromatography. A gradient of elution CH_2Cl_2 : EtOH : CH_3CN of 98 : 1 : 1 to 96 : 2 : 2 gave 36 mg (11.6 μmol) of rotaxane (46% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 9.49 (d, J^3 = 8.9 Hz, 2H), 8.72 (d, J^3 = 8.1 Hz, 2H), 8.58 (d, J^3 = 8.2 Hz, 4H), 8.57 (d, J^3 = 8.2 Hz, 2H), 8.50 (s, 2H), 8.47 (dd, J^3 = 8.3 Hz, J^4 = 1.9 Hz, 2H), 8.19 (s, 2H), 8.07 (s, 4H), 7.94 (d, J^3 = 8.1 Hz, 4H), 7.34 (s, 2H), 7.22 (d, J^3 = 8.6 Hz, 12H), 7.21 (d, J^3 = 8.9 Hz, 4H), 7.15 (d, J^3 = 7.9 Hz, 8H), 7.11 (d, J^3 = 8.8 Hz, 12H), 6.78 (d, J^3 = 8.9 Hz, 4H), 6.00 (d, J^3 = 7.9 Hz, 8H), 4.65 (t, J^3 = 6.8 Hz, 4H), 3.99 (t, J^3 = 5.4 Hz, 4H), 3.92–3.70 (m, 40H), 2.43 (q, J^3 = 6.1 Hz, 4H) and 1.26 (s, 54H). MS (ES): m/z (%) = 1409.0656 (100) [M^{2+}]/2 (calc. 1409.1217).

Demetallated [3]rotaxane 12

Metallated [3]rotaxane $\mathbf{1}^{2+}(PF_6^-)_2$ (10 mg, 3.22 μmol) and KCN (9 mg, 138 μmol) were diluted in 1 mL of CH_2Cl_2, 0.5 mL of CH_3CN and 0.5 mL of distilled water, and stirred for 3 h. Then, 10 mL of water and 10 mL of CH_2Cl_2 were added and the two layers separated. The aqueous layer was extracted three times with 10 mL of CH_2Cl_2 and the organic layer dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by alumina chromatography. A gradient of elution CH_2Cl_2 : EtOH of 100 : 0 to 98 : 2 gave 8.3 mg (3.1 μmol) of demetallated rotaxane (96% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 9.16 (d, J^3 = 8.9 Hz, 2H), 9.07 (d, J^4 = 1.4 Hz, 2H), 8.81 (s, 2H), 8.77 (d, J^3 = 8.6 Hz, 2H), 8.64 (d, J^3 = 8.2 Hz, 2H), 8.31 (s, 2H), 8.26 (d, J^3 = 8.4 Hz, 4H), 8.15 (d, J^3 = 8.2 Hz, 2H), 8.14 (d, J^3 = 8.7 Hz, 8H), 7.95 (d, J^3 = 8.4 Hz, 4H), 7.77 (s, 4H), 7.24 (d, J^3 = 8.6 Hz, 12H), 7.14 (d, J^3 = 8.7 Hz, 12H), 7.09 (d, J^3 = 8.8 Hz, 4H), 6.78 (d, J^3 = 9.0 Hz, 4H), 6.72 (d, J^3 = 8.7 Hz, 8H), 4.31 (t, J^3 = 7.1 Hz, 4H), 3.92–3.85 (m, 12H), 3.64 (s, 8H), 3.55–3.45 (m, 24H), 2.21 (q, J^3 = 6.4 Hz, 4H) and 1.29 (s, 54H). MS (ES): m/z (%) = 2754.3143 (100) $[M + H]^+$ (calc. 2754.1696).

Crystallography

Data were recorded with a Bruker-Nonius Kappa APEX II diffractometer using graphite-monochromatized Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 123.0(1) K. The data were processed with Denzo-SMN v0.95.373,[17] and the structure was solved by direct methods.[18] Refinements based on F^2 were made by full-matrix least-squares techniques.[19] No absorption correction was applied. The hydrogen atoms were calculated in their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and refined as riding atoms. Severe disorder in one of the macrocycles, one of the PF_6^- anions and one of the solvent acetone molecules in **8** was treated with robust restraints to prevent chemically unreasonable bond distances and angles. The crystal lattice contained voids and the electron density within them was treated with the SQUEEZE program.[20]

Crystal data for 8

Formula: $C_{123.5}H_{142}N_8O_{17}Cu_2F_{12}P_2Si_2$, crystal size: 0.25 × 0.25 × 0.45 mm, triclinic, space group: P-1, a = 13.3567(7), b = 20.1482(7), c = 26.926(1) Å, α = 69.490(2), β = 88.660(2), γ = 74.205(3)°, V = 6509.8(5) Å^3, Z = 2, D_{calc} = 1.267 g cm^{-3}, μ = 0.45 mm^{-1}, 25 576 reflections measured ($2\theta_{max}$ = 22.5°), 16 719 independent reflections, 7862 with $I > 2\sigma(I)$, number of parameters = 1509, number of restraints = 389, R_{int} = 0.0532, R = 0.1327 [$I > 2\sigma(I)$], wR^2 = 0.379 (all data), GOF = 1.149. Maximum and minimum peaks in the difference map: 0.993 and −0.491 eÅ^{-3}. The severe disorder and large thermal movement of the isopropyl methyl carbon renders the positions of the methyl hydrogens inaccurate.†

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