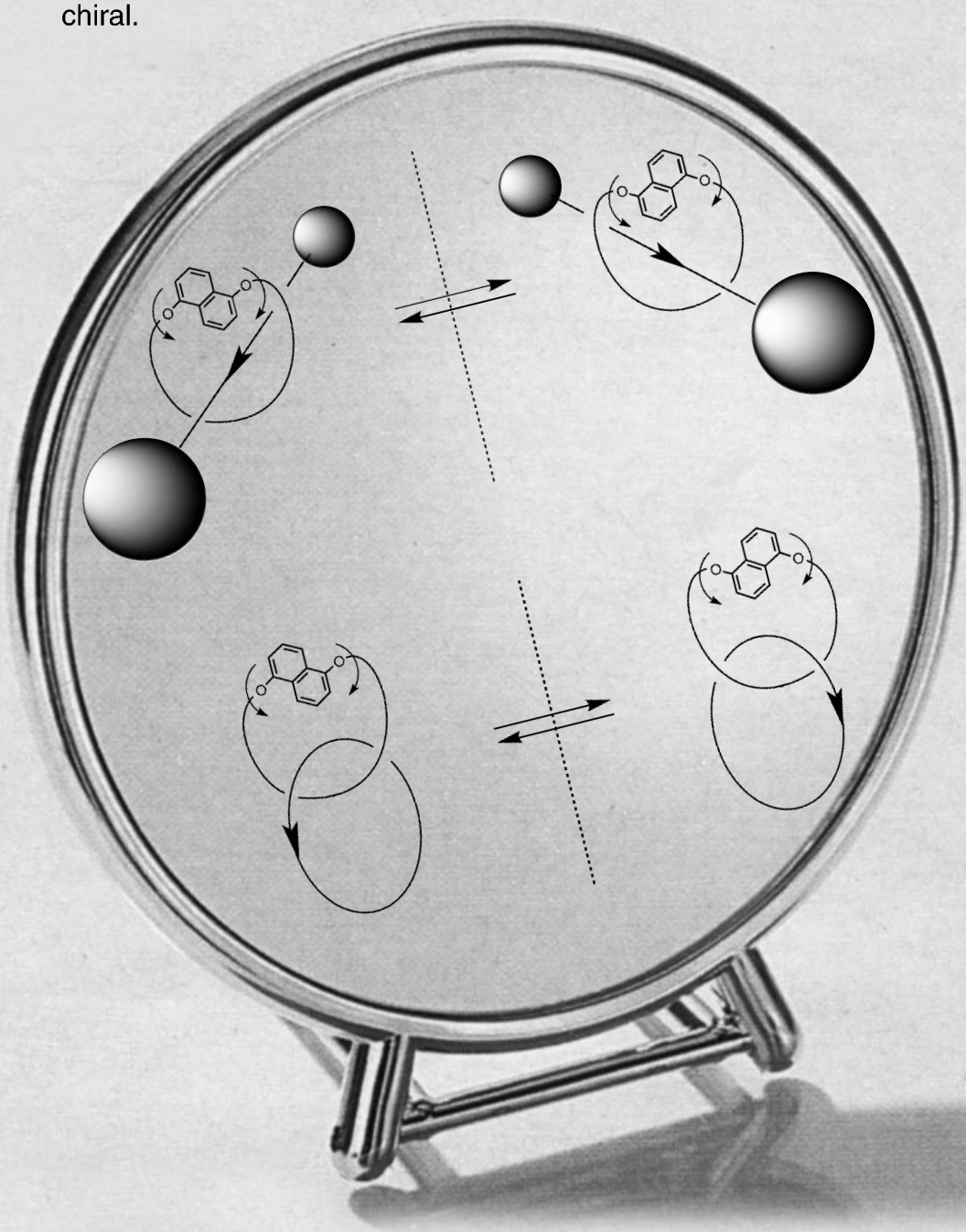
The [2]-rotaxane and [2]-catenane shown below are chemically achiral. However, their mirror images are exchanged by a chiral pathway, that is, any possible conformation of these molecules is chiral.



The [2]-rotaxane is an example of an Euclidean rubber glove molecule. By contrast, the [2]-catenane, which cannot be flattened to a planar figure, is the prototype of the topological rubber glove.

For more information see the following pages.

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A [2]Catenane and a [2]Rotaxane as Prototypes of Topological and Euclidean Molecular "Rubber Gloves"

Jean-Claude Chambron,*[a] Jean-Pierre Sauvage,*[a] Kurt Mislow,*[b] André De Cian,[c] and Jean Fischer[c]

Abstract: A [2]catenane and a [2]rotaxane have been prepared from a C_2-symmetric, 2,9-diphenyl-1,10-phenanthroline-based (dpp-based) macrocycle incorporating a 1,5-dioxynaphthalene subunit by means of the transition metal templated technique. In the case of the catenane, this macrocycle is interlocked with a dpp-based macrocycle that is oriented through the location of a *p*-tolyl substituent in the 4-position of the phenanthroline subunit. In the case of the rotaxane, the C_2-symmetric macrocycle is threaded onto an oriented, dumbbell-shaped molecule, based on the same 4-*p*-tolyl-1,10-phenanthroline subunit, which bears tetraarylmethane stoppers. Both species are chemically achiral molecules, yet they are composed entirely of asymmetric, mirror-image conformations. Conformational enantiomerization processes therefore take place exclusively by chiral pathways, conferring on these molecules the "rubber glove" property. However, while the molecular graph (constitutional formula) of the [2]rotaxane can be deformed into a planar and, hence, rigidly achiral representation, a feature shared by a few other compounds in the literature that have been characterized as "Euclidean rubber gloves", the molecular graph of the [2]catenane cannot be deformed in this way. It therefore has the unique property of being a chemically achiral "topological rubber glove".

Keywords: catenanes · copper · rotaxanes · rubber glove molecule

Introduction

While the vast majority of chemically achiral molecules display at least one achiral conformation (usually with a mirror plane or an inversion center), a few of them possess the intriguing property of being composed *entirely* of rigidly chiral conformations. Conformational enantiomerization processes are, therefore, different for the two cases. Specifically, in the latter case they can only take place by way of chiral pathways, as in the process of removing a right-handed rubber glove from the right hand by "peeling" it off while turning it inside-out; the resulting object is superimposable on a left-handed glove, yet at no time does the glove ever attain a symmetrical (achiral) shape.[1]

The first member of this family of stereochemical curiosities [(1*R*)-menthyl (1*S*)-menthyl 2,2′,6,6′-tetranitro-4,4′-diphenate (**1**) in Figure 1] was conceived and synthesized in the mid-1950s.[2] Other examples of this type have since been reported, including chiral molecular propellers such as compound **2** in Figure 1, enantiomerization of which by the two-ring flip mechanism involves an exclusively chiral pathway,[3] and certain bis(9-triptycyl)methane derivatives such as **3**, in which two triptycyl groups behave as highly mobile and tightly meshed bevel gears.[4] In addition, we note that certain *meso* compounds recently described by Sharpless and co-workers[5] show the same kind of property; all chemically accessible conformations of **4** (Figure 1) are chiral, yet they are interconvertible by rotation of the *trans* double bond by 180°.

The graphs (constitutional formulae) of the molecules in Figure 1 can be embedded in the plane without the crossing of any edges (bonds), in the same way that a rubber glove can be deformed, in principle, into a flat sheet of rubber. Note that metrics and energetics play no role in this deformation, which is a purely topological transformation. The resulting planar presentation[6] is achiral in three-dimensional space. How-

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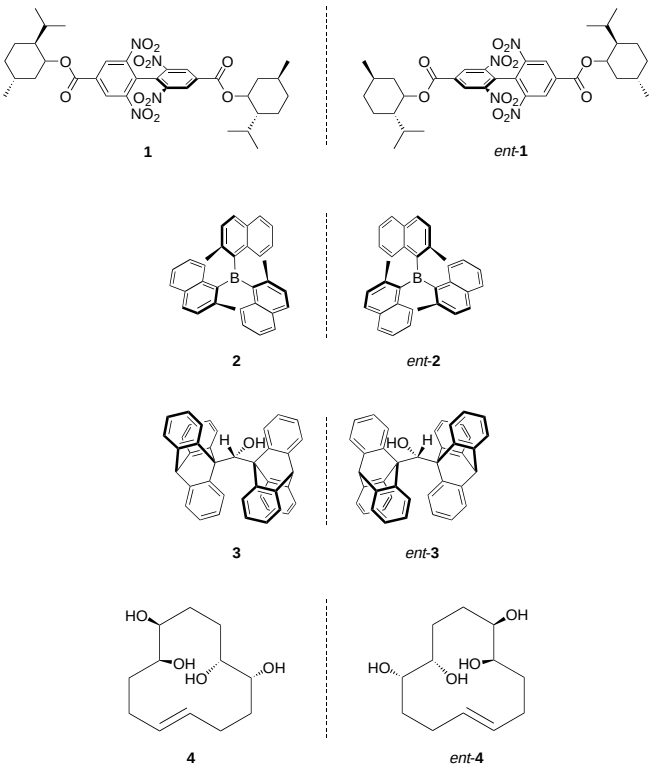

Figure 1. Examples of chemically achiral molecules displaying exclusively chiral conformations. For each compound **1**–**4**, two interconverting enantiomorphous conformations are shown. They are related by the mirror plane marked with a dashed line.

ever, the chirality of individual conformations requires the maintenance of chemically reasonable bonding parameters (bond angles and lengths). Such molecules have therefore been termed "Euclidean rubber gloves".

A few years ago, we reported in brief on the first example of a molecule that is not only chemically achiral, but the molecular graph of which, unlike those of the "Euclidean rubber glove" molecules **1**–**4** in Figure 1, is also rigidly (geometrically) chiral in every possible presentation.[7] This molecule, the [2]catenane **5** in Figure 2, was properly characterized as a chemically achiral "topological rubber glove".

In this paper, we describe the preparation of [2]catenane **5** and compare its properties with those of its "Euclidean rubber glove" analogue, [2]rotaxane **6** (Figure 2), and also compare the corresponding copper(I) complexes, $[Cu(\mathbf{5})]^+$ and $[Cu(\mathbf{6})]^+$.

Results and Discussion

Design, principle of construction, and synthesis: The [2]catenane **5** and [2]rotaxane **6** in Figure 2 can be prepared from the same C_2-symmetric macrocycle incorporating a 1,5-dioxynaphthalene subunit, which was designed for making a hybrid Cu^I [2]catenate based on transition metal complexation and aromatic donor–acceptor interactions.[8a] In the case of the catenane, this macrocycle is interlocked with a macrocycle that is oriented by the location of a *p*-tolyl substituent in the 4-position of the 1,10-phenanthroline subunit.[8b] In the case of the rotaxane, the C_2-symmetric macrocycle is threaded onto an oriented, dumbbell-shaped molecule based on the same 4-*p*-tolyl-1,10-phenanthroline subunit, which bears tetraarylmethane stoppers that have been extensively used in the construction of rotaxanes.[9] Catenation of the C_2-symmetric ring with the oriented ring (in the case of **5**) or threading of the former onto the oriented dumbbell (in the case of **6**) destroys the C_2 axis of the 1,5-dioxynaphthalene-containing macrocycle in both molecules. As shown in Figure 2, the mirror image of an asymmetric conformation of either **5** or **6** is obtained by rotation of the 1,5-dioxynaphthalene plane by 180°. All chemically accessible conformations encountered along this or any other enantiomerization pathway are asymmetric. The time-averaged symmetry of **5** or **6** is C_s, which expresses the chemical achirality of the molecule, even though no individual conformation of the molecule can possibly belong to this point group. There is, however, a

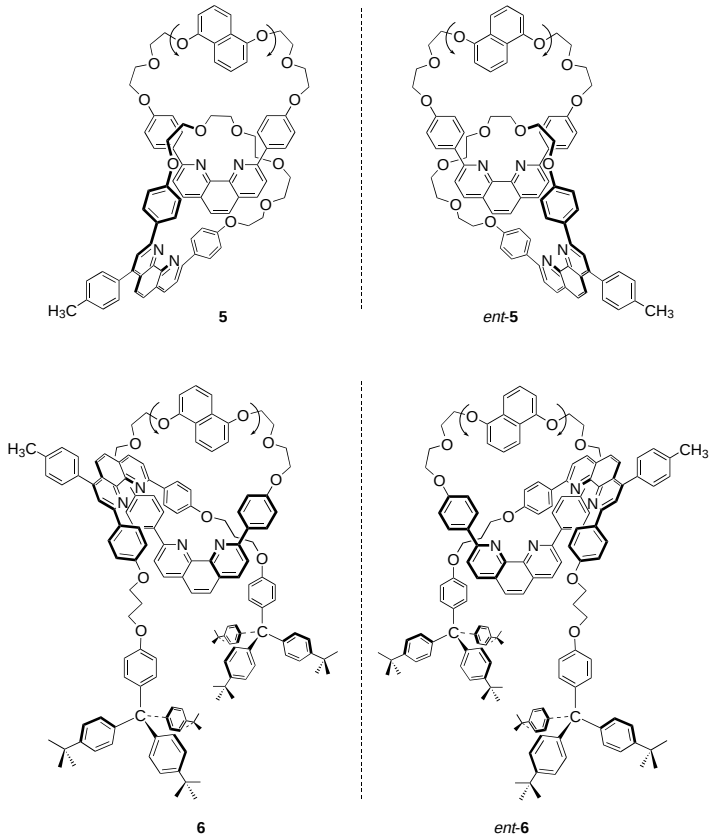

Figure 2. Enantiomorphous conformations of [2]catenane **5** and [2]rotaxane **6**. The enantiomorphs are related by the mirror plane marked with a dashed line and are interconverted by rotation of the 1,5-dioxynaphthalene moiety about the C–O bonds (arrows).

crucial difference between **5** and **6** as far as topological properties are concerned. In contradistinction to **5**, which cannot be separated into its macrocyclic components without bond breaking, **6** can, in principle, be disassembled by dethreading of the ring from the oriented molecular dumbbell, and the molecular graphs of the individual components can be deformed into planar and, hence, achiral presentations. The former therefore qualifies as a "topological rubber glove", whereas the latter is "only" a "Euclidean rubber glove".

The target [2]catenane **5** and [2]rotaxane **6** were synthesized by means of the transition metal templated technique developed and used extensively for making various catenanes, rotaxanes, and knots.[10] The general principle of construction is shown in Figure 3. The molecular precursors, macrocyclic A and acyclic B, both incorporate the same bidentate chelating subunit. In the presence of copper(I), they give rise to the exclusive formation of intermediate C by virtue of the stereoelectronic preferences of this d^{10} transition metal cation. Reaction of C with the appropriate linker or stopper affords the copper(I) complexes of the desired catenane D or rotaxane F, respectively. Finally, removal of the metal template affords the free catenane E or rotaxane G species, in which the components are held together only by mechanical bonds. In this study, we arbitrarily chose complementary routes for the preparation of the catenane and the rotaxane. Pre*catenate* C was formed with the oriented macrocycle A, and the second interlocking C_2-symmetric macrocycle was generated in the next step, whereas pre*rotaxane* C was formed with the C_2-symmetric macrocycle, and the oriented threading dumbbell was constructed in the next step.

The macrocyclic and acyclic precursors and components (**7**–**10**) are shown in Figure 4, while the trityl-containing precursors (**11**–**14**) and dumbbell component **15** are shown in

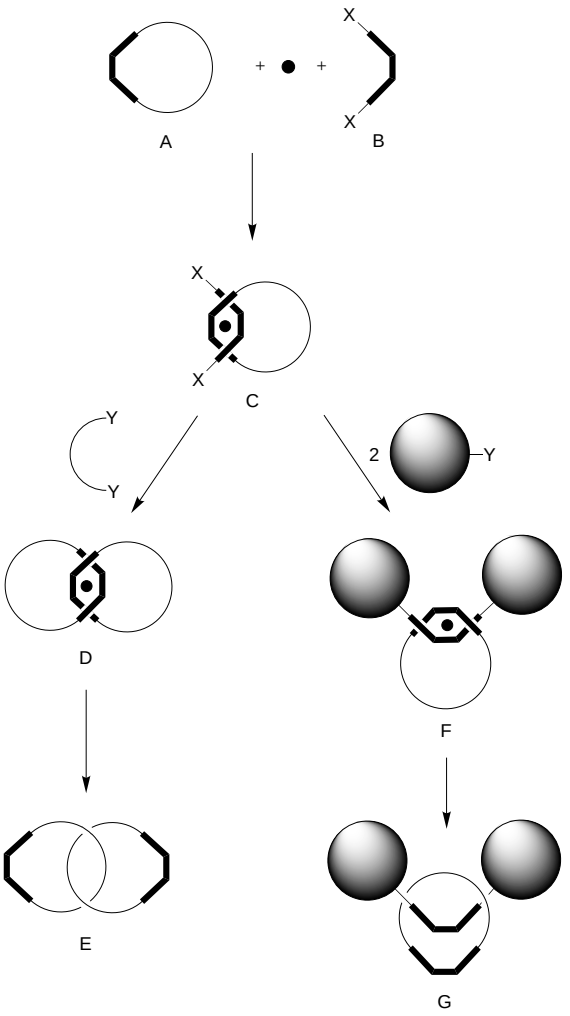

Figure 3. Transition metal templated strategy for the construction of catenanes and rotaxanes. Thick lines represent bidentate chelates. The black disk represents a transition metal cation. X and Y are complementary functions, such as nucleophilic and electrophilic groups. The metal controls threading of macrocycle A onto acyclic fragment B. Intermediate C can be used as a precursor for the formation of either catenane D or rotaxane F, depending on the nature of the other reactant (chain-like fragment or stopper, respectively). Removal of the metal template provides access to either free catenane E or free rotaxane G.

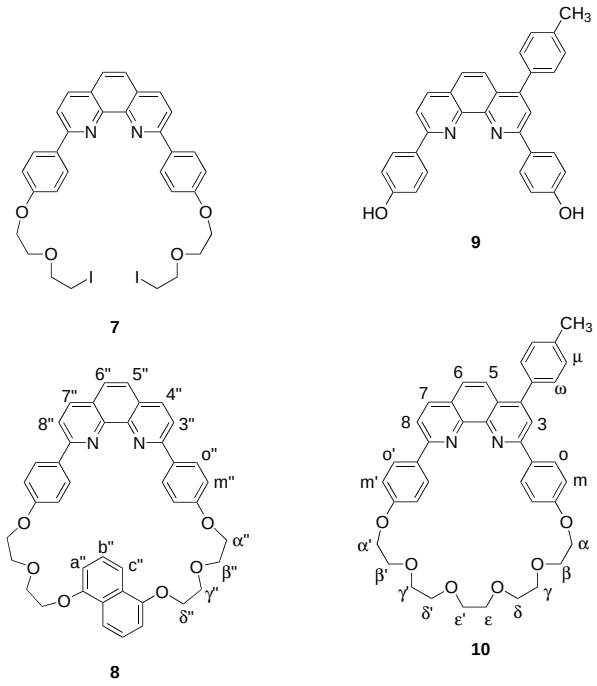

Figure 4. Acyclic (**7**, **9**) and cyclic (**8**, **10**) 2,9-diphenyl-1,10-phenanthroline-based precursors and components used in the synthesis of catenane **5** and rotaxane **6**.

Figure 5. Macrocycle **8** was synthesized in 37% yield by reaction of the phenanthroline derivative **7** with 1,5-naphthalenediol under high dilution conditions, with Cs_2CO_3 as a base in DMF at 60–64 °C. This method turned out to be less efficient than the synthesis described by Amabilino and coworkers,[8a] which involved 2,9-di(4-hydroxyphenyl)-1,10-phenanthroline as a nucleophile and 1,5-bis{2-[2-(toluene-*p*-sulfonyl)ethoxy]ethoxy}naphthalene as an electrophile and gave a yield of 55%. The individual steps leading to [2]catenane **5** are depicted in Schemes 1 and 2. Precatenate $[Cu(\mathbf{7})(\mathbf{10})]PF_6$ was prepared in quantitative yield by first mixing $[Cu(CH_3CN)_4]PF_6$ and macrocycle **10** in CH_3CN/CH_2Cl_2 under argon and then adding a stoichiometric amount of the diiodo derivative **7**. Its formation was accompanied by a

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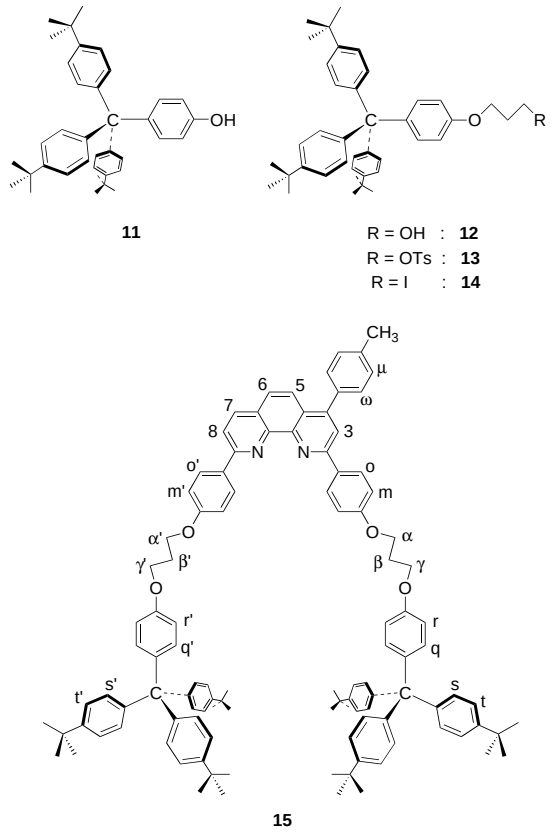
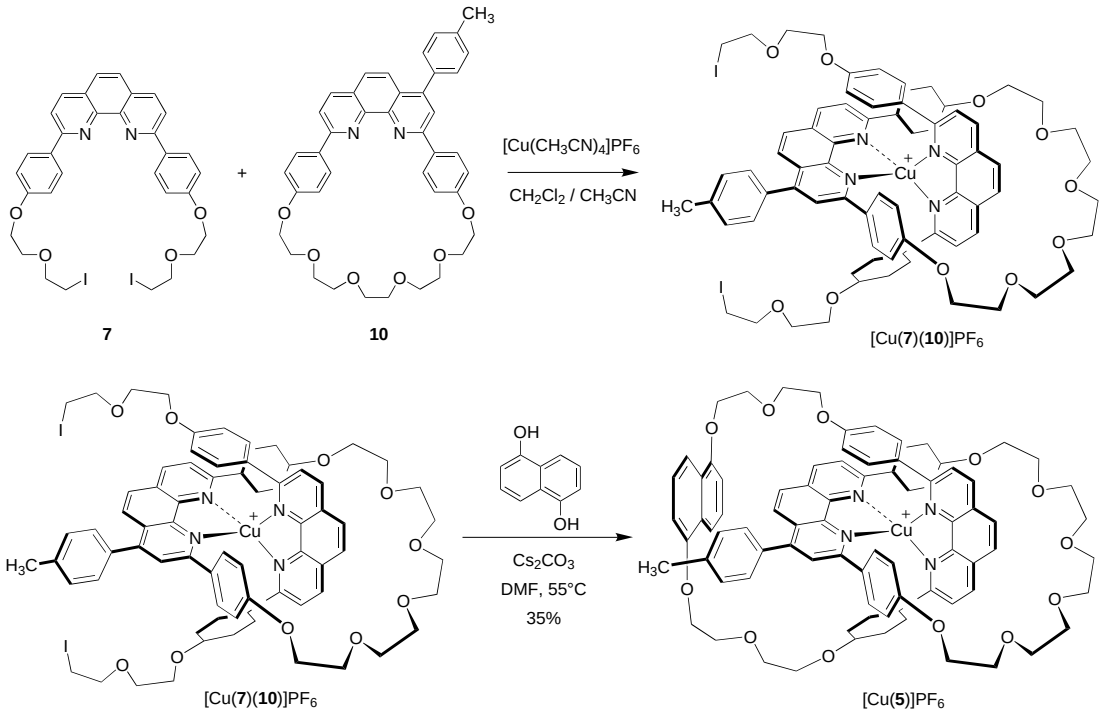


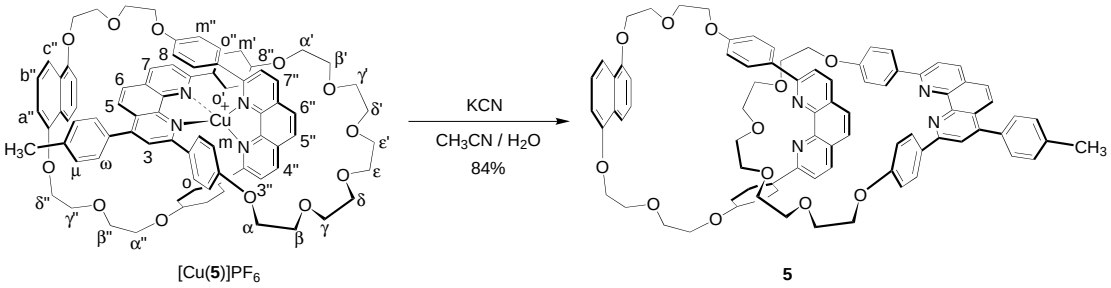
Figure 5. Precursors (**11**–**14**) and dumbbell component (**15**) of rotaxane **6** based on the tris(4-*tert*-butylphenyl)phenylmethane blocking group.

marked color change from orange to brown-red in the final step. Subsequently, a mixture of [Cu(**7**)(**10**)]PF_6 and 1,5-dihydroxynaphthalene in DMF was added dropwise to a suspension of Cs_2CO_3 in DMF at 60 °C under argon over a period of 7 h. The reaction was followed by counterion exchange (KPF_6) and chromatography. It gave the desired Cu^I [2]catenate [Cu(**5**)]PF_6 in 35 % yield and macrocycle **8** in 6 % yield, while around 59% of the starting macrocycle **10** was recovered. Demetallation of [Cu(**5**)]PF_6 to give catenane **5** was accomplished by treating a solution of the Cu^I [2]catenate in acetonitrile with a large excess of aqueous KCN solution. The metal-free [2]catenane was obtained in 84 % yield after chromatography.

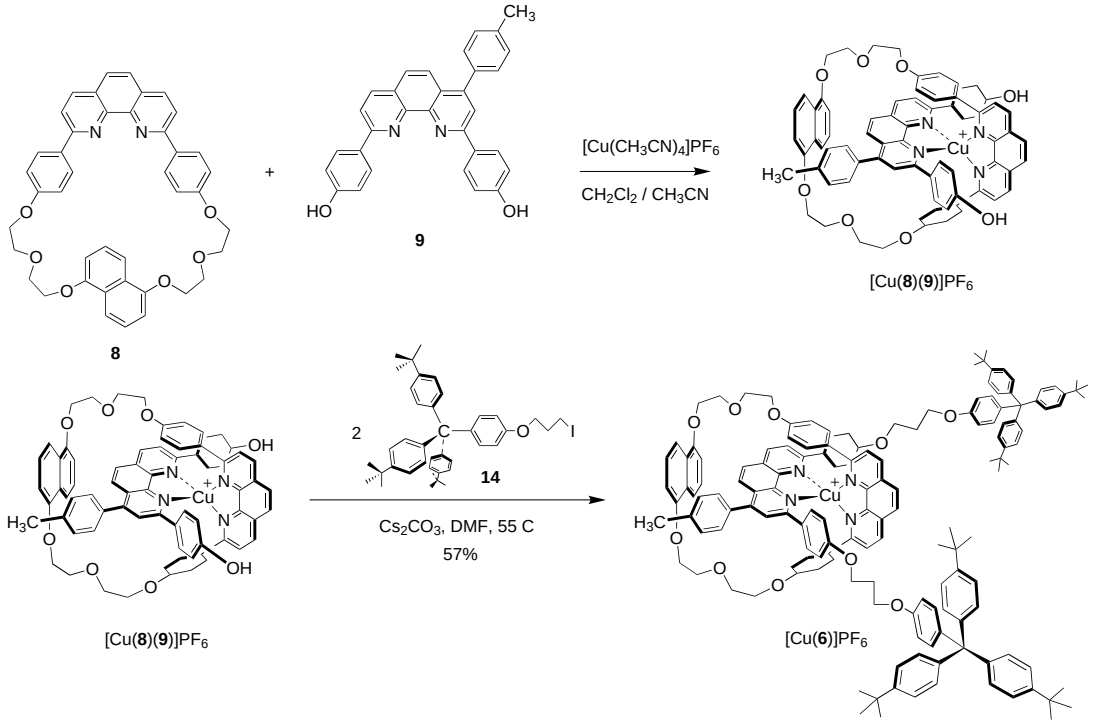
The synthesis of [2]rotaxane **6** is shown in Schemes 3 and 4. The tetraarylmethane electrophile **14** was prepared in four steps from tris(4-*tert*-butylphenyl)(4-hydroxyphenyl)methane (**11**) (Figure 5).[9f] In the first step, **11** was treated with 2-(3-chloropropyloxy)tetrahydro-2*H*-pyran[11] in the presence of a stoichiometric amount of KOH in butan-1-ol. Acid hydrolysis afforded **12** in 54 % yield.[9f] Tosylation was performed by treating **12** with tosyl chloride in dichloromethane in the presence of triethylamine at 0 °C; compound **13** was obtained in 56 % yield after chromatography. Displacement of tosylate by iodide by treating **13** with an excess of NaI heated under reflux in acetone led to the quantitative isolation of **14**. Prerotaxane [Cu(**8**)(**9**)]PF_6 was quantitatively obtained from macrocycle **8** and diphenol **9** as reported for the precatenane analogue. The rotaxane complex [Cu(**6**)]PF_6 was prepared as follows. Aliquots of a suspension of Cs_2CO_3 in DMF and a solution of the iodo derivative **14** in DMF were alternately added to a solution of the prerotaxane in DMF at 60 °C under argon over a period of 1 h. It was found that the extent of dethreading, which occurs in hot and basic media, could be suppressed using this procedure.[9l, 12] After counterion exchange and chromatography, the copper complex [Cu(**6**)]PF_6 was obtained in 57 % yield, along with free dumbbell **15** (34 %) and some released macrocycle **8** (32 %). The relatively



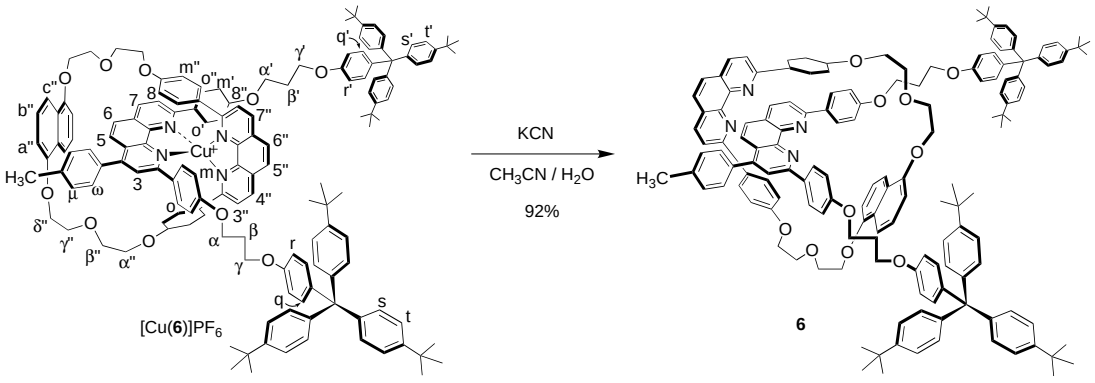
Scheme 1. Synthesis of Cu^I [2]catenate [Cu(**5**)]PF_6.



Scheme 2. Demetallation of [Cu(**5**)]PF_6 to give **5**.



Scheme 3. Synthesis of Cu^{I} [2]rotaxane [Cu(**6**)]PF_6.



Scheme 4. Demetallation of [Cu(**6**)]PF_6 to give **6**.

high yield of the rotaxane formation, in agreement with the relatively small amount of free macrocycle recovered, is noteworthy. Demetallation of [Cu(**6**)]PF_6 to give rotaxane **6** was performed as described for catenane **5**. The metal-free [2]rotaxane was obtained in 92 % yield after chromatography.

X-ray molecular structure of the Cu^{I} [2]catenate [Cu(6)]PF_6: The X-ray structure of the Cu^{I} [2]catenate [Cu(**6**)]PF_6 (Table 1) is reproduced in Figure 6a, and a view of the unit cell with its two pairs of enantiomorphous occupants is given in Figure 6b. This view nicely shows the interlocking of the C_2-

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Table 1. X-ray experimental data for $[Cu(\mathbf{5})]PF_6$.

formula	$C_{83}H_{76}CuN_4O_{12} \cdot PF_6$
M_r	1530.06
crystal system	monoclinic
space group	$P12_1/n1$
a [Å]	14.944(1)
b [Å]	23.186(1)
c [Å]	20.921(1)
β [°]	96.45(6)
V [Å^3]	7203.1(7)
Z	4
color	red
size [mm]	$0.18 \times 0.15 \times 0.10$
ρ_{calcd} [g cm^{-1}]	1.41
$F(000)$	3184
μ [mm^{-1}]	0.404
T [K]	173
λ	0.71073
radiation	$Mo_{K\alpha}$ graphite-monochromated
scan mode	Ψ scans
hkl limits	0,18/0,28/ – 26,25
θ limits [°]	2.5/26.37
reflections measured	47344
reflections obsevered [$I > 3\sigma(I)$]	7709
parameters	964
R[a]	0.046
R_w[a]	0.075
GoF[a]	1.442
Largest peak in final difference [e Å^{-3}]	0.421

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o - F_c)^2]^{1/2}$; GOF $= [\Sigma w(F_o - F_c)^2/(\text{no. of reflns.} - \text{no. of params.})]^{1/2}$.

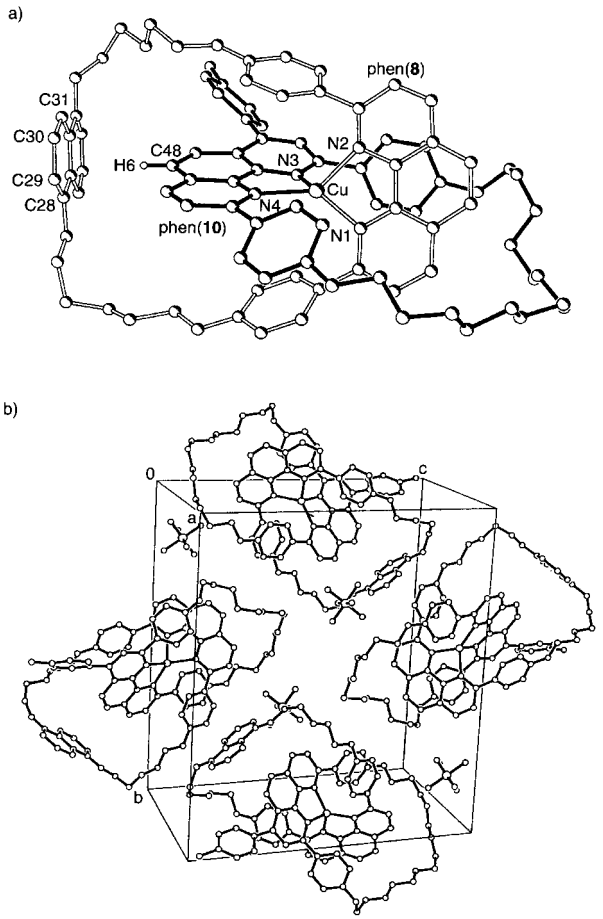

Figure 6. X-ray crystal structure of $[Cu(\mathbf{5})]PF_6$. a) Molecular structure. b) View of the unit cell.

symmetric and the oriented macrocycles. Overall, this structure is very similar to that found for a related Cu^I [2]catenate.[13] The copper atom is bound to the two phenanthroline (phen) subunits through the four nitrogen atoms. The N–Cu bond lengths range from 2.018 to 2.052 Å. As expected, the coordination polyhedron around Cu^I is highly distorted with respect to a tetrahedral geometry. The angle between the phenanthroline planes deviates from orthogonality by 28°. As a consequence, if the chelate bite of the phen ligand imposes two N–Cu–N angles of 82.3(1)° (C_2-symmetric macrocycle) and 82.6(1)° (oriented macrocycle), the other N–Cu–N angles will vary from 105.0(1)° to 135.2(1)°. In previous work, the pronounced distortion around the copper atom was interpreted as the result of acceptor/donor stacking interactions between the phen nucleus of one macrocyclic subunit and an anisyl moiety of the other.[13] This is indeed what is observed in the present case; as shown in Figure 6a, phen(**10**) is almost parallel to the phenyl group of phen(**8**) above it, with an angle of 11° between the mean planes and a centroid-to-centroid distance of 3.69 Å. In comparison, the corresponding values for phen(**8**) and the phenyl group of phen(**10**) *cis* to the *p*-tolyl substituent are 27° and 4.16 Å, respectively. Furthermore, the two remaining phenyl groups are also parallel to one another and are also in very close proximity (3.5 Å). Remarkably, the naphthyl moiety of the C_2-symmetric macrocycle lies perpendicular to the phenanthroline nucleus of the oriented macrocycle, with the C48–H6 bond of the latter pointing to the center of one of the fused six-membered rings of the former, the distances between H6 and the C27–C32 atoms ranging from 2.84 to 3.21 Å. This strongly suggests the existence of an edge-to-face aromatic interaction between the two polycyclic systems.

^{1}H NMR spectroscopic and FAB-MS characterization of [2]catenane 5, [2]rotaxane 6, and their complexes: The room temperature ^{1}H NMR spectra of [2]catenate $[Cu(\mathbf{5})]^+$ and catenane **5** are compared in Figures 7 (low-field region) and 8 (high-field region). Notably, only one set of signals is seen for the naphthyl moiety, despite the two different environments created by the non-symmetric substitution of H4 and H7 on the oriented ring; this shows that, at least at room temperature, the naphthyl group rotates freely, and that on the NMR timescale the enantiomers exchange rapidly. The *meta* protons of the phenyl 2,9-substituents (*m*, *m*′, and *m*″) give rise to a cluster of signals between $\delta = 5.8$ and 6.2 in the spectrum of $[Cu(\mathbf{5})]^+$. As discussed in earlier work, the *meta* protons of a phenyl group attached to a given phen lie in the shielding field of the other phen chelate of the molecule.[14] The same is true for $[Cu(\mathbf{6})]^+$. The shielding of the H6 proton of the oriented macrocycle is particularly remarkable: it has a chemical shift of $\delta = 6.494$ in the Cu^I catenate and of $\delta = 6.402$ in the Cu^I rotaxane, while the adjacent proton H5 resonates downfield, at $\delta = 7.221$ in the case of $[Cu(\mathbf{5})]^+$ and at $\delta = 7.244$ in the case of $[Cu(\mathbf{6})]^+$. This result is in good agreement with what is observed in the solid state for the catenate. Whereas δH5 – δH6 = 0.727 ppm for catenate $[Cu(\mathbf{5})]^+$ and 0.842 ppm for rotaxane $[Cu(\mathbf{6})]^+$, in the case of macrocycle **10** this difference is just 0.150 ppm, highlighting the anisotropy created by the naphthyl group in the vicinity of protons H5 and H6. As

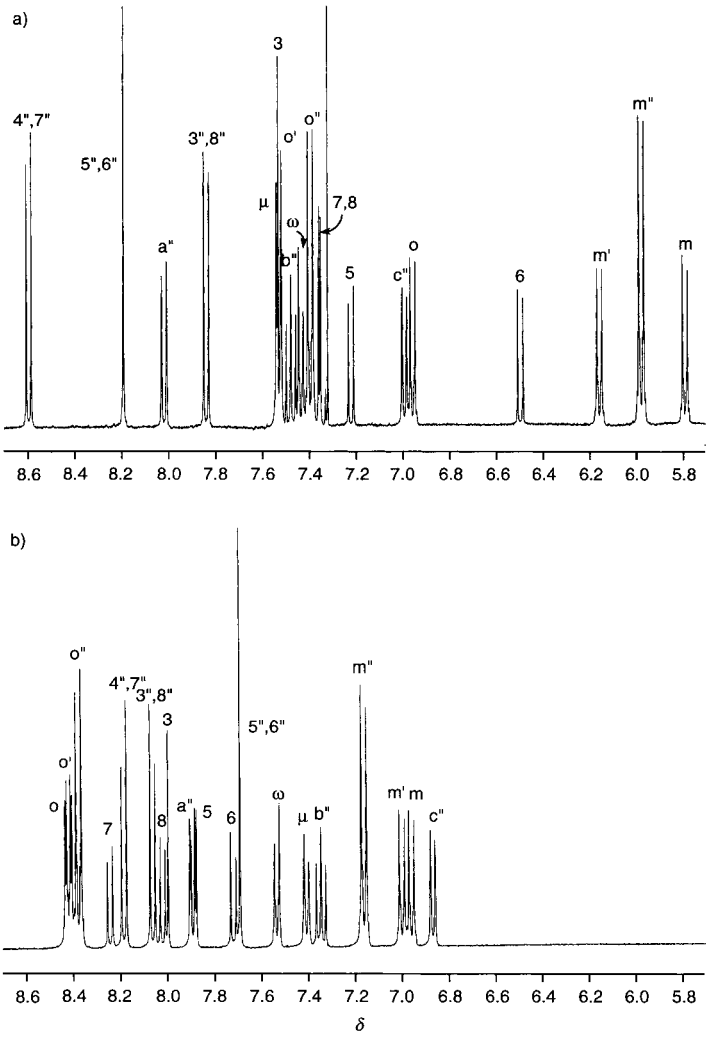

Figure 7. ^{1}H NMR spectra (low-field region) of a) Cu^{I} [2]catenate [Cu(**5**)]$^+$ and b) [2]catenane **5**. Atom labeling is as shown in Scheme 2.

shown in Figure 7, the ^{1}H NMR spectrum of the free catenane **5** is dramatically different from that of its copper complex, suggesting that a complete reorganization of the molecule occurs upon decomplexation. The same is true for the rotaxane species. The aromatic interactions present in the Cu^{I} complexes are no longer seen, as indicated by the downfield shifts of the signals of the *meta* protons (*m*, *m*′, *m*″), which appear in the range $\delta = 6.9 - 7.2$, and the downfield shift of the signal due to H6 ($\Delta\delta = 1.229$ ppm for **5**, 1.257 ppm for **6**). Consistently, the values of δH5 – δH6 are 0.168 ppm for **5** and 0.176 ppm for **6**, which are very close to the shift difference measured for macrocycle **10** (0.150 ppm). Nevertheless, the spectrum of a 1:1 mixture of macrocycles **8** and **10** is not superimposable on that of the free catenane, even if its overall appearance is rather similar. This may be explained by the fact that catenane **5** has several aromatic groups held in close proximity by mechanical bonding, which may influence each other through a subtle combination of ring current effects. The same is true for the spectrum of [2]rotaxane **6**, which is not merely the sum of the spectra of the individual components **8** and **15**. Similar observations have been made for related molecules.[9c,9l] Comparison of the high-field regions of the relevant spectra of the catenated species (Figure 8) shows that demetallation of [Cu(**5**)]$^+$ to give **5** allows some flexibility of the polyether chain of the C_2-symmetric macrocyclic component, as manifested, for example, in the changes in the pattern of the signals of the diastereotopic methylene Hδ''.

The ES mass spectrum of [2]catenate [Cu(**5**)]PF_6 shows two peaks, the molecular peak at *m*/*z* 1384.0, corresponding to loss of the PF_6^- anion, and a peak at *m*/*z* 692.5, corresponding to a doubly charged species. The FAB mass spectra of the metal-free catenane **5** and the metal-free rotaxane **6** are shown in Figure 9. The spectrum of the catenane (Figure 9a) shows the molecular peak at *m*/*z* 1321.5, as well as peaks corresponding to each individual macrocycle at *m*/*z* 665.2 for C_2-symmetric **8** and *m*/*z* 657.3 for oriented **10**. As expected on the basis of earlier studies, there is no peak between the molecular peak and those of the individual components, and this was recognized as a signature of catenated species.[10a,15] The FAB mass spectrum of the rotaxane (Figure 9b) also shows the molecular peak, at *m*/*z* 2209.2, and peaks corresponding to each individual component, at *m*/*z* 1544.9 for dumbbell **15** and *m*/*z* 665.2 for macrocycle **8**. A similar spectrum is obtained for the Cu^{I}-complexed [2]rotaxane [Cu(**6**)]PF_6, with a shift of +63.5 amu relative to the values reported above. In this latter case, two clusters of peaks centered at *m*/*z* 1738.8 and *m*/*z* 1073.5 correspond to the fragmentation of the dumbbell

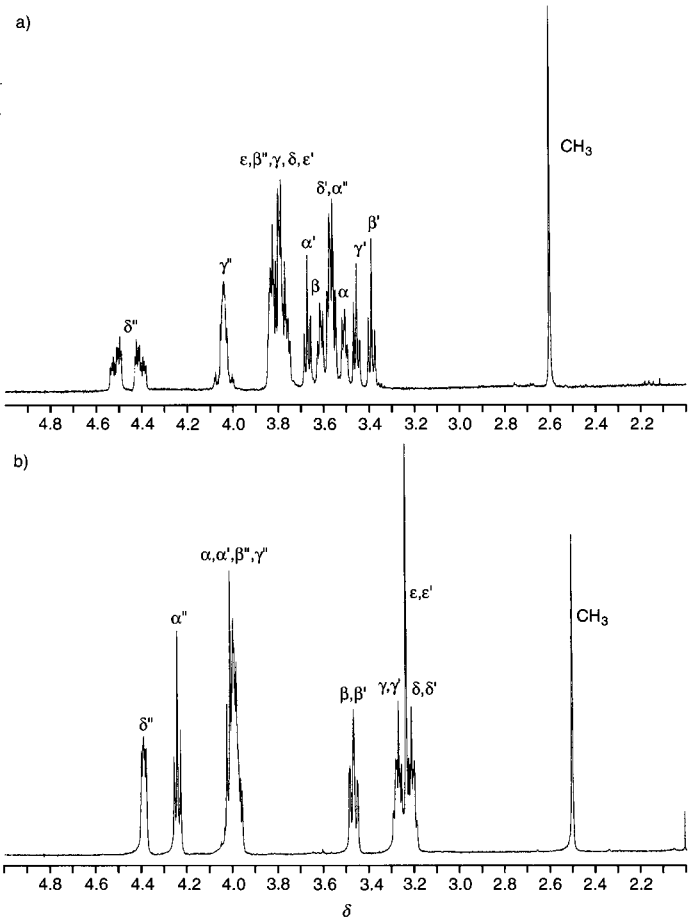

Figure 8. ^{1}H NMR spectra (high-field region) of a) Cu^{I} [2]catenate [Cu(**5**)]$^+$ and b) [2]catenane **5**. Atom labeling is as shown in Scheme 2.

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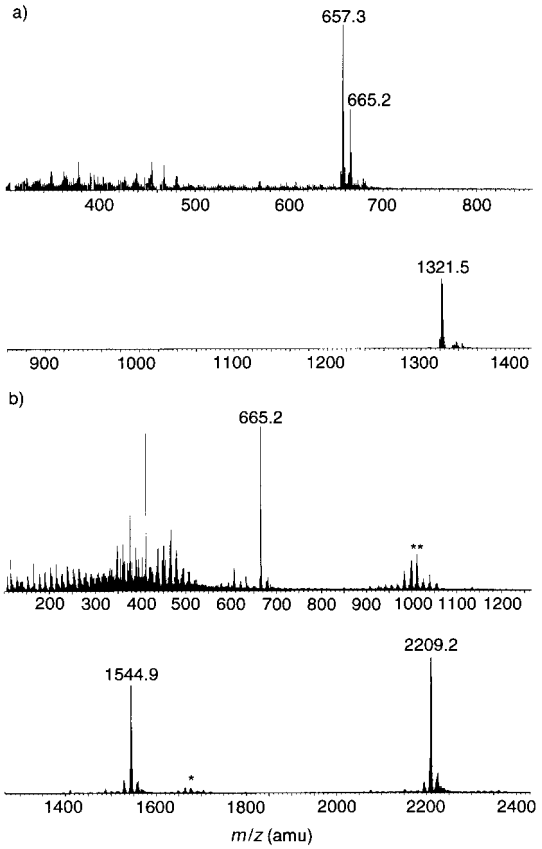

Figure 9. FAB$^+$ mass spectra of a) [2]catenane **5** and b) [2]rotaxane **6**. The asterisks in b) show the fragmentation patterns of the threaded (*) and unthreaded (**) dumbbell species.

component, either as part of the rotaxane or as Cu^I-complexed species. In support of this interpretation, the difference between the maxima corresponds to the mass of the C_2-symmetric macrocycle **8**. As expected, in the case of the metal-free rotaxane, the fragmentation patterns corresponding to the dethreaded dumbbell are present at around 1010 amu. Surprisingly, those corresponding to the threaded dumbbell are also seen in the spectrum (at around 1675 amu), albeit to a much lesser extent than in the case of the Cu^I complex; this is an indication that fragmentation of the threaded dumbbell may occur without disassembly of the system. Since ionization processes of the metal-free phenanthroline-based rotaxanes and catenanes usually occur by protonation, it is assumed that the fragments of the threaded species (which can be characterized as semi-rotaxane species) are held together by proton complexation.[16]

^{1}H NMR studies at variable temperatures or in the presence of a chiral shift reagent: As mentioned in the previous section, ^{1}H NMR studies in CD_2Cl_2 at room temperature showed the rates of the exchange processes between enantiomeric conformations to be fast on the NMR timescale in all four cases (catenane **5**, rotaxane **6**, and their copper complexes). As illustrated in Figure 2, enantiomerization takes place by a rotation of the naphthyl group by 180° about the C–O bonds. Cooling solutions of these compounds to $-90\,^\circ$C generally led to a simple broadening of the peaks. Only in the case of the Cu^I complex of [2]rotaxane **6** were remarkable features seen in the ^{1}H NMR spectra (Figure 10). Specifically, the doublets due to the 4″,7″ protons (phen moiety) and a″ = a_1″, a_2″ protons (naphthyl moiety) of the C_2-symmetric macrocycle,

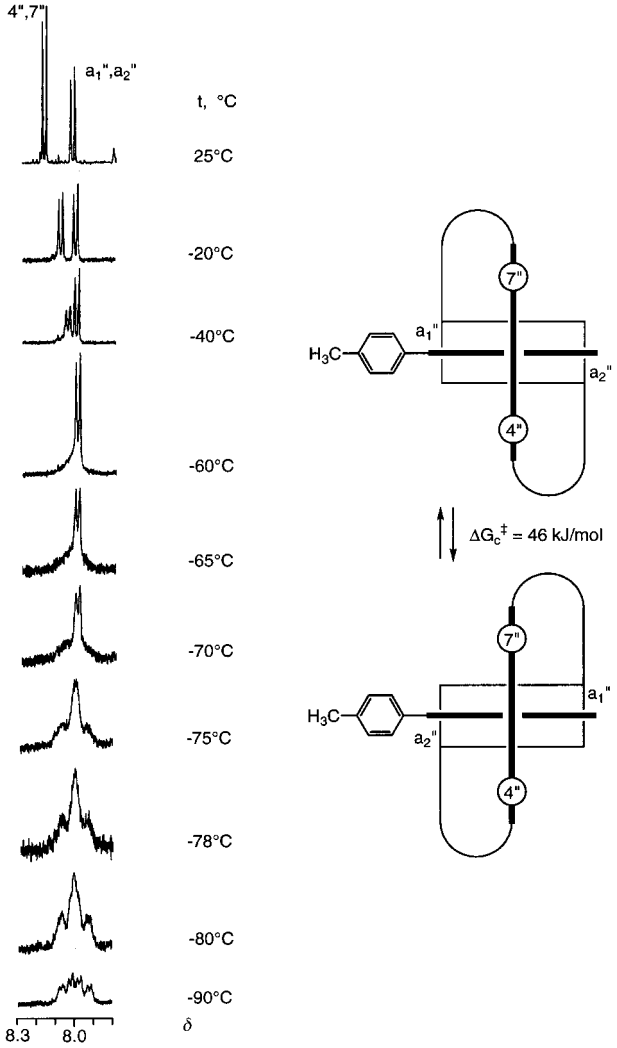

Figure 10. Selected low-field region of the variable-temperature ^{1}H NMR spectra of Cu^I [2]rotaxane [Cu(**6**)]PF_6 (CD_2Cl_2, 400 MHz) and the enantiomerization mechanism that exchanges 4″ and 7″ on the one hand and a_1″ and a_2″ on the other.

which are well-separated from the other low-field peaks, undergo the changes shown in Figure 10. Each doublet is split into a set of two doublets, which are nicely resolved at $-90\,^\circ$C. The coalescence temperature is $-78\,^\circ$C (195 K), corresponding to an enantiomerization barrier of about 46 kJ mol^{-1}. These observations are easily explained in terms of hindered rotation of the naphthyl moiety at low temperatures (Figure 10). Thus, at $-90\,^\circ$C, the enantiomeric conformations do not exchange on the NMR timescale. Whereas the splitting of the doublet due to Ha″ can readily be understood, this is not the case for the doublet due to H4″,7″, since these protons are quite remote from the perturbing area.

Non-interconverting enantiomorphous conformations could be observed for [Cu(**5**)]$^+$ by ^{1}H NMR spectroscopy in the presence of Pirkle's reagent (*S*)-(+)-2,2,2-trifluoro-1-(9-

anthryl)ethanol[17] at room temperature. Addition of a small amount of the chiral shift reagent produced a clear, nicely resolved splitting of the doublet due to the c′′ protons of the naphthyl moiety.

Experimental Section

General methods: Oxygen- or water-sensitive reactions were conducted under a positive pressure of argon in oven-dried glassware with Schlenk techniques. CH_2Cl_2 was distilled from P_2O_5, CH_3CN was distilled from CaH_2, and DMF was filtered through a pad of alumina prior to use. Common reagents and materials were purchased from commercial sources. The following materials were prepared according to literature procedures: 2,9-bis{4-{2-[2-iodoethoxy(ethoxy)]}phenyl}-1,10-phenanthroline (**7**),[18] 2,9-bis(4-hydroxyphenyl)-4-(*p*-tolyl)-1,10-phenanthroline (**9**),[8b] macrocycle **10**,[8b] tris(*p*-*tert*-butylphenyl)(4-hydroxyphenyl)methane (**11**),[9f] 2-(3-chloropropyloxy)tetrahydro-2*H*-pyran,[11] and $[Cu(CH_3CN)_4]PF_6$.[19] Thin-layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254} (Merck). Column chromatography was carried out on silica gel 60 (Merck, 70–230 mesh). ^{1}H NMR spectra were recorded on either a Bruker WP 200 SY (200 MHz) or a Bruker AM 400 (400 MHz) spectrometer. NMR chemical shifts (δ) are expressed in ppm relative to the solvent peaks as internal standards. Coupling constants (J) are given in Hz. Splitting patterns are designated as s, d, t, q, p, sx, m, and br, indicating singlet, doublet, triplet, quartet, pentet, sextet, multiplet, and broad, respectively. The labeling scheme of the protons of the [2]catenane and [2]rotaxane and their precursors is indicated in the Schemes 2 and 4 and Figures 4 and 5. Fast-atom bombardment mass spectrometry (FAB MS) data were recorded in the positive-ion mode with a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a ZAB-HF mass spectrometer. A VG BIOQ triple-quadrupole spectrometer was used for the electrospray mass spectrometry measurements, which was also operated in the positive-ion mode. Melting points were determined in open capillary tubes on a Büchi 530 apparatus; the values quoted are uncorrected. Elemental analyses were performed by the Service de Microanalyse de l'Institut de Chimie de Strasbourg.

Macrocycle (8): Method A, 55% yield.[8a] Method B: Compound **7** (1.00 g, 1.32 mmol) and 1,5-dihydroxynaphthalene (0.198 g, 1.239 mmol) were dissolved in dry, degassed DMF (115 mL). The resulting solution was added dropwise to a vigorously stirred suspension of Cs_2CO_3 (1.716 g, 5.27 mmol) in dry degassed DMF (230 mL) maintained at 60–64 °C over a period of 18 h. After the addition was complete, the dropping funnel was rinsed with DMF (20 mL), and further Cs_2CO_3 (0.479 g, 1.47 mmol) was added. Stirring and heating were maintained for a further day, after which the solvent was removed in vacuo. The brown residue was partitioned between CH_2Cl_2 and H_2O. The organic phase was washed twice with water, dried with $MgSO_4$, and concentrated to dryness. The crude product (0.926 g) was subjected to column chromatography (SiO_2, 56 g; CH_2Cl_2), affording pure macrocycle **8** (0.323 g) in 37% yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 8.434$ (d, $J = 8.96$ Hz, 4H; Ho′′), 8.292 (d, $J = 8.45$ Hz, 2H; H4′′,7′′), 8.111 (d, $J = 8.45$ Hz, 2H; H3′′,8′′), 7.975 (d, $J = 8.57$ Hz, 2H; Ha′′), 7.773 (s, 2H; H5′′,6′′), 7.467 (t, $J = 8.00$ Hz, 2H; Hb′′), 7.132 (d, $J = 8.96$ Hz, 4H; Hm′′), 7.033 (d, $J = 7.55$ Hz, 2H; Hc′′), 4.396 (q, $J = 4.74$ Hz, 4H; Hδ′′), 4.281 (q, $J = 4.74$ Hz, 4H; Hα′′), 4.076 (q, $J = 4.74$ Hz, 4H; Hγ′′), 4.025 (q, $J = 4.74$ Hz, 4H; Hβ′′).

Cu^{I} precatenate [Cu(7)(10)]PF$_6$: Under argon, a solution of $[Cu(CH_3CN)_4]PF_6$ (0.174 g, 0.467 mmol) in CH_3CN (15 mL) was transferred to a solution of macrocycle **10** (0.302 g, 0.46 mmol) in dichloromethane (10 mL). The resulting mixture immediately turned amber-orange. After stirring for 20 min at room temperature, a solution of compound **7** (0.349 g, 0.459 mmol) in CH_2Cl_2 (10 mL) was added to the reaction mixture, producing a color change to dark red-brown. The resulting mixture was stirred overnight under argon. The solvents were then removed in vacuo to leave pure precatenate [Cu(**7**)(**10**)]PF_6 in quantitative yield. ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 8.640$ (d, $J = 8.43$ Hz, 2H; H4′′,7′′), 8.514 (d, $J = 8.44$ Hz, 1H; H7), 8.238 (s, 2H; H5′′,6′′), 8.116 (d, $J = 9.04$ Hz, 1H; H6), 8.010 (d, $J = 9.03$ Hz, 1H; H5), 7.900 (d, $J = 8.44$ Hz, 2H; H3′′,8′′), 7.880 (d, $J = 8.23$ Hz, 1H; H8), 7.753 (s, 1H; H3), 7.578 (d, $J = 7.83$ Hz, 2H; Hω), 7.551 (d, $J = 8.63$ Hz, 4H; Ho′′), 7.493 (d, $J = 8.03$ Hz, 2H; Hμ), 7.340 (d, $J = 8.63$ Hz, 2H; Ho′), 7.298 (d, $J = 8.63$ Hz, 2H; Ho), 6.158 (d, $J = 8.63$ Hz, 4H; Hm′′), 6.028 (d, $J = 8.83$ Hz, 2H; Hm′), 5.964 (d, $J = 8.64$ Hz, 2H; Hm), 3.845 (s, 4H; Hε,ε′), 3.757 (t, $J = 6.53$ Hz, 4H; Hγ′′), 3.735 (m, 12H; Hα′′,β′′,δ,δ′), 3.612 (m, 4H; Hγ,γ′), 3.578 (t, 2H; Hα′), 3.534 (t, 2H; Hα), 3.517 (t, 4H; Hβ,β′), 3.275 (t, $J = 6.53$ Hz, 4H; Hδ′′), 2.546 (s, 3H; CH_3).

Cu^{I} [2]catenate [Cu(5)]PF$_6$: Under argon, a mixture of precatenate [Cu(**7**)(**10**)]PF_6 (0.46 mmol) and 1,5-dihydroxynaphthalene (0.067 g, 0.418 mmol) in DMF (40 mL) was added dropwise to a suspension of Cs_2CO_3 (0.534 g, 1.64 mmol) in DMF (80 mL) at 60 °C over a period of 7 h. The solvent was then evaporated in vacuo and the solid residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed three times with H_2O and concentrated to a volume of 50 mL. It was stirred overnight with a 5% aqueous solution of KPF_6 (20 mL). The organic layer was separated, washed three times with H_2O, and concentrated to dryness. The residue (0.813 g) was fractionated by passage through silica, eluting with CH_2Cl_2/CH_3OH. Each fraction was repurified by chromatography on silica to afford 0.019 g (6% yield) of macrocycle **8** (CH_2Cl_2/0.25–1% CH_3OH) and 0.187 g (62%) of recovered macrocycle **10** ($CHCl_3$/0.1–0.7% CH_3OH). The fractions containing the desired catenate were further purified by chromatography on alumina (gradient elution with hexane/$CHCl_3$, 40:60, to $CHCl_3$/0.1% CH_3OH). From the combined fractions, 0.227 g of [Cu(**5**)]PF_6 was obtained (35% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 8.595$ (d, $J = 8.30$ Hz, 2H; H4′′,7′′), 8.193 (s, 2H; H5′′,6′′), 8.021 (d, $J = 8.57$ Hz, 2H; Ha′′), 7.840 (d, $J = 8.57$ Hz, 2H; H3′′,8′′), 7.534 (s, 1H; H3), 7.530 (d, $J = 8.57$ Hz, 2H; Hμ), 7.530 (d, $J = 8.57$ Hz, 2H; Ho′), 7.479 (t, $J = 8.03$ Hz, 2H; Hb′′), 7.436 (d, $J = 8.03$ Hz, 2H; Hω), 7.396 (d, $J = 8.83$ Hz, 4H; Ho′′), 7.356 (AB, $J = 8.30$ Hz, 2H; H7,8), 7.221 (d, $J = 9.10$ Hz, 1H; H5), 6.992 (d, $J = 7.76$ Hz, 2H; Hc′′), 6.956 (d, $J = 8.56$ Hz, 2H; Ho), 6.494 (d, $J = 9.10$ Hz, 1H; H6), 6.154 (d, $J = 8.56$ Hz, 2H; Hm′), 5.975 (d, $J = 8.84$ Hz, 4H; Hm′′), 5.787 (d, $J = 8.84$ Hz, 2H; Hm), 4.464 (2m, 4H; Hδ′′), 4.041 (m, 4H; Hγ′′), 3.84–3.75 (hidden, 4H; Hε,ε′), 3.832 (m, $J = 1.88$ Hz, 2H; Hγ), 3.802 (t, $J = 4.69$ Hz, 4H; Hβ′′), 3.758 (m, hidden, 2H; Hδ), 3.674 (t, $J = 5.76$ Hz, 2H; Hα′), 3.618 (t, $J = 4.69$ Hz, 2H; Hβ), 3.575 (t, $J = 4.69$ Hz, 4H; Hα′′), 3.560 (t, $J = 4.42$ Hz, 2H; Hδ′), 3.509 (t, $J = 4.69$ Hz, 2H; Hα), 3.457 (t, $J = 5.35$ Hz, 2H; Hγ′), 3.391 (t, $J = 5.76$ Hz, 2H; Hβ′), 2.604 (s, 3H; CH_3); ES-MS: m/z (%): 1384.0 (100) $[M - PF_6]^+$, 692.5 (6) $[M - PF_6 + H]^{2+}/2$.

[2]Catenane 5: Cu^{I} [2]catenate [Cu(**5**)]PF_6 (0.042 g, 0.0277 mmol) was dissolved in CH_3CN (7 mL) and mixed with a solution of KCN (0.049 g, 0.75 mmol) in H_2O (4 mL). A white precipitate of free [2]catenane **5** appeared. After complete bleaching, the reaction mixture was diluted with CH_2Cl_2 to dissolve the precipitate and washed three times with H_2O. The organic layer was separated and concentrated to dryness, and the residue was purified by chromatography on a column of silica gel (hexane/CH_2Cl_2, 80:20, to CH_2Cl_2/CH_3OH, 100:4). Finally, the product was filtered through a pad of alumina (CH_2Cl_2/1% CH_3OH) to afford 0.031 g (84%) of pure [2]catenane **5**. ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 8.425$ (d, $J = 9.10$ Hz, 2H; Ho), 8.419 (d, $J = 9.10$ Hz, 2H; Ho′), 8.380 (d, $J = 9.10$ Hz, 4H; Ho′′), 8.248 (d, $J = 8.57$, 1H; H7), 8.188 (d, $J = 8.29$ Hz, 2H; H4′′,7′′), 8.067 (d, $J = 8.57$ Hz, 2H; H3′′,8′′), 8.025 (d, $J = 8.30$ Hz, 1H; H8), 8.001 (s, 1H; H3), 7.898 (d, $J = 8.56$ Hz, 2H; Ha′′), 7.891 (d, $J = 9.10$ Hz, 1H; H5), 7.723 (d, $J = 9.10$ Hz, 1H; H6), 7.694 (s, 2H; H5′′,6′′), 7.537 (d, $J = 8.03$ Hz, 2H; Hω), 7.411 (d, $J = 7.76$ Hz, 2H; Hμ), 7.349 (t, $J = 8.03$ Hz, 2H; Hb′′), 7.164 (d, $J = 9.11$ Hz, 4H; Hm′′), 7.002 (d, $J = 8.83$ Hz, 2H; Hm′), 6.961 (d, $J = 9.10$ Hz, 2H; Hm), 6.870 (d, $J = 7.50$ Hz, 2H; Hc′′), 4.391 (p, $J = 4.28$ Hz, 4H; Hδ′′), 4.244 (t, $J = 5.62$ Hz, 4H; Hα′′), 4.012 (t, $J = 5.62$ Hz, 4H; Hβ′′), 3.999 (m, 4H; Hγ′′), 3.985 (m, hidden, 4H; Hα,α′), 3.470 (t, $J = 6.16$ Hz, 4H; Hβ,β′), 3.272 (t, $J = 5.35$ Hz, 4H; Hγ,γ′), 3.238 (s, 4H; Hε,ε′), 3.214 (t, $J = 5.08$ Hz, 4H; Hδ,δ′), 2.504 (s, 3H; CH_3); FAB-MS: m/z (%): 1321.5 (42) $[M+H]^+$, 665.2 (48) [**8**+H]$^+$, 657.3 (100) [**10**+H]$^+$.

Tris(*p*-*tert*-butylphenyl)(4-hydroxypropyloxyphenyl)methane (12): Tris(*p*-*tert*-butylphenyl)(4-hydroxyphenyl)methane (**11**) (5.226 g, 10.4 mmol) was heated in butan-1-ol (100 mL) until it dissolved. A solution of KOH (1.21 g, 21.6 mmol) in H_2O (5 mL) was then added, and the reaction mixture was heated under reflux for 1 h. A solution of 2-(3-chloropropyloxy)tetrahydro-2*H*-pyran (4.17 g, 23.4 mmol) in butan-1-ol (20 mL) was then added dropwise, and the resulting mixture was refluxed for 3 days. The solvents were subsequently removed in a rotary evaporator, and the residue was

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partitioned between dichloromethane and water. The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated to dryness. The solid was redissolved in a mixture of dichloromethane (100 mL) and methanol (50 mL) and treated with concentrated HCl (2.1 mL) for 3 h at room temperature. After evaporation of the solvents, the residue was redissolved in dichloromethane, and the resulting solution was washed three times with water and dried over $MgSO_4$. Filtration and removal of the solvent left a white solid (6.394 g), which was purified by chromatography on silica (200 g), eluting with hexane/dichloromethane (30:70). Yield of pure product: 3.141 g (54%); m.p. > 260 °C; ^{1}H NMR (CD_2Cl_2, 200 MHz): $\delta = 7.27$ (d, $J = 8.7$ Hz, 6H; Hs or Ht), 7.16 (d, $J = 8.8$ Hz, 6H; Ht or Hs), 7.16 (d, $J = 8.9$ Hz, 2H; Hq), 6.79 (d, $J = 8.9$ Hz, 2H; Hr), 4.08 (t, $J = 6$ Hz, 2H; Hγ), 3.80 (q, $J = 5.7$ Hz, 2H; Hα), 2.00 (p, $J = 6.0$ Hz, 2H; Hβ), 1.68 (t, $J = 5.4$ Hz, 1H; OH), 1.31 (s, 27H; CH_3); elemental analysis calcd (%) for $C_{40}H_{50}O_2 \cdot H_2O$ (580.86): C 82.71, H 9.02; found: C 82.87, H 8.95.

Tris(*p*-*tert*-butylphenyl)[4-(4-toluenesulfonyl)propyloxyphenyl]methane (13): A solution of tosyl chloride (0.957 g, 5 mmol) in dichloromethane (40 mL) was added to a solution of **12** (2.007 g, 3.6 mmol) in dichloromethane (350 mL) at 0 °C. Triethylamine (1.2 mL, 8.6 mmol) and DMAP (0.006 g, 0.05 mmol) were subsequently added. The reaction mixture was stirred at 0 °C for 4 h and then allowed to warm to room temperature. After stirring overnight at room temperature, it was poured onto ice and neutralized with 5% aqueous HCl. The organic layer was separated, washed with water, and dried over $MgSO_4$. The crude product was purified by chromatography on silica, eluting with hexane/dichloromethane (1:1). Yield of pure product: 2.85 g (56%); m.p. 223–225 °C; ^{1}H NMR (CD_2Cl_2, 200 MHz): $\delta = 7.72$ (d, $J = 8.3$ Hz, 2H; H_{tosyl}), 7.28 (d, $J = 8.8$ Hz, 6H; Hs or Ht), 7.24 (d, $J = 8.6$ Hz, 2H; H_{tosyl}), 7.16 (d, $J = 8.8$ Hz, 6H; Ht or Hs), 7.13 (d, $J = 8.7$ Hz, 2H; Hq), 6.64 (d, $J = 9.0$ Hz, 2H; Hr), 4.20 (t, $J = 6.1$ Hz, 2H; Hγ), 3.92 (t, $J = 5.9$ Hz, 2H; Hα), 2.34 (s, 3H; CH_3), 2.08 (p, $J = 5.9$ Hz, 2H; Hβ), 1.31 (s, 27H; CH_3); elemental analysis calcd (%) for $C_{47}H_{56}O_4S$ (717.02): C 78.73, H 7.87; found: C 78.84, H 8.06.

Tris(*p*-*tert*-butylphenyl)(4-iodopropyloxyphenyl)methane (14): A solution of NaI (1.0 g, 6.7 mmol) in acetone (5 mL) was added to a hot solution of **13** (0.392 g, 0.55 mmol) in acetone (20 mL). The reaction mixture was heated under reflux for 3 h. The solvent was then evaporated, and the residue was partitioned between CH_2Cl_2 (40 mL) and H_2O (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness to leave 0.366 g of pure **14** (quantitative yield); m.p. 232–238 °C; ^{1}H NMR (CD_2Cl_2, 200 MHz): $\delta = 7.27$ (d, $J = 8.6$ Hz, 6H; Hs or Ht), 7.16 (d, $J = 8.8$ Hz, 6H; Ht or Hs), 7.16 (d, $J = 8.8$ Hz, 2H; Hq), 6.78 (d, $J = 9.0$ Hz, 2H; Hr), 4.01 (t, $J = 5.8$ Hz, 2H; Hγ), 3.38 (t, $J = 6.8$ Hz, 2H; Hα), 2.25 (p, $J = 6.3$ Hz, 2H; Hβ), 1.31 (s, 27H; CH_3); elemental analysis calcd (%) for $C_{40}H_{49}IO$ (672.73): C 71.42, H 7.34; found: C 72.31, H 7.39.

Cu^{I} prerotaxane [Cu(8)(9)]PF$_6$: Under argon, a solution of $[Cu(CH_3CN)_4]PF_6$ (0.084 g, 0.226 mmol) in CH_3CN (5 mL) was transferred to a solution of macrocycle **8** (0.150 g, 0.226 mmol) in dichloromethane (7 mL). The solution immediately turned bright orange with the simultaneous formation of a small amount of precipitate, which redissolved upon addition of DMF (2 mL). After stirring for 45 min at room temperature, a solution of diphenol **9** (0.105 g, 0.23 mmol) in DMF (3 mL) was added, which resulted in a color change to dark red. The solution was stirred overnight under argon. The solvents were then removed in vacuo to leave pure prerotaxane [Cu(**8**)(**9**)]PF_6 in quantitative yield. ^{1}H NMR (CD_2Cl_2, 200 MHz): $\delta = 8.42$ (d, $J = 8.4$ Hz, 2H; H4″,7″), 8.03 (d, $J = 8.4$ Hz, 2H; Ha″), 7.95 (s, 2H; H5″,6″), 7.80 (d, $J = 8.4$ Hz, 2H; H3″,8″), 7.60 (d, $J = 8.5$ Hz, 2H; Ho′), 7.50 (s, 1H; H3), 7.46 (d, $J = 7.9$ Hz, 4H; Hμ,b″), 7.42 (d, $J = 8.3$ Hz, 2H; Hω), 7.33 (d, $J > 6.5$ Hz, 1H; H8), 7.32 (d, $J = 8.6$ Hz, 4H; Ho″), 7.26 (d, $J = 9.1$ Hz, 1H; H7), 7.16 (d, $J = 8.5$ Hz, 1H; H5), 7.01 (d, $J = 7.7$ Hz, 2H; Ho), 6.94 (d, $J = 8.5$ Hz, 2H; Hc″), 6.40 (d, $J = 9.1$ Hz, 1H; H6), 6.23 (d, $J = 8.5$ Hz, 2H; Hm′), 5.94 (d, $J = 8.7$ Hz, 4H; Hm″), 5.78 (d, $J = 8.4$ Hz, 2H; Hm), 4.48 (m, $J = 4.1$ Hz, 4H; Hδ″), 4.05 (t, $J = 3.8$ Hz, 4H; Hγ″), 3.80 (t, $J = 4.5$ Hz, 4H; Hβ″), 3.56 (t, $J = 4.5$ Hz, 4H; Hα″), 2.59 (s, 3H; CH_3).

Cu^{I} [2]rotaxane [Cu(6)]PF$_6$: Portions of a suspension of Cs_2CO_3 (0.264 g, 0.81 mmol) in DMF (10 mL) and a solution of compound **14** (0.387 g, 0.575 mmol) in DMF (20 mL) were alternately added over a period of 1 h to a solution of prerotaxane [Cu(**8**)(**9**)]PF_6 (0.21 mmol) in DMF (10 mL) at 60 °C under argon. The reaction mixture was then stirred at 60 °C for a further 20 h, after which the solvent was evaporated in vacuo. The solid residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was washed with H_2O and concentrated to a volume of 30 mL. It was then stirred overnight with a solution of KPF_6 (0.430 g, 2.37 mmol) in H_2O (10 mL). The organic layer was separated, washed twice with H_2O, and concentrated to dryness. The residue (0.626 g) was purified by chromatography on SiO_2 (40 g). Gradient elution with hexane/CH_2Cl_2, 20:80, to CH_2Cl_2/0.25% CH_3OH afforded pure compound **15** (0.112 g). Elution from CH_2Cl_2/0.25% CH_3OH to 0.5% CH_3OH afforded impure Cu^{I} [2]rotaxane [Cu(**6**)]PF_6. Finally, elution with CH_2Cl_2/0.5% CH_3OH yielded pure macrocycle **8** (0.006 g). The fractions containing the desired rotaxane complex were combined and freed of **8** (0.039 g) by column chromatography on alumina. Elution with hexane/CH_2Cl_2, 55:45, afforded a total of 0.289 g (57% yield) of pure Cu^{I} [2]rotaxane [Cu(**6**)]PF_6; m.p. 224–225 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 8.180$ (d, $J = 8.44$ Hz, 2H; H4″,7″), 8.030 (d, $J = 8.81$ Hz, 2H; Ha″), 7.712 (s, 2H; H5″,6″), 7.688 (d, $J = 8.43$ Hz, 2H; H3″,8″), 7.632 (d, $J = 8.81$ Hz, 2H; Ho′), 7.527 (s, 1H; H3), 7.517 (d, $J = 8.07$ Hz, 2H; Hμ), 7.483 (t, $J = 8.07$ Hz, 2H; Hb″), 7.422 (d, $J = 8.07$ Hz, 2H; Hω), 7.376 (d, $J = 8.43$ Hz, 1H; H8), 7.294 (d, $J = 8.44$ Hz, 4H; Ho″), 7.246 (d, $J = 9.17$ Hz, 2H; Hq), 7.244 (d, hidden, 1H; H5), 7.234 (d, $J = 8.81$ Hz, 6H; Ht′), 7.231 (d, $J = 8.81$ Hz, 6H; Ht), 7.230 (d, hidden, 1H; H7), 7.209 (d, $J = 9.17$ Hz, 2H; Hq′), 7.166 (d, $J = 8.80$ Hz, 6H; Hs′), 7.146 (d, $J = 8.80$ Hz, 6H; Hs), 7.040 (d, $J = 8.81$ Hz, 2H; Ho), 7.013 (d, $J = 7.71$ Hz, 2H; Hc″), 6.893 (d, $J = 9.17$ Hz, 2H; Hr), 6.824 (d, $J = 9.17$ Hz, 2H; Hr′), 6.402 (d, $J = 9.54$ Hz, 1H; H6), 6.239 (d, $J = 8.80$ Hz, 2H; Hm′), 5.932 (d, $J = 8.80$ Hz, 4H; Hm″), 5.823 (d, $J = 8.81$ Hz, 2H; Hm), 4.478 (m, 4H; Hδ″), 4.107 (t, $J = 5.69$ Hz, 4H; Hγ,γ′), 4.053 (m, $J = 5.27$ Hz, 4H; Hγ″), 3.847 (t, $J = 5.87$ Hz, 2H; Hα′), 3.793 (t, $J = 4.77$ Hz, 4H; Hβ″), 3.683 (t, $J = 5.87$ Hz, 2H; Hα), 3.537 (t, $J = 4.77$ Hz, 4H; Hα″), 2.601 (s, 3H; CH_3), 2.110 (m, $J = 5.87$ Hz, 4H; Hβ,β′), 1.273 (s, 27H; CH_3), 1.263 (s, 27H; CH_3); FAB-MS: *m*/*z* (%): 2272.2 (100) $[M - PF_6]^+$, 1606.9 (31) [**15**+Cu]$^+$, 727.2 (70) [**8**+Cu]$^+$; elemental analysis calcd (%) for $C_{153}H_{154}CuF_6N_4O_{10}P$ (2417.43): C 76.02, H 6.42, N 2.32; found: C 76.95, H 6.63, N 2.30.

[2]Rotaxane 6: Cu^{I} [2]rotaxane [Cu(**6**)]PF_6 (0.064 g, 0.0264 mmol) was dissolved in CH_3CN (9 mL), and a solution of KCN (0.047 g, 0.72 mmol) in H_2O was added in four portions over a period of 6 h. A white precipitate of free [2]rotaxane **6** gradually appeared. After complete bleaching, the reaction mixture was diluted with CH_2Cl_2 to dissolve the precipitate and washed three times with H_2O. The organic layer was separated and concentrated to dryness, and the residue was purified by chromatography on alumina (hexane/CH_2Cl_2, 75:25, to pure CH_2Cl_2) to afford 0.0541 g of pure [2]rotaxane **6** (yield: 92%). ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 8.404$ (d, $J = 8.86$ Hz, 2H; Ho), 8.294 (d, $J = 8.86$ Hz, 4H; Ho″), 8.145 (d, $J = 8.44$ Hz, 2H; H4″,7″), 8.107 (d, $J = 8.54$ Hz, 1H; H7), 8.009 (d, $J = 9.92$ Hz, 2H; Ho′), 7.997 (s, 1H; H3), 7.946 (d, $J = 8.44$ Hz, 2H; H3″,8″), 7.946 (d, $J = 8.44$ Hz, 2H; Hc″), 7.835 (d, $J = 9.02$ Hz, 1H; H5), 7.716 (d, $J = 8.50$ Hz, 1H; H8), 7.659 (s, 2H; H5″,6″), 7.659 (d, $J = 8.71$ Hz, 1H; H6), 7.508 (d, $J = 8.04$ Hz, 2H; Hω), 7.404 (d, $J = 7.84$ Hz, 2H; Hμ), 7.338 (t, $J = 8.02$ Hz, 2H; Hb″), 7.255 (d, $J = 8.70$ Hz, 6H; Ht′), 7.203 (d, $J = 8.63$ Hz, 6H; Hs or Ht), 7.156 (d, $J = 8.71$ Hz, 6H; Ht or Hs), 7.144 (d, $J = 8.96$ Hz, 2H; Hq), 7.047 (d, $J = 8.62$ Hz, 6H; Hs′), 7.038 (d, $J = 8.92$ Hz, 2H; Hm), 6.861 (d, $J = 7.67$ Hz, 2H; Ha″), 6.788 (d, $J = 8.87$ Hz, 4H; Hm″), 6.796 (d, $J = 8.91$ Hz, 2H; Hq′), 6.784 (d, $J = 8.91$ Hz, 2H; Hr), 6.726 (d, $J = 8.86$ Hz, 2H; Hm′), 6.338 (d, $J = 8.95$ Hz, 2H; Hr′), 4.163 (t, $J = 6.86$ Hz, 2H; Hα), 4.390 (sx, $J = 4.99$ Hz, 4H; Hδ″), 4.129 (t, $J = 6.17$ Hz, 2H; Hγ), 3.926 (br s, 4H; Hγ″), 3.853 (m, 4H; Hα″), 3.791 (p, $J = 5.59$ Hz, 4H; Hβ″), 3.583 (t, $J = 6.10$ Hz, 2H; Hα′), 3.380 (t, $J = 6.13$ Hz, 2H; Hγ′), 2.499 (s, 3H; CH_3), 2.243 (p, $J = 6.05$ Hz, 2H; Hβ), 1.714 (p, $J = 6.09$ Hz, 2H; Hβ′), 1.287 (s, 27H; CH_3), 1.286 (s, 27H; CH_3) ; FAB-MS: *m*/*z* (%): 2209.2 (81) $[M+H]^+$, 1544.9 (65) [**15**+H]$^+$, 665.2 (100) [**8**+H]$^+$; elemental analysis calcd (%) for $C_{153}H_{154}N_4O_{10}$ (2208.92): C 83.19, H 7.03, N 2.54; found: C 82.97, H 7.19, N 2.56.

Compound 15: See preparation of [Cu(**6**)]PF_6. M.p. 178–191 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) $\delta = 8.436$ (d, $J = 8.80$ Hz, 2H; Ho), 8.430 (d, $J = 9.17$ Hz, 2H; Ho′), 8.270 (d, $J = 8.44$ Hz, 1H; H7), 8.107 (d, $J = 8.44$ Hz, 1H; H8), 8.020 (s, 1H; H3), 7.862 (d, $J = 9.17$ Hz, 1H; H5), 7.698 (d, $J = 9.17$ Hz, 1H; H6), 7.511 (d, $J = 8.07$ Hz, 2H; Hω), 7.407 (d, $J = 7.70$ Hz, 2H; Hμ), 7.262 (d, $J = 8.44$ Hz, 6H; Ht or Ht′), 7.258 (d, $J = 8.80$ Hz, 6H; Ht′ or Ht), 7.163 (d, $J = 8.81$ Hz, 2H; Hq or Hq′), 7.163 (d, $J = 8.81$ Hz, 6H; Hs or Hs′), 7.159 (d, $J = 8.80$ Hz, 2H; Hq′ or Hq), 7.159 (d, $J = 8.80$ Hz, 6H; Hs′ or Hs), 7.150 (d, $J = 8.80$ Hz, 2H; Hm′), 7.137 (d, $J = 9.17$ Hz, 2H; Hm), 6.831 (d, $J = 8.81$ Hz, 2H; Hr or Hr′), 6.825 (d, $J = 8.81$ Hz, 2H; Hr′ or Hr), 4.295 (t, $J = 5.31$ Hz, 2H; Hα or Hα′), 4.281 (t, $J = 5.14$ Hz, 2H; Hα′ or Hα), 4.200

(t, $J = 6.05$ Hz, 2H; Hγ or Hγ'), 4.193 (t, $J = 6.05$ Hz, 2H; Hγ' or Hγ), 2.50 (s, 3H; CH_3), 2.317 (t, $J = 6.05$ Hz, 2H; Hβ or Hβ'), 2.309 (t, $J = 6.05$ Hz, 2H; Hβ' or Hβ), 1.296 (s, 27H; CH_3), 1.292 (s, 27H; CH_3); FAB-MS: *m*/*z* (%): 1544.9 (67) $[M+H]^+$; elemental analysis calcd (%) for $C_{111}H_{118}N_2O_4 \cdot H_2O$ (1562.18): C 85.34, H 7.74, N 1.79; found: C 85.66, H 7.99, N 1.81.

X-ray crystallography: Suitable single crystals of [Cu(**6**)]PF_6 were obtained by the slow diffusion method at room temperature: 6 mm test tube; lower layer: 11 mg of the compound in 0.4 mL CH_2Cl_2/0.3 mL benzene; intermediate layer: 1 mL of benzene/ethanol: 50/50; upper layer: 2.5 mL ethanol. A systematic search in reciprocal space with a Nonius Kappa CCD diffractometer showed that crystals of [Cu(**6**)]PF_6 belonged to the monoclinic system. Quantitative data were obtained at $-100\,^{\circ}C$. All experimental parameters used are given in Table 1. The resulting data set was transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package[20] was used. The structure was solved by direct methods. After refinement of the heavy atom positions, a difference Fourier map revealed residual electronic density maxima close to the expected positions of the hydrogen atoms. These were introduced as fixed contributors in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as $U(H) = 1.3\ U_{eq}(C)$ Å,[21] but were not refined. Full-matrix least-squares refinements were made against $|F|$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients are from ref. [21]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158093. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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