Synthesis, Characterization, and a Proton NMR Study of Topologically Chiral Copper(I) [2]-Catenates and Achiral Analogues

Jean-Claude Chambron,* Dennis K. Mitchell,† and Jean-Pierre Sauvage*

Contribution from the Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS, Université Louis Pasteur, Faculté de Chimie, 1, rue Blaise Pascal, 67000 Strasbourg, France.
Received August 9, 1991

Abstract: Cu(I) catenates and the corresponding metal-free catenands in which one or both constitutive rings are oriented have been synthesized and characterized. Ring orientation is achieved by an appropriate substitution on the phenanthroline core of the macrocycle. Cu(I) catenates which contain two oriented rings are topologically chiral. Their chirality has been observed by ^{1}H-NMR spectroscopy in an optically active medium. Indeed, a splitting of the signals of the aromatic protons, which are enantiotopic by *external* comparison, is observed. In the case of the achiral Cu(I) catenate with only one oriented ring, the signals of the aromatic protons of the nonoriented macrocycle (enantiotopic by *internal* comparison) are also split. Those of the oriented macrocycle are equivalent by external comparison and thus do not show any splitting. In the field of topological chirality, this study illustrates the fact that only a careful analysis of the topicity of the protons allows the possibility of distinguishing chiral molecules from achiral ones by ^{1}H-NMR in an optically active medium.

Introduction

Topologically chiral molecules are those chiral molecules whose enantiomers cannot be conceptually converted into one another by continuous deformation in three-dimensional space.[1] Continuous deformation means that bond breaking and reforming are not allowed in this process. As a result, no molecular rigidity at all is required for topological enantiomers to remain distinct. This is not the case for the so-called Euclidean enantiomers: for example, the chiral tetrasubstituted carbon center could be racemized by deformation of the tetrahedron into its mirror image via a square-planar intermediate. Of course, the two mirror images of the asymmetric carbon and the hypothetical square-planar intermediate are topologically indistinguishable; but the latter is too high in energy for the chemical process to take place. It has been conjectured that topological chirality may be achieved only by chiral molecules having a nonplanar graph, either intrinsically (Kuratowski's K_5 or $K_{3,3}$ graphs) or extrinsically (oriented links, chiral links, and chiral knotted rings).[1] The first examples of topologically chiral molecules having intrinsically nonplanar K_5 and $K_{3,3}$ molecular graphs are shown in Figure 1. They are the centered polyquinane derivative (Figure 1a), independently synthesized by Simmons and Maggio[2] and Paquette and Vazeux,[3] and the so-called three-rung Möbius ladder (Figure 1b), synthesized by Walba and co-workers.[4] The topological nature of the chirality of these molecules has been demonstrated by mathematical methods,[5] and their chemical chirality has been tested by NMR spectroscopy in optically active media. The most fascinating example of topologically chiral molecules having an extrinsically nonplanar graph is the molecular trefoil knot recently synthesized in this laboratory[6] (Figure 1c). Unlike all the other known topologically chiral molecules, the molecular trefoil knot does not require any condition (such as bonds of different order or ring orientation, see below) to be chiral. Molecular links, or catenanes, can also be unconditionally topologically chiral. This is the case for the chiral link whose presentation has a minimum number of four crossings (Figure 2a). At present, the corresponding molecule is still highly speculative.[7]

Conditionally topologically chiral links are oriented linked rings (Figure 2b).[8] As discussed years ago,[7,8] they are prototypical topologically chiral objects and the simplest ones, since their presentation in the plane has a minimum number of two crossings only. The first synthesis of an *isolated* topologically chiral catenane, containing two interlocked directed rings, was recently performed in this laboratory (Figure 2b).[9] Orientation of the individual rings was achieved by anchoring a phenyl group in position 4 of the phenanthroline nucleus. Such a use of oriented macrocycles in the design of chiral molecules has been reported for systems showing Euclidean chirality.[10] The chemical chirality of the latter catenane was tested experimentally using its Cu(I) catenate complex, by proton NMR spectroscopy in the presence of Pirkle's reagent, (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol,[11] as the optically active medium. In this paper, we present the synthesis and a detailed proton NMR study of chiral catenates and achiral analogues in optically active media, as an illustration of the scope and limitations of this method for probing chirality.

Results and Discussion

1. Synthesis of Topologically Chiral [2]-Catenands and Achiral Analogues. The [2]-catenates synthesized for this study are represented in Figure 3. ([2] means that the number of interlocking rings is 2.) The constitutive rings are phenanthroline-containing macrocycles either unsubstituted or substituted with aryl groups in position 4 of the phenanthroline nucleus. Thus, catenates $[\mathbf{2}Cu]^+$ and $[\mathbf{4}Cu]^+$ are symmetrically substituted with phenyl and *p*-tolyl groups, respectively, whereas catenate $[\mathbf{3}Cu]^+$ is substituted with one *p*-tolyl group. Copper(I) [2]-catenates have

* Author to whom correspondence should be addressed.
† On sabbatical leave from Los Angeles City College, 855 North Vermont Avenue, Los Angeles, CA 90029.

(1) Walba, D. M. *Tetrahedron* **1985**, *41*, 3161–3212. The intrinsic topology of a molecule is described by its molecular graph or its bond connectivity. The extrinsic topology appears when its graph is embedded in 3-D space and is endowed with complete flexibility.
(2) Simmons, H. E., III; Maggio, J. E. *Tetrahedron Lett.* **1981**, *22*, 287–290.
(3) Paquette, L. A.; Vazeux, M. *Tetrahedron Lett.* **1981**, *22*, 291–294.
(4) Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 3219–3221.
(5) Simons, J. *Topology* **1986**, *25*, 229–235.
(6) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 189–192.
(7) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789–3795.
(8) Schill, G. In *Catenanes, Rotaxanes and Knots*; Academic Press: New York, 1971; p 11. The orientation of a macrocycle is provided, for example, by a chosen sequence of substituents at the periphery of the macrocycle. The order of the sequence will determine the sense of the arrow on a very schematic representation like that in Figure 2. In this particular case, the arrow goes from the small substituent (H) to the large one (aryl) through the 1,10-phenanthroline nucleus.
(9) Mitchell, D. K.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 930–931.
(10) Kubo, H.; Aida, T.; Inoue, S.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1015–1017.
(11) Pirkle, W. H.; Sikkenga, D. L.; Pavlin, M. S. *J. Org. Chem.* **1977**, *42*, 384–387.

0002-7863/92/1514-4625$03.00/0

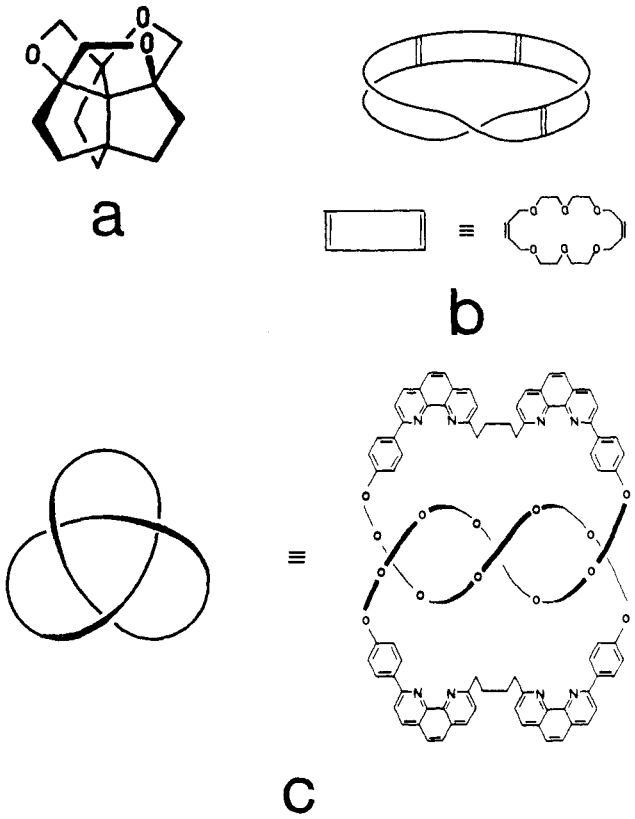


Figure 1. Examples of topologically chiral molecules.

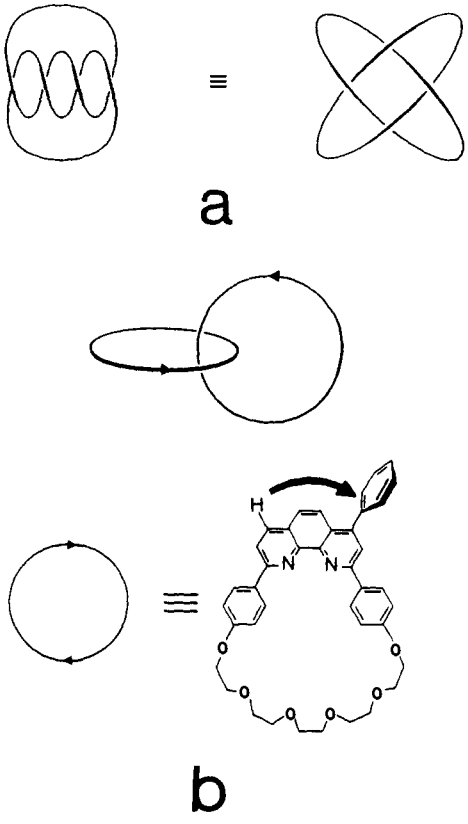
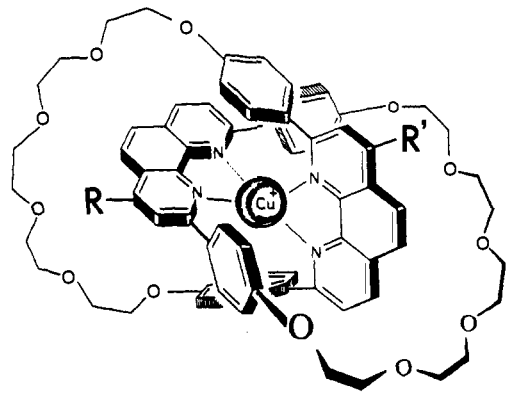


Figure 2. Examples of topologically chiral catenanes.

been synthesized using a three-dimensional template synthesis, which has been extensively discussed previously.[12-16] The two



R = R′ = H : [1Cu]$^+$
R = R′ = Ph : [2Cu]$^+$
R = H, R′ = PhCH$_3$: [3Cu]$^+$
R = R′ = PhCH$_3$: [4Cu]$^+$

Figure 3. Structure and nomenclature of the catenates synthesized. The corresponding catenands (metal-free) are not represented.

strategies shown in Figure 4 have been used; strategy A is a one-pot double-cyclization reaction, whereas strategy B requires the preliminary synthesis of a coordinating macrocycle. Fortunately, the latter involves only four reacting centers in the final cyclization reaction. Another advantage of strategy B is that it allows preparation of catenates containing two differently substituted interlocking macrocycles.[14,17] This is of particular usefulness for the present study. The precursors are represented in Figure 5. The 4-aryl-1,10-phenanthrolines **9** and **13** are the key compounds, since they determine the orientation of the individual rings of the catenanes. 4-Phenyl-1,10-phenanthroline (**9**) was prepared first by Case.[18] 4-(*p*-Tolyl)-1,10-phenanthroline (**13**) was prepared by the same method. Introduction of the anisyl groups in positions 2 and 9 of the phenanthrolines **9** and **13** was performed as described previously for **6**, that is, reaction at room temperature with *p*-lithioanisole followed by hydrolysis and rearomatization with manganese dioxide.[14,19] Cleavage of the methyl ether groups proceeded as described for **7**,[14] and the 2,9-bis(4-hydroxyphenyl)-1,10-phenanthrolines **11** and **15** were obtained quantitatively as red-orange solids when dry.

The synthesis of catenates [**2**Cu]$^+$ and [**4**Cu]$^+$ was performed using strategy A, i.e., the one-pot synthesis. Accordingly, the respective precursor copper complexes [(**11**)$_2$Cu]$^+$ and [(**15**)$_2$Cu]$^+$ were generated and reacted under high-dilution conditions with 1,14-diiodo-3,6,9,10-tetraoxatetradecane (diiodo derivative of pentaethyleneglycol) in DMF at 65 °C in the presence of cesium carbonate as a base.[14] The yields were respectively 12% and 15%, which is much lower than the yield obtained for [**1**Cu]$^+$ under the same conditions (e.g., 27%).[14] Possibly, the presence of a bulky aryl group in the "back" of the phenanthroline nucleus hampers the approach of 1,14-diiodo-3,6,9,10-tetraoxatetradecane. Catenate [**3**Cu]$^+$ was prepared using strategy B. Among the two possible precatenates, the one containing the unsubstituted macrocycle **8** (i.e., [(**8**,**15**)Cu]$^+$) was used in order to minimize steric hindrance in the ultimate macrocyclization reaction. Thus, the macrocycle **8** was prepared as previously described,[14] and the

(12) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P. *Tetrahedron Lett.* **1983**, *24*, 5095–5098.
(13) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1984**, *106*, 3043–3045.
(14) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Tetrahedron* **1990**, *46*, 503–512.
(15) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795–810.
(16) Sauvage, J.-P. *Acc. Chem. Res.* **1990**, *23*, 319–327.
(17) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Weiss, J. *Tetrahedron Lett.* **1986**, *27*, 2257–2260.
(18) Case, F. H. *J. Org. Chem.* **1951**, *16*, 1541–1545.
(19) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P. *Tetrahedron Lett.* **1982**, *23*, 5291–5294.

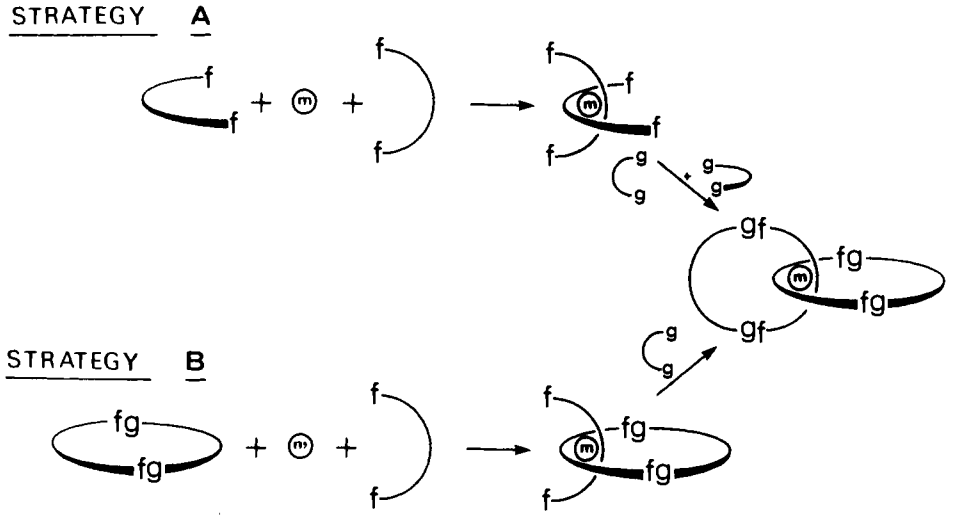
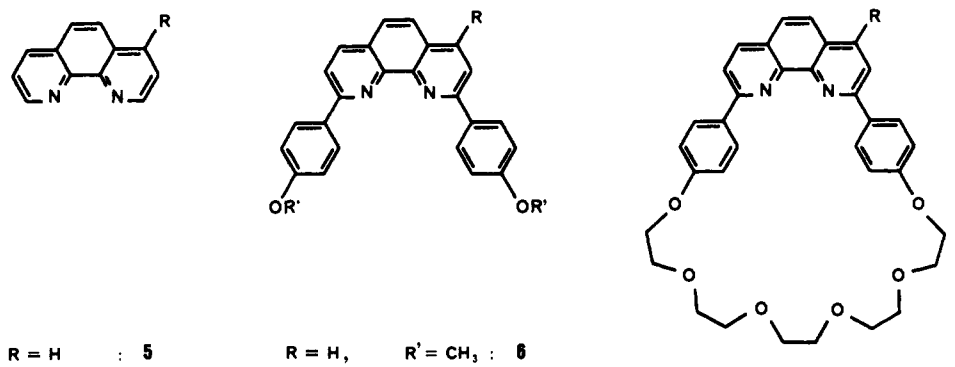


Figure 4. Synthetic strategies for the synthesis of [2]-catenates based on a three-dimensional template effect induced by a transition metal. Functions f and g react to form the links. The molecular fragments f–f interact with a transition metal (m) bearing or not bearing auxiliary ligands. This metal disposes fragments f–f (linear or already included in a macrocycle) perpendicular to one amother.



R = H : **5**

R = H, R' = CH_3 : **6**

R = H, R' = H : **7**

R = H : **8**

R = Ph : **9**

R = Ph, R' = CH_3 : **10**

R = Ph, R' = H : **11**

[R = Ph : **12**]

R = $PhCH_3$: **13**

R = $PhCH_3$, R' = CH_3 : **14**

R = $PhCH_3$, R' = H : **15**

R = $PhCH_3$: **16**

Figure 5. Structural formulas of the precursors to the catenates synthesized (macrocycle **12** in brackets has not been prepared).

precatenate species [(**8**,**15**)Cu]$^+$ was generated and subsequently reacted under high-dilution conditions with 1,14-diiodo-3,6,9,10-tetraoxatetradecane, as above. The desired compound [**3**Cu]$^+$ was contaminated with catenate [**4**Cu]$^+$ (ca. 2%) which had formed during the reaction. The formation of the latter is due to the relative instability of precatenate [(**8**,**15**)Cu]$^+$ under the reaction conditions, which may equilibrate to [(**15**)$_2$Cu]$^+$ and uncomplexed **8**. Removal of [**4**Cu]$^+$ from [**3**Cu]$^+$ proved to be extremely difficult (the two compounds are not separated on TLC silica plates) but could be achieved by repeated (up to 20 times) medium-pressure liquid chromatography of the reaction mixture which had been previously purified by gravity liquid chromatography. The yield of [**3**Cu]$^+$ obtained in the last step was 19%. Large amounts (ca. 50%) of the macrocyclic precursor **8** were recovered. Catenands **2**, **3**, and **4** were quantitatively obtained by treatment of acetonitrile solutions of the corresponding copper(I) catenates [**2**Cu]$^+$, [**3**Cu]$^+$, and [**4**Cu]$^+$ with excess aqueous KCN, as described previously for catenand **1**.[13,14]

2. Characterization of the New Compounds. Catenates [**2**Cu]$^+$, [**3**Cu]$^+$, and [**4**Cu]$^+$ and the corresponding catenands **2**, **3**, and **4** were characterized by elemental analysis, ^{1}H- and ^{13}C-NMR spectroscopies, and FAB-mass spectrometry. As an example, the positive FAB mass spectrum of [**3**Cu]$^+$ is reproduced in Figure 6. It shows a pattern that had been observed already for catenand **1**, but by chemical ionization.[13] The spectrum shows the molecular peak ([**3**Cu]$^+$), and the next lower peaks are those of each constitutive macrocycle *complexed by a copper(I) ion* (i.e., [**16**Cu]$^+$ and [**8**Cu]$^+$ respectively). This characteristic feature (the fact that practically no ion is detected in between the molecular peak and the peak corresponding to an individual macrocycle) has been recognized by Schill et al. as a fingerprint of catenanes.[20]

The catenates [**2**Cu]$^+$ and [**4**Cu]$^+$ are the first members of this family of molecules to be devoid of any symmetry plane. Thus, their ^{1}H-NMR spectra are much more complicated than that of [**1**Cu]$^+$. In the case of [**4**Cu]$^+$, for example, signals due to protons ortho (H_o and $H_{o'}$) and meta (H_m and $H_{m'}$) to the phenyl substituents in positions 2 and 9 of the phenanthroline split, since these positions are no longer exchanged by a symmetry element (Figure 7). Protons 5 and 6, which are equivalent in [**1**Cu]$^+$, show a nice AB pattern in [**4**Cu]$^+$. ^{1}H-NMR spectra of [**2**Cu]$^+$ and [**4**Cu]$^+$ were assigned using data from NOESY experiments and from data previously obtained for [**1**Cu]$^+$.[21] The NOESY connectivity map of [**4**Cu]$^+$ is shown in Figure 8. The full sequence $H_{m'} \rightarrow H_{o'} \rightarrow H_8 \rightarrow H_7 \rightarrow H_6 \rightarrow H_5 \rightarrow H_{o''} \rightarrow H_3 \rightarrow H_o \rightarrow H_m$ can be easily followed. Not shown in the figure is the branched sequence $H_{o'} \rightarrow H_{m''} \rightarrow$ methyl H. The spectrum of [**3**Cu]$^+$ is nearly a superposition of those of [**1**Cu]$^+$ and [**4**Cu]$^+$.

(20) Vetter, W.; Logemann, E.; Schill, G. *Org. Mass Spectrom.* **1977**, *12*, 351–369 and references cited therein.

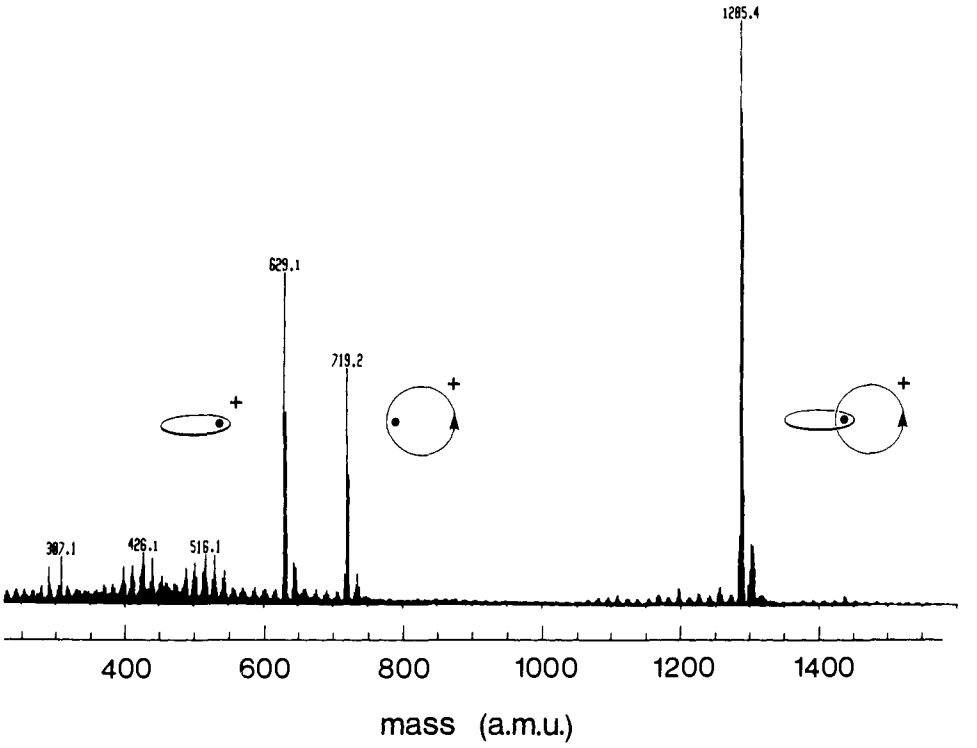


Figure 6. Positive FAB mass spectrum of $[4Cu]^+BF_4^-$ in *p*-nitrobenzyl alcohol matrix.

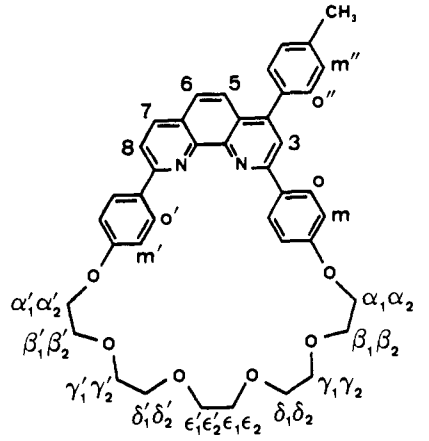


Figure 7. Atomic numbering scheme of macrocycle **16** and related molecules.

The spectra of the catenates $[2Cu]^+$, $[3Cu]^+$, and $[4Cu]^+$ show several features that had been recognized previously for $[1Cu]^+$ and its noninterlocked precursor, namely, $[(6)_2Cu]^+$.[21,22] In particular, the shielding of the ortho and meta protons of a macrocycle was attributed to the strong ring current effect of the phenanthroline nucleus of the other interlocking macrocycle. This feature is a NMR fingerprint of the entwining of two diphenylphenanthroline units around a metal center.

The $^{13}C\{^1H\}$-NMR spectra were recorded for catenates $[3Cu]^+$ and $[4Cu]^+$. In the case of the latter, a $^1H-^{13}C$ correlation was performed. This experiment, with the additional help of previous data on $[1Cu]^+$,[21] allowed unambiguous attribution of most of the peaks of the spectra of $[3Cu]^+$ and $[4Cu]^+$. Several features of the ^{13}C spectra will be discussed in detail in the next section.

3. Study of the Chirality of [2]-Catenates by NMR Methods. In this section, we present a detailed comparison of catenates $[1Cu]^+$, $[3Cu]^+$, and $[4Cu]^+$, using the concepts of topicity introduced and developed by Mislow.[23,24] The study of $[2Cu]^+$ has been reported earlier.[9] All three catenates are represented schematically in Figure 9. In the case of $[1Cu]^+$ and $[4Cu]^+$, the two interlocked macrocycles (respectively **8** and **16**) are

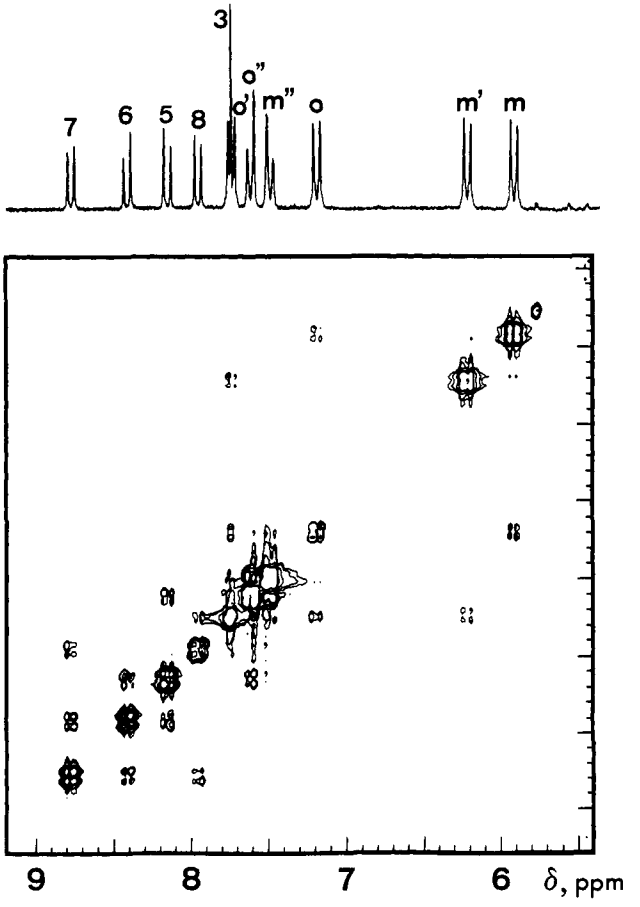


Figure 8. NOESY connectivity map of $[4Cu]^+$.

(21) Edel. A. PhD Thesis, Université Louis Pasteur, Strasbourg. 1987.
(22) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P.; Kintzinger. J.-P.; Maltêse, P. *New J. Chem.* **1984**, *8*, 573–582.
(23) Mislow. K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1–37.
(24) Eliel, E. L. *Top. Curr. Chem.* **1982**, *105*, 1–76.

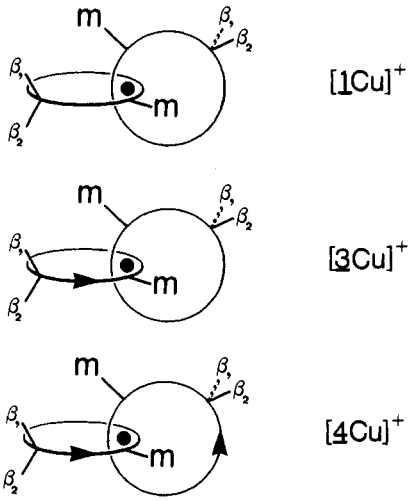


Figure 9. Schematic representation of catenates $[1Cu]^+$, $[3Cu]^+$, and $[4Cu]^+$ showing atoms whose topicity is discussed in the text.

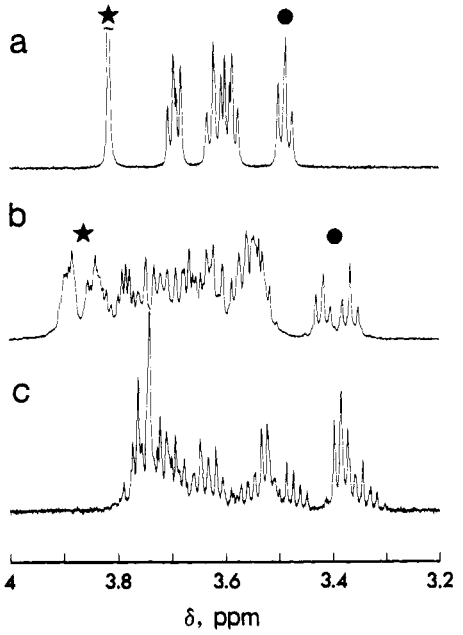


Figure 10. ^{1}H-NMR spectra (400-MHz) of (a) $[1Cu]^+$, (b) $[3Cu]^+$, and (c) $[4Cu]^+$ in the region of the protons belonging to the polyoxyethylenic chains. The black dots show the signals of β-protons, and the stars show the signals of ϵ-protons.

equivalent (i.e., they are related by a C_2 symmetry axis). In the case of $[3Cu]^+$, they are different. Catenates $[1Cu]^+$ and $[3Cu]^+$ are achiral, since they contain at least one plane of symmetry. But unlike $[1Cu]^+$, $[3Cu]^+$ does not contain any C_2 symmetry axis. Catenate $[4Cu]^+$ is chiral: its only symmetry element is a C_2 axis. The symmetry properties of these catenates are nicely illustrated by an analysis of the ^{13}C-NMR lines of the β-carbon atoms of the polyoxyethylenic chains (see Figure 7 for atomic numbering). In the case of $[1Cu]^+$, C_β and $C_{\beta'}$ are equivalent or homotopic and show a single line. But in the case of $[4Cu]^+$, C_β and $C_{\beta'}$ are different or heterotopic. As a result, two lines are observed. Finally, in the case of $[3Cu]^+$, three lines are observed: two corresponding to heterotopic C_β and $C_{\beta'}$ belonging to the substituted macrocycle as noted for $[4Cu]^+$, and one corresponding to enantiotopic C_β and $C_{\beta'}$ belonging to the unsubstituted macrocycle.

Figure 10 shows the 400-MHz ^{1}H-NMR spectra of $[1Cu]^+$, $[3Cu]^+$, and $[4Cu]^+$ in the region of the protons belonging to the polyoxyethylenic chains. The spectra of $[3Cu]^+$ and $[4Cu]^+$ are much more complicated than that of $[1Cu]^+$. As in the case of the ^{13}C-NMR spectra, this can be understood after an analysis of the topic relationships of the atoms of these chains has been

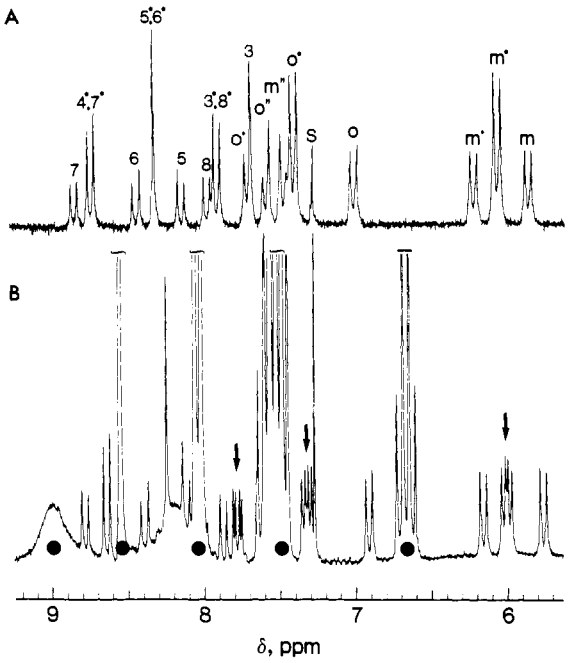


Figure 11. (a) ^{1}H-NMR spectrum (200-MHz) of $[4Cu]^+$ (aromatic region) in $CDCl_3/D_2O$ + sodium dithionite. The stars mark the peaks of the unsubstituted macrocycle. (b) Same as part a + a 12-fold excess of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol. The arrows show the peaks which are split; the black dots mark the signals of the optically active reagent.

done. Let us take the β-protons as a typical example. They can be separated into two groups which show the same relationships as those shown by the β-carbon atoms bearing them. Now, we consider the protons within a methylene group. In the case of $[1Cu]^+$, $H_{\beta 1}$ and $H_{\beta 2}$ are related by a symmetry plane and are thus enantiotopic. Since they are coupled to α-protons, they should generate the AA′ part of an AA′XX′ spin system.[21] Actually, this is an A_2X_2 system, since a triplet is observed (Figure 10a). This shows that there are rapid conformational equilibria exchanging $H_{\alpha 1}$ and $H_{\alpha 2}$ sites on the one hand and $H_{\beta 1}$ and $H_{\beta 2}$ sites on the other hand on the NMR time scale. In addition, there is only one triplet, since the two systems $(H_{\beta 1},H_{\beta 2})$ and $(H_{\beta' 1},H_{\beta' 2})$ are equivalent.[25] In the case of $[4Cu]^+$, $H_{\beta 1}$ and $H_{\beta 2}$ are now diastereotopic. Thus they give rise to the AB half of an ABXY spin system. A second one arises from the system $(H_{\beta' 1},H_{\beta' 2})$ which is different from $(H_{\beta 1},H_{\beta 2})$. In this case, the analysis accounts only *qualitatively* for the complexity of the spectrum observed (Figure 10c). The case of $[3Cu]^+$ is even more complex, since this catenate contains two different macrocycles. $H_{\beta 1}$ and $H_{\beta 2}$ belonging to the unsubstituted macrocycle are diastereotopic, and we are brought back to the case of $[4Cu]^+$. But only one ABXY system is expected, since the two groups $(H_{\beta 1},H_{\beta 2})$ and $(H_{\beta' 1},H_{\beta' 2})$ are enantiotopic in the unsubstituted macrocycle. $H_{\beta 1}$ and $H_{\beta 2}$ as well as $H_{\beta' 1}$ and $H_{\beta' 2}$ belonging to the oriented macrocycle are enantiotopic, since this macrocycle lies in the symmetry plane of the molecule. Thus, according to the analysis detailed for $[1Cu]^+$, two triplets are expected: one for the system $(H_{\beta 1},H_{\beta 2})$ and the other for the system $(H_{\beta' 1},H_{\beta' 2})$. This is what is actually observed (Figure 10b). A similar discussion could be set forth for protons H_ϵ. It would account for the singlet observed in the case of $[1Cu]^+$ and the symmetrical pattern observed in the same frequency domain for $[3Cu]^+$.

Whereas diastereotopic atoms can be evidenced and distinguished (in principle!) in an achiral environment, enantiotopic atoms can be distinguished only in a chiral medium. This is the reason why the ^{1}H-NMR spectra of the three catenates $[1Cu]^+$, $[3Cu]^+$, and $[4Cu]^+$ were also recorded in a chiral environment,

(25) Notice that in macrocycle **16** and catenands **2** and **4** the triplets of heterotopic protons α and α' on the one hand and β and β' on the other hand are degenerate (see Experimental Section).

using Pirkle's reagent (S)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol. Only the changes in the region of the aromatic protons were investigated. In the case of $[1Cu]^+$, no splitting at all was observed. In the case of $[3Cu]^+$ (Figure 11), *only the signals of the aromatic protons belonging to the unsubstituted macrocycle were split*, and in the case of $[4Cu]^+$, most of the peaks were split as previously observed for $[2Cu]^+$,[9] i.e., those of H_7, H_8, H_o, $H_{o'}$, H_m, and $H_{m'}$. Splitting of H_3 was unclear, but signals of H_5 and H_6 were not split, and those of $H_{o''}$ and $H_{m''}$ were hindered by the peaks of Pirkle's reagent. To rationalize these results, let us consider one of the two sets of meta protons (H_m for example; see Figures 9 and 7). In the case of $[1Cu]^+$, meta protons belong to two equivalent sets since H_m and $H_{m'}$ are related by an axis of symmetry. Their equivalence results from both internal and external (i.e., when a pair of molecules is considered) comparison. Thus a chiral medium has no effect on the chemical shifts of these protons, as it is actually observed. In the case of $[4Cu]^+$, let us consider a pair of enantiomeric molecules. Protons H_m of a given enantiomer are related by a symmetry plane to protons H_m of the other enantiomer; protons H_m are enantiotopic by external comparison in $[4Cu]^+$. Therefore, in the presence of a chiral shift reagent, their signal is split; this is what is indeed observed. Finally, in the case of $[3Cu]^+$, there are two sets of protons H_m: those belonging to the unsubstituted macrocycle and those belonging to the substituted macrocycle, which is the symmetry plane of the molecule. Therefore, the former are outside this symmetry plane, whereas the latter are inside this symmetry plane. Let us consider a pair of molecules of $[3Cu]^+$. H_m protons of the substituted macrocycle are equivalent by external comparison, and a chiral shift reagent will not split their signal, as observed. On the contrary, H_m and $H_{m'}$ protons of the unsubstituted macrocycle are related by a symmetry plane by internal as well as external comparisons. They are therefore enantiotopic. As expected, their signal is split in the presence of Pirkle's chiral shift reagent. What has been illustrated with protons H_m is valid for all the other protons of the phenanthroline nucleus. In a few cases, the lack of any splitting when splitting was in fact expected is certainly accidental.

Similar experiments (i.e., use of the Pirkle reagent) were conducted with the corresponding metal-free catenanes. However, a general broadening of the peaks in the NMR spectra was observed, and no conclusion could be drawn from these experiments. Probably, too many conformations of the catenane are available to the Pirkle reagent on the NMR time scale to give a well-defined, single interaction, and only the average of all possible interactions is observed. Therefore, another optically active NMR shift reagent (the lanthanide shift reagent europium tris[3-[(trifluoromethyl)hydroxymethylene]-(+)-camphorato]][26] was used in the presence of catenand **2**. Unfortunately, in the solvent used ($CDCl_3$), protonation of the catenand occurred.[27] Very few peaks were split (i.e., H_8, $H_{o'}$, and $H_{m'}$), and some of them (H_7,H_6) underwent a slight upfield paramagnetic shift. Again, chirality could not be tested with the pure catenand. Therefore, this experiment was limited to catenand **2**.

Conclusion

In this study, we have synthesized a series of copper catenates and metal-free catenands, two of them exhibiting topological chirality. The chemical chirality has been proven by proton NMR spectroscopy in the presence of chiral shift reagents, owing to a careful analysis of the topicity of protons and sets of protons in the chiral catenates as well as in the achiral analogues. The topological nature of the chirality of the catenates studied is only conjecture at the present moment.

Much work remains to be done in the field of topologically chiral catenates, such as resolution of the enantiomers. Preliminary experiments[28,29] indicate that this should be feasible, starting from Cu(I) catenates and using HPLC on chiral stationary phases. Thus, measurement of the optical activity of a catenane would be possible. Finally, the unknown unconditionally topologically chiral catenane shown in Figure 2a remains a fascinating synthetic challenge.

Experimental Section

General. Macrocycle **8**, catenate $[1Cu]^+$, and catenand **1** were synthesized as previously described.[14] 3-Chloro-1-(4-methylphenyl)-propanone was prepared according to the literature.[30] All other chemicals were of the best commercially available grade and were used without further purification. ^{1}H-NMR spectra were recorded at 200 or 400 MHz; ^{13}C-NMR spectra were recorded at 50 MHz. The spectrometers used were Bruker WP 200 SY and AM 400 instruments. Chemical shifts are given in parts per million downfield vs Me_4Si. Low-resolution FAB mass spectra were recorded with a VG Instruments ZAB-HF mass spectrometer.

4-Phenyl-1,10-phenanthroline (9). This compound was synthesized according to the procedure of Case[18] (see also preparation of **13**) but was purified by chromatography (silica gel, 2% MeOH in CH_2Cl_2): yield, 6.9 g (45%); ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 9.16 (dd, 1 H, J_2 = 1.1 Hz, J_1 = 4.4 Hz, H_9), 9.15 (d, 1 H, J = 4.6 Hz, H_2), 8.27 (dd, 1 H, J_2 = 1.8 Hz, J_1 = 8.1 Hz, H_7), 7.92 (d, 1 H, J = 9.2 Hz, H_6), 7.76 (d, 1 H, J = 9.2 Hz, H_5), 7.65 (dd, 1 H, J_1 = 8.1 Hz, J_2 = 4.4 Hz, H_8), 7.58 (d, 1 H, J = 4.5 Hz, H_3), 7.56–7.51 (m, 5 H, $H_{o'',m'',p''}$).

2,9-Dianisyl-4-phenyl-1,10-phenanthroline (10). This compound was synthesized as described for **6**[14] and purified by chromatography (silica gel, 1% MeOH in $PhCH_3$) and crystallization from benzene–hexane: yield, 1.9 g (32%); mp 161–165 °C; ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 8.46 (d, 2 H, J = 8.9 Hz, $H_{o'}$), 8.45 (d, 2 H, J = 8.9 Hz, H_o), 8.28 (d, 1 H, J = 8.5 Hz, H_7), 8.12 (d, 1 H, J = 8.5 Hz, H_8), 8.05 (s, 1 H, H_3), 7.84 (d, 1 H, J = 9 Hz, H_6), 7.70 (d, 1 H, J = 9.1 Hz, H_5), 7.65–7.54 (m, 5 H, $H_{o'',m'',p''}$), 7.15 (d, 2 H, J = 9.0 Hz, $H_{m'}$), 7.14 (d, 2 H, J = 9.0 Hz, H_m), 3.93 (s, 3 H, methoxy H), 3.92 (s, 3 H, methoxy H). Anal. Calcd for $C_{32}H_{24}O_2N_2$: C, 82.03; H, 5.16; N, 5.98. Found: C, 82.28; H, 5.39; N, 5.94.

2,9-Bis(4-hydroxyphenyl)-4-phenyl-1,10-phenanthroline (11). This compound was synthesized as described for **7**:[14] quantitative yield (3 g); ^{1}H-NMR (200 MHz, d^7-DMF) δ 9.81 (s, 2 H, phenol OH), 8.64 (d, 2 H, J = 8.8 Hz, $H_{o'}$), 8.58 (d, 2 H, J = 8.8 Hz, H_o), 8.55 (d, 1 H, J = 8.5 Hz, H_7), 8.39 (d, 1 H, J = 8.5 Hz, H_8), 8.28 (s, 1 H, H_3), 7.96 (d, 1 H, J = 9.1 Hz, H_6), 7.85 (d, 1 H, J = 9.0 Hz, H_5), 7.82–7.66 (m, 5 H, $H_{o'',m'',p''}$), 7.16 (d, 4 H, J = 8.2 Hz, $H_{m,m'}$). Anal. Calcd for $C_{30}H_{20}O_2N_2 \cdot H_2O$: C, 78.58; H, 4.83; N, 6.11. Found: C, 78.44; H, 5.11; N, 6.09.

Copper Catenate $[2Cu]^+$. This compound was synthesized as described for $[1Cu]^+$[14] and purified by chromatography (silica gel, 1.5% MeOH in CH_2Cl_2) and crystallization from hot methanol: yield, 0.35 g (12.6%); mp 229–230 °C; ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 8.78 (d, 2 H, J = 8.5 Hz, H_7), 8.43 (d, 2 H, J = 9.2 Hz, H_6), 8.13 (d, 2 H, J = 9.1 Hz, H_5), 7.97 (d, 2 H, J = 8.4 Hz, H_8), 7.77 (s, 2 H, H_3), 7.73–7.66 (m, 14 H, $H_{o'',m'',p'',o'}$), 7.22 (d, 4 H, J = 8.7 Hz, H_o), 6.23 (d, 4 H, J = 8.8 Hz, $H_{m'}$), 5.93 (d, 4 H, J = 8.7 Hz, H_m), 3.75–3.58 (m, 24 H, $H_{\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$), 3.53 (t, 8 H, J = 4.7 Hz, $H_{\alpha,\alpha'}$), 3.39 (m, 8 H, $H_{\beta,\beta'}$). Anal. Calcd for $C_{80}H_{76}BCuF_4N_4O_{12}$: C, 66.92; H, 5.34; N, 3.90. Found: C, 67.02; H, 5.53; N, 3.94.

Catenand 2. This compound was obtained as described for **1**.[14] It was purified by chromatograpy (silica gel, 3% MeOH in CH_2Cl_2): yield, 0.019 g (51%); ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 8.50 (d, 4 H, J = 8.8 Hz, $H_{o'}$), 8.48 (d, 4 H, J = 8.7 Hz, H_o), 8.27 (d, 2 H, J = 8.4 Hz, H_7), 8.11 (d, 2 H, J = 8.5 Hz, H_8), 8.07 (s, 2 H, H_3), 7.84 (d, 2 H, J = 9.1 Hz, H_6), 7.71 (d, 2 H, J = 9.1 Hz, H_5), 7.62–7.49 (m, 10 H, $H_{o'',m'',p''}$), 7.17 (d, 4 H, J = 8.9 Hz, $H_{m'}$), 7.16 (d, 4 H, J = 9 Hz, H_m), 4.24 (t, 8 H, J = 6.9 Hz, $H_{\alpha,\alpha'}$), 3.74 (t, 8 H, J = 6.8 Hz, $H_{\beta,\beta'}$), 3.69–3.63 (m, 24 H, $H_{\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$). Anal. Calcd for $C_{80}H_{76}N_4O_{12}$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.85; H, 6.15; N, 3.91.

4-(*p*-Tolyl)-1,10-phenanthroline (13). A mixture of 8-aminoquinoline (20 g, 0.139 mol), arsenic pentaoxide (18.7 g, 0.0814 mol), concentrated H_2SO_4 (30 mL), and water (10 mL) was heated at 100 °C, and 3-chloro-1-(4-methylphenyl)propanone (36 g, 0.878 mol) was added rapidly. The reaction mixture was heated at reflux (ca. 135 °C) for 2.5 h. Then it was poured onto ice and basified with concentrated aqueous potassium hydroxide. The crude product obtained after acid–base ex-

(26) McCreary, M. D.; Lewis, D. W.; Wernick, L. D.: Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038–1054.
(27) Cesario, M.; Dietrich-Buchecker, C. O.; Edel, A.; Guilhem, J.; Kintzinger, J.-P.; Pascard, C.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 6250–6254.
(28) Tachibana, K.; Chambron, J.-C.: Mitchell, D. K.; Sauvage, J.-P. Unpublished results.
(29) Okamoto, H.; Chambron, J.-C.: Mitchell, D. K.; Sauvage, J.-P. Work in progress.
(30) Kenner, J.: Statham, F. S. *J. Chem. Soc.* **1935**, 16–18.

traction was submitted to repeated chromatography (alumina, CH_2Cl_2) and recrystallized from ethyl acetate. Yield, 8 g (21%); mp 166.5–167.5 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 9.22 (dd, 1 H, J_1 = 1.9 Hz, J_2 = 4 Hz, H_9), 9.20 (d, 1 H, J = 4.5 Hz, H_2), 8.24 (dd, 1 H, J_1 = 8.1 Hz, J_2 = 1.7 Hz, H_7), 7.95 (d, 1 H, J = 9.1 Hz, H_6), 7.72 (d, 1 H, J = 9.2 Hz, H_5), 7.64 (dd, 1 H, J_1 = 8.1 Hz, J_2 = 4.3 Hz, H_8), 7.56 (d, 1 H, J = 4.5 Hz, H_3), 7.44 (d, 2 H, J = 8.3 Hz, $H_{o''}$), 7.37 (d, 2 H, J = 8.3 Hz, $H_{m''}$), 2.49 (s, 3 H, methyl H). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.11; H, 5.34; N, 10.30.

2,9-Dianisyl-4-(*p*-tolyl)-1,10-phenanthroline (14). This compound was synthesized as described for **6**[14] and purified by chromatography (silica gel, 0.1% MeOH in CH_2Cl_2): yield, 12.9 g (65%); mp 195–197 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.48 (d, 2 H, J = 8.9 Hz, $H_{o'}$), 8.47 (d, 2 H, J = 8.8 Hz, H_o), 8.24 (d, 1 H, J = 8.5 Hz, H_7), 8.09 (d, 1 H, J = 8.5 Hz, H_8), 8.01 (s, 1 H, H_3), 7.86 (d, 1 H, J = 9.0 Hz, H_6), 7.66 (d, 1 H, J = 9 Hz, H_5), 7.51 (d, 2 H, J = 8.0 Hz, $H_{o''}$), 7.39 (d, 2 H, J = 8.0 Hz, $H_{m''}$), 7.14 (d, 2 H, J = 8.9 Hz, $H_{m'}$), 7.12 (d, 2 H, J = 8.9 Hz, H_m), 3.94 (s, 6 H, methoxy H), 2.51 (s, 3 H, methyl H). Anal. Calcd for $C_{33}H_{26}N_2O_2 \cdot {}^1/_2H_2O$: C, 80.63; H, 5.54; N, 5.70. Found: C, 80.61; H, 5.51; N, 5.54.

2,9-Bis(4-hydroxyphenyl)-4-(*p*-tolyl)-1,10-phenanthroline (15). This compound was synthesized as described for **7**:[14] quantitative yield (4.30 g); ^{1}H-NMR (200 MHz, d^7-DMF) δ 10.18 (s, br, 1 H, phenol OH), 8.65 (d, 2 H, J = 8.7 Hz, $H_{o'}$), 8.59 (d, 2 H, J = 8.6 Hz, H_o), 8.55 (d, 1 H, J = 7.6 Hz, H_7), 8.40 (d, 1 H, J = 8.6 Hz, H_8), 8.27 (s, 1 H, H_3), 7.96 (d, 1 H, J = 9.0 Hz, H_6), 7.89 (d, 1 H, J = 9 Hz, H_5), 7.68 (d, 2 H, J = 8.0 Hz, $H_{o''}$), 7.53 (d, 2 H, J = 7.9 Hz, $H_{m''}$), 7.16 (d, 4 H, J = 7.5 Hz, $H_{m',m}$), 2.55 (s, 3 H, methyl H). Anal. Calcd for $C_{31}H_{22}N_2O_2 \cdot 2H_2O$: C, 75.90; H, 5.34; N, 5.71. Found: C, 75.56; H, 5.03; N, 5.70.

Macrocycle 16. This compound was synthesized as described for **8**:[14] yield: 1 g (37%); mp 163–164 °C; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.45 (d, 2 H, J = 8.7, $H_{o'}$), 8.44 (d, 2 H, J = 8.7 Hz, H_o), 8.25 (d, 1 H, J = 8.5 Hz, H_7), 8.08 (d, 1 H, J = 8.4 Hz, H_8), 7.99 (s, 1 H, H_3), 7.87 (d, 1 H, J = 9.1 Hz, H_6), 7.68 (d, 1 H, J = 9.1 Hz, H_5), 7.51 (d, 2 H, J = 8.0 Hz, $H_{o''}$), 7.40 (d, 2 H, J = 7.9 Hz, $H_{m''}$), 7.21 (d, 2 H, J = 8.9 Hz, $H_{m'}$), 7.19 (d, 2 H, J = 8.8 Hz, H_m), 4.36 (t, 4 H, J = 4.9 Hz, $H_{\alpha,\alpha'}$), 3.87 (t, 4 H, J = 5.0 Hz, $H_{\beta,\beta'}$), 3.77–3.73 (m, 12 H, $H_{\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$), 2.51 (s, 3 H, methyl H). Anal. Calcd for $C_{41}H_{40}N_2O_6$: C, 74.98; H, 6.14; N, 4.27. Found: C, 74.97; H, 6.16; N, 4.33.

Copper Catenate [3Cu]$^+$. This compound was obtained as described for [**1**Cu]$^+$ (strategy B), starting from [(**8**,**15**)Cu]$^+$.[14] It was purified first by gravity chromatography (silica gel, 2% MeOH in CH_2Cl_2) and then by repeated medium-pressure liquid chromatography (silica gel, 1–1.2% MeOH in CH_2Cl_2 at 1.2 bar) to remove [**4**Cu]$^+$ which had formed as a side product (2%). Fractions were monitored by ^{1}H-NMR: yield, 0.239 g (19%); ^{1}H-NMR (400 MHz, $CDCl_3/D_2O$/sodium dithionite; underlined protons are those of the unsubstituted macrocycle) δ 8.83 (d, 1 H, J = 8.4 Hz, H_7), 8.72 (d, 2 H, J = 8.3 Hz, $H_{4,7}$), 8.42 (d, 1 H, J = 9.2 Hz, H_6), 8.31 (s, 2 H, $H_{5,6}$), 8.13 (d, 1 H, J = 9.1 Hz, H_5), 7.96 (d, 1 H, J = 8.4 Hz, H_8), 7.90 (d, 2 H, J = 8.3 Hz, $H_{3,8}$), 7.70 (d, 2 H, J = 8.8 Hz, $H_{o'}$), 7.68 (s, 1 H, H_3), 7.58 (d, 2 H, J = 8.1 Hz, $H_{o''}$), 7.46 (d, 2 H, J = 7.9 Hz, $H_{m''}$), 7.40 (d, 4 H, J = 8.7 Hz, H_o), 7.00 (d, 2 H, J = 8.6 Hz, H_o), 6.22 (d, 2 H, J = 8.7 Hz, $H_{m'}$), 6.07 (d, 4 H, J = 8.7 Hz, H_m), 5.86 (d, 2 H, J = 8.7 Hz, H_m), 3.90–3.35 (m, 40 H, $H_{\alpha,\alpha',\beta,\beta',\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$, $H_{\alpha,\beta,\gamma,\delta,\epsilon}$), 2.54 (s, 3 H, methyl H); ^{13}C-NMR (50 MHz, CD_2Cl_2; underlined carbons are those of the unsubstituted macrocycle) δ 159.80, 159.58, 159.17, 156.57, 156.42, 156.26, 150.17, 144.37, 143.78, 139.99 (quaternary C), 138.85 (C_7), 138.15 ($C_{4,7}$), 134.77, 132.97, 132.82 (quaternary C), 130.14, 129.88 ($C_{o',o'',m''}$), 129.35 (C_o), 128.74 (C_o), 128.65 (C_6), 127.60 ($C_{5,6}$), 126.72 (quaternary C), 124.67, 124.26, 124.19, 124.04 ($C_{3,5,8}$, $C_{3,8}$), 113.86 ($C_{m'}$), 113.45 (C_m), 113.04 (C_m), 71.65, 71.59, 71.52, 71.09, 70.89 ($C_{\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$, $C_{\gamma,\delta,\epsilon}$), 69.38 ($C_\beta$), 69.83, 69.00 ($C_{\beta,\beta'}$), 67.55 ($C_\alpha$), 67.92, 67.30 ($C_{\alpha,\alpha'}$), 30.17 (not attributed), 21.26 (methyl C). Anal. Calcd for $C_{75}H_{74}BCuF_4N_4O_{12}$: C, 65.58; H, 5.43; N, 4.08. Found: C, 65.40; H, 5.70; N, 3.79. FAB-MS: m/z found 1285.4 ($M - BF_4^-$), 719.2 ([**16**Cu]$^+$), 629.1 ([**8**Cu]$^+$); calcd 1286.9, 720.3, 630.2.

Catenand 3. This compound was obtained as described for **1**:[14] yield, 0.041 g (90%); ^{1}H-NMR (200 MHz, CD_2Cl_2) 8.53 (d, 2 H, J = 8.8 Hz, $H_{o'}$), 8.51 (d, 2 H, J = 8.9 Hz, H_o), 8.44 (d, 4 H, J = 8.9 Hz, H_o), 8.29 (d, 2 H, J = 8.5 Hz, $H_{4,7}$), 8.27 (d, 1 H, J = 8.6 Hz, H_7), 8.12 (d, 1 H, J = 8.5 Hz, H_8), 8.09 (d, 2 H, J = 8.7 Hz, $H_{3,8}$), 8.07 (s, 1 H, H_3), 7.85 (d, 1 H, J = 9.1 Hz, H_6), 7.79 (s, 2 H, $H_{5,6}$), 7.70 (d, 1 H, J = 9.0 Hz, H_5), 7.46 (d, 2 H, J = 8.0 Hz, $H_{o''}$), 7.31 (d, 2 H, J = 8.0 Hz, $H_{m''}$), 7.19 (d, 2 H, J = 8.9 Hz, $H_{m'}$), 7.16 (d, 2 H, J = 8.6 Hz, H_m), 7.12 (d, 4 H, J = 8.8 Hz, H_m), 4.23 (m, 8 H, $H_{\alpha'}$, $H_{\alpha'}$, $H_{\alpha'}$), 3.77–3.63 (m, 32 H, $H_{\beta,\beta',\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$, $H_{\beta,\gamma,\delta,\epsilon}$), 2.46 (s, 3 H, methyl H). Anal. Calcd for $C_{75}H_{74}N_4O_{12}$: C, 73.63; H, 6.10; N, 4.58. Found: C, 73.14; H, 6.05; N, 4.02. FAB-MS: m/z found 1223.3 (M^+), 657.2 (**16**$^+$), 567.2 (**8**$^+$); calcd 1223.4, 656.8, 566.7.

Copper Catenate [4Cu]$^+$. This compound was synthesized as described for [**1**Cu]$^+$[14] and purified by column chromatography (silica gel, 1–5% MeOH in $CHCl_3$) and preparative TLC (silica gel, 15% MeOH in $CHCl_3$): yield, 0.392 g (14.6%); mp 219–221 °C; ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 8.78 (d, 2 H, J = 8.5 Hz, H_7), 8.41 (d, 2 H, J = 9.2 Hz, H_6), 8.15 (d, 2 H, J = 9.1 Hz, H_5), 7.95 (d, 2 H, J = 8.4 Hz, H_8), 7.74 (s, 2 H, H_3), 7.73 (d, 4 H, J = 8.7 Hz, $H_{o'}$), 7.61 (d, 4 H, J = 8.1 Hz, $H_{o''}$), 7.49 (d, 4 H, J = 8.0 Hz, $H_{m''}$), 7.19 (d, 4 H, J = 8.6 Hz, H_o), 6.21 (d, 4 H, J = 8.8 Hz, $H_{m'}$), 5.91 (d, 4 H, J = 8.7 Hz, H_m), 3.67–3.60 (m, 24 H, $H_{\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$), 3.57–3.47 (m, 8 H, $H_{\alpha,\alpha'}$), 3.44–3.29 (m, 8 H, $H_{\beta,\beta'}$), 2.53 (s, 6 H, methyl H); ^{13}C-NMR (50 MHz, CD_2Cl_2) δ 160.72, 160.12, 157.02, 150.94, 145.10, 140.63 (quaternary C), 139.41 (C_7), 135.44, 133.71, 133.46 (quaternary C), 130.86, 130.71 ($C_{o',o'',m''}$), 130.03 (C_o), 129.20 (C_6), 127.37 (quaternary C), 125.20 (C_3), 124.94 (C_5), 124.57 (C_8), 114.36 ($C_{m'}$), 113.62 (C_m), 71.80, 71.64, 71.08, 70.97, ($C_{\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$), 69.95, 69.23 ($C_{\beta,\beta'}$), 68.08, 67.57 ($C_{\alpha,\alpha'}$), 21.39 (methyl C). Anal. Calcd for $C_{82}H_{80}CuBF_4N_4O_{12}$: C, 67.27; H, 5.51; N, 3.83. Found: C, 67.18; H, 5.59; N, 3.68. FAB-MS: m/z found 1375.50 ($M - BF_4^-$), 719.2 ([**16**Cu]$^+$); calcd 1377.0, 720.3.

Catenand 4. This compound was obtained as described for **1**.[14] It was purified by chromatography (silica gel, 2% MeOH in CH_2Cl_2): yield, 0.124 (93%), ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.45 (d, 4 H, J = 8.9 Hz, $H_{o'}$), 8.43 (d, 4 H, J = 8.9 Hz, H_o), 8.23 (d, 2 H, J = 8.5 Hz, H_7), 8.06 (d, 2 H, J = 8.4 Hz, H_8), 7.99 (s, 2 H, H_3), 7.86 (d, 2 H, J = 9.0 Hz, H_6), 7.65 (d, 2 H, J = 9.1 Hz, H_5), 7.50 (d, 4 H, J = 8.1 Hz, $H_{o''}$), 7.38 (d, 4 H, J = 8.0 Hz, $H_{m''}$), 7.20 (d, 4 H, J = 8.9 Hz, $H_{m'}$), 7.19 (d, 4 H, J = 8.9 Hz, H_m), 4.36 (t, 8 H, J = 5.0 Hz, $H_{\alpha,\alpha'}$), 3.86 (t, 8 H, J = 5.2 Hz, $H_{\beta,\beta'}$), 3.77–3.67 (m, 24 H, $H_{\gamma,\gamma',\delta,\delta',\epsilon,\epsilon'}$), 2.50 (s, 6 H, methyl H). Anal. Calcd for $C_{82}H_{80}N_4O_{12}$: C, 74.98; H, 6.14; N, 4.27. Found: C, 74.42; H, 6.55; N, 4.02. FAB-MS: m/z found 1313.6 (M^+), 657.3 (**16**$^+$); calcd 1313.5, 656.8.

Acknowledgment. We acknowledge the financial contribution of the CNRS. D.K.M. thanks the Ministère des Affaires Etrangères for a fellowship. Dr. R. Graff and Mr. J.-D. Sauer are gratefully acknowledged for the high-resolution and bidimensional NMR spectra, and Mr. R. Hueber is thanked for the FAB mass spectra. Dr. J.-P. Kintzinger is thanked for fruitful discussions.