# Electrochemically and Photochemically Driven Ring Motions in a Disymmetrical Copper [2]-Catenate

**Aude Livoreil,[†] Jean-Pierre Sauvage,\*,[†] Nicola Armaroli,[‡,§] Vincenzo Balzani,\*,[‡] Lucia Flamigni,[§] and Barbara Ventura[‡]**

*Contribution from the Laboratoire de Chimie Organo-Minérale, URA 422 du CNRS, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg, France, Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, and Istituto FRAE/CNR, Via Gobetti 101, 40129 Bologna, Italy*

*Received June 23, 1997*[⊗]

**Abstract:** By applying the three-dimensional template effect of copper(I), previously used for making various interlocking ring systems, a new disymmetrical [2]-catenate has been made which consists of two different interlocking rings. One ring contains a 2,9-diphenyl-1,10-phenanthroline (dpp) unit whereas the other cycle incorporates both a dpp motif and a 2,2′,6′,2″-terpyridine (terpy) fragment, the coordination site of these two chelates pointing toward the inside of the ring. Depending on the oxidation state of the central metal (Cu(I) or Cu(II)), and thus on its preferred coordination number, two distinct situations have been observed. With monovalent copper, the two dpp units interact with the metal and the terpy fragment remains free, at the outside of the molecule. By contrast, when the catenate is complexed to divalent copper, the terpy motif is bonded to the metal and it is now a dpp ligand which lies at the periphery of the complex. This dual coordination mode leads to dramatically different molecular shapes and properties for both forms. The molecular motion which interconverts the four- and the five-coordinate complexes can be triggered chemically, electrochemically, or photochemically by changing the oxidation state of the copper center (II/I). The process has been studied by electrochemistry and by UV-vis spectroscopy. Interestingly, once the stable 4-coordinate copper(I) complex has been oxidized to a thermodynamically unstable pseudo-tetrahedral copper-(II) species, the rate of the gliding motion of the rings which will afford the stable 5-coordinate species (copper(II) coordinated to dpp and terpy) can be controlled at will. Under certain experimental conditions, the changeover process is extremely slow (weeks), and the 4-coordinate complex is more or less frozen. By contrast, addition of a coordinating counterion to the medium (Cl⁻) enormously speeds up the rearrangement and leads to the thermodynamically stable 5-coordinate complex within minutes.

## Introduction

The fascination exerted by catenanes stems mainly from their unusual topological properties (nonplanar molecular graph),[1] but it also originates from the potential novel properties displayed by molecular systems containing virtually nonconstrained constitutive elements, such as interlocking rings able to glide freely within one another. Although catenanes have been known for several decades,[2] their chemical and physical characteristics have been little studied, mostly due to the difficulty of synthesizing them at a really preparative scale. In spite of this limitation, dynamic studies using NMR relaxation time measurements have been carried out on simple systems, showing fast intramolecular molecular motions.[3]

Clearly, little constrain between interlocking rings of sufficient size can in principle be extended to polymers. It is thus expected that macromolecular systems incorporating interlocking ring units will lead to interesting systems related to the high mobility and flexibility of their polymer backbone.[4] Another new area

of research, in which catenanes and other related systems containing rings threaded by stringlike molecules (rotaxanes and pseudo-rotaxanes) are particularly promising, is that of the so called "molecular machines"[5] or molecular assemblies whose shape, physical, chemical, and dynamic properties can be controlled by using an external signal. The general idea of inducing a profound molecular rearrangement by reducing or

---

† Université Louis Pasteur.

‡ Università di Bologna.

§ Istituto FRAE/CNR.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

(1) For a representative collection of papers, see *New. J. Chem.* special issue, **1993,** vol 17, 10−11. Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961,** *83,* 3789. Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995,** *95,* 2725−2828. Sauvage, J. P.; Hosseini, M. W., Eds.; Templating, Self-Assembly, and Self-Organization. *Comprehensive Chemistry,* Pergamon: New York, 1996, Vol. 9. Walba, D. M. *Tetrahedron* **1985,** *41,* 3161−3212.

(2) Wasserman, E. *J. Am. Chem. Soc.* **1960,** *82,* 4433. Schill, G. *Catenanes, Rotaxanes and Knots*; Academic Press: New-York, London, 1971.

(3) Fritz, H.; Hug, P.; Sauter, H.; Logemann, E. *J. Mag. Reson.* **1976,** *21,* 373−375. Kintzinger, J. P.; Bourgeois, H.; Edel, A.; Graff, R.; Chambron, J. C.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *Computational Approaches in Supramolecular Chemistry*; Wipff, G., Ed.; Kluwer Academic Publishers: Boston, 1994; pp 391−398. Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin A. M. Z.; Spencer, N.; Stoddart J. F.; Vicent, C.; Williams D. J. *J. Am. Chem. Soc.* **1992,** *114,* 193−218.

(4) Weidmann, J. L.; Kern, J. M.; Sauvage, J. P.; Geerts, Y.; Muscat, D.; Müllen, K. *Chem. Commun.* **1996,** 1243−1244.

(5) Ballardini, R.; Balzani, V.; Gandolfi, M. T., Prodi, L.; Venturi, M.; Philp, D.; Ricketts, H. G.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1301−1303. Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; Gòmez-Lòpez, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur.J.* **1997,** *3,* 152−170. Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Langford, S. J.; Menzer, S.; Prodi, L.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 978−981. Bissel, R. A.; Còrdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994,** *369,* 133−137. Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Menzer, S.; Pérez-Garcìa, L.; Prodi, L.; Stoddart, J. F.; Venturi, M.; White, A.J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1995,** *117,* 11171−11197. Credi, A.; Balzani, V.; Longford, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **1997,** *119,* 2679−2681. For a photoswitchable catenane, see: Bauer, M.; Müller, W. M.; Müller, U.; Rissanen, K.; Vögtle, F. *Liebigs Ann.* **1995,** 649−656. Vögtle, F.; Müller, W. M.; Müller, U.; Bauer, M.; Rissanen, K. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1295−1297.

oxidizing a constitutive element of a chemical system is certainly of great interest in itself, but it is also related to biological systems. Many proteins undergo dramatic conformational changes in relation with their biological action although electron-transfer proteins undergo very limited changes. Recent work has stressed the importance of redox processes in folding−unfolding reactions of redox proteins incorporating heme groups and acting as electron-transfer agents (cytochrome).[6] Among synthetic systems, a non-catenane example mimics the action of a brake by using the coordination properties of a fragment of the compound to slow down a rotation process about a C−C bond.[7] A two-coordination site ligand has also been used to demonstrate that hopping of a metal center (Fe(II) or Fe(III)) between two remote positions in the compound can be induced by simply oxidizing or reducing the metal.[8]

Other elegant examples based on catenanes, rotaxanes, and rotaxane-like systems exhibiting donor−acceptor interactions have recently been described.[5] They make use of chemical, electrochemical, or photochemical properties to induce conformational changes. Recently, a transition metal-bonded [2]-catenane has been described, which undergoes a complete changeover process (gliding of one ring within the other) under the action of an electrochemical signal.[9] We would now like to report the synthesis of the compound, its electrochemically and photochemically driven motions, as well as the effect of various experimental factors, such as nature of the solvent or coordinating ability of the counterions used, on the rate of the molecular rearrangement.

### Results and Discussion

**Design and Synthesis of the Catenane.** Thanks to the topological link[1] existing between its two constitutive rings, a [2]-catenane can adopt several geometries, defined by the respective positions of both rings, while keeping its global topology unchanged. This makes it a potential multistable molecule, the interconversion from one stable state to the next one consisting of the gliding motion of one ring into the other. As illustrated by previous work in our group,[10] a catenane can also sometimes act as a ligand and form stable complexes with several transition metal atoms such as copper, cobalt, zinc... We thus synthesized a copper catenate,[9] i.e. a copper complex whose organic backbone is a [2]-catenane, able to adjust its coordination geometry to the oxidation state of the metal by changing the respective position of its rings. This catenane offers two different coordination sites to the metal, each one stabilizing a different oxidation state: a tetrahedral site consisting of two bidentate chelates favors Cu(I), whereas a 5-coordinating atom site, consisting of bidentate and terdentate chelates stabilizes Cu(II). Consequently, oxidation or reduction of both stable states generates a "metastable" compound, which rearranges through a gliding motion of one ring into the other, leading to the complex which best fits the new coordination geometry of the metal center. These linkage isomerisms are illustrated in Figure 1.
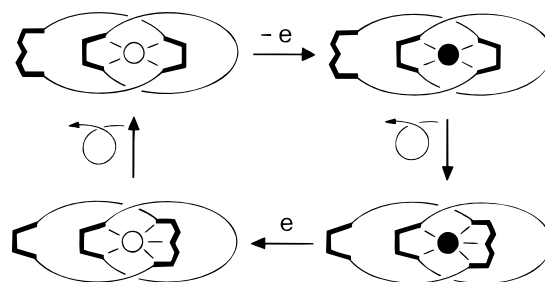


**Figure 1.** The linkage isomerisms subsequent to modification of the metal center oxidation state. The white and black circles stand, respectively, for Cu(I) and Cu(II), whereas the chelates (bi- or terdentate coordinating fragments) incorporated in the rings are drawn with bold broken lines. Once the Cu(I) complex gathering two bidentate chelates is oxidized, the resulting Cu(II) complex undergoes a changeover process leading to the catenate second coordination mode, based on complexation of a bidentate and a terdentate ligand. Reversibly, reduction of this complex regenerates the original coordination mode, through a similar gliding motion of the rings.

This square scheme reminds of the one obtained by Sano and Taube for ruthenium complexes showing linkage isomerism with sulfoxide ligands.[11] Thanks to their very different physicochemical properties, e.g. redox potentials, those complexes show cyclic voltammograms characteristic of a molecular hysteresis phenomenon. Other transition metal complexes have also been shown to undergo rearrangement following reduction or oxidation of the metal center.[12] Similarly, our compound is an example of hysteresis at the molecular level, but as we will see later, the isomerism kinetics are even slower in our case. This hysteresis property could be of great interest in the field of information storage.

Our disymmetrical catenane consists of two different rings (Figure 2): one includes the classical bidentate chelate, 2,9-diphenyl-1,10-phenanthroline (dpp) and a polyethyleneglycol fragment, the other comprises a dpp moiety and a terdentate ligand, 2,2′:6′,2″-terpyridine (terpy), both units being linked by three methylene groups. Both macrocycles have a 33 atom-long inner rim in order to minimize steric hindrance toward rotation of one ring through the other. In order to distinguish the different coordination modes, we introduce a notation indicating the oxidation state of the metal and the number of nitrogen atoms surrounding it in each case: the tetrahedral complex is noted $Cu^{(I/II)}N_4$ and the 5-coordinate one $Cu^{(I/II)}N_5$. The catenate is obtained as a Cu(I) pseudo-tetrahedral complex ($Cu^I N_4$) using a two-step procedure, as shown in Figure 2.

A threaded precursor is synthesized by complexation of a Cu(I) cation by an acyclic dpp unit and a macrocycle consisting of a second dpp motif. The sequential addition of the metal cation to a solution of the macrocycle, followed by addition of the open ligand, prevents formation of a mixture of complexes, and allows quantitative obtention of the precursor. The reaction of this complex with the missing fragment in high dilution conditions leads to the desired catenate. The copper cation is used as a template, its tetrahedral coordination geometry inducing the threading and the subsequent interlocking of the two rings.

(6) Bixler, J.; Bakker, G.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6938−6939. Pascher, T.; Chesick, J. P.; Winkler, J. R.; Gray, H. *Science* **1996**, *271*, 1558−1560.

(7) Kelly, T. R.; Bowyer, M. C.; Bhaskar, K. V.; Bebbington, D.; Garcia, A.; Lang, F.; Kim, M. H.; Jette, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 3657−3658

(8) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, *374*, 790−792.

(9) Livoreil, A.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 9399−9400.

(10) Dietrich-Buchecker, C.; Sauvage, J. P. *Tetrahedron* **1990**, *46*, 2, 503−512. Dietrich-Buchecker, C.; Kintzinger, J. P.; Sauvage, J. P. *Tetrahedron Lett.* **1983**, *24*, 5095−5098. Dietrich-Buchecker, C.; Sauvage, J. P.; Kern, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 7791−7800.

(11) Tomita, A.; Sano, M. *Inorg. Chem.* **1994**, *33*, 5825−5830 and references cited therein: Sano, M.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 2327−2328..

(12) Geiger, W. E.; Salzer, A.; Edwin, J.; Von Philipsborn, W.; Piantini, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113−7121. Katz, N. E.; Fagalde, F. *Inorg. Chem.* **1993**, *32*, 5391−5393. Joulié, L. F.; Schatz, E.; Ward, M. D.; Weber, F.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1994**, 799−804. Bond, A. M.; Hambley, T. W.; Mann, D. R.; Snow, M. R. *Inorg. Chem.* **1987**, *26*, 2257−2265.
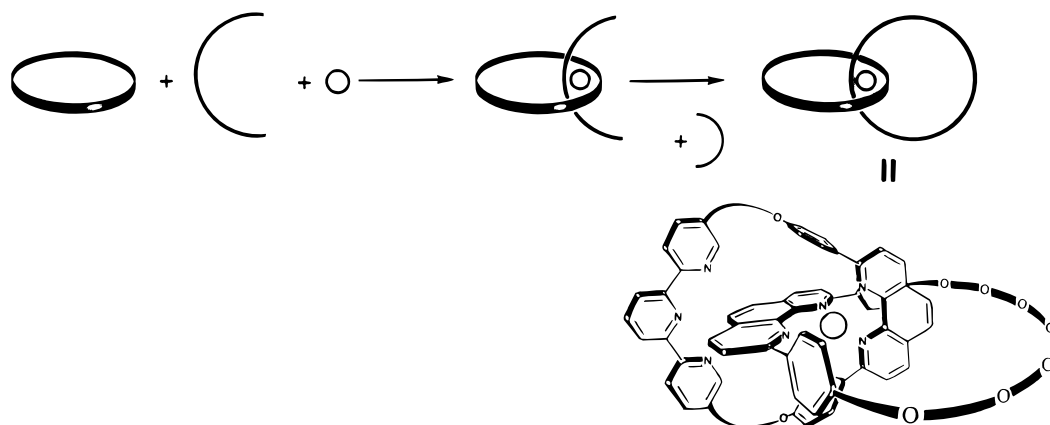
**Figure 2.** The synthesic strategy and the target molecule: the template effect of Cu(I) induces threading of the acyclic chelate through the macrocyclic ligand, resulting in the formation of a tetrahedral precursor complex; reaction of this complex with the complementary fragment gives the catenate. In our case, this molecule is comprised of two different chelates: a bidentate 2,9-diphenyl-1,10-phenanthroline (two units) and a terdentate 2,2′: 6′:2″-terpyridine.



R = Me : **2**

= (CH₂)₃OTHP : **3**

= (CH₂)₃OH : **4**

= (CH₂)₃OSO₂Me : **5**

= (CH₂)₃Br : **6**
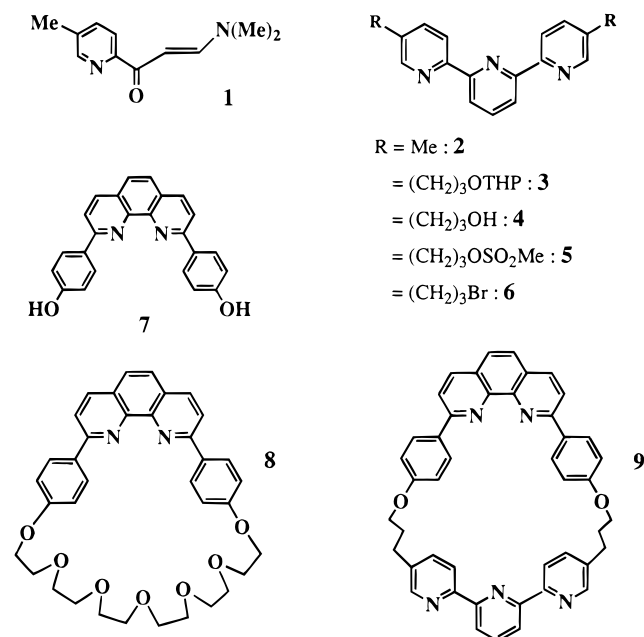
**Figure 3.** Intermediate key-compounds synthesized.

The synthesis of the different moieties relies on already described methodologies, especially the synthesis of 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline[10] (**7**) (Figure 3).

5,5″-Dimethyl-2,2′:6′,2″-terpyridine (**2**) was prepared from 2-acetyl-5-methylpyridine, first converted to **1**, according to the method used by Jameson and al.[13] **2** was transformed into the organolithium derivative by action of LDA[14] at low temperature and added to a solution of protected bromoethanol, tetrahydropyranyl-2-bromoethyl ether,[15] giving **3**. **4** was obtained by deprotection of both alcohol functions in slightly acidic media[15] and converted into **5** by reaction with mesylate chloride in CH₂-Cl₂.[16] **6** was finally obtained from **5** and anhydrous LiBr in acetone.[17] **6** and **7** were reacted in DMF (60 °C under argon) in presence of Cs₂CO₃, in high dilution conditions, leading to the macrocycle **9** with 58% yield. Using similar conditions, the macrocycle **8**, containing only one dpp unit and no terpy

moiety, was prepared from **7** and the hexaethyleneglycol diiodo derivative (yield 60%). Since our target-catenate is disymmetrical, two different precursors are possible, according to the two-step synthesis described above (vide supra). Both possibilities are illustrated in Figure 4.

The threaded precursor **10**⁺ can be prepared from the macrocycle **8** and the acyclic ligand **7** and then reacted with the terpy-containing fragment **6**. The precursor **12**⁺ can also be constructed with the macrocycle **9** and the acyclic ligand **7**, thus reacted afterwards with the hexaethyleneglycol diiodo derivative. In both cases, the formation of the precursor is quantitative thanks to the sequential addition of reactants and is confirmed by ¹H-NMR spectroscopy. Due to the presence of the second chelate (terpy) in the macrocycle **9**, a mixture of two copper precursors could have been formed: one consisting of the desired tetrahedral Cu(dpp)₂⁺ complex, the other containing the 4-coordinate Cu(dpp)(η²-terpy)⁺. Neither TLC experiments, nor NMR spectrocopy indicated formation of the latter, leading to the conclusion that the complex Cu(dpp)₂⁺ is thermodynamically more stable. This conclusion is supported by literature,[18] mentioning the better π-accepting properties of a phenanthroline as compared to a bipyridine unit, as well as the strong stabilizing effect of substituents on α positions for Cu(I) complexes. From this point of view, the dpp unit, with its two phenyl groups, is better suited than the terpy unit, one pyridine playing the role of the α-substituent but the other ortho position to a nitrogen atom being unsubstituted. This remark will be of some importance in the following electrochemical experiments (vide infra). In both cases, the target compound **11**·PF₆ is obtained with 8−10% yield, via simultaneous addition of reactants in a hot Cs₂CO₃/DMF suspension, and subsequent ion exchange and chromatographies on silica gel columns. It is characterized by NMR spectroscopy and elemental analysis, and the characteristic fragmentation pattern was obtained by mass-spectrometry asserting its topology.[19] By action of KCN on the catenate **11**⁺, the free ligand **13** is obtained and characterized[10] (Figure 5). Its topology is also confirmed by mass spectrometry. Reaction of **13** with a copper(II) salt (Cu(BF₄)₂) leads to the most stable coordination geometry, i.e. CuᴵᴵN₅, where the metal is complexed by one dpp unit and the terpy nucleus. The composition of the complex is confirmed by mass spectrometry and elemental analysis, its physicochemical properties supporting the 5-coordination hypothesis (vide infra).

(13) Guise, L.; Jameson, D. L. *Tetrahedron Lett.* **1991**, *32*, 1999−2002.

(14) Crane, J.; Sauvage, J. P. *New. J. Chem.* **1992**, *16*, 649−650. Chambron, J. C.; Sauvage, J. P. *Tetrahedron* **1987**, *43*, no. 5, 895−904.
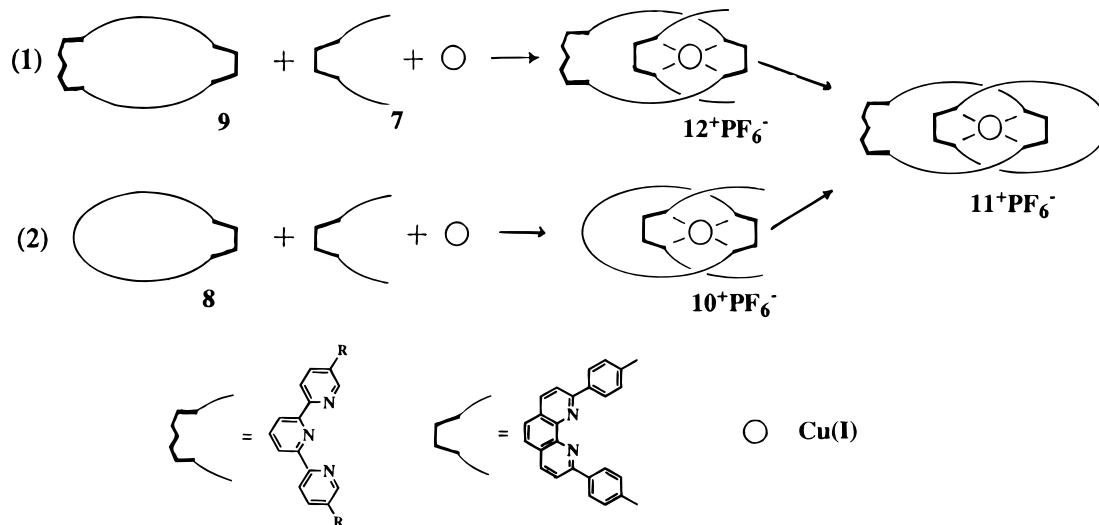
(15) Wälchi, P. C.; Engster, R. *Helv. Chim. Acta* **1978**, *61*, 885−898.

(16) Martin, A. E.; Bulkowski, J. E. *J. Org. Chem.* **1982**, *47*, 415−418.

(17) Nierengarten, J. F.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 375−376.

(18) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007−2019.

(19) Vetter, W.; Logemann, E.; Schill, G. *Org. Mass. Spectrom.* **1977**, *12*, 351; Dietrich-Buchecker, C. O.; Sauvage, J. P. *Chem. Rev.* **1987**, *87*, 795.

**Figure 4.** The two strategies based on a two-step approach: two threaded precursor (**10$^+$** and **12$^+$**) are possible, depending on which macrocycle is used (**8** and **9**, respectively). Reaction of each precursor with the complementary fragment affords the target disymmetrical catenate **11$^+$**. In both cases a 10% yield was obtained.
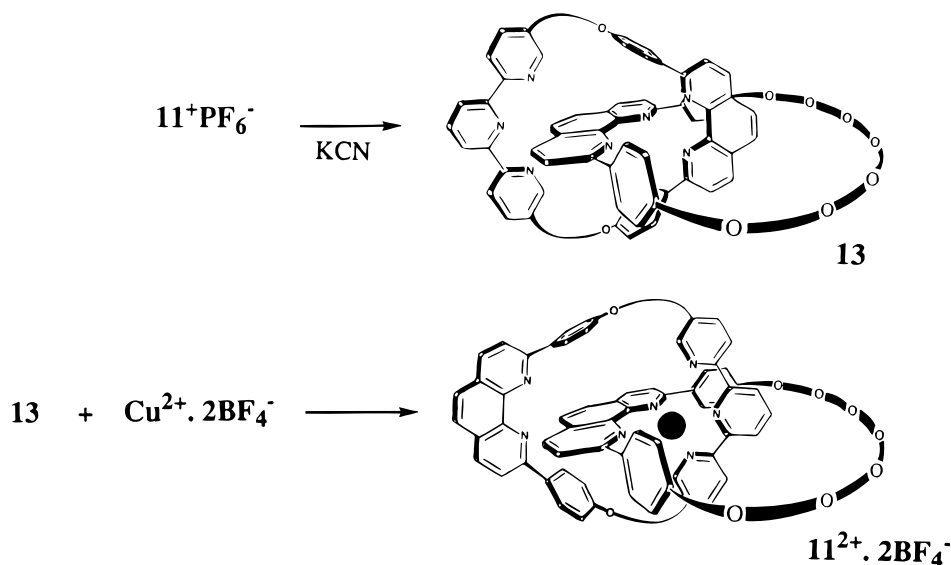


**Figure 5.** Decomplexation of the copper(I) catenate by reaction with KCN gives the free ligand **13**. Remetalation leads to the thermodynamically stable 5-coordinate Cu(II) catenate.

In the square scheme describing the behavior of our catenate (Figure 1), two specific complexes can be directly obtained via synthesis and thus be fully characterized: Cu$^I$N$_4$ and Cu$^{II}$N$_5$. Cu$^I$N$_4$ corresponds to the coordination of both dpp units around the cation, a complex already present in other catenates synthesized previously in our group.[10] Analysis of the data given by $^1$H-NMR spectroscopy, electrochemistry, and UV-visible absorption spectroscopy provides the characteristics of the pseudo-tetrahedral Cu$^I$(dpp)$_2$ complex: (1) the signals of the phenyl protons in position 2,9 are shifted to high field because of the phenanthroline ring current;[20] (2) the redox potential of the Cu$^{I/II}$N$_4$ couple in acetonitrile is +0.63V vs SCE, indicating a strong stabilization of the low oxidation state;[10] (3) a MLCT absorption band is observed at 437 nm ($\epsilon$ 2500) in acetonitrile, resulting in a red-brown solution. This confirms the entwined arrangement of both dpp units around Cu(I).

The geometry of the copper(II) catenate obtained via decomplexation and remetalation has been confirmed by comparison of its physical and chemical properties with those of the literature

compounds, whose structures have already been established. Its redox potential is −0.07V vs SCE in acetonitrile, indicating a good stabilization of the copper(II) state. UV-visible absorption spectroscopy reveals a band centered at 636 nm ($\epsilon$ 125) in acetonitrile, corresponding to a d-d transition, resulting in a pale olive-green solution. This value can be compared with the one obtained for the 5-coordinated complex Cu$^{II}$(terpy)(bipy)(ClO$_4$)$_2$: 640 nm ($\epsilon$ 120),[21] as well as for the same complex present in a copper(II) helicate recently synthesized.[22] In collaboration with Kaim and Baumann, EPR spectroscopy measurements on the catenate[23] were recently performed, which showed an anisotropic signal characteristic of an axial symmetry coordination around Cu(II) ($g_{||}$ = 2.233; $g_\perp$ = 2.045; $A_{||}$ = 16.6 mT in acetonitrile at 110 K). We compared these data with those measured for a 5-coordinate complex [Cu($\eta^3$-L)($\eta^2$-L)]-

(20) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P.; Kintzinger, J. P.; Maltese, P. *Nouv. J. Chim.* **1984**, *8*, 573−582.

(21) Harris, C. M.; Lockyer, T. N. *Aust. J. Chem.* **1970**, *23*, 673−682. Arena, G.; Bonomo, R. P.; Musumeci, S.; Purello, R.; Rizzarelli, E.; Sammartano, S. *J. Chem. Soc., Dalton Trans.* **1983**, 1279−1283.

(22) Hasenknopf, B.; Lehn, J.-M.; Baum, G.; Fenske, D. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 1397−1400.

(23) Baumann, F.; Livoreil, A.; Kaim; W.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1996**, 35−36.
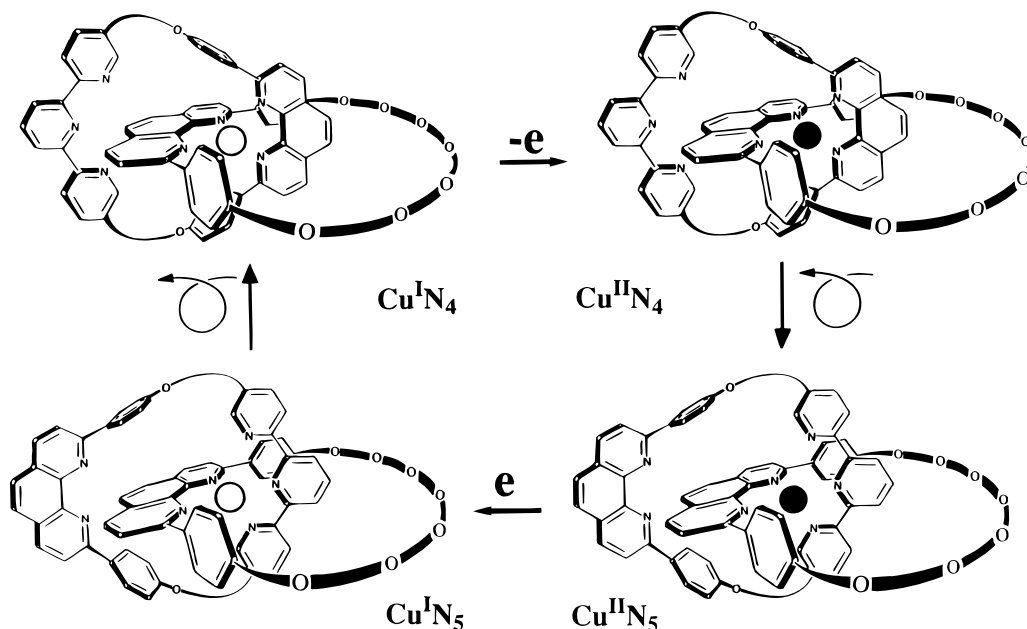
**Figure 6.** The molecular square scheme illustrating the response of the catenate to an electrochemical signal: oxidation or reduction generates a metastable complex which rearranges to adopt the coordination mode best fitting the new oxidation state of the metal center. The white and black circles stand, respectively, for Cu(I) and Cu(II). Each complex is distinguished through its number of coordinated nitrogen atoms (CuN$_x$, $x = 4$ or 5).

(ClO$_4$)$_2$, containing the potential terdentate 2,6-bis(benzimidazol-2′-yl)pyridine ligand L and showing square-pyramidal configuration at the metal ion ($g_{||} = 2.23$, $g_\perp = 2.03$; $A_{||} = 16.7$ mT).[24] The similarity of all these data tends to confirm the 5-coordination of the metal cation in our catenate through entwining of one dpp and the terpy, as summarized in the notation Cu$^{II}$N$_5$. It also seems reasonable to suggest a square-pyramidal configuration of the metal.

**The Copper Catenate in Motion.** The scheme we used to describe the concept of the catenate motions (Figure 1) can now be transcripted in terms of molecules, as illustrated in Figure 6.

As discussed in the previous section, we could isolate and characterize the two most stable states Cu$^I$N$_4$ and Cu$^{II}$N$_5$. In addition, there are two states, corresponding to a nonappropriate coordination of the metal center: Cu$^{II}$N$_4$ and Cu$^I$N$_5$. Our aim was to generate *in situ* a metastable state by oxidation or reduction, and at monitoring its linkage isomerism toward the stable complex best fitting the new oxidation state of the metal. Each time, we compare the properties of the new species with those of the two characterized stable complexes Cu$^I$N$_4$ and Cu$^{II}$N$_5$. We first monitored this process via UV-visible absorption spectroscopy. A solution of Cu$^I$N$_4$ in acetonitrile, showing an intense red-brown color, is oxidized by addition of Br$_2$ in solution in acetonitrile or NOBF$_4$ as a solid (Figure 7). The solution turns deep green (pine-tree green), the spectrum indicating a d-d absorption band at 670 nm ($\epsilon$ 800). The spectrum is superimposable with those of catenates or complexes containing the same Cu(dpp)$_2$$^{2+}$ unit.[10]

The intensity of this absorption band decreases with time, accompanied by a 30 nm hypsochromic shift, resulting in a change of the solution color from pine-tree to pale olive green (Figure 8). After several hours, the absorption band is centered at 640 nm ($\epsilon$ 125). This spectrum is completely superimposable with the one obtained for the copper(II) catenate Cu$^{II}$N$_5$, under the same conditions of concentration and solvent. This shift

(24) Sanni, S. B.; Behm, H. J.; Beurskens, P. T.; Van Albada, G. A.; Reedijk, J.; Lenstra, A. T. H.; Addison, A. W.; Palaniandavar, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1429−1435.
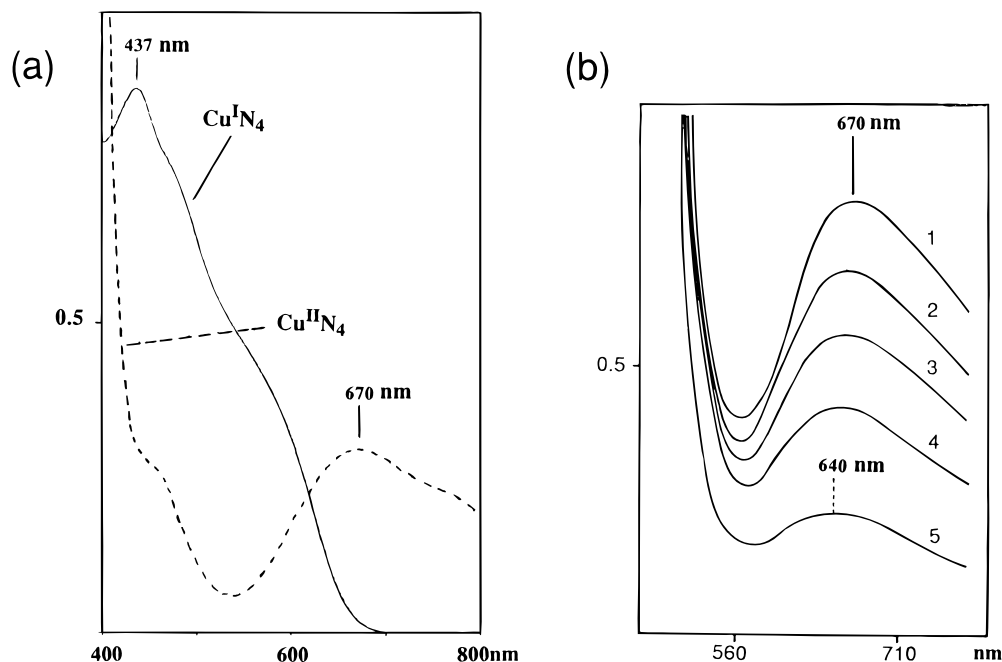
can be explained in terms of a stronger ligand field around the cation because of an increased coordination number, as well as a modification of the coordination geometry (from pseudo-tetrahedral to square-pyramidal).

We thus conclude that after oxidation of Cu$^I$N$_4$, the catenate underwent a linkage isomerization through a gliding motion of one ring in the other, transforming the metastable complex Cu$^{II}$N$_4$ into the more favorable one Cu$^{II}$N$_5$. Addition of hydrazine monohydrate or ascorbic acid triggers the reverse process: the solution turns red-brown and shows an absorption identical to that of the Cu$^I$N$_4$ starting complex. It is reasonable to suggest that this form consists of both dpp units entwined around the metal cation, since this complex appeared as the most thermodynamically stable on synthesis of the precursor **12$^+$** (vide supra). This hypothesis was also confirmed by the following electrochemical experiments.

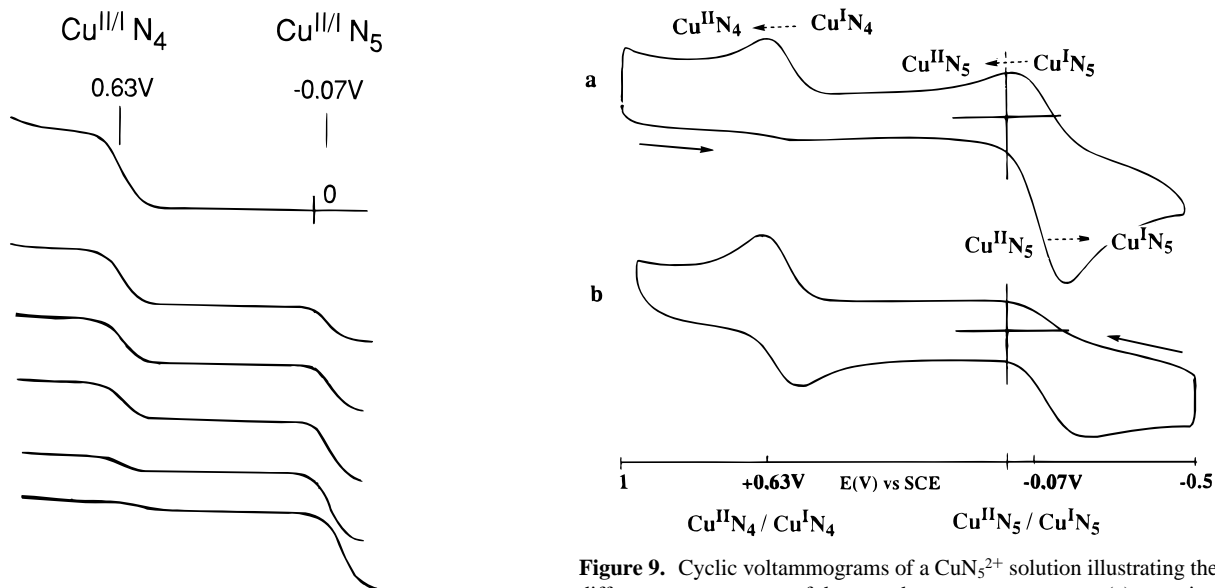**Electrochemically-Driven Motion.** An acetonitrile electrolyte solution of the copper(I) catenate (Cu$^I$N$_4$), was oxidized on a platinum electrode (0.1 M TBABF$_4$, applied potential = +0.8V vs SCE, 1.5 h). The red solution progressively turns deep green. A cyclic voltammogram of the solution shows a reversible signal at 200 mV/s, centered at +0.63V vs SCE, i.e. corresponding to the couple Cu$^{II/I}$N$_4$. A series of linear-sweep voltammetries were then carried out, indicating a decrease of the signal at +0.63 V with time, while a new signal at −0.07 V appeared (Figure 8). After several hours, the signal of the new species has gained the original intensity of the tetrahedral species Cu$^{II}$N$_4$, the signal of the latter having almost disappeared. The color of the solution is then olive green.

The potential −0.07V is identical to the one measured for the copper(II) metalated catenane, i.e. Cu$^{II}$N$_5$. Inversely, a reductive electrolysis of the solution (−0.4 V, 1.5 h) regenerates the original red color, as well as a unique signal at +0.63 V. No signal corresponding to free copper in solution is observed, nor has the intensity of the signal decreased. An electrospray mass spectrometry experiment carried out on a sample of this solution reveals no traces of free ligand. This indicates that we have monitored electrochemically the oxidation of the complex Cu$^I$N$_4$ and its subsequent linkage isomerism leading

**Figure 7.** (a) Visible absorption spectra of a $0.35 \times 10^{-4}$ M solution of the tetrahedral Cu(I) complex $Cu^IN_4$ ($\lambda_{max} = 437$ nm, MLCT d $\rightarrow \pi^*$ transition) and of its oxidized form $Cu^{II}N_4$ ($\lambda_{max} = 670$ nm, d-d transition) in acetonitrile (oxidant: solid $NOBF_4$) and (b) visible absorption spectroscopy monitoring of the Cu(II) changeover process: (**1**) freshly oxidized solution of $Cu^IN_4$, (2) after 11h, (3) after 24h, (4) after 34h, (5) after 70 h, the process is almost completed, $Cu^{II}N_5$ is the major species; (acetonitrile solution, $10^{-3}$ M, room temperature, oxidant $Br_2$ in acetonitrile).



**Figure 8.** Electrochemical monitoring of the Cu(II) changeover process: after oxidative electrolysis of an acetonitrile solution of $Cu^IN_4$ ($10^{-3}$ M), linear-sweep voltammetry is carried out. The upper curve is obtained immediately after electrolysis and corresponds predominently to the 4-coordinate species. After 20 h, the bottom voltammogram is obtained and shows almost exclusively the response of the 5-coordinate complex. Redox Potentials ($E_{1/2}$): $Cu^{II/I}N_4 + 0.63$V; $Cu^{II/I}N_5 - 0.07$ V; (0.1 M $nBu_4NBF_4$, $BF_4$, Pt electrode, SCE, 5 mV/s, 1 V to $-0.5$ V).



**Figure 9.** Cyclic voltammograms of a $CuN_5{}^{2+}$ solution illustrating the different rate constants of the two changeover processes: (a) scanning from 1 V to $-0.5$ V first, (b) scanning from $-0.5$ V to 1 V first. ($CH_3$-CN, 0.1 M $nBu_4NBF_4$, $BF_4$, Pt electrode SCE, 200 mV/s).

to the complex $Cu^{II}N_5$. Inversely, the reduction of this complex has triggered the reformation of the complex $Cu^IN_4$, by an opposite gliding motion of the ring.

A similar experiment was conducted in collaboration with Kaim and Baumann:[23] after electrochemical oxidation of an acetonitrile electrolyte solution of the complex $Cu^IN_4$, the changeover process was monitored by EPR spectroscopy. The evolution of the spectra with time indicated a relaxation of the

coordination geometry around the Cu(II) cation, in agreement with the conversion of the pseudo-tetrahedral configuration in $Cu^{II}N_4$ into the square-pyramidal configuration assumed in $Cu^{II}N_5$.

As indicated by the above-mentioned experiments, the two changeover processes, $Cu^{II}N_4$ to $Cu^{II}N_5$ and $Cu^IN_5$ to $Cu^IN_4$, do not proceed at the same speed. The first one is a slow evolution allowing to characterization of the metastable complex $Cu^{II}N_4$, whereas the second one was too fast to allow isolation of the complex $Cu^IN_5$. This discrepancy clearly appears in the cyclic voltammograms of a solution of the 5-coordinate complex $Cu^{II}N_5$ (Figure 9).

Cyclic voltammetry is carried out between $+1.0$ V and $-0.5$ V vs SCE, on platinum, using an acetonitrile electrolyte solution (0.1 M $nBu_4NBF_4$, 200 mV/s). Starting at $+1$ V (voltammo-

gram a), the first wave represents the reduction of $Cu^{II}N_5$ into $Cu^IN_5$ at $-0.07$ V. On the reverse sweep, the corresponding oxidation wave has a much smaller intensity, whereas a second oxidation wave has appeared at $+0.63$ V, the characteristic potential of the redox couple $Cu^{II/I}N_4$. This indicates that as soon as it was reduced at the electrode, a certain amount of the 5-coordinate complex $Cu^IN_5$ rearranged rapidly into the 4-coordinate form $Cu^IN_4$. When the scan direction is reversed (voltammogram b), i.e. starting at $-0.5$ V, the first wave at $-0.07$ V represents the oxidation of the electrode-generated 5-coordinate complex $Cu^IN_5$, where as the second wave at $+0.63$ V corresponds to the oxidation of the complex $Cu^IN_4$. The second wave is much higher than the first one, indicating a *rapid* changeover from $Cu^IN_5$ to $Cu^IN_4$. By contrast, the signal of the 4-coordinate complex is almost symmetrical, indicating that the metastable species $Cu^{II}N_4$ evolves *slowly*. The height of the reduction wave at $-0.07$ V ($Cu^{II}N_5$ to $Cu^IN_5$) comes from a diffusion phenomenon since we are in a $Cu^{II}N_5$ solution. An approximate value of the rate constant of the changeover process from $Cu^IN_5$ to $Cu^IN_4$ can be obtained using the method described by Nicholson and Shain.[25] By measuring the relative intensity of oxidation and reduction waves of the $Cu^{II/I}N_5$ couple as a function of scan-rate, we obtained a value of $1$ s$^{-1}$ for the changeover rate. This value is very small as compared to usual substitution rate constants observed for copper(I) complexes.[26] A topological effect is supposedly responsible for this comparatively slow process, similar to what had been observed in the study of formation kinetics of copper(I) catenate.[27] Nonetheless, one can also reasonably assume that this rate is sensitive toward the coordinative properties of the solvent and the presence of any coordinating species in the medium. Indeed such an influence has been observed and studied in detail in the case of substitution of biquinoline by dimethylphenanthroline on copper(I),[28] indicating a strong accelerating effect of acetonitrile as well as iodide ions. A more accurate study of the kinetics of the Cu(I) changeover process in our catenate is conducted at the moment.
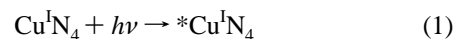
As for the Cu(II) changeover process, leading to $Cu^{II}N_5$ from $Cu^{II}N_4$, the spectroscopic monitoring experiments carried out in various conditions indicate a drastic influence on the kinetics of the solvent, the traces of water, and the presence of chloride ions. In each case, an electrolyte solution of the complex $Cu^IN_4$ is chemically oxidized, and the intensity of the absorption band characteristic of the complex $Cu^{II}N_4$ (670 nm) is monitored as a function of time. The presence of water strongly slows down the linkage isomerism process, supporting the hypothesis of formation of a 5-coordinate complex including a water molecule, $Cu^{II}N_4OH_2$. This has been already observed[29,30] for the related complex $Cu(dmp)_2^{+2}$ and suspected for the complex $Cu(dap)_2^{+2}$, where dmp is 2,9-dimethyl-1,10-phenanthroline and dap is 2,9-diphenyl-1,10-phenanthroline. As compared to the metastable form $Cu^{II}N_4$, this 5-coordinate complex is kinetically stabilized. By contrast, in the presence of chloride ions, the changeover process is strongly accelerated.

The formation of the $Cu^{II}-Cl$ bond is mentioned in the literature,[31] its strength depending on the polarity of the solvent. In dichloromethane, which is less polar than acetonitrile, the isomerism process is slower, but the addition of chloride ions (as a solution of $nBu_4NCl$ in $CH_2Cl_2$) increases the changeover rate in a drastic manner: the total reaction time required for complete transformation of $Cu^{II}N_4$ diminishes from hours to 2 min. We suspect that formation of a Cu-Cl bond weakens the other Cu$-$N bonds in $Cu^{II}N_4$ (similar to a ligand-assisted removal[32]) and thus enables the faster substitution of the dpp unit by the terpy unit. In addition, in the course of the changeover process, removal of a dpp unit from the copper(II) coordination sphere has to proceed before any interaction between the metal center and the entering terpy ligand is possible. This implies that the copper(II) atom be "half-naked" at some stage. If Cl$^-$ is present in the medium, it could interact with the metal in this coordinatively unsaturated complex, in a transitory fashion, and thus lower the activation barrier of the rearrangement by stabilizing intermediate states.

The same rearrangement experiments performed in a Cu(II)- or Cu(I)-containing medium indicates no influence of free copper on the changeover rate constant. This supports the hypothesis of an intramolecular process. As a conclusion, concerning the kinetic aspects of the present system, the strong dependence of the isomerism rate constants on the experimental conditions can be considered as a "solvent and ion tuning" opportunity. One can then determine the response of the catenate to the signal, by including deliberately "accelerating" or "decelerating" agents in the medium, such as chloride ions or water, respectively.

**Photochemically-Driven Motion.** It is well known that in Cu(I) complexes of polypyridine ligands the lowest triplet MLCT excited state is luminescent, has a reasonably long lifetime, and can play the role of electron-transfer reagent.[33-35] $Cu^IN_4$ shows a MLCT emission band (Figure 12, inset) with $\lambda_{max} = 750$ nm and $\tau = 60$ ns in aerated acetonitrile solution at 298 K (730 nm and 115 ns in aerated $CH_2Cl_2$). Therefore, it should be possible to cause the first step of the overall swinging process indicated in Figure 6, namely the conversion of $Cu^IN_4$ into $Cu^{II}N_4$, by photoexcitation (eq 1) followed by an excited state oxidation process in the encounter with a suitable oxidant (eq 3):

$$Cu^IN_4 + h\nu \rightarrow {}^*Cu^IN_4 \qquad (1)$$

$$^*Cu^IN_4 \rightarrow Cu^IN_4 + \text{heat or } h\nu' \qquad (2)$$

$$^*Cu^IN_4 + Ox \rightarrow Cu^{II}N_4 + Red \qquad (3)$$

$$Cu^{II}N_4 + Red \rightarrow Cu^IN_4 + Ox \qquad (4)$$

$$Red \rightarrow products \qquad (5)$$

The occurrence of the excited state electron transfer process (eq 3) competes with the luminescence (eq 2) which is therefore a useful tool to evaluate whether reaction 3 takes place.

The reduction potential of the $Cu^{II}N_4/^*Cu^IN_4$ couple can be evaluated from the reduction potential of the $Cu^{II}N_4/Cu^IN_4$

(25) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 4, 706−723.

(26) *Inorg. Chem.* **1975**, *14*, 1716−1717.

(27) Albrecht-Gary, A. M.; Dietrich-Buchecker, C. O.; Saad, Z.; Sauvage, J. P. *J. Am. Chem. Soc.* **1988**, *110*, 1467−1472.

(28) Frei, U. M.; Geier, G. *Inorg. Chem.* **1992**, *31*, 3132−3137.

(29) Hall, J. R.; Marchant, N. K.; Plowman, R. A. *Aust. J. Chem.* **1963**, *16*, 34−41. Sundararajan, S.; Wehry, E. L. *J. Phys. Chem.* **1972**, *76*, 1528−1536. Al-Shatti, N.; Lappin, A. G.; Sykes, A. G. *Inorg. Chem.* **1981**, *20*, 1466−1469.

(30) Geoffroy, M.; Wermeille, M; Dietrich-Buchecker, C. O.; Sauvage, J. P.; Bernardinelli, G. *Inorg. Chim. Acta* **1990**, *167*, 157−164.

(31) McConnell, H. M.; Weaver, H. E. *J. Chem. Phys.* **1956**, *25*, 307−311. Khan, M. A.; Schwing-Weill, M. J. *Inorg. Chem.* **1976**, *15*, 2202−2205. Hall, J. R.; Marchant, N. K., Plowman, R. A. *Aust.J. Chem.* **1962**, *15*, 480−485. Krüger, H. J. *Chem. Ber.* **1995**, *128*, 531−539.

(32) R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; VCH: New York, 1991; p 214.

(33) Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Inorg. Chem.* **1989**, *28*, 4070−4072. Everly, R. M.; McMillin, D. R. *J. Phys. Chem.* **1991**, *95*, 9071−9075, and references therein. Dietrich-Buchecker, C. O.; Nierengarten, J.-F.; Sauvage, J.-P.; Armaroli, N.; Balzani, V.; De Cola, L. *J. Am. Chem. Soc.* **1993**, *115*, 11237−11244. Armaroli, N.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Sauvage, J.-P.; Hemmert, C. *J. Am. Chem. Soc.* **1994**, *116*, 5211−5217.

couple (+0.63 V vs SCE, in acetonitrile) and the energy of the $*Cu^IN_4$ excited state (about 1.65 eV, as estimated from the maximum of the emission band in the same solvent) by the following equation:[36]

$$E°(Cu^{II}N_4/*Cu^IN_4) \approx E°(Cu^{II}N_4/Cu^IN_4) - E' = -1.02 \text{ V}$$

$$(7)$$

where $E'$ is the one-electron potential corresponding to the spectroscopic energy of $*Cu^IN_4$ excited state. This shows that even a mild oxidant should be sufficient to oxidize the photoexcited $*Cu^IN_4$ catenate (eq 3). Nevertheless, the choice of the oxidant is not a trivial matter because other important requirements have to be satisfied: (i) the oxidant should not compete with $Cu^IN_4$ for light absorption, (ii) the reaction between $*Cu^IN_4$ and the oxidant (eq 3) should be fast enough to compete with the intrinsic excited state decay (eq 2), and (iii) after reduction, the oxidant should undergo a very fast, irreversible decomposition reaction (eq 5) in order to prevent the occurrence of the back electron-transfer reaction (eq 4). In the case of Ru(II) polypyridine compounds, photooxidation is usually performed by using Co(III) amine complexes.[37] We have tried to use $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5(NO_2)]^{2+}$, but we have found that, because of the short excited state lifetime and the slow rate of the bimolecular process (eq 3), the concentrations of the Co(III) complexes should have been so high as to prevent light absorption by the $Cu^IN_4$ catenate. Therefore we have decided to use *p*-nitrobenzylbromide, *p*-$NO_2C_6H_4CH_2Br$, which satisfies requirements i and iii,[38] and had previously been used to quench the excited state of other Cu(I) complexes.[39] By a Stern–Volmer analysis[40] (Figure 10), we have found that the rate constant of the quenching process (eq 3) was $4.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile solution. Since the lifetime of $*Cu^IN_4$ in air-equilibrated acetonitrile at 25 °C is 60 ns, we have therefore estimated that a sufficiently large fraction of the $*Cu^IN_4$ excited states can react with the quencher even using reasonably low concentrations ($10^{-1}-10^{-2}$ M) of *p*-$NO_2C_6H_4CH_2Br$.

The photochemical experiments were performed by exciting with 464 nm light acetonitrile solutions containing $1.0 \times 10^{-4}$ M $Cu^IN_4$ and $5.0 \times 10^{-2}$ M *p*-$NO_2C_6H_4CH_2Br$. Under these conditions, all the exciting light is absorbed by the Cu(I) catenate. Light excitation was found to cause the spectral changes shown in Figure 11. Such spectral changes clearly indicate the disappearance of $Cu^IN_4$ and the concomitant formation of $Cu^{II}N_4$ as the only reaction product. The overall quantum yield of the photoreaction was about 3%. Since the

(34) Kirchoff, J. R.; Gamache, R. E., Jr.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380–2384. Blaskie, M. W.; McMillin, D. R. *Inorg.Chem.* **1980**, *19*, 3519–3522.

(35) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P.; Kirchhoff, J. R.; McMillin, D. R. *J. Chem. Soc. Chem. Commun.* **1983**, 513–515. Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C.; Sauvage, J. P. *Inorg.Chem.* **1989**, *28*, 4070–4072. Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Tetrahedron Lett.* **1982**, *23*, 5291–5294. Edel, A.; Marnot, P. A.; Sauvage, J. P. *Nouv. J. Chim.* **1984**, *8*, 495–498.

(36) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1–64.

(37) See e. g. Sandrini, D.; Gandolfi, M. T.; Maestri, M.; Bolletta, F.; Balzani, V.; *Inorg.Chem.* **1984**, *23*, 3017–3023. Zahir, K.; Boettcher, W.; Haim, A. *Inorg. Chem.* **1985**, *24*, 1966–1968.
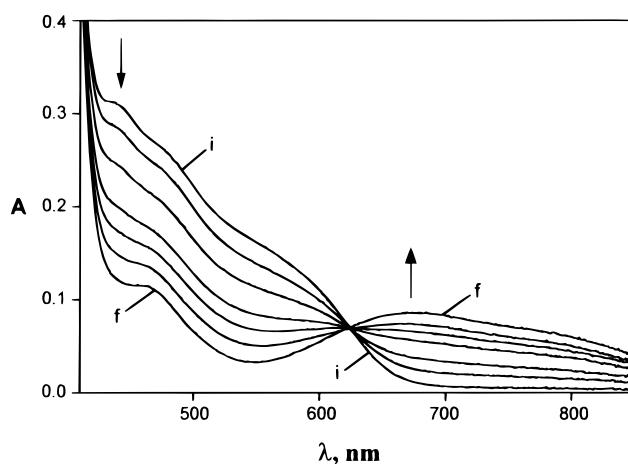
(38) In acetonitrile solution, *p*-$NO_2C_6H_4CH_2Br$ shows a band with $\lambda_{max}$ = 273 nm which does not interfere in the visible light absorption by $Cu^IN_4$. On reduction of *p*-$NO_2C_6H_4CH_2Br$, a benzylic radical is formed which undergoes a fast dimerization reaction. In the presence of dioxygen, the benzylic radical gives rise to a series of reactions which end with formation of *p*-nitrobenzaldeyde.[39]

(39) Kern, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 546–548.

(40) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.
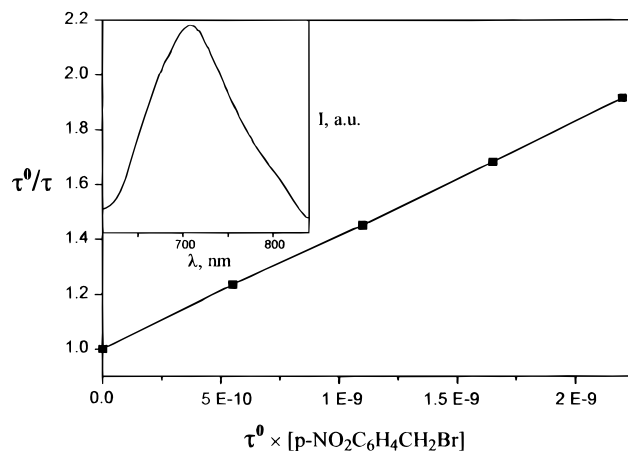


**Figure 10.** Stern–Volmer plot for the quenching of the $Cu^IN_4$ luminescence by *p*-$NO_2C_6H_4CH_2Br$ in acetonitrile solution at 298 K. The inset shows the uncorrected luminescence spectrum of $Cu^IN_4$ in acetonitrile solution at 298 K.



**Figure 11.** Spectral changes caused by photoexcitation of an acetonitrile solution containing $1.0 \times 10^{-4}$ M $Cu^IN_4$ and $5.0 \times 10^{-2}$ M *p*-$NO_2C_6H_4CH_2Br$. The isosbestic point is at 625 nm. (i) The initial spectrum; (f) the final spectrum obtained after 20 min of irradiation.

fraction of $*Cu^IN_4$ excited states reacting with the quencher is 55%, the fraction of quenching events that give rise to a permanent formation of $Cu^{II}N_4$ is $\approx 5\%$. Since *p*-$NO_2C_6H_4$-$CH_2Br$ cannot quench $*Cu^IN_4$ by energy transfer, the low efficiency of the photoinduced process has to be attributed to a competition between reactions 4 and 5. Under the experimental conditions used, practically complete transformation of $Cu^IN_4$ into $Cu^{II}N_4$ was achieved in about 20 min. The results obtained also showed that $Cu^{II}N_4$ is not photosensitive.

At the end of the photoreaction, the irradiated solution was kept in the dark at 298 K. Spectrophotometric measurements showed that a slow reaction was occurring, causing a general decrease in absorbance, particularly in the 600–800 nm region, as expected for the transformation of $Cu^{II}N_4$ into the more stable $Cu^{II}N_5$ species (Figure 6). After about 48 h, no further spectral change was observed. At this stage, the spectrum of the solution (curve c in Figure 12) was that of the stable $Cu^{II}N_5$ species. In order to complete the cycle (Figure 6), we added to the solution an excess of ascorbic acid (dissolved in MeOH). We observed a gradual reappearance of the spectrum of $Cu^IN_4$. After about 30 min, the spectrum was practically coincident with the initial spectrum (Figure 12), showing that the cyclic process (Figure 6) was completed.

One can wonder whether, besides the oxidation step, the reduction step can also be induced by light. We believe that
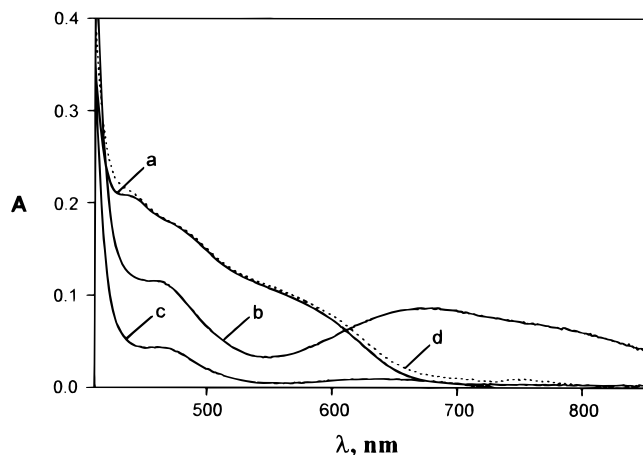
**Figure 12.** Absorption spectra of $Cu^IN_4$ in acetonitrile solution: (a) before light excitation; (b) at the end of the photoreaction with $p$-$NO_2C_6H_4CH_2Br$ (20 min irradiation); (c) after subsequent 24 h in the dark; (d) 30 min after subsequent addition of an excess of ascorbic acid.

this cannot be the case for the following reasons. $Cu^{II}N_5$ is not photosensitive and does not exhibit any luminescence. This is an expected result since in Cu(II) complexes ($d^9$ electronic configuration) the lowest excited state is a low energy, distorted ligand-field level which undergoes very fast radiationless decay to the ground state.[41] Therefore it is not possible to involve $Cu^{II}N_5$ in a bimolecular reaction where an excited state of the complex should play the role of electron donor. On the other hand, even a photochemical reaction based on the addition of an electron donor photosensitizer seems impracticable not only for the extreme complexity of the system (at this stage, the solution would also contain a large amount of unreacted $p$-$NO_2C_6H_4$-$CH_2Br$), but also because of the quenching by energy transfer of the photosensitizer by $Cu^{II}N_5$.

**Conclusion.** The three-dimensional matrix effect of the copper(I) cation has allowed the synthesis of a new copper [2]-catenate. Thanks to its topology and to the different composition of its constitutive macrocycles, this catenate is able to adopt two geometries, each stabilizing preferentially a different oxidation state of the metal center. The changeover process from one geometry to the other can be triggered by chemical, electrochemical, and photochemical stimuli. Its cyclic functioning is reversible, reproducible and easily followed through color changes. The speed of the response (changeover) is controlled at will by the experimental conditions, allowing a great variability of rates.

## Experimental Section

**Materials and General Procedures.** The following chemicals were obtained commercially and were used without further purification: $Cs_2$-$CO_3$ (Aldrich), KCN (Jannsen), $KPF_6$ (Jannsen), *N,N*-dimethylforma-mide dimethylacetal (DMFDMA), tBuOK, LDA, MesCl, LiBr. $nBu_4$-$NBF_4$ was recrystallized twice in a mixture of methanol and water and dried under vacuum at 60 °C overnight. The following materials were prepared according to literature procedures: $Cu(MeCN)_4PF_6$,[42] 2,9-bis-(*p*-hydroxyphenyl)-1,10-phenanthroline,[10] 2-acetyl-5-methyl-pyridine,[43] tetrahydropyranyl-2-bromoethanol.[15] Dry solvents were distilled from suitable desiccants ($Et_2O$ and THF from Na, MeCN and $CH_2Cl_2$ from $P_2O_5$) according to literature methods. Thin-layer chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 $F_{254}$ (Merck 5554), or coated with neutral alumina 60 $F_{254}$ (Merck 5550).

After elution, the plates were either scrutinized under a UV lamp or exposed to $I_2$, or, for terpyridine derivatives, put in a solution of $(NH_4)_2$-$Fe^{II}(SO_4)_2,6H_2O$ in $MeOH/H_2O$ 50:50. Column chromatography was carried out on silica gel 60 (Merck 9385, 230−400 mesh) and neutral alumina 90 (Merck 1076, 0.060−0.200mm). UV-visible spectra were recorded on a Kontron Instruments UVIKON 860 spectrophotometer. Fast atom bombardment mass spectrometry (FABMS), was recorded in the positive ion mode with either a krypton primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a Kratos MS80RF mass spectrometer coupled to a DS90 system, or a xenon primary atom beam with the same matrix and a ZAB-HF mass spectrometer. Electrospray mass spectrometry was recorded in the positive ion mode by dissolving the compound or complex in MeCN or $CH_2Cl_2$ at a concentration of 50 pmol $mL^{-1}$, and injecting the solution into a VG BioQ triple quadrupole spectrometer (VG BioTech Ltd., Altrincham, UK), with a mass-to-charge (*m/z*) range of 4000, using a cone voltage ($V_c$) of 40 V, with a source temperature of approximately 30 °C. The $^1H$ NMR spectra were recorded on either Bruker AC 300 (300 MHz), WP200 SY (200 MHz) or WP400SY (400 MHz) spectrometers (using the deuterated solvent as the lock and residual solvent as the internal reference).

**Electrochemistry.** Electrochemical experiments were performed with a three-electrode system consisting of a platinum working electrode, a platinum-wire counter-electrode, and a standard reference calomel electrode, versus which all potentials are reported. All measurements were carried out under argon, in degassed spectroscopic grade solvents, using 0.1 M $nBu_4NBF_4$ solutions as electrolytes. A potentiostat EG&G Princeton Applied Research Model 273A connected to a computer was used (software: Programme Research Electrochem-istry Software), as well as a potentiostat Bruker E130M, connected to a printing table.

**Photochemistry.** All the photochemical experiments were per-formed in acetonitrile (Carlo Erba for spectroscopy). The concentration of $Cu^IN_4$ (as $PF_6^-$ salt) was $1.0 \times 10^{-4}$ M and that of $p$-$NO_2C_6H_4CH_2$-Br was $5.0 \times 10^{-2}$ M. The solutions, continuously stirred, were irradiated with a 150 W xenon lamp (Osram XBOW/1) at 464 nm using a slit of 2.5 mm (9.4 nm). The absorption spectra were recorded with a Perkin-Elmer l5 spectrophotometer, using 1 cm path length cuvettes. The quantum yield of the photoreaction was calculated by measuring the intensity of the light source with the "micro-version" of the ferric oxalate actinometer.[44] Emission spectra were recorded with a Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R-928 phototube. The spectra were corrected for the instrumental response. An IBH single photon counting equipment $N_2$ lamp, $\lambda_{exc} = 337$ nm) was used to obtain the excited state lifetime.

***β*-(Dimethylamino)vinyl 2-(5-Methyl)pyridyl Ketone 1.** A mixture of 2-acetyl-5-methylpyridine (10 g, 0.074 mol) and *N,N*-dimethylfor-mamide dimethylacetal (DMFDMA) (12 mL; 0.089 mol) in anhydrous toluene (40 mL) was refluxed for 7 h under argon. Two fractions of DMFDMA (5 mL, 2 mL) were added after 2.5 h and 6 h heating, respectively, the methanol produced being continuously distilled from the mixture. Evaporation of solvent followed by addition of hexane triggered precipitation of a brown powder (11.4 g, 0.06 mol, 81% yield). Analytical sample was recrystallized from $CH_2Cl_2$/hexane. $^1H$ NMR (200 MHz, $CDCl_3$): 8.04 (d, 1H, *J* = 8 Hz); 7.59 (d, 1H, *J* = 0.6 Hz); 8.44 (q, 1H, *J* = 1.3 Hz); 7.89 (d, 1H, *J* = 12.7 Hz); 6.42 (d, 1H, *J* = 12.7 Hz); 2.38 (s, 3H); 2.99 (s, 3H); 3.16 (s, 3H). Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45, H, 7.42, N, 14.72. Found: C, 69.44, H, 7.44, N, 14.68.

**5,5″-Dimethylterpyridine 2.** A THF solution (25 mL) of 2-acetyl-5-methylpyridine (0.8 g, 6 mmol) and tBuOK in THF (12 mL, 12 mmol) was stirred under argon at room temperature for 2 h. Then **1** (1 g, 6 mmol) was added as a solid. During 20 h stirring, the pink solution progressively turned bright red. Addition of $NH_4OAc$ (4.6 g, 0.06 mol) followed by 15 mL acetic acid caused the solution to turn light brown. THF was distilled off over 3 h, acetic acid was evaporated under vacuum, and the resulting black oil was treated with 40 mL of $H_2O$. This solution was neutralized with aqueous $Na_2CO_3$ solution (end-point indicated by pH-paper) and extracted three times with $CH_2Cl_2$. The combined organic layers were dried over $MgSO_4$, filtered, and

(41) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33−146.

(42) Kubas, G. J.; Monzyk, B.; Crumbliss, A. L. *Inorg. Synth.* **1990**, *28*, 68−70.

(43) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organometal. Chem.* **1973**, *56*, 53−66.

(44) Fischer, E. *EPA Newsl.* **July 1984**, 33−34.

concentrated to a black solid. This solid was dissolved in toluene (40 mL), filtered on paper, and separated on alumina (eluent hexane/ether), to give terpyridine (0.721 g, 2.8 mmol, 45% yield). Analytical sample was recrystallized from ethanol. $^1$H NMR (200 MHz, CDCl$_3$): 2.42 (s, 6H); 8.40 (d, 2H, $J = 8.5$ Hz); 7.67 (d, 2H); 8.53 (s, 2H); 8.51 (d, 2H, $J = 8.08$ Hz); 7.93 (t, 1H). Anal. Calcd for C$_{17}$H$_{15}$N$_3$: C, 78.13, H, 5.79, N, 16.08. Found: C, 78.20, H, 5.79, N, 16.18.

**5,5''-Bis(γ-(tetrahydropyranyl)propyl)terpyridine 3.** Lithium diisopropylamid (LDA) (1.8 mL, titrated commercial solution 1.41 M) was added dropwise to a suspension of **2** (0.3 g, 1.15 mmol) in anhydrous THF (20 mL) at −81 °C. After 2 h stirring at −80 °C the violet solution was allowed to reach 0°C and then cooled back to −78 °C. A separate solution of protected bromoethanol (tetrahydropyranyl-2-bromoethanol, 0.621 g, 2.99 mmol) in 10 mL anhydrous THF was refrigerated to 0 °C. By the double-ended needle transfer technique the organolithium solution was added to the alcohol solution. Within 20 h stirring the intense blue-green mixture was allowed to slowly warm up to room temperature and was hydrolyzed with 10 mL water. After evaporation of solvent and extraction with CH$_2$Cl$_2$, the organic phases were gathered, dried over MgSO$_4$, filtered, and concentrated to an orange oil. It was separated by column chromatography on alumina (eluent ether/hexane 40/60), giving a white powder (317 mg, 0.63 mmol, 55% yield). $^1$H NMR (200 MHz, CD$_2$Cl$_2$): 8.52 (d, 2H, $J = 7.8$ Hz); 8.54 (s, 2H); 8.38 (d, 2H, $J = 7.8$ Hz); 7.92 (t, 1H, $J = 7.8$ Hz); 7.68 (dd, 2H, $J = 2.4$ Hz), 4.59 (t, 2H, $J = 2.98$ Hz); 3.84 (complex, 4H); 3.47 (complex, 4H); 2.80 (t, 4H, $J = 6.1$ Hz); 1.98 (q, 4H, $J = 6.1$ Hz); global peak between 1.3 and 1.7 ppm.

**5,5''-Bis(γ-hydroxypropyl)terpyridine 4.** The previously obtained **3** was diluted in ethanol (30 mL and a few drops of chloroform) and heated to reflux. On addition of a drop of concd HCl$_{(aq)}$ the solution turned pale yellow. The reaction was followed by thin layer chromatography. After 3 h refluxing, the ethanol was evaporated and the resulting solid was partitioned between CH$_2$Cl$_2$ and H$_2$O. The organic phase was dried over MgSO$_4$, filtered, and concentrated to give a white powder (0.633 g), which was purified by column chromatography on alumina (eluent CH$_2$Cl$_2$/MeOH). The pure diol **4** (293 mg, 0.84 mmol) was isolated in 81% yield. $^1$H NMR (200 MHz, CDCl$_3$): 8.53 (d, 2H, $J = 8$ Hz); 8.56 (s, 2H); 8.39 (d, 2H, $J = 7.8$ Hz); 7.94 (t, 1H, $J = 8$ Hz); 7.70 (dd, 2H, $J = 2.2$ Hz), 3.73 (t, 4H, $J = 6.3$ Hz); 2.81 (t, 4H, $J = 7.3$ Hz); 1.95 (tt, 4H, $J = 7.3$ Hz and 6.3 Hz).

**5,5''-Bis(γ-mesylpropyl)terpyridine 5.** A suspension of **4** (193 mg, 0.55 mmol) in anhydrous CH$_2$Cl$_2$ (35 mL) and freshly distilled NEt$_3$ (0.88 mL, 6.3 mmol) was cooled down to −5 °C. Mesyl chloride (0.22 mL, 2.86 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added dropwise (−5 < $t$ < −2 °C) to the suspension, which turned progressively clear yellow. According to thin layer chromatography, end-point was reached within 2 h stirring below 0 °C. The reaction mixture was washed with water, the organic phase was dried over MgSO$_4$, filtered, and concentrated to a beige powder. It was purified by column chromatography on alumina (eluent CH$_2$Cl$_2$/hexane and then pure CH$_2$Cl$_2$), giving an amorphous white powder (198 mg, 0.39 mmol, 71% yield). $^1$H NMR (200 MHz, CD$_2$Cl$_2$): 8.55 (d, 2H, $J = 8$ Hz); 8.56 (d, 2H, $J = 2$ Hz); 8.41 (d, 2H, $J = 7.8$ Hz); 7.95 (t, 1H, $J = 8$ Hz); 7.71 (dd, 2H, $J = 2$ Hz and 7.8 Hz), 4.26 (t, 4H, $J = 6$ Hz); 3.04 (s, 6H); 2.86 (t, 4H, $J = 7.2$ Hz); 2.14 (complex, 4H, $J = 7.2$ Hz and 6 Hz).

**5,5''-Bis(γ-bromopropyl)terpyridine 6.** A mixture of **5** (402 mg, 0.8 mmol) and anhydrous LiBr (0.7 g, 8 mmol) in analytical grade acetone (25 mL) was heated at reflux for 1 h under argon. After evaporation of solvent, the crude mixture was partitioned between CH$_2$Cl$_2$ and H$_2$O. The organic phases were gathered, dried over MgSO$_4$, filtered, and concentrated to give a yellowish glassy solid (0.369 g). $^1$H-NMR spectrum indicated at least a 90% proportion was the desired product (95% yield). The solid was utilized in following steps without further purification, owing to its poor stability. $^1$H NMR (200 MHz, CD$_2$Cl$_2$): 8.67 (d, 2H, $J = 8$ Hz); 8.67 (s, 2H); 8.57 (d, 2H, $J = 7.8$ Hz); 8.01 (t, 1H, $J = 8$ Hz); 7.90 (dd, 2H, $J = 2.2$ Hz); 3.44 (t, 4H, $J = 6.3$ Hz); 2.94 (t, 4H, $J = 7.3$ Hz); 2.25 (tt, 4H, $J = 7.3$ Hz and 6.3 Hz).

**Macrocycle 9.** A degassed solution of **7** (2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline, 0.292 g, 0.8 mmol) and **6** (0.369 g, 0.78 mmol) in analytical grade DMF (80 mL) was added dropwise to a stirred suspension of Cs$_2$CO$_3$ (0.82 g, 2.51 mmol) in 150 mL of DMF analytical

grade at 60 °C. After the 13 h-long addition, the reaction mixture was heated and stirred for another 16 h, its orange color progressively intensifying. The solvent was evaporated under high vacuum and the crude product was partitioned between CH$_2$Cl$_2$ and H$_2$O. The organic phases were gathered, dried over MgSO$_4$, filtered, and concentrated to leave a brown glassy solid. It was purified by column chromatography over alumina (eluent CH$_2$Cl$_2$/hexane) to give a white powder (300 mg, 0.44 mmol; 57% yield). $^1$H NMR (200 MHz, CD$_2$Cl$_2$): 8.72 (d, 2H, $J = 8$ Hz); 8.60 (d, 2H, $J = 2$ Hz); 8.39 (d, 2H, $J = 8$ Hz); 8.29 (d, 2H, $J = 8$ Hz); 8.27 (d, 4H, $J = 8$ Hz); 8.06 (d, 2H); 7.94 (t, 1H, $J = 8$ Hz); 7.86 (dd, 2H); 7.77 (s, 2H); 7.03 (d, 4H); 4.04 (t, 4H, $J = 6$ Hz); 3.01 (complex peak, 4H); 2.25 (complex peak, 4H). Anal. Calcd for C$_{45}$H$_{35}$N$_5$O$_2$ (sample recrystallized from benzene): C, 79.74, H, 5.20. Found C, 79.86, H, 5.43. FABMS 678 [MH]$^+$.

**Macrocycle 8.** A solution of **7** (970 mg, 2.6 mmol) and 1,12-diiodohexaethyleneglycol (1.440 g, 2.8 mmol) in analytical grade DMF (180 mL) was added dropwise to a stirred suspension of Cs$_2$CO$_3$ (2.72 g, 8.4 mmol) in analytical grade DMF (360 mL) at 60 °C. Another 0.1 equiv of diiodohexaethyleneglycol was added after 24 h, and the solution was stirred under argon for 48 h, successively showing an orange then yellow color. After evaporation of solvent under high vacuum, the residual solid was partitioned between CH$_2$Cl$_2$ and H$_2$O, and the organic phases were gathered, dried over MgSO$_4$, filtered, and concentrated to an orange oil (2.9 g). A column chromatography over silica gel (eluent CH$_2$Cl$_2$/MeOH, 98/2) yielded a yellow glassy product (978 mg, 1.6 mmol, 61% yield). $^1$H NMR (200 MHz, CDCl$_3$): 8.46 (d, 4H, $J = 6$ Hz); 8.26 (d, 2H, $J = 8$ Hz); 8.07 (d, 2H); 7.75 (s, 2H); 7.17 (d, 4H, $J = 6$ Hz); 4.31 (t, 4H, $J = 5$ Hz); 3.90 (t, 4H, $J = 5$ Hz); 3.90 (complex signal, 16H).

**Precatenate 10$^+$·PF$_6^-$.** The method is exactly the one used for synthesis of **12**·PF$_6$.

**Precatenate 12$^+$·PF$_6^-$.** Using the double-ended needle transfer technique, a degassed solution of Cu(CH$_3$CN)$_4$PF$_6$ (182 mg, 0,49 mmol) in analytical grade acetonitrile (15 mL) was added under argon to a degassed solution of macrocycle **9** (300 mg, 0.44 mmol) in analytical grade CH$_2$Cl$_2$ (25 mL). A red-brown color formed immediately. After stirring for 30 min, a solution of **7** (171 mg, 0.44 mmol) in analytical grade DMF (25 mL) was similarly added under argon without any further color change. After 2 h stirring at room temperature, the solvent mixture was evaporated under high vacuum, giving an intensely red-colored powder (0.56 g, 0.44 mmol). NMR analysis showed almost quantitative formation of the precursor. $^1$H NMR (200 and 400 MHz, COSY, DMSO-$d_6$): 8.72 (d, 2H, $J = 8$ Hz); 8.64 (d, 2H); 8.53 (d, 2H, $J = 8$ Hz); 8.42 (d, 2H, $J = 7.72$ Hz); 8.34 (d, 2H, $J = 8.38$ Hz); 8.13 (s, 2H); 7.75 (s, 2H); 8.05 (t, 1H, $J = 8$ Hz); 7.80 (d, 2H, $J = 8.4$ Hz); 7.70 (d, 2H, $J = 8.4$ Hz); 7.68 (dd, 2H, $J = 8$ Hz and 2 Hz); 7.38 (d, 4H, $J = 8.8$ Hz); 7.23 (d, 4H, $J = 8.8$ Hz); 5.98 (d, 8H, $J = 7.8$ Hz); 3.23 (t, 4H, $J = 6.9$ Hz); 2.93 (4H, complex peak); 2.12 (4H, complex peak).

**Catenate 11$^+$·PF$_6^-$.** A degassed solution of precatenate **12**$^+$ (0.55 g, 0.44 mmol) and diiodohexaethyleneglycol (0.260 g, 0.52 mmol) in analytical grade DMF (90 mL) was slowly added under argon to a suspension of Cs$_2$CO$_3$ (0.55 g, 1.4 mmol) in analytical grade DMF (80 mL) at 60 °C. After the 10 h-long addition, the stirred solution was maintained at 60 °C for another 48 h, after which it was filtrated on paper and concentrated under high vacuum. The residual cherry-red solid was partitioned between CH$_2$Cl$_2$ and H$_2$O, the organic phases were gathered and dried over MgSO$_4$. After filtration, a saturated aqueous solution of KPF$_6$ was then added, and the mixture was allowed to stand for 5 h at room temperature with good stirring. The brownish organic phase was separated, washed with water, and dried over MgSO$_4$. The filtered solution was concentrated under high vacuum leaving a red-brown powder (0.579 g). By successive column chromatographies over silica gel and alumina (eluent CH$_2$Cl$_2$/hexane and CH$_2$Cl$_2$/MeOH), an intense red powder was obtained (80 mg, 0.05 mmol; 10% yield) and recrystallized from a mixture of CH$_2$Cl$_2$ and C$_6$H$_6$. $^1$H NMR (200 and 400 MHz, COSY, CD$_2$Cl$_2$): 8.72 (d, 2H, $J = 8$ Hz); 8.64 (d, 2H); 8.53 (d, 2H, $J = 8$ Hz); 8.42 (d, 2H, $J = 7.72$ Hz); 8.34 (d, 2H, $J = 8.38$ Hz); 8.13 (s, 2H); 8.05 (t, 1H, $J = 8$ Hz); 7.80 (d, 2H, $J = 8.4$ Hz); 7.75 (s, 1H); 7.70 (d, 2H, $J = 8.36$ Hz); 7.68 (dd, 2H, $J = 8$ Hz and 2 Hz); 7.38 (d, 4H, $J = 8.8$ Hz); 7.23 (d, 4H, $J = 8.8$ Hz); 5.98 (d, 8H, $J = 7.8$ Hz); 3.74 (t, 4H); complex peak 3.68 (20H); 3.23 (t,

4H, $J = 6.9$ Hz); 2.93 (4H, complex peak); 2.12 (4H, complex peak). Anal. Calcd for $C_{81}H_{73}N_7O_9CuPF_6$, (sample recrystallized from benzene): C, 64.98, H, 4.91, N, 6.17. Found: C, 64.99, H, 5.22, N, 6.22. FABMS: 1350 $[M - PF_6]^+$.

**Catenand 13.** The copper catenate **11** (112 mg, 0.07 mmol) was dissolved in acetonitrile (30 mL), and an aqueous KCN solution (100 mg in 2 mL) was added, triggering spontaneous precipitation of a white powder, which was dissolved on adding $CH_2Cl_2$ (3 mL). The resulting beige solution was left overnight with stirring at room temperature. After evaporation of solvent, the solid was partitioned between $CH_2Cl_2$ and $H_2O$; the organic phase was washed with water, dried over $MgSO_4$, filtered, and concentrated to leave a yellowish glassy product (100 mg). $^1$H NMR (200 and 400 MHz, NOESY, $CD_2Cl_2$): 8.87 (d, 2H, $J = 8$ Hz); 8.62 (d, 2H); 8.45 (d, 4H, $J = 8.8$ Hz); 8.45 (d, 2H, $J = 8$ Hz); 8.30 (d, 4H, $J = 8.8$ Hz); 8.27 (d, 4H, $J = 7.7$ Hz); 8.06 (d, 4H, $J = 8.4$ Hz); 7.97 (t, 1H, $J = 8$ Hz); 7.75 (s, 4H); 7.76 (dd, 2H, $J = 8$ Hz and 2 Hz); 7.05 (d, 4H, $J = 7.8$ Hz); 6.09 (d, 4H, $J = 7.8$ Hz); 3.92 (t, 4H); 3.92 (t, 4H, $J = 6.9$ Hz); 3.64 (t, 4H); 3.49 (16H, complex signal); 2.91 (4H, complex signal); 2.16 (4H, complex signal). FABMS: 1288 $[MH]^+$.

**Copper(II) Catenate $10^{2+}\cdot2BF_4^-$.** A solution of **13** (30 mg, $2.3 \times 10^{-5}$ mol) in 20 mL of $CH_2Cl_2$ was added to a solution of Cu-$(BF_4)_2.xH_2O$ (8 mg, $2.3 \times 10^{-5}$ mol) in 5 mL of acetonitrile. The resulting pale olive-green solution was left overnight with stirring at room temperature. After evaporation of solvent, the solid was partitioned between $CH_2Cl_2$ and $H_2O$; the organic phase was washed with water, dried over $MgSO_4$, filtered, and concentrated to leave a bright pale green powder (29 mg, 85% yield), recrystallized from a mixture of acetone and diisopropyl ether. ESMS in $CH_2Cl_2$: 675.9 $[M]^{2+}$. Anal. Calcd for $C_{81}H_{73}N_7O_9Cu(BF_4)_2$: C, 63.77, H, 4.82, N, 6.43. Found: C, 63.56, H, 4.87, N, 6.49.

JA9720826