A Switchable Hybrid [2]-Catenane Based on Transition Metal Complexation and π-Electron Donor−Acceptor Interactions

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Abstract: A bimodal [2]-catenane has been synthesized via a copper(I) templated synthesis. The compound contains both a transition metal coordination site and a set of π-electron rich and π-electron deficient aromatic units suitable for the formation of acceptor-donor complexes. Each constituent ring is thus different from the other, and the organic backbone can adopt two favored contrasting orientations by circumrotation of one ring within the other: (i) in the metal complex mode, each dpp unit (dpp = 2,9-diphenyl-1,10-phenanthroline) is entwined about the other, while a cationic species is complexed in the coordination site thus created; (ii) in the organic π-electron acceptor-donor complex mode, the dpp fragments are remote from one another, and the π-electron rich and π-electron deficient units stack to form a complex. The conversion of one binding mode to the other implies complete topographical rearrangement of the molecule. It can be triggered by adding or removing the cation center (Cu^+, Li^+, or H^+), bonded to the dpp-containing complexing site. Interestingly, this switching process can be easily monitored by ^1H NMR, since it involves drastic relative orientational changes. It can also be evidenced by electronic spectroscopy. In particular, the proton-driven rearrangement reactions lead to significant changes in the absorption spectrum, which correspond to the appearance (by deprotonation) and disappearance (by protonation of the dpp) of a charge transfer band (around 470 nm) resulting from the π-electron donor−acceptor noncovalent interaction.

The very elegant and intellectually-appealing early syntheses of catenanes[1,2] created interlocked rings with little functionality, apart from those chemical groups required to make them. More recent template-directed strategies reliant on transition metal complexation,[3] π-electron donor−acceptor interactions,[4] and steric fit/hydrogen bonding between amide[5] and related moieties[6] have not only made the synthesis of interlocking rings more accessible[7] but have also allowed the preparation of compounds incorporating chemically, electrochemically, and photochemically accessible functionalities. These sites provide a handle which permits the control of their physical and chemical properties, such as molecular geometry,[8] coordination ability toward transition metal ions,[9] electronic and electrochemical behavior,[10] spectroscopic and photochemical parameters,[11] and so on, from the outside.

With the aim of increasing the degree of control over the properties of this type of compound, we decided to combine *two* template concepts and to incorporate the two types of building block into one and the same catenane. The resulting molecular system would thus have properties governed by either of the template binding modes, with the possibility of switching the system from one type of interaction to the other, provided that coexistence of both binding modes was prohibited. The combination of transition metal ion chelating units and π-electron donor−acceptor complexes comprised of π-electron rich

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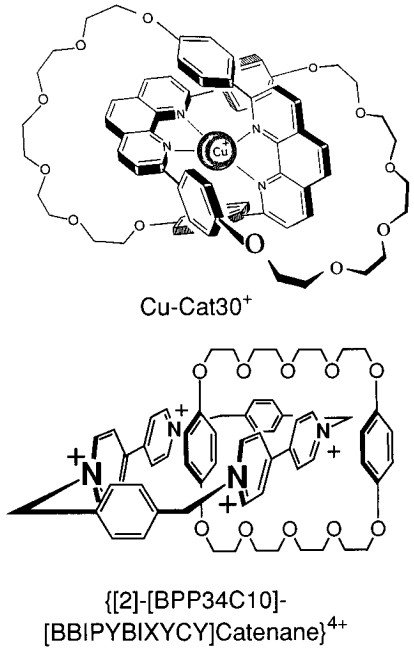

Figure 1. The first members in families of metal ion templated (Cu-cat-30^{+}) and self-assembled ({[2]-[BPP34C10]-[BBIPYBIXYCY]-catenane}$^{4+}$) [2]-catenates and [2]-catenanes.

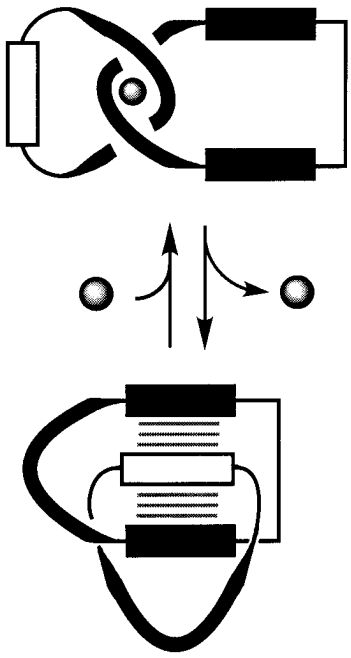

Figure 2. The concept behind a switchable [2]-catenane based on metal ion (dark ball) chelation (by the crescents) and π-electron donor (clear rectangle) to acceptor (dark rectangle) interactions. The molecule is switched by complexation or removal of the chelated ion.

aromatic rings and π-electron deficient moieties seemed especially appealing and promising. We would now like to report the synthesis and properties of such a hybrid catenane and, in particular, describe the switchable nature of the compound.

Results and Discussion

Design Considerations. The archetypal catenanes made some years ago by our two groups are represented in Figure 1. The [2]-catenate Cu-cat-30^{+} contains two interlocked 30-membered rings,[12] the core of the molecule consisting of the templating set of two dpp-type ligands (dpp = 2,9-diphenyl-1,10-phenanthroline) entwined around a copper(I) center. The two different rings in {[2]-[BPP34C10]-[BBIPYBIXYCY]-catenane}$^{4+}$ interlock as a result of the ability of BPP34C10 to template the formation of the tetracationic cyclophane component.[13] The rings interact noncovalently by $\pi-\pi$ stacking between π-electron rich and π-electron deficient units as well as through CH$\cdots$O hydrogen bonds and CH$\cdots\pi$ interactions.

The cation complexation properties (in Cu-cat30^{+}) and the noncovalent interactions between π-electron donors and acceptors (in {[2]-[BPP34C10]-[BBIPYBIXYCY]catenane}$^{4+}$) can be combined into a single molecular species, as depicted schematically in Figure 2. Such a hybrid catenane has two modes of interaction which govern the relative geometries of the component macrocycles. These different modes should be interchanged by the inclusion or expulsion of some cation chelated by the catenand.

Synthesis. A molecular realization of the conceptual design, along with its template-directed synthesis, is depicted in Scheme 1. The target compound is the copper(I) [2]-catenate **1**$^{5+}$. For the sake of clarity, we shall refer to the ring incorporating the bipyridinium units as the "tetracationic macrocycle", while the neutral ring will be termed "**2**". The route by which we chose to construct the catenate **1**$^{5+}$ requires the closure of the tetracationic macrocycle to be the final catenating cyclization. This approach was selected because the bipyridinium moieties are the most chemically labile part of this catenate, and so their formation in the last step of the synthesis was desirable. Therefore, the macrocycle **2**—incorporating one π-electron rich 1,5-dioxynaphthalene residue and one 1,10-phenanthroline unit in a 34-membered ring—was prepared by reacting the ditosylate[14] **3** with the diphenol[12] **4** in DMF under high dilution conditions using cesium carbonate as the base.[15] The dication **5**$^{2+}$—the precursor to the tetracationic macrocycle of the catenate—was prepared by reacting 4,4′-bipyridine with the bisbromomethyl phenanthroline[16] derivative **6**. An excess of 4,4′-bipyridine was employed to avoid the formation of oligomers. The dication **5**$^{2+}$ was isolated as its bishexafluorophosphate salt after column chromatography and counterion exchange.

The threaded complex **7**$^{3+}$ was formed quantitatively[17] by first of all combining the macrocycle **2** with Cu(MeCN)$_4$PF$_6$ in CH_2Cl_2/MeCN under argon, to generate the Cu(I) complex of the macrocycle, and then adding the dication **5**$^{2+}$ as its bishexafluorophosphate salt. The formation of **7**$^{3+}$ was con-

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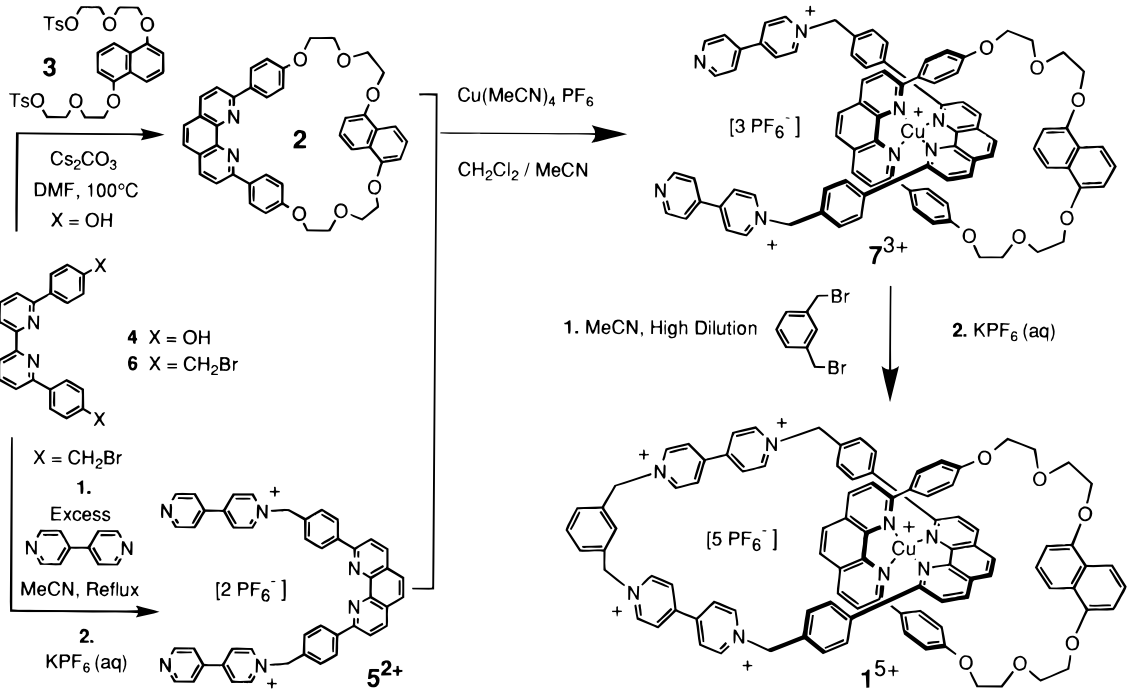
(17) This threaded complex can be regarded as a precatenate (see ref 9) as well as a precursor to a family of rotaxanes. The reaction of suitably large stopper groups bearing chloro- or bromomethyl groups with the "precatenate" would afford rotaxanes. For examples of this kind of approach to rotaxanes, see: (a) Ashton, P. R.; Philp, D.; Spencer, N.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1992**, 1124−1128. For a more recent account with references, see: (b) Amabilino, D. B.; Ashton, P. R.; Bélohradsky, M.; Raymo, F. M.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1995**, 751−753.

Scheme 1



firmed by one- and two-dimensional ^{1}H NMR spectroscopy (vide infra) as well as by electrospray mass spectrometry[18] (ESMS), which showed peaks *m/z* values of 1688, 772, and 466, corresponding to the $[M\text{-}PF_6]^+$, $[M\text{-}2PF_6]^{2+}$, and $[M\text{-}3PF_6]^{3+}$ ions, respectively.[19]

Formation of [2]-catenanes of the type {[2]-[BPP34C10]-[BBIPYBIXYCY]catenane}$^{4+}$ by self-assembly is very sensitive to constitutional change in the components,[20] because the active role of the template during catenation relies upon molecular recognition. By contrast, the procedures used to form catenates of the type Cu-cat30$^+$ are generally carried out under high dilution conditions,[12] since the metal ion template is remote from the reactive termini and interacts with the ligands through coordinative bonds. Therefore, since the tetracationic macrocycle to be created is very different from those formed by self-assembly, the reaction of 1,3-bisbromomethyl benzene with the precatenate **7**$^{3+}$ was performed under high dilution conditions in refluxing MeCN. The [2]-catenate **1**$^{5+}$ was isolated as its pentakis(hexafluorophosphate) salt, following column chromatography, counterion exchange, and crystallization, as a red solid in 40% yield.

The composition of the [2]-catenate was confirmed by both electrospray (ES) and fast atom bombardment (FAB) mass spectroscopies. The spectrum resulting from the former (softer) ionization technique has peaks with *m/z* values of 969 and 597, corresponding to the $[M\text{-}2PF_6]^{2+}$ and $[M\text{-}3PF_6]^{3+}$ ions, respectively. The FAB mass spectrum (Figure 3) of the catenate is very characteristic of interlocked molecular compounds containing bipyridinium residues.[21] Peaks are observed for the $[M\text{-}PF_6]^+$, $[M\text{-}2PF_6]^+$, $[M\text{-}3PF_6]^+$, and $[M\text{-}4PF_6]^+$ ions, respectively. In addition, fragmentation of the molecule occurs,[22] and peaks corresponding to the copper complex of **2** as well as a fragment of the tetracationic macrocycle are observed. The ^{1}H NMR spectrum of the catenate also confirmed its interlocked nature (vide infra).

The topology of a catenate is ultimately proved upon removal of the templating metal ion and by characterization of the resulting catenand. When the catenate **1**$^{5+}$ was treated (Scheme 2) with KCN in aqueous MeCN,[23] the [2]-catenand **8**$^{4+}$ was isolated in 81% yield as its hexafluorophosphate salt. It precipitated as an orange solid from the reaction medium upon addition of KPF_6(aqueous). The material was characterized as the catenand in the first instance by FAB-MS, which gave a spectrum with peaks having *m/z* values of 1879, 1729, 1583, and 1439, corresponding to the singly charged ions resulting from the loss of one, two, three, and four hexafluorophosphate counterions, respectively, from the molecule. In addition, peaks corresponding to **2**, as well as to fragments of the tetracationic macrocycle, were observed.

^{1}H NMR Spectra of the Catenate and Catenand. An ^{1}H NMR spectroscopic study of **8**.4PF_6 strongly suggests that, upon demetalation from **1**.5PF_6, the two interlocked rings undergo a reorientation relative to one another. It is necessary to compare

(18) Electrospray mass spectrometry has been used for the characterization of both families of catenanes from which the 'hybrid' catenane is derived as well as related copper(I) complexes, see: (a) Ashton, P. R.; Brown, C. L.; Chapman, J. R.; Gallagher, R. T.; Stoddart, J. F. *Tetrahedron Lett.* **1992**, *33*, 7771−7774. (b) Bitsch, F.; Dietrich-Buchecker, C.; Khémiss, A. K.; Sauvage, J.-P.; van Dorsselaer, *J. Am. Chem. Soc.* **1991**, *113* , 4023−4025; A. Bitsch, F.; Hegy, G.; Dietrich-Buchecker, C.; Leize, E.; Sauvage, J.-P.; van Dorsselaer, A. *New J. Chem.* **1994**, *18*, 801−807. (c) Moucheron, C.; Dietrich-Buchecker, C. O.; Sauvage, J.-P.; van Dorsselaer, A. *J. Chem. Soc., Dalton Trans.* **1994**, 885−893.

(19) Peaks from the free thread and copper complex of the macrocycle as a result of partial decomposition of the complex during the mass spectroscopic experiment, were also observed.

(20) Amabilino, D. B.; Ashton, P. R.; Pérez-García, L.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2378−2380.

(21) Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Córdova, E.; Godínez, L. A.; Goodnow, T. T.; Kaifer, A. E.; Newton, S. P.; Pietraszkiewicz, M.; Philp, D.; Raymo, F. M.; Reder, A. S.; Rutland, M.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 1271−1293.

(22) The characteristics of the mass spectra of catenanes—in which the interlocked structure gives a peak, and then there is a "desert" in the spectrum until the component rings are observed—were first noted in the following seminal publications: (a) Vetter, W.; Schill, G. *Tetrahedron* **1967**, *23*, 3079−3093. (b) Vetter, W.; Logemann, E.; Schill, G. *Org. Mass. Spectrom.* **1977**, *12*, 351−369.

(23) When **1**.5PF_6 is treated with KCN in aqueous acetone, decomposition of the resulting catenand—specifically the tetracationic cyclophane component—means that the only isolable compound is the component neutral macrocycle. The decomposition is presumably a result of nucleophilic attack of the cyanide ion at the methylene groups adjacent to the quaternary nitrogen atom in the bipyridinium unit.

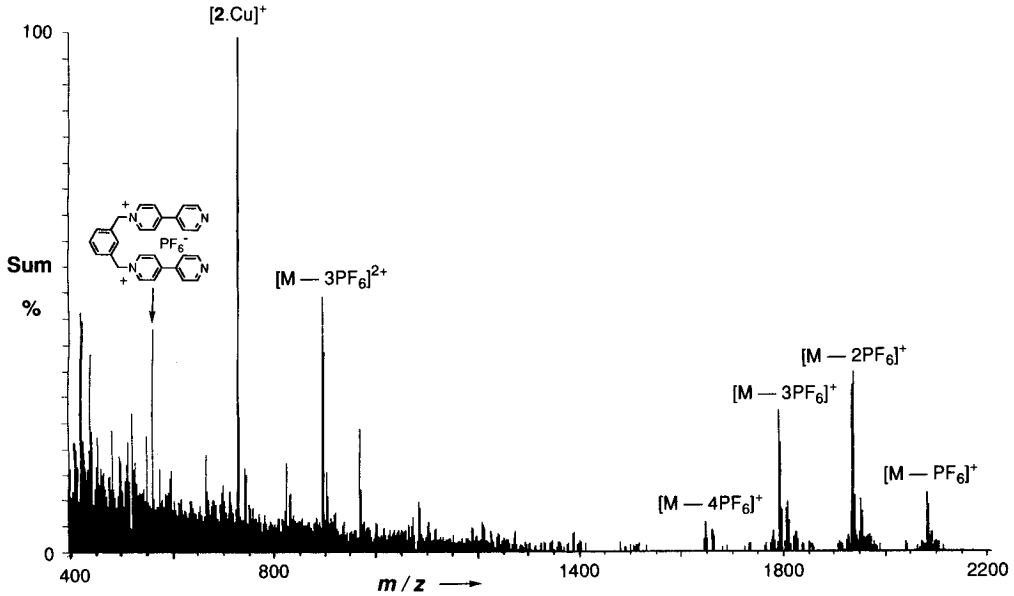
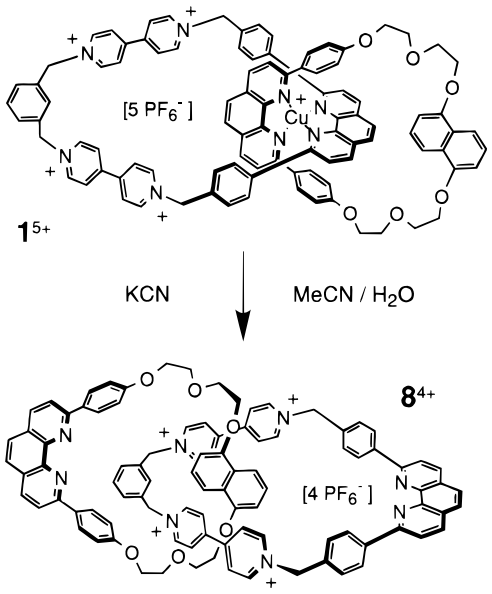


Figure 3. The fast atom bombardment mass spectrum of **1**.5PF_6.

Scheme 2



the ^{1}H NMR spectra of the precatenate, catenate, and catenand—all of which were fully assigned using COSY and ROESY two-dimensional spectroscopy—in order to understand the nature of this geometrical change. The ^{1}H NMR spectra of **1**.5PF_6 and **8**.4PF_6 are shown in Figure 4, along with the numbering scheme used for the hydrogen atoms in the two rings. Table 1 compares the ^{1}H NMR chemical shifts arising from some of the key probe hydrogen atoms in the three species, along with the chemical shift changes taking place upon removal of the templating copper(I) ion from the catenate.

In the ^{1}H NMR spectrum of **1**.5PF_6 (CD_3CN, 400 MHz, 298 K), the resonances arising from the hydrogen atoms attached to the phenanthroline moiety in **2** have chemical shifts which are in the expected positions for such a copper(I) catenate. On the other hand, the corresponding hydrogen atoms of the chelate in the tetracationic macrocycle give peaks at higher field positions, particularly $pnH_{5,6}B$, an observation which is believed to be a result of shielding induced by the proximal 1,5-dioxynaphthalene unit in the interlocked macrocycle.[24] A similar shielding of the corresponding hydrogen atoms is also observed in the ^{1}H NMR spectrum of the precatenate **7**.3PF_6 under the same conditions. The phenyl substituents of the phenanthroline moieties in **1**.5PF_6 have hydrogen atoms which give peaks which reside, as expected, at high field compared with the same signals for the free components, as a result of the chelation of the copper(I) ion and their resulting proximity. An NOE between H_oA and H_oB was observed in the ROESY spectrum of **1**.5PF_6 providing experimental evidence for this effect. Peaks are observed arising from each of the four nonequivalent hydrogen atoms in the bipyridinium units. The chemical shifts for those protons attached to the pyridinium unit nearest to the template center correspond to the signals at highest field—probably as a result of shielding by the phenanthroline unit in **2** which they "sandwich"—while those protons on the pyridinium group nearest to the *m*-xylyl linker have chemical shifts similar to those in related uncomplexed tetracationic cyclophanes.[25]

The ^{1}H NMR spectrum of **8.**4PF_6 has several major differences to that of the corresponding copper(I) catenate. The resonances arising from the hydrogen atoms β to the quaternary nitrogen atom of the pyridinium rings in **8.**4PF_6 have chemical shifts at much higher field than those in **1.**5PF_6, the $\Delta\delta$ upon removal of the copper(I) ion being 0.70 and 0.46 ppm for βCH_A and βCH_B, respectively. Additionally, the signals for $npH_{2,6}$, $npH_{3,7}$, and $npH_{4,8}$ in the catenand are shielded by 0.64, 1.00, and 0.95 ppm, respectively, when compared with the catenate. Interestingly, the resonances arising from H_oA and H_mA in the catenand, although appearing at lower field than those in the catenate, retain relatively high field chemical shifts at δ 7.53 and 6.38, respectively, compared with δ 8.51 and 7.36 for the hydrogen atoms attached to the corresponding group in the tetracationic macrocycle component. Examination of a CPK space-filling molecular model of the catenand suggests that both these phenyl rings and the 1,5-dioxynaphthalene unit enter into $\pi-\pi$ stacking interactions with the tetracationic macrocycle at the same time. This phenomenon would explain the high field positions of the resonances arising from the hydrogen atoms attached to these phenyl rings.

All these comparative ^{1}H NMR data, along with the observation of a charge transfer band in the UV−vis spectrum of the catenand (vide infra), suggest strongly that cation-free **8.**4PF_6

(24) A similar shielding effect has been noted by Momenteau and coworkers in catenates incorporating porphyrins. See ref 9b.

(25) Amabilino, D. B.; Ashton, P. R.; Tolley, M. S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1297−1301.

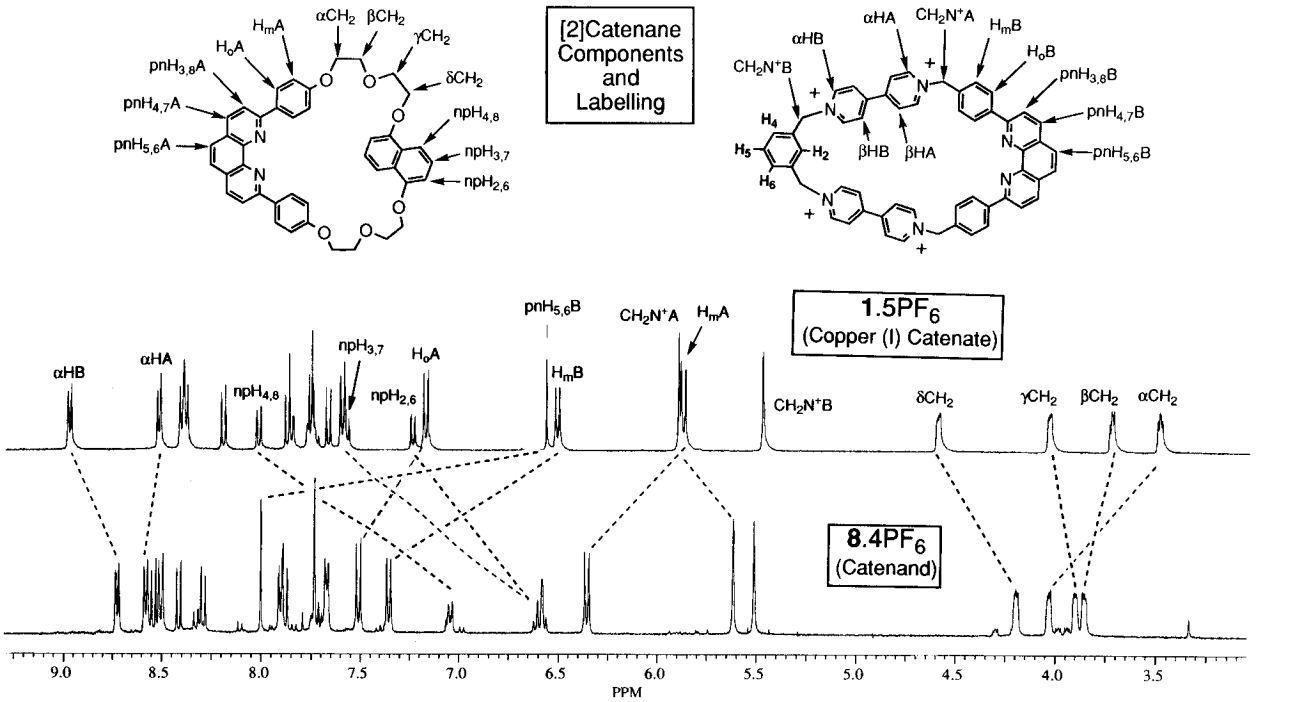


Figure 4. A comparison of the ^{1}H NMR spectra (400 MHz) of **1**.5PF$_6$ and **8**.4PF$_6$, both in CD$_3$CN at room temperature, and the numbering used to refer to the hydrogen atoms in the component interlocked rings. The dashed lines show some of the key changes in the spectra upon removal of the copper(I) ion from **1**.5PF$_6$ which demonstrate the dramatic relative reorientation of the rings.

Table 1. Selected ^{1}H NMR Chemical Shift Data (400 MHz, CD$_3$CN,[a] 298 K) for the Catenate **1**.5PF$_6$, the Catenand **8**.4PF$_6$, the Intermediate Precatenate **7**.3PF$_6$, and the Free Components **2** and **5**.2PF$_6$ as well as the $\Delta\delta$ Values[b] upon Removal of the Copper(I) Ion from **1**.5PF$_6$

H^1 probe[c]	"Free" **2** and **5**.2PF$_6$	precatenate **7**.3PF$_6$	Cu(I) catenate **1**.5PF$_6$	catenand **8**.4PF$_6$	$\Delta\delta$ catenate vs catenand
npH$_{2,6}$	6.99[a]	7.21	7.24	6.60	−0.64
npH$_{3,7}$	7.45[a]	7.58	7.60	6.60	−1.00
npH$_{4,8}$	7.99[a]	7.75	8.03	7.08	−0.95
H$_m$A	7.11[a]	5.91	5.89	6.38	+0.49
H$_o$A	8.44[a]	7.15	7.19	7.53	+0.34
pnH$_{3,8}$A	8.06[a]	7.56	7.68	7.88	+0.20
pnH$_{4,7}$A	8.23[a]	8.02	8.22	8.42	+0.20
pnH$_{5,6}$A	7.71[a]	7.95	7.77	7.75	−0.02
CH$_2$N$^+$A	5.86	5.32	5.49	5.53	+0.04
CH$_2$N$^+$B			5.91	5.63	−0.28
H$_m$B	7.69	6.61	6.53	7.36	+0.83
H$_o$B	8.50	7.45	7.60	8.51	+0.91
pnH$_{3,8}$A	8.31	7.81	7.77	8.30	+0.53
pnH$_{4,7}$A	8.56	8.45	7.87	8.55	+0.68
pnH$_{5,6}$A	7.96	7.04	6.60	8.01	+1.41
αHA	8.89	8.57	8.53	8.60	+0.07
αHB	8.83	8.92	8.98	8.74	−0.24
*β*HA	8.29	8.29	8.39	7.69	−0.70
*β*HB	7.77	7.88	8.42	7.94	−0.46

[a] The chemical shift data for **2** refer to a CDCl$_3$ solution. The compound is almost insoluble in CD$_3$CN. [b] The $\Delta\delta$ values are presented such that a negative value indicates a chemical shift change to high field upon conversion of **1**.5PF$_6$ to **8**.4PF$_6$. [c] See Figure 4 for the proton designation.

has a preferred geometry in solution determined by noncovalent interactions between the π-electron rich and π-electron deficient units, which is completely different to that in the copper(I) catenate.

In order to investigate the significance of the noncovalent interactions between the neutral and charged rings in **8**.4PF$_6$, a variable temperature ^{1}H NMR spectroscopic study (400 MHz) was undertaken. When a CD$_3$CN solution of the catenand **8**.4PF$_6$ is cooled down, significant changes in the chemical shifts of the peaks in the ^{1}H NMR spectrum are observed. In particular, the peaks arising from npH$_{2,6}$, npH$_{3,7}$, and npH$_{4,8}$ move significantly to high field (Figure 5). At 308 K, they resonate at δ 6.60, 6.63, and 7.08, while at 247 K, the broadened

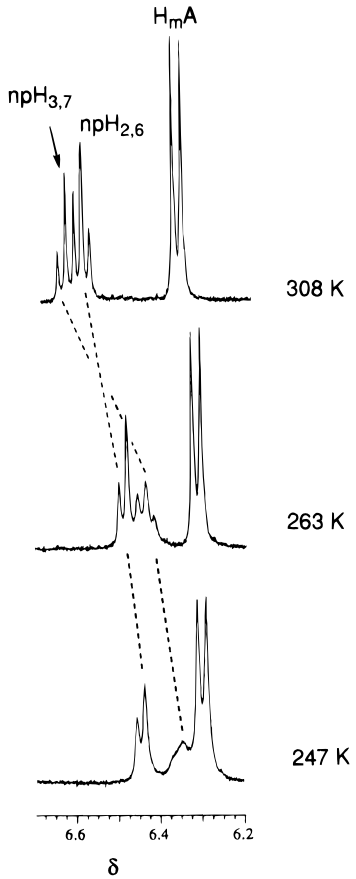


Figure 5. Partial ^{1}H NMR spectra (400 MHz) of **8**.4PF$_6$ in CD$_3$CN at various temperatures, illustrating the high field movement of the peaks arising from the hydrogen atoms attached to the 1,5-dioxynaphthalene ring.

peaks appear at δ 6.44 ($\Delta\delta$ 0.16 ppm), 6.37 ($\Delta\delta$ 0.26 ppm), and 6.76 ($\Delta\delta$ 0.32 ppm), respectively. The peak arising from HoA is also shifted slightly to high field. In addition, the peaks from the hydrogen atoms β- to the quaternary nitrogen atoms in the tetracationic macrocycle component are increasingly shielded. The ^{1}H NMR spectrum of **8**.4PF_6 showed no concentration dependence in CD_3CN at room temperature. These observations indicate an enhancement of the noncovalent interactions between the two rings upon cooling down solutions of **8**.4PF_6, an effect that is more pronounced for the 1,5-dioxynaphthalene unit than for the phenylene rings attached to the phenanthroline unit in **2**. The two rings are apparently free to reorient and spin around and through one another at a rate which is fast on the ^{1}H NMR time scale, even in CD_3COCD_3 at 203 K. Presumably, this lack of order is partially a result of the shape and large size of the tetracationic macrocycle component (37-membered ring) of this catenand when compared with, for example, cyclobis(paraquat-*p*-phenylene) (28-membered ring),[13] which is a very snug host for π-electron rich units such as 1,5-dioxynaphthalene.

Electrochemistry of the Catenate and Catenand. The cyclic voltammogram of **1**.5PF_6 (MeCN, 0.1 M TBA.PF_6) exhibits three reversible waves centered on +0.68, −0.38, and −0.82 V vs SCE. The wave at +0.68 V corresponds to the redox couple Cu^{2+}/Cu^+ and is slightly more positive than those usually observed in related copper catenates.[10a] This difference could be attributed to an electrostatic effect: the four positive charges on the bipyridium units are relatively close to the copper(I) center, and thus slightly disfavor its oxidation.[26] The interval between the anodic and cathodic waves for the Cu^{2+}/Cu^+ redox couple (ΔEp = 190 mV at 100 mV·s^{-1}) indicates a slow electron transfer rate compared with classical Nernstian systems.[27] This effect was confirmed by carrying out several cyclic voltammograms with increasing scan rates and observing an increase in the interval between the anodic and cathodic waves.

The negative current peak at −0.38 V corresponds to the simultaneous single electron reduction of both 4,4′-bipyridinium units. The second negative current peak at −0.82 V is a result of their further single electron reduction to yield the neutral units.[13] Compared to the reduction potentials of cyclobis(paraquat-*p*-phenylene (−0.29 and −0.71 V vs SCE), consisting of two bipyridinium units linked by paraphenylene units, the observed potentials are 100 mV more negative and closer to those in paraquat (-0.38 and −0.80 V vs SCE).[28] The reason for this similarity to paraquat, as opposed to a free tetracationic macrocycle, is partially a result of charge−charge interactions in the latter[13] as well as the large size of the tetracationic macrocycle in $\mathbf{1}^{5+}$. The proximity of the copper(I) complex to the bipyridinium moieties does not induce much perturbation on the redox potentials values, which indicates no very significant interaction between both redox units.

The cyclic voltammogram of the free ligand **8**.4PF_6 (MeCN, 0.1 M TBA.PF_6) exhibits two reduction waves at −0.46 and −0.80 V vs SCE. The first reduction is quasi-reversible (ΔEp = 150 mV) and reproducible. Its more negative potential than the corresponding wave for the copper(I) catenate **1**.5PF_6 can be attributed to the presence of an intramolecular π-electron donor−acceptor complex: the bipyridinium units interact with the 1,5-dioxynaphthalene moiety and are thus less easily reduced. For symmetry reasons, unlike {[2]-[BPP34C10]-[BBIPYBIXYCY]-catenane}$^{4+}$, the first reduction wave in **8**.4PF_6 is not split into two single-electron waves. Nonetheless, surprisingly, the first reduction potential is 20 mV more negative than the second single electron reduction potential of {[2]-[BPP34C10]-[BBIPYBIXYCY]catenane}$^{4+}$. This situation could be a result of the stronger charge-transfer interaction in $\mathbf{8}^{4+}$, arising from the greater π-electron-donating ability of 1,5-dioxynaphthalene compared with hydroquinone. The second reduction in **8**.4PF_6 is not reversible: following the reduction, an electrochemically inert species is deposited on the electrode. The potential value is close to the second reduction potential of **1**.5PF_6 and is 50 mV higher than the second reduction potential of {[2]-[BPP34C10]-[BBIPYBIXYCY]catenane}$^{4+}$. This observation indicates that the donor−acceptor complex is negligible after the first reduction of the bipyridinium units, a phenomenom which was observed in related catenanes and rotaxanes.[13]

As a conclusion, the electrochemical behavior of **1**.5PF_6 is consistent with a superimposition of the "classical" behavior of both its components: the copper complex and the bipyridinium units. In contrast, the free ligand shows behavior consistent with the presence of intramolecular π-π stacking interactions.

External Control of Catenane Topography and Interaction Mode. We have shown that the copper(I) catenate $\mathbf{1}^{5+}$ adopts an entwined topography based on the tetrahedral bis(diphenylphenanthroline) complexation of the templating ion. On the other hand, the topography of the free ligand $\mathbf{8}^{4+}$ is governed by $\pi-\pi$ donor−acceptor interactions. We now sought suitable chemical systems which could make the catenate switch reversibly from one topography to the other. We chose two systems: the lithium ion (reversed by addition of DMF) and the proton (reversed by addition of base).

Complexation with Li^+. According to previous studies on related bis(diphenylphenanthroline) catenates,[10a] a lithium catenate derived from Cu-cat30$^+$ can easily be synthesized and shows tetrahedral coordination around the metal ion center. The Li^+ ion can be displaced by addition of DMF to a catenate solution.[29] The conformational change of the free ligand $\mathbf{8}^{4+}$ upon addition of Li^+ was studied using UV−vis spectroscopy and ^{1}H NMR spectroscopy.

The UV−vis spectrum of $\mathbf{8}^{4+}$ in MeCN exhibits a broad charge-transfer band centered at 470 nm, corresponding to the intramolecular π-electron donor−acceptor complex. This value is consistent with related catenanes (478 nm) and similar complexes.[13] Addition of $LiBF_4$ to the solution causes disappearance of the charge-transfer band, and the spectrum obtained is similar to those of bis(diphenylphenanthroline) Li^+ complexes.[10a] Attempts to restore the original charge-transfer band seen in $\mathbf{8}^{4+}$ by removing Li^+ were unsuccessful. We conclude that the first attempt at "switching" from the π-electron donor−acceptor complex to the metal ion complex is rapid and complete, but the reverse direction is apparently not facile in this catenate. This realization led us to investigate the behavior of the catenane in acidic and basic media.

Switching with Acid−Base. Previous studies of the catenand cat30 show that a proton catenate can be synthesized in solution by adding trifluoroacetic acid to a solution of free ligand.[30] The 1:1 complex is stable and was characterized by NMR, UV−vis spectroscopy, and X-ray crystallography. Addition of base (for example, pyridine) to the proton catenate

(26) A similar effect has been observed in a fullerene-stoppered rotaxane, see: Diederich, F.; Dietrich-Buchecker, C. O.; Nierengarten, J.-F.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 781−782.

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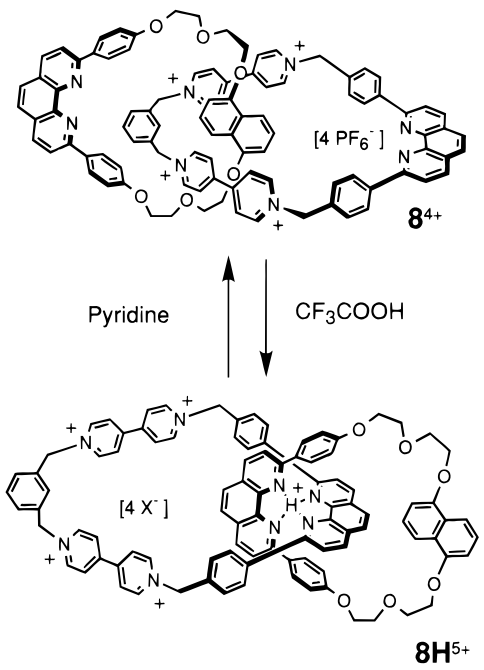
Scheme 3



solution triggers equilibration with the free ligand whose position is dependent upon the pK_a of the base. Therefore, by alternately adding acid or base to a solution of the catenane, we expected it to adjust its topography, i.e., to switch between the complex in which the phenylphenanthroline units surround an included cation and the form in which π-electron donor−acceptor interactions determine the relative orientation of the rings (Scheme 3). The changes were monitored by ^{1}H NMR and UV−vis spectroscopy.

Addition of trifluoroacetic acid (TFA, 1.5 equiv) to a solution of **8**.4PF$_6$ in CD$_3$CN causes significant changes in the catenane's ^{1}H NMR spectrum (Figure 6, hydrogen atoms labeling is as in Figure 4). The signals of methylene hydrogen atoms α, β, γ, and δ of the polyethylene glycol chain are shifted downfield ($\Delta\delta$ 0.1−0.2 ppm), and the signals of npH$_{2,6}$, npH$_{3,7}$, and npH$_{4,8}$ of the 1,5-dioxynaphthalene residue are shifted significantly downfield ($\Delta\delta$ 0.25, 0.40, and 0.30 ppm, respectively). These changes are consistent with the replacement of the $\pi-\pi$ donor−acceptor complex between the 1,5-dioxynaphthalene and bipyridinium moieties with a proton catenate: the $\pi-\pi$ stacking interaction vanishes, resulting for the 1,5-dioxynaphthalene in a strong downfield shift of its hydrogen atoms signals. On addition of C$_5$D$_5$N, the resonances of the hydrogen atoms of the 1,5-dioxynaphthalene residue and the polyethyleneglycol chain were restored to their previous positions, indicating reformation of the donor−acceptor complex. The protonated molecule is in rapid exchange with free **8**$^{4+}$ as witnessed by the averaged signals obtained for the two species upon addition of substoichiometric amounts of acid or base (Figure 6). Repeated sequential additions of acid and base showed reversible switching of the peak positions between the values corresponding to the first addition of acid and the subsequent additions of pyridine and TFA.[31]

An MeCN solution of **8**.4PF$_6$ exhibits the characteristic charge-transfer band centered at 470 nm (vide supra), indicating a topography determined by the donor−acceptor complex (Figure 7). On addition of TFA, this absorption band vanishes. Since the phenanthroline residues are the only basic moieties present in solution, we could attribute this absorption change to their protonation,[30] leading to the formation of the proton catenate, thus inducing a reorientation of the interlocked rings such that the intramolecular π-electron donor−acceptor complex is destroyed. Upon addition of pyridine, the original spectrum of **8**.4PF$_6$ was fully reconstituted, indicating complete recovery of the π-electron donor−acceptor complex.

(31) Other peaks arising from hydrogen atoms attached to the bipyridinium unit in particular are sensitive to solvent polarity, and are thus nonreversibly shifted by consecutive additions of TFA and C$_5$D$_5$N.

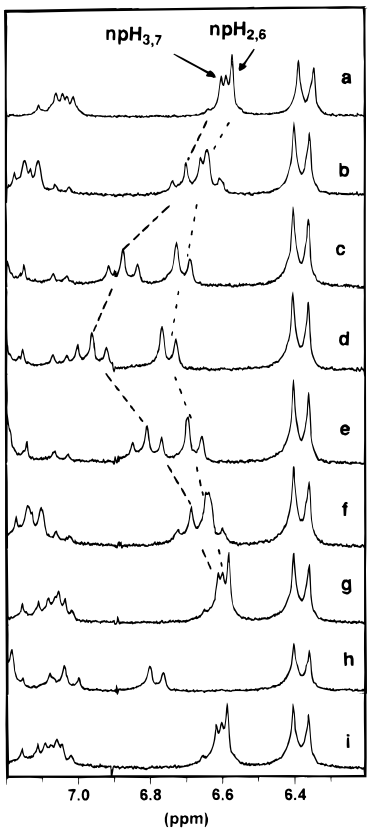


Figure 6. The switching of the [2]-catenand **8**.4PF$_6$ in CD$_3$CN (**a**: **8**.4PF$_6$) by sequential additions of acid (TFA; **b**: 0.5 equiv; **c**: 1 equiv; **d**: 1.5 equiv) then base (C$_5$D$_5$N; **e**: 1.5 equiv of TFA + 0.5 equiv of C$_5$D$_5$N; **f**: 1.5 equiv of TFA + 1 equiv of C$_5$D$_5$N; **g**: 1.5 equiv of TFA + 1.5 equiv of C$_5$D$_5$N) and repeated switching (**h**: 1.5 equiv of TFA + 1.5 equiv of C$_5$D$_5$N + 1.5 equiv of TFA; **i**: 1.5 equiv of TFA + 1.5 equiv of C$_5$D$_5$N + 1.5 equiv of TFA + 1.5 equiv of C$_5$D$_5$N) as monitored by ^{1}H NMR spectroscopy (200 MHz).

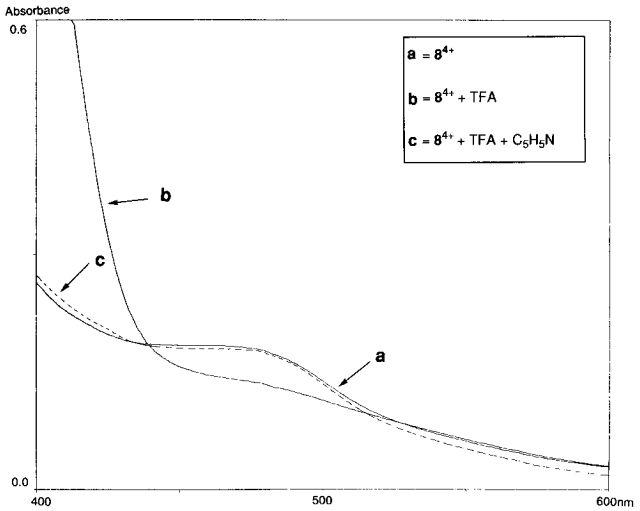


Figure 7. The switching of the [2]-catenand **8**.4PF$_6$ in MeCN by addition of acid (TFA) then base (pyridine) as monitored by UV−vis spectroscopy.

Conclusion. In summary, a [2]-catenane **1**$^{5+}$ has been

prepared by a metal-ion templated strategy. Modifications in the ^{1}H NMR and especially UV−vis spectra of the derived [2]-catenand **8**$^{4+}$ on additions of acid and base illustrate the changes in the molecular topography, as the interlocked molecular system switches reversibly between a proton catenate and a $\pi-\pi$ donor−acceptor complex.

Experimental Section

Materials and General Procedures. The following chemicals were obtained commercially and were used without further purification: 4,4′-bipyridine (Aldrich), 1,3-bisbromomethyl benzene (Aldrich), Cs_2CO_3 (Aldrich), KCN (Janssen), KPF_6 (Janssen), nitromethane (Fluka), d_5-pyridine (Aldrich), and tetrabutylammonium hexafluorophosphate (Fluka). The following materials were prepared according to literature procedures: $Cu(MeCN)_4PF_6$,[32] 2,9-bis(4-phenoxy)-1,10-phenanthroline,[12] 1,5-bis[2-(2-(toluene-*p*-sulfonyl)ethoxy)ethoxy]naphthalene,[14] and 2,9-bis-(4-bromomethylphenyl)-1,10-phenanthroline.[16] Dry solvents were distilled from suitable dessicants (DMF from CaH_2 in vacuo, MeCN from P_2O_5) according to literature methods.[33] Thin-layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F_{254} (Merck 5554). After elution, the plates were either scrutinized under a UV lamp or exposed to I_2. Column chromatography was carried out on silica gel 60 (Merck 9385, 230−400 mesh). UV−vis spectra were recorded on a Kontron Instruments UVIKON 860 spectrophotometer. Fast atom bombardment mass spectrometry (FABMS) were 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 were recorded in the positive ion mode by dissolving the compound or complex in MeCN at a concentration of 50 pmol μL^{-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 (Vc) of 40 V, with a source temperature of approximately 30 °C. The ^{1}H 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).

Macrocycle 2. 2,9-Bis-(4-hydroxyphenyl)-1,10-phenanthroline (**4**) (1.10 g, 3.02 mmol) and 1,5-bis[2-(2-(toluene-*p*-sulfonyl)ethoxy)ethoxy]-naphthalene (**3**) (1.95 g, 3.02 mmol) were dissolved in dry degassed DMF (300 mL) and were added dropwise over 48 h to a vigorously stirred suspension of Cs_2CO_3 (3.25 g, 9.97 mmol) and Cs0Ts (1.84 g, 6.04 mmol) in dry degassed DMF (480 mL) maintained at 70 °C under an atmosphere of argon. After the addition was complete, stirring and heating were continued for a further 3 days, after which the solvent was removed in vacuo. The brown residue was partitioned between CH_2Cl_2 (200 mL) and 10% aqueous $NaHCO_3$ solution (200 mL). The separated organic layer was then washed with a saturated aqueous NaCl solution (200 mL), dried over Na_2SO_4, and filtered. The solvent was removed in vacuo. Then the residue was redissolved in CH_2Cl_2 and was subjected to column chromatography (SiO_2, gradient elution, CH_2Cl_2 to 2% EtOAc in CH_2Cl_2). The product (1.10 g, 55%) was afforded as a white solid which turned yellow on standing in light and air: mp 39−40 °C; FABMS 665 (M^+); ^{1}H NMR ($CDCl_3$, 300.13 MHz) δ 4.02 (t, J = 4.7 Hz, 4H), 4.08 (t, J = 4.7 Hz, 4H), 4.25 (t, J = 4.7 Hz, 4H), 4.38 (t, J = 4.7 Hz, 4H), 6.99 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 8.4 Hz, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.71 (s, 2H), 7.99 (d, J = 7.7 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H), 8.23 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 67.8, 68.2, 70.1, 70.4, 106.4, 114.9, 115.1, 119.1, 125.3, 125.6, 127.1, 127.5, 129.0, 132.4, 136.7, 146.0, 154.6, 156.1, 160.2. Anal. Calcd for $C_{42}H_{36}N_2O_6$: C, 75.87, H, 5.46, N, 4.27. Found: C, 75.98, H, 5.20, N, 4.50.

5.2PF$_6$. A solution of 4,4′-bipyridine (6.30 g, 40 mmol) in dry MeCN (200 mL) was warmed to 60°C with stirring under a silica gel guard. 2,9-Bis-(4-bromomethylphenyl)-1,10-phenanthroline (**6**) (1.04 g, 2.0 mmol) was added as a solid to this solution over a period of 24 h. The resulting suspension was heated with stirring for a further 24 h. The cool reaction mixture was filtered, and the solid residue was washed with Et_2O (100 mL) and then redissolved in a mixture of MeCN (50 mL) and H_2O (50 mL). This solution was filtered, and then a saturated solution of KPF_6 in H_2O (50 mL) was added, causing the precipitation of a pale yellow solid. After standing overnight, the solid was filtered under gravity and washed with H_2O (50 mL) before being dissolved in 7:2:1 MeOH: 2 M NH_4Cl (aqueous):$MeNO_2$ and subjected to column chromatography (SiO_2) using the same solvent mixture as eluent. The fractions containing the product (as determined by TLC) were stripped off solvent and redissolved in a mixture of MeCN and H_2O (1:10). The product was precipitated as its bishexafluorophosphate salt by the addition of a saturated solution of KPF_6 in H_2O, filtered, and dried in vacuo. The product (765 mg, 40%) was a pale brown solid: mp dec 240 °C; FABMS 815 ($[M-PF_6]^+$), 669 ($[M-2PF_6]^+$), 514 ($[M-4,4'\text{-bipy}-PF_6]^+$), 357.1 ($[M-2\times 4,4'\text{-bipy}]^+$); ESMS 815 ($[M-PF_6]^+$), 335 ($[M-2PF_6]^{2+}$); ^{1}H NMR ($CD_3CN$, 200.13 MHz) δ 5.86 (s, 4H), 7.69 (d, J = 8.3 Hz, 4H), 7.77 (bd, J = 5.8 Hz, 4H), 7.96 (s, 2H), 8.25−8.35 (m, 6H), 8.48−8.58 (m, 6H), 8.83 (bd, J = 5.8 Hz, 4H), 8.89 (d, J = 6.9 Hz, 4H); ^{13}C NMR (CD_3CN, 50.32 MHz) δ 64.86, 121.45, 122.76, 127.15, 127.64, 129.49, 130.82, 134.93, 138.64, 141.65, 141.94, 145.88, 146.64, 152.09, 155.44, 156.01. Anal. Calcd for $C_{46}H_{34}N_6P_2F_{12}.1.5H_2O$: C, 55.93, H, 3.77, N, 8.51. Found: C, 55.63, H, 3.42, N, 8.77.

7.3PF$_6$. A solution of $Cu(MeCN)_4PF_6$ (132 mg, 0.35 mM) in dry degassed MeCN (2 × 30 mL) was transferred via a cannula to a stirred solution of the macrocycle **2** (233 mg, 0.35 mM) in CH_2Cl_2 (35 mL) all under an atmosphere of argon at room temperature. The resulting yellow solution was stirred for 5 min. Then a solution of **5.2PF$_6$** in dry degassed MeCN (50 mL) was transfered via a cannula into it, resulting in the immediate formation of a deep red solution which was stirred for 14 h at room temperature. The solvent was removed in vacuo, leaving a deep red solid (660 mg, 100%): ESMS 1688 ($[M-PF_6]^+$), 815 ($[\mathbf{7}.PF_6]^+$), 772 ($[M-2PF_6]^{2+}$), 727 ($[\mathbf{4}+Cu]^+$), 465.5 ($[M-3PF_6]^{3+}$); ^{1}H NMR (CD_3CN, 400.13 MHz) δ 3.62 (t, J = 4.3 Hz, 4H), 3.77 (t, J = 4.3 Hz, 4H), 4.00−4.07 (m, 4H), 4.55−4.59 (m, 4H), 5.32 (s, 4H), 5.91 (d, J = 8.7 Hz, 4H), 6.61 (d, J = 8.1 Hz, 4H), 7.04 (s, 2H), 7.15 (d, J = 8.7 Hz, 4H), 7.21 (d, J = 7.5 Hz, 2H), 7.45 (d, J = 8.1 Hz, 4H), 7.56 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 7.5 Hz, 2H), 7.75 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 7.88 (vbd, 4H), 7.95 (s, 2H), 8.02 (d, J = 8.4 Hz, 2H), 8.29 (d, J = 6.9 Hz, 4H), 8.45 (d, J = 8.4 Hz, 2H), 8.57 (d, J = 6.9 Hz, 4H), 8.92 (vbd, 4H). This material was used in the next stage of the synthesis without further purification.

1.5PF$_6$. Solutions of **7.3PF$_6$** (660 mg, 0.35 mM) in MeCN (200 mL) and 1,3-bis-bromomethylbenzene (95 mg, 0.36 mM) were added simultaneously to a refluxing, stirred and degassed solution of $Cu(MeCN)_4PF_6$ (50 mg, 0.13 mM) in dry MeCN (350 mL) over a period of 4 days under an atmosphere of argon. After the addition was complete, an extra amount of 1,3-bisbromomethylbenzene (15 mg, 0.06 mM) was added as a solid, and the whole was maintained at reflux for a further 4 days. The solvent was evaporated, and the residue was redissolved in 7:2:1 MeOH: 2 M NH_4Cl (aqueous):$MeNO_2$ and subjected to column chromatography (SiO_2) using the same solvent mixture as eluent. The fractions containing the product were stripped off solvent and redissolved in H_2O, and then KPF_6 (aqueous) was added to precipitate the product as its hexafluorophosphate salt. This material was subjected to further column chromatography (SiO_2) using 7:2:1 MeOH: 2 M NH_4Cl (aqueous):$MeNO_2$ as eluent. The product was obtained as its hexafluorophosphate salt as before and was then crystallized from MeCN, EtOAc, and *i*-Pr_2O by the vapor diffusion method. The product (311 mg, 40%) was a deep red color: mp > 280 °C; FABMS 2082 ($[M-PF_6]^+$), 1937 ($[M-2PF_6]^+$), 1792 ($[M-3PF_6]^+$), 1648 ($[M-4PF_6]^+$), 896 ($[M-2PF_6]^{2+}$), 727 ($[\mathbf{4}+Cu]^+$), 561 (fragment containing two pyridine-pyridinium groups spaced by a *m*-xylyl unit ($[M-PF_6]^+$) resulting from the breakage of the cyclophane component of the catenate); ESMS 968.5 ($[M-2PF_6]^{2+}$), 597 ($[M-3PF_6]^{3+}$); ^{1}H NMR (CD_3CN, 400.13 MHz) δ 3.50 (t, J = 4.3 Hz, 4H), 3.73 (t, J = 4.3 Hz, 4H), 4.01−4.08 (m, 4H), 4.57−4.64 (m, 4H), 5.49 (s, 4H), 5.89 (d, J = 8.4 Hz, 4H), 5.91 (s, 4H), 6.53 (d, J = 8.4 Hz, 4H), 6.60 (s, 2H), 7.19 (d, J = 8.8 Hz, 4H), 7.24 (d, J = 7.6 Hz, 2H), 7.55−7.63 (m, 6H), 7.68 (d, J = 8.4 Hz, 2H), 7.74−7.81 (m,

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6H), 7.84−7.92 (m, 4H), 8.03 (d, J = 7.6 Hz, 2H), 8.22 (d, J = 8.4 Hz, 2H), 8.39 (d, J = 6.9 Hz, 4H), 8.42 (d, J = 6.8 Hz, 4H), 8.53 (d, J = 6.9 Hz, 4H), 8.98 (d, J = 6.8 Hz, 4H). Anal. Calcd for $C_{96}H_{78}N_8O_6P_5F_{30}Cu.H_2O$: C, 51.37, H, 3.59, N, 4.99. Found: C, 51.10, H, 3.85, N, 4.83.

8.4PF$_6$. To a stirred solution of the copper(I) catenate **1.5PF$_6$** (68 mg, 0.03 mM) in H_2O:MeCN (2:1, 50 mL) with KCl (10 mg, 0.13 mM) was added KCN (5 mg, 0.08 mM) as a solid. The mixture partially decolored instantaneously to afford an orange color, and some precipitation was observed. Stirring was continued at ambient temperature for 20 min. Then KPF_6 (aqueous, 20 mL) was added, causing further precipitation. After 10 min, the solid was filtered under gravity and carefully washed with H_2O (40 mL). The solid was redissolved in MeCN (20 mL), and filtered, and then the solvent was removed in vacuo. The remaining solid was washed several times with CH_2Cl_2 (4 × 20 mL) and was then dried. The orange solid (50 mg, 81%) was characterized as **8.4PF$_6$**: mp dec 260 °C; FABMS 1874 ($[M-PF_6]^+$), 1729 ($[M-2PF_6]^+$), 1583 ($[M-3PF_6]^+$), 1439 ($[M-4PF_6]^+$), 1064 (tetracationic cyclophane component $[M-2PF_6]^+$), 920 (tetracationic cyclophane component $[M-3PF_6]^+$), 665 ([**4**]$^+$), 561 (fragment containing two pyridine-pyridinium groups spaced by a *m*-xylyl unit ($[M-PF_6]^+$) resulting from the breakage of the cyclophane component of the catenate). ^{1}H NMR (CD_3CN, 400.13 MHz, 298 K) δ 3.84−3.88 (m, 4H), 3.89−3.93 (m, 4H), 4.03−4.07 (m, 4H), 4.29−4.34 (m, 4H), 5.53 (s, 4H), 5.63 (s, 4H), 6.38 (d, J = 8.6 Hz, 4H), 6.56−6.64 (m, 4H), 7.08 (d, J = 7.7 Hz, 2H), 7.36 (d, J = 8.2 Hz, 4H), 7.53 (d, J = 8.6 Hz, 4H), 7.65−7.72 (m, 5H), 7.74−7.79 (m, 5H), 7.88 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 6.7 Hz, 4H), 8.01 (s, 2H), 8.30 (d, J = 8.4 Hz, 2H), 8.42 (d, J = 8.4 Hz, 2H), 8.51 (d, J = 8.2 Hz, 4H), 8.55 (d, J = 8.4 Hz, 2H), 8.60 (d, J = 6.7 Hz, 4H), 8.74 (d, J = 6.7 Hz, 4H).

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 MeCN, using 0.1 M nBu_4PF_6 solutions as electrolytes.

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