Dual-Mode "Co-Conformational" Switching in Catenanes Incorporating Bipyridinium and Dialkylammonium Recognition Sites**

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Abstract: Three [2]catenanes and three [3]catenanes incorporating one or two π-electron-rich macrocyclic polyethers and one π-electron-deficient polycationic cyclophane have been synthesized in yields ranging from 4 to 38%. The π-electron-rich macrocyclic components possess either two 1,4-dioxybenzene or two 1,5-dioxynaphthalene recognition sites. The π-electron-deficient cyclophane components incorporate two bipyridinium and either one or two dialkylammonium recognition sites. The template-directed syntheses of these catenanes rely on i) π⋯π stacking interactions between the dioxyarene and bipyridinium recognition sites, ii) C–H⋯O hydrogen bonds between some of the bipyridinium hydrogen atoms and some of the polyether oxygen atoms, and iii) C-H⋯π interactions between some of the dioxyarene hydrogen atoms and the aromatic spacers separating the bipyridinium units. The six catenanes were characterized by mass spectrometry and by both ^{1}H and ^{13}C NMR spectroscopy. The absorption spectra and the electrochemical properties of the catenanes have been investigated and compared with those exhibited by the component macrocycles and by related known catenanes. Broad and weak absorption bands in the visible region, originating from charge-transfer (CT) interactions between electron-donor and electron-acceptor units, have been observed. Such charge-transfer interactions are responsible for the quenching of the potentially fluorescent excited states of the aromatic units of the macrocyclic polyether components. The redox behavior of these novel compounds has been investigated and correlations among the observed redox potentials are illustrated and discussed. The catenanes undergo co-conformational switching upon one-electron reduction of the two bipyridinium units. One of them—in its reduced form—can be also switched by acid/base inputs and exhibits AND logic behavior. The co-conformational rearrangements induced by the redox and acid/base stimulations lend themselves to exploitation in the development of molecular-level machines and logic gates.

Keywords: catenanes · cyclophanes · electrochemistry · molecular machines · template synthesis

Introduction

Molecules incorporating mechanically-interlocked components,[1] that is, the so-called catenanes and rotaxanes, are ideal candidates for the generation of molecular-sized switches[2] and machines.[3] Indeed, bistable [2]catenanes[4] and [2]rotaxanes[5] can be designed and constructed by introducing chemically-, electrochemically-, and/or photochemically-active recognition sites into one of their two interlocked components. By employing chemical, electrochemical, and/or photochemical stimuli, the recognition properties of these units can be altered, inducing the movement of one of the interlocked components relative to the other. By exploiting such externally triggered dynamic processes, switching between two stable states becomes possible. Recently, we designed[6] and synthesized a series of [2]rotaxanes that incorporate a bipyridinium and a dialkylammonium recognition site in their dumbbell-shaped components, which are encircled by a π-electron-rich macrocyclic

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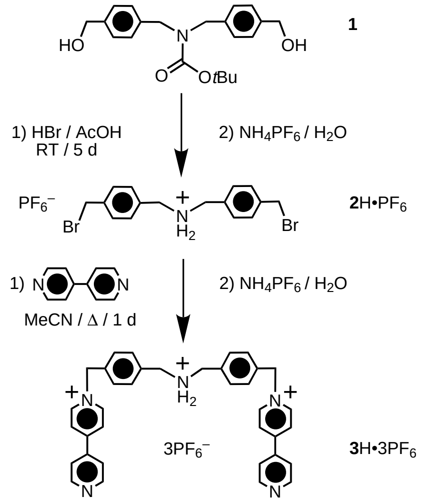
polyether. These [2]rotaxanes can be switched reversibly between two states by deprotonation/protonation of the dialkylammonium recognition site as these processes are accompanied by the shuttling of the macrocyclic component from the dialkylammonium to the bipyridinium recognition site and vice versa. Furhermore, the recognition properties of the bipyridinium unit can be modulated electrochemically.[7] Therefore, the presence of two recognition sites of a different nature leads to the possibility of dual-mode[8] (acid/base and redox) stimulation of the system. In order to generate switchable catenanes, we have taken the opportunity to synthesize molecules incorporating π-electron-rich macrocyclic polyethers interlocked with polycationic cyclophanes that possess bipyridinium and dialkylammonium recognition sites. Here, we report the template-directed syntheses[9, 10] of three [2]catenanes and three [3]catenanes in which cyclophanes of this type are interlocked with 1,4-dioxybenzene- or 1,5-dioxynaphthalene-based macrocyclic polyethers. The absorption spectra and electrochemical properties of the novel catenanes have been investigated and compared with those exhibited by the component macrocycles and by related known catenanes. One of these catenanes reveals an interesting machine-like behavior and logic gate performance.

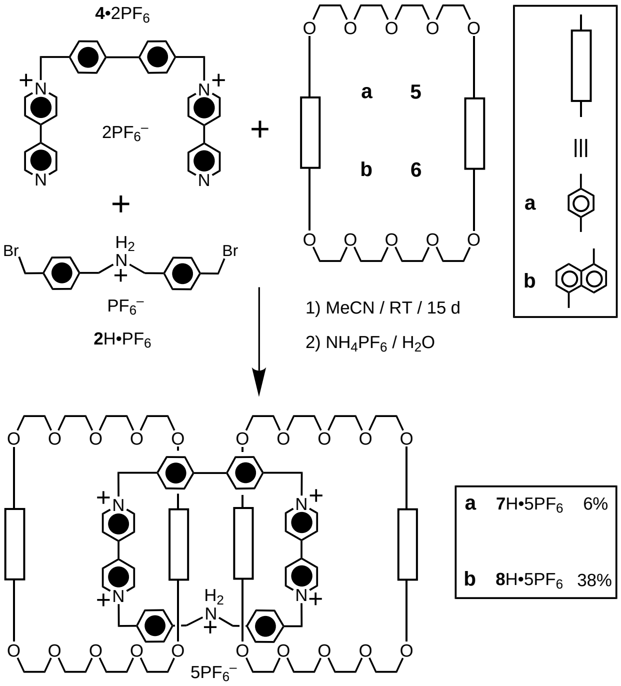
Abstract in Italian: *Sono stati sintetizzati tre [2]catenani e tre [3]catenani contenenti un ciclofano policationico π elettron accettore e, rispettivamente, uno e due polieteri macrociclici π elettron donatori, con rese comprese fra 4 e 38 %. I componenti macrociclici π donatori possiedono due unità 1,4-diossibenzene o due unità 1,5-diossinaftalene, mentre il componente π accettore contiene due gruppi dipiridinio ed uno o due gruppi dialchilammonio. La sintesi templata di questi catenani si basa su i) interazioni π···π fra i siti di riconoscimento diossiaromatici e dipiridinio, ii) legami a idrogeno C–H···O fra atomi di idrogeno dei gruppi dipiridinio ed atomi di ossigeno delle catene polieteree e iii) interazioni C–H···π fra atomi di idrogeno delle unità diossiaromatiche e gli spaziatori p-fenilenici che separano i gruppi dipiridinio. I sei catenani sono stati caratterizzati mediante spettrometria di massa e spettroscopia* ^{1}*H e* ^{13}*C NMR. Il comportamento elettrochimico e gli spettri di assorbimento dei catenani sono stati esaminati e confrontati con quelli dei componenti macrociclici e di altri catenani simili studiati in precedenza. Si osservano bande di assorbimento deboli e allargate nella regione del visibile, attribuite alle interazioni di trasferimento di carica fra le unità π elettron donatrici e quelle π elettron accettrici. Tali interazioni sono responsabili anche dello spegnimento degli stati eccitati, potenzialmente fluorescenti, localizzati sulle unità aromatiche dei polieteri macrociclici. Dalle correlazioni fra i potenziali dei processi redox osservati si può concludere che i catenani subiscono riarrangiamenti co-conformazionali in seguito a riduzione monoelettronica dei due gruppi dipiridinio. Uno dei catenani esaminati, nella forma ridotta, dà luogo a riarrangiamenti strutturali anche a seguito di stimoli chimici di tipo acido/base, evidenziando un comportamento logico di tipo AND. I movimenti co-conformazionali indotti mediante stimoli redox e acido/base suggeriscono la possibilità di impiegare questi nuovi catenani per la realizzazione di macchine e porte logiche a livello molecolare.*

Results and Discussion

Synthesis: Treatment of **1** with HBr afforded the hexafluorophosphate salt **2**H · PF$_6$ (Scheme 1), which was reacted with 4,4′-bipyridine to give the tris(hexafluorophosphate) salt **3**H · 3PF$_6$. Reaction of **2**H · PF$_6$ and **4** · 2PF$_6$ in the presence of the 1,4-dioxybenzene-based macrocyclic polyether **5** (BPP34C10) afforded the [3]catenane **7**H · 5PF$_6$ in a yield of 6% (Scheme 2), after counterion exchange. When the 1,5-dioxy-

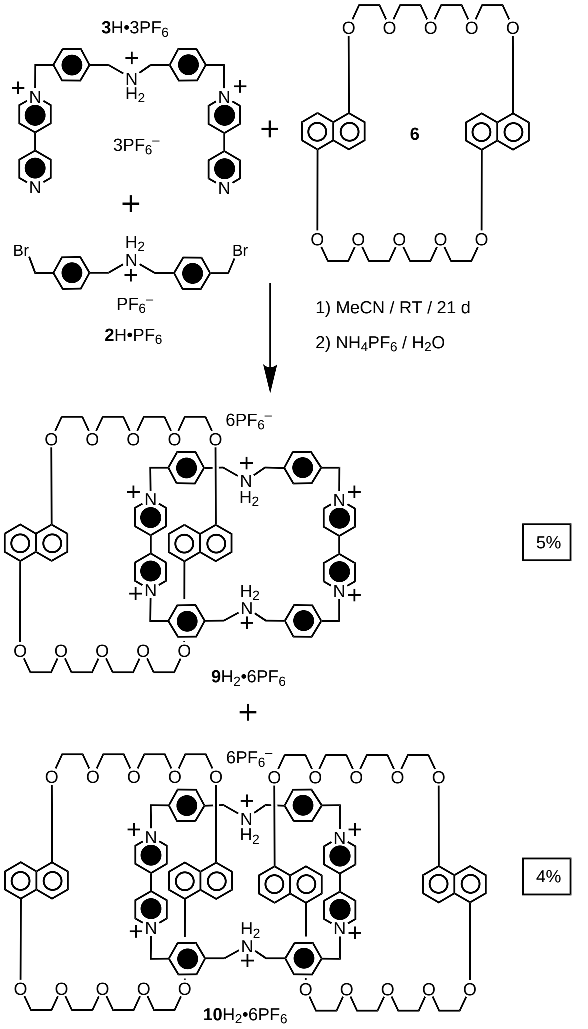


Scheme 1. The synthesis of the tris(hexafluorophosphate) salt **3**H · 3PF$_6$.

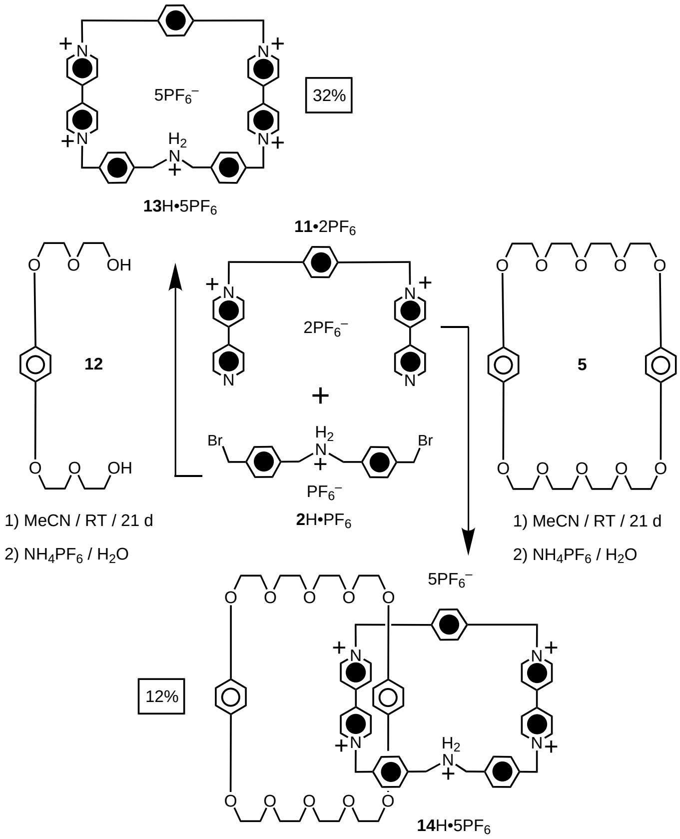


Scheme 2. The template-directed syntheses of the [3]catenanes **7**H · 5PF$_6$ and **8**H · 5PF$_6$.

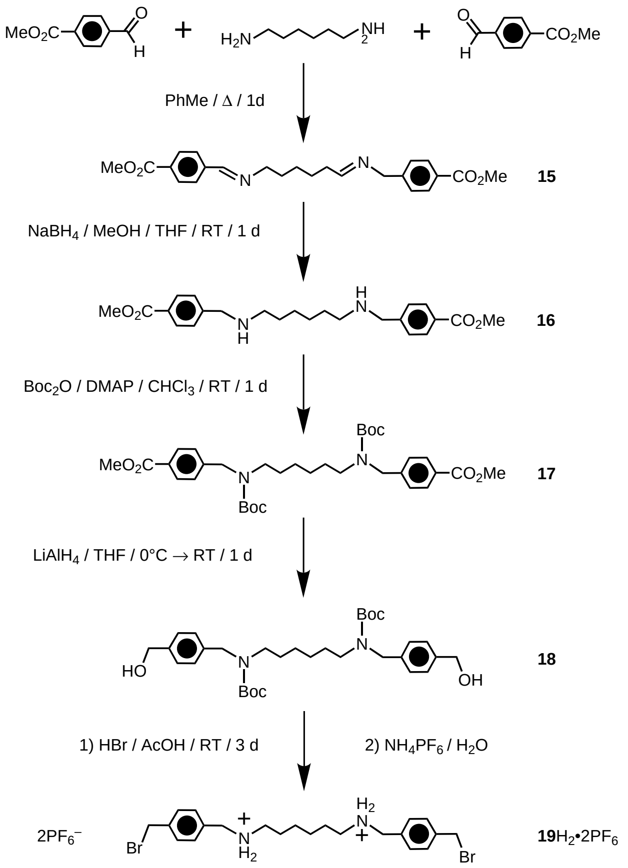
naphthalene-based macrocyclic polyether **6** (1/5DN38C10) was used instead, under otherwise identical conditions, the [3]catenane **8**H $\cdot$ 5PF$_6$ was isolated in a yield of 38%. The efficiency of the catenation diminished significantly when the tris(hexafluorophosphate) salt **3**H $\cdot$ 3PF$_6$ was treated with **2**H $\cdot$ PF$_6$ in the presence of **6** (Scheme 3). In this instance, however, the [2]catenane **9**H$_2$ $\cdot$ 6PF$_6$ was obtained, together with the [3]catenane **10**H$_2$ $\cdot$ 6PF$_6$, in yields of 5 and 4%, respectively. No catenanes were isolated when the reaction was carried out in the presence of **5** instead. The template-directed synthesis of the pentacationic cyclophane **13**H $\cdot$ 5PF$_6$ was realized (Scheme 4) by treating **2**H $\cdot$ PF$_6$ with **11** $\cdot$ 2PF$_6$ in the presence of the 1,4-dioxybenzene-based template **12**. When **5** was employed instead, under otherwise identical conditions, the [2]catenane **14**H $\cdot$ 5PF$_6$ was isolated in a yield of 12%. Condensation of 1,6-diaminohexane with methyl 4-formylbenzoate, followed by the reduction of the resulting bisimine **15**, gave the bisamine **16** (Scheme 5). Protection of **16**, followed by the reduction of the resulting compound **17**, yielded the diol **18** which was treated with HBr to afford the bis(hexafluorophosphate) salt **19**H$_2$ $\cdot$ 2PF$_6$. Reaction of **11** $\cdot$



Scheme 3. The template-directed synthesis of the [2]catenane **9**H$_2$ $\cdot$ 6PF$_6$ and of the [3]catenane **10**H$_2$ $\cdot$ 6PF$_6$.

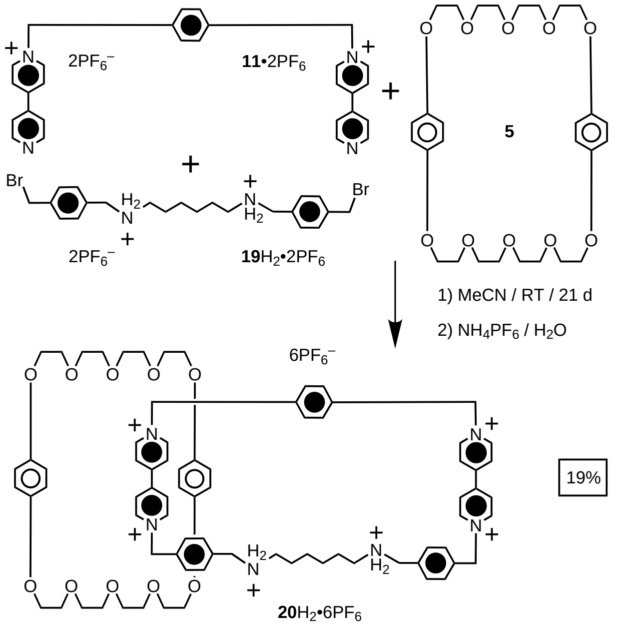


Scheme 4. The template-directed synthesis of the cyclophane **13**H $\cdot$ 5PF$_6$ and of the [2]catenane **14**H $\cdot$ 5PF$_6$.



Scheme 5. The synthesis of the bis(hexafluorophosphate) salt **19**H$_2$ $\cdot$ 2PF$_6$.

$2PF_6$ with **19**$H_2 \cdot 2PF_6$ in the presence of **5** gave the [2]catenane **20**$H_2 \cdot 6PF_6$ in a yield of 19% (Scheme 6), after counterion exchange.



Scheme 6. The template-directed synthesis of the [2]catenane **20**$H_2 \cdot 6PF_6$.

Mass spectrometry: The [2]catenanes and the [3]catenanes were characterized (Table 1) by liquid secondary ion mass spectrometry (LSIMS). In all instances, the spectra revealed peaks at *m*/*z* values for $[M-3PF_6]^+$ and $[M-4PF_6]^+$ corresponding to the losses of three and four hexafluorophosphate counterions, respectively. For the [3]catenanes **7**$H \cdot 5PF_6$ and **8**$H \cdot 5PF_6$, peaks at *m*/*z* values for $[M-PF_6]^+$ and $[M-2PF_6]^+$ were also observed. The spectra of the [3]catenane **10**$H_2 \cdot 6PF_6$ and of the [2]catenane **14**$H \cdot 5PF_6$ revealed peaks at *m*/*z* values for $[M-2PF_6]^+$. For the [2]catenanes **9**$H_2 \cdot 6PF_6$ and **20**$H_2 \cdot 6PF_6$, and for the [3]catenane **10**$H_2 \cdot 5PF_6$, peaks at *m*/*z* values for $[M-5PF_6]^+$ were also observed.

Table 1. Liquid secondary ion mass spectrometric (LSIMS) data[a] for the [2]catenanes **9**$H_2 \cdot 6PF_6$, **14**$H \cdot 5PF_6$, and **20**$H_2 \cdot 6PF_6$ and for the [3]catenanes **7**$H \cdot 5PF_6$, **8**$H \cdot 5PF_6$, and **10**$H_2 \cdot 6PF_6$.

Catenane	$[M-PF_6]^+$	$[M-2PF_6]^+$	$[M-3PF_6]^+$	$[M-4PF_6]^+$	$[M-5PF_6]^+$
7$H \cdot 5PF_6$	2369	2224	2079	1933	[b]
8$H \cdot 5PF_6$	2570	2424	2279	2134	[b]
9$H_2 \cdot 6PF_6$	[b]	[b]	1829	1685	1540
10$H_2 \cdot 6PF_6$	[b]	2613	2467	2322	2176
14$H \cdot 5PF_6$	[b]	1611	1466	1320	[b]
20$H_2 \cdot 6PF_6$	[b]	[b]	1712	1567	1422

[a] The spectra were recorded on a VG ZabSpec mass spectrometer using 3-nitrobenzyl alcohol as matrix. The measured masses correspond to the centroids of unresolved isotopic distributions. [b] Not observed.

^{1}H NMR spectroscopy: The macrocyclic receptors BPP34C10 and 1/5DN38C10 bind bipyridinium dications as a result of strong π···π stacking and C–H···O interactions. Their *N*,*N*′-dimethyl-4,4′-bipyridinium dication complexes have stability constants of 240 and 1190 M^{-1}, respectively, in MeCN at 25 °C.[9m] These macrocycles, however, are relatively large. Only one of their two polyether loops can sustain $^+N-H \cdots O$ and $C-H \cdots O$ interactions with a dialkylammonium recognition site residing in the macrocyclic cavity. The lack of cooperative binding is reflected in the low stability constants for the corresponding 1:1 complexes.[11] The marked preference of BPPP34C10 and 1/5DN38C10 for bipyridinium recognition sites dictates the co-conformation of the catenanes (Figure 1), as demonstrated by the pronounced chemical shift changes suffered by the bipyridinium protons (vide infra). The cyclophane **13**H^{5+}, the [2]catenanes **9**H_2^{6+}, **14**H^{5+}, and **20**H_2^{6+}, and the [3]catenanes **7**H^{5+}, **8**H^{5+}, and **10**H_2^{6+} were analyzed by ^{1}H NMR spectroscopy at temperatures higher than or equal to 298 K. Under these conditions, the dynamic processes (vide infra) associated with the catenanes are fast on the ^{1}H NMR timescale, and, as a result, their ^{1}H NMR spectra are relatively simple. The chemical shifts (δ) for the α- and β-bipyridinium protons H_α and H_β are listed in Table 2. Two sets of signals are observed for the protons H_α and H_β of the [3]catenanes **7**H^{5+} and **8**H^{5+}. In the ^{1}H NMR spectrum of the [3]catenane **7**H^{5+}, which incorporates the BPP34C10 macrocycle, the H_α protons resonate at $\delta = 9.28$ and 9.13, and the H_β protons at $\delta = 8.09$ and 8.07. For the [3]catenane **8**H^{5+}, incorporating the 1/5DN38C10, the signals for the H_α protons shift upfield by about $\Delta\delta = 0.4$ ppm. A more pronounced

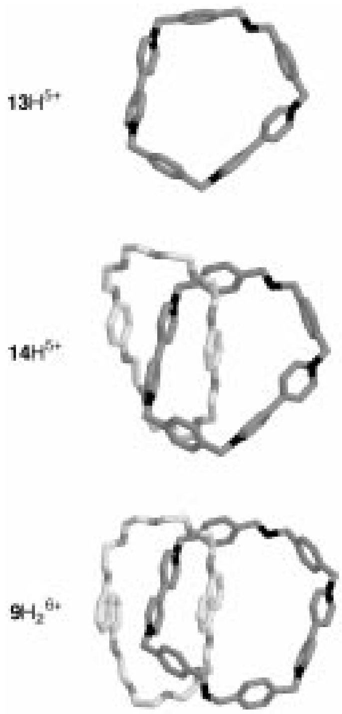


Figure 1. MMFF minimized (PC Spartan Pro) geometry of the cyclophane **13**H^{5+} and co-conformations of the [2]catenanes **14**H^{5+} and **9**H_2^{6+} in which the macrocyclic polyether encircles one of the two bipyridinium recognition sites of the pentacationic cyclophane. Hydrogen atoms have been omitted for clarity.

Table 2. Chemical shifts (δ) for the α- and β-bipyridinium protons H_α and H_β of the cyclophane **13**H^{5+}, the [2]catenanes **9**H$_2$$^{6+}$, **14**H^{5+}, and **20**H$_2$$^{6+}$, and the [3]catenanes **7**H^{5+}, **8**H^{5+}, and **10**H$_2$$^{6+}$.

Compound	H_α	H_β	Solvent	Temperature [K]
7H^{5+}	9.28/9.13[a]	8.09/8.07[a]	$(CD_3)_2CO$	304
8H^{5+}	8.85/8.74[a]	7.03/7.00[a]	$(CD_3)_2CO$	304
9H$_2$$^{6+}$	8.76[b]	7.53 [b]	CD_3CN	344
10H$_2$$^{6+}$	8.84[b]	7.15 [b]	CD_3CN	304
13H^{5+}	9.37[b]	8.62/8.59[a]	$(CD_3)_2CO$	298
14H^{5+}	8.91/8.84[a]	7.91/7.88[a]	CD_3CN	298
20H$_2$$^{6+}$	9.32/9.26[a]	8.46/8.44[a]	$(CD_3)_2CO$	298

[a] Two sets of signals, centered on the δ values listed, are observed in the ^{1}H NMR spectrum. [b] One set of signals, centered on the δ value listed, is observed in the ^{1}H NMR spectrum.

upfield shift is observed for the resonances of the H_β protons, which move by approximately $\Delta\delta = 1.0$ ppm. These observations indicate that the 1,5-dioxynaphthalene units of the macrocyclic polyether of **8**H^{5+} exert a more pronounced shielding effect upon the bipyridinium protons than the 1,4-dioxybenzene rings of **7**H^{5+}. Comparison of the chemical shifts of the bipyridinium protons of the [2]catenane **9**H$_2$$^{6+}$ and the [3]catenane **10**H$_2$$^{6+}$, both incorporating the same hexacationic cyclophane component, shows a small difference in the δ values for the H_α protons and a change of about $\Delta\delta = 0.4$ ppm for the H_β protons. These observations confirm that the H_β protons are more sensitive than the H_α protons to the shielding effects exerted by the sandwiching dioxyarene units.

In the case of the [3]catenane **7**H^{5+}, the temperature dependence of the ^{1}H NMR spectrum was investigated. At 294 K in CD_2Cl_2/CD_3CN, the circumrotation of the two BPP34C10 macrocycles (Figure 2) through the cavity of the pentacationic cyclophane is fast on the ^{1}H NMR timescale. As a result, the 1,4-dioxybenzene rings located inside and alongside the cavity of the pentacationic cyclophane cannot be distinguished. All their protons resonate (Figure 2a) as a singlet centered at $\delta = 6.08$. Upon cooling down, the rate of the dynamic process decreases, and this signal becomes broad (Figure 2b) and then merges into the baseline (Figure 2c). At 270.8 K, the half-height broadening ($\Delta\tilde{\nu}$) of this resonance is 66 Hz. This value corresponds to a rate constant of 207 Hz and a free energy barrier of 12.9 kcal mol^{-1} for the circumrotation.[12]

Absorption, emission, and electrochemical properties: The compounds we have investigated are illustrated schematically in Figure 3. Unfortunately, the cyclophane components (represented within square brackets in Figure 3) of the catenanes **7**H^{5+}, **8**H^{5+}, **9**H$_2$$^{6+}$, and **10**H$_2$$^{6+}$ could not be isolated, while the [2]catenane **20**H$_2$$^{6+}$ was not available in a sufficient amount to perform the spectroscopic and electrochemical investigations. For comparison, we have also taken into consideration the cyclophane **21**$^{4+}$, its [2]catenanes **22**$^{4+}$ and **23**$^{4+}$, the cyclophane **24**$^{4+}$, and its [3]catenanes **25**$^{4+}$ and **26**$^{4+}$. The spectroscopic and electrochemical properties of these compounds, which do not contain ammonium recognition sites, have been investigated previously.[4g, 13, 14] The absorption and emission properties of all these compounds are summarized in Tables 3 and 4. All the [2]catenanes and [3]catenanes exhibit low-energy charge-transfer bands caused by the interactions between the electron deficient bipyridinium units contained in the polycationic cyclophanes and the electron-rich dioxyarene units of the macrocyclic polyethers, BPP34C10 (**5**) and 1/5DN38C10 (**6**).[4f–i, 5a,f,g] Such low-energy excited states are responsible for the quenching of the higher energy, potentially

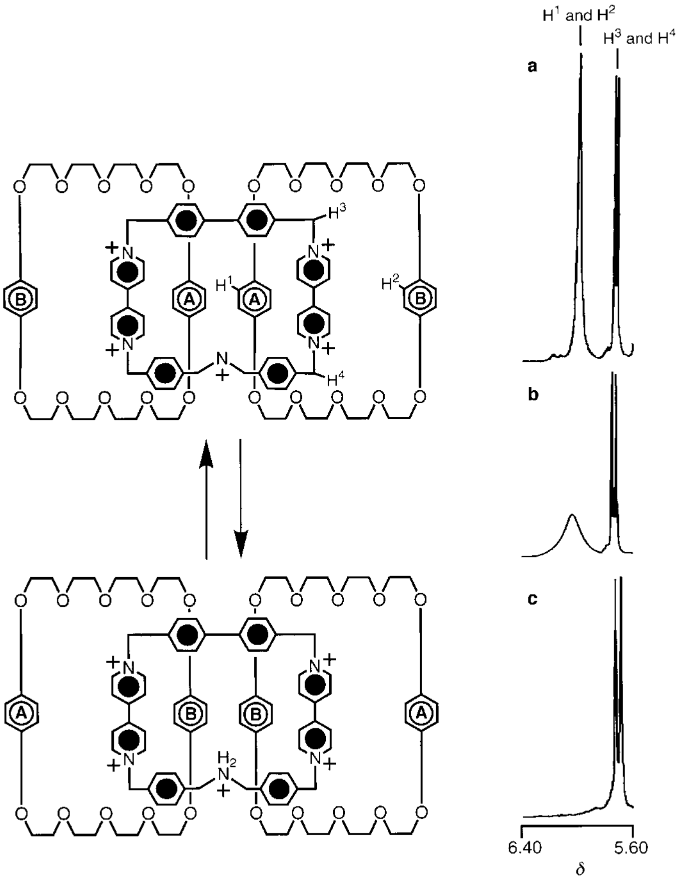


Figure 2. Circumrotation of the two macrocycles **5** of the [3]catenane **7**H^{5+} through the cavity of the pentacationic cyclophane exchanging the 1,4-dioxybenzene rings A and B. Partial ^{1}H NMR spectra of **7**H^{5+} in CD_2Cl_2/CD_3CN at a) 294, b) 273, and c) 253 K.

Table 3. Absorption and electrochemical data (MeCN, 298 K) of the macrocyclic polyether **5**, the cyclophanes **21**$^{4+}$, **24**$^{4+}$ and **13**H^{5+}, the reference [2]catenane **22**$^{4+}$, the reference [3]catenane **25**$^{4+}$, the [2]catenane **14**H^{5+}, and the [3]catenane **7**H^{5+}.

Compound	Absorption[a]		Electrochemical reduction[b]
	λ_{max} [nm]	ε [M^{-1}cm^{-1}]	$E_{1/2}$ [V] (vs SCE)
5[c]	290	5200	–
21^{4+}[c]	261	40000	– 0.29 (2); – 0.71 (2)
25^{4+}[d]			– 0.46 (2); – 0.88 (2)
13H^{5+}	258	43000	– 0.33 (2); – 0.74 (2)
13^{4+}[e]	258	43000	– 0.32 (2); – 0.74 (2)
22^{4+}[c]	478	700	– 0.31 (1); – 0.44 (1); – 0.84 (2)
14H^{5+}	456	370	– 0.32 (1); – 0.40 (1); – 0.76 (2)
14^{4+}[e]	452	420	– 0.32 (1); – 0.43 (1); – 0.77 (1); – 0.85 (1)
7H^{5+}	459	830	– 0.44 (2); – 0.85 (2)
7^{4+}[e]	463	960	– 0.46 (2); – 0.87 (2)

[a] For the catenanes, only the data regarding the CT absorption band are reported. [b] Argon purged solution, tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte, glassy carbon as working electrode; all processes are reversible; halfwave potential values in V vs SCE; the number of exchanged electrons is indicated in parentheses. [c] Data from Ref. [4g]. [d] Data from Ref. [14]. [e] Obtained by addition of one equivalent of n-Bu$_3$N.

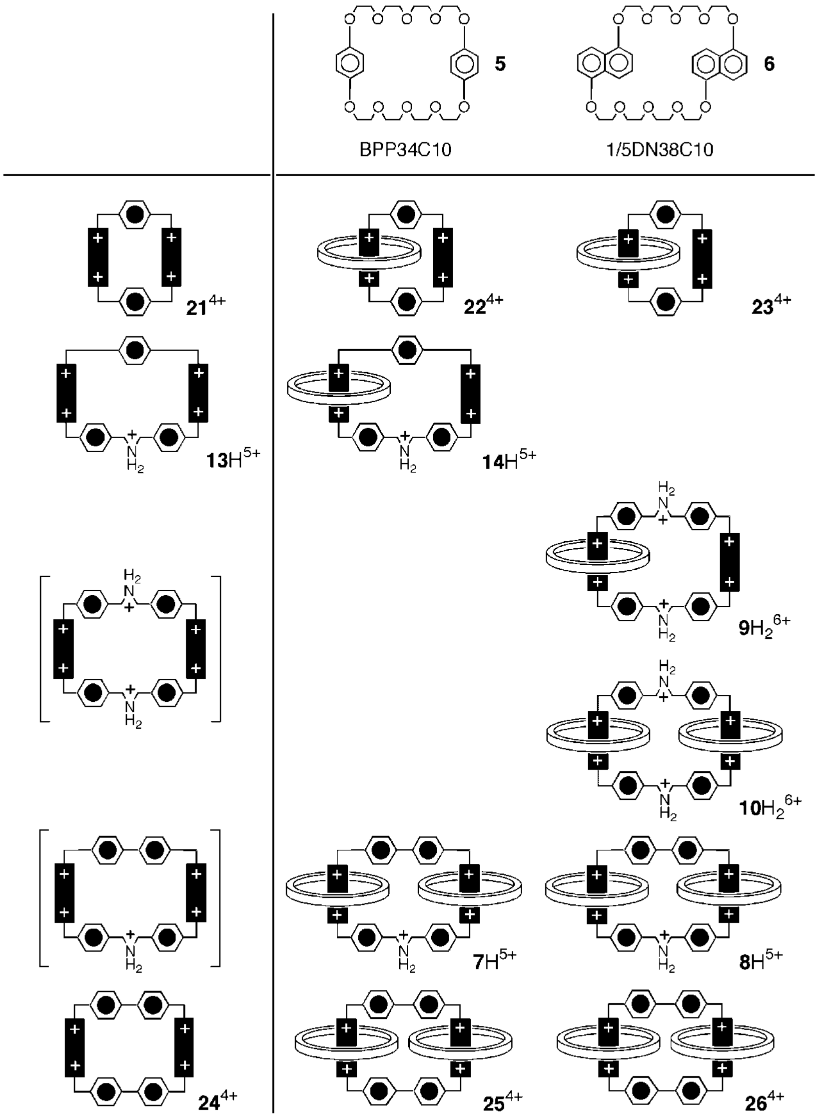


Figure 3. Graphical representation of the macrocyclic polyether, cyclophanes, and catenanes whose absorption spectra, luminescence properties, and electrochemical behavior are discussed. The cyclophanes enclosed within square brackets could not be synthesized.

luminescent excited states of the dioxyarene units.[4f–i, 5f,g] For each compound, a great number of redox processes are observed. They are related to the presence of the bipyridinium and dioxyarene electroactive units. It is well known that the potential values associated with such processes are diagnostic of the presence of donor/acceptor interactions[4f–i, 5a,f,g, 6c] and can therefore reveal the nature of the "co-conformations" adopted by the catenanes in their various redox and acid/base forms.[15]

The novelty of the compounds described in this paper is related to the presence in the polycationic cyclophanes of both bipyridinium units and dialkylammonium centers, which can play the roles of recognition sites for the aromatic crown ethers **5** and **6**. In order to understand the effects caused by the simultaneous presence of these two types of recognition sites, it is useful to compare the properties of these novel catenanes with those exhibited by related compounds that contain only the bipyridinium units within their cyclophane components.

For the sake of simplicity, we will discuss the compounds that contain the macrocyclic polyethers **5** and **6** separately.

*Catenanes containing BPP34C10 (**5**)*: The absorption and redox properties of [2]catenane **14**H^{5+} and [3]catenane **7**H^{5+} are summarized in Table 3, in which the properties of the novel cyclophane **13**H^{5+} and of the previously studied macrocyclic polyether BPP34C10 (**5**),[4g] the cyclophane **21**$^{4+}$,[4g] and the catenanes **22**$^{4+}$[4g] and **25**$^{4+}$[14] are also displayed for comparison.

The absorption spectrum of cyclophane **13**H^{5+} is similar to that of cyclophane **21**$^{4+}$ and does not undergo any appreciable change upon deprotonation. This result is an expected one, since the ammonium/amine centers do not exhibit absorption bands in the near UV-visible absorption region. On reduction, both **13**H^{5+} and its deprotonated form exhibit the two bielectronic processes characteristic of the cyclophanes that contain two equivalent, noninteracting bipyridinium units. The reduction potentials are slightly more negative than those of **21**$^{4+}$. Presumably, the different sizes and flexibilities of the two cyclophanes impose different strains on the bipyridinium units and, thus, affect the reduction potentials.

The [2]catenane **14**H^{5+} (Figure 4, full line) and the [3]catenane **7**H^{5+} show a charge-transfer (CT) absorption band at a wavelength similar to that of [2]catenane **22**$^{4+}$ (Figure 4, dashed line).[4g] The molar absorption coefficient of the CT band of **14**H^{5+}, however, is about half that of **22**$^{4+}$ and close to that exhibited by a closely-related rotaxane.[16] This observation suggests that **5**, when interlocked with the relatively large cyclophane, surrounds a bipyridinium unit but, contrary to what happens in the case of the [2]catenane **22**$^{4+}$, which contains the smaller cyclophane, it does not interact with the second (alongside) bipyridinium unit. Accordingly, the [3]catenane **7**H^{5+} exhibits a molar absorption coefficient twice that of **14**H^{5+}. Since the unprotonated catenanes possess only bipyridinium recognition sites, and deprotonation of **14**H^{5+} and **7**H^{5+} does not cause any substantial change in the absorption spectra,[17] we conclude that the polyether macrocycle surrounds a bipyridinium recognition site even in the

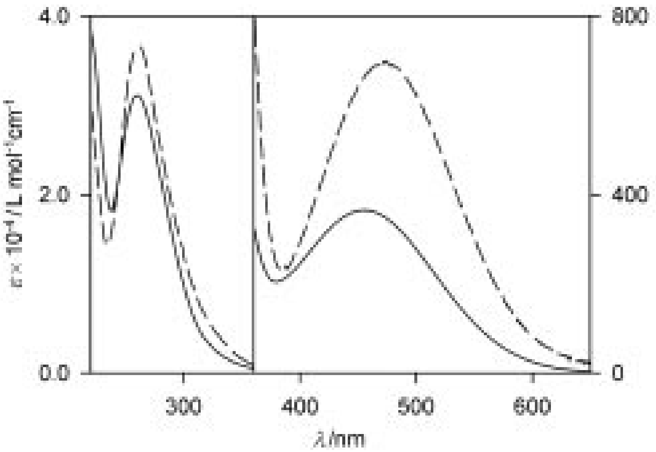


Figure 4. Absorption spectra (MeCN, 298 K) of the catenanes **14**H^{5+} (full line) and **22**$^{4+}$ (dashed line). Note that the visible CT bands are represented on a magnified scale (see right hand axis).

protonated species. None of the catenanes exhibits the characteristic fluorescence of free **5** because of the quenching effect of the low-energy CT levels.

The electrochemical results confirm fully that in **14**H^{5+} the macrocyclic polyether **5** surrounds one of the two bipyridinium units. The first bielectronic reduction process of the cyclophane splits into two monoelectronic processes, one occurring at almost the same potential as that of the free cyclophane **13**H^{5+}, and the other at a potential that is strongly displaced toward a more negative value (Table 3 and Figure 5). In the catenane **22**$^{4+}$, whose cyclophane ring is smaller, the reduction of the alongside bipyridinium unit is only slightly affected by the macrocycle **5**. Although deprotonation of **14**H^{5+} does not affect the first reduction process (assigned to the alongside bipyridinium unit), it moves the second reduction process (assigned to the inside bypiridinium unit) to slightly more negative values. This observation indicates that a stabilizing interaction exists between **5** and the ammonium center when both the bipyridinium units have been monoreduced (vide infra), and that such an interaction can be switched off by addition of base. In **14**H^{5+}, the second bielectronic reduction process of the cyclophane is only slightly shifted and does not split, showing that when both the bipyridinium units have been monoreduced, the macrocycle **5** resides on the ammonium center. In the deprotonated catenane, however, the second reduction process of the two bipyridinium units splits into two monoelectronic processes, with, once again, one occurring at almost the same potential as that of **13**H^{5+}, and with the other one shifted to more negative potentials. Such a behavior suggests that, when the ammonium recognition center is switched off, the macrocycle resides on one of the two monoreduced bipyridinium units—a situation that permits some donor/acceptor stabilization to occur.

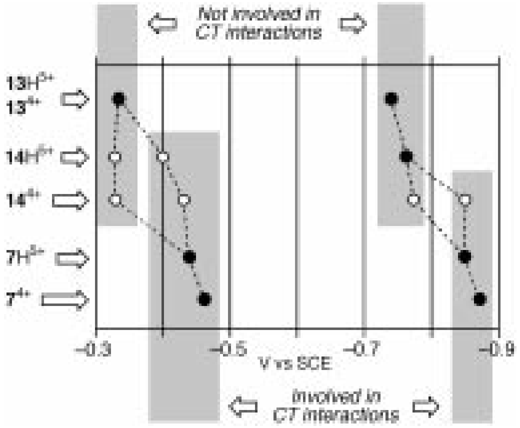


Figure 5. Correlation diagram for the reduction processes (MeCN, 298 K) of the cyclophane **13**H^{5+} and its [2]catenane **14**H^{5+} and [3]catenane **7**H^{5+}, as well as of their deprotonated forms, obtained by addition of one equivalent of n-Bu$_3$N to the solution. ○: monoelectronic processes; ●: bielectronic processes..

In the [3]catenane **7**H^{5+}, which contains two polyether macrocyclic rings and only one ammonium recognition center, the first reduction process of both the bipyridinium units takes place simultaneously and is displaced toward more negative potentials (Table 3, Figure 5) in a manner that is expected for a structure in which both the bipyridinium units are surrounded by a macrocyclic polyether. Since the second reduction of the two bipyridinium units in **7**H^{5+} does not split and occurs at a potential expected for such units surrounded by macrocycle **5**, switching of one of the two rings onto the ammonium center apparently cannot occur. This behavior can be explained by considering that the movement of one molecule of **5** to the ammonium center is prevented by the presence of the other ring, which exhibits the same tendency. Such an explanation is fully consistent with the behavior exhibited (vide infra) by the [3]catenanes **25**$^{4+}$, **26**$^{4+}$ and **8**H^{5+}, whose cyclophane components do not possess enough recognition sites to receive the two macrocyclic rings after reduction of the bipyridinium units. Of course, the same results are obtained for the deprotonated species, **7**$^{4+}$.

On oxidation, the [2]catenane **22**$^{4+}$ has two distinct one-electron processes at +1.42 and +1.72 V,[18] which can be assigned to the alongside and inside dioxybenzene units, respectively. In the catenane **14**H^{5+}, whose cyclophane is larger, both the dioxybenzene units are oxidized at the same potential, confirming that **5** interacts only with the inside bipyridinium unit (vide supra). Since the oxidation processes are not fully reversible, we will avoid any further speculation on this issue.

In conclusion, the absorption spectra and electrochemical properties show that in the [2]catenane **14**H^{5+}, as well as in its deprotonated form, the macrocyclic ring **5** surrounds one of the two bipyridinium units and does not interact with the alongside one. Therefore, protonation/deprotonation does not cause any switching of the ring position. However, after one-electron reduction of both the bipyridinium units, the macrocyclic ring **5** is displaced onto the ammonium center in a process which means that an electrochemically induced "co-conformational" switching occurs (Figure 6, left-hand side). Furthermore, after the two-electron reduction of **14**H^{5+}, the macrocyclic ring **5** is not only located on the ammonium center, but it also moves back onto one of the monoreduced bipyridinium units upon deprotonation (**14**$^{2+}$ in Figure 6). Thus, the [2]catenane **14**$^{4+}$ behaves (Figure 7) according to an AND binary logic.[19]

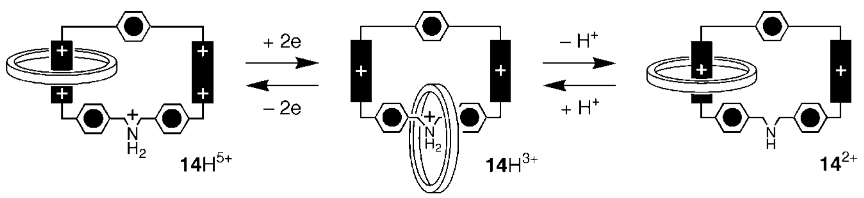


Figure 6. Schematic representation of the "co-conformational" switching processes associated with redox and acid/base stimulation of catenane **14**H^{5+}.

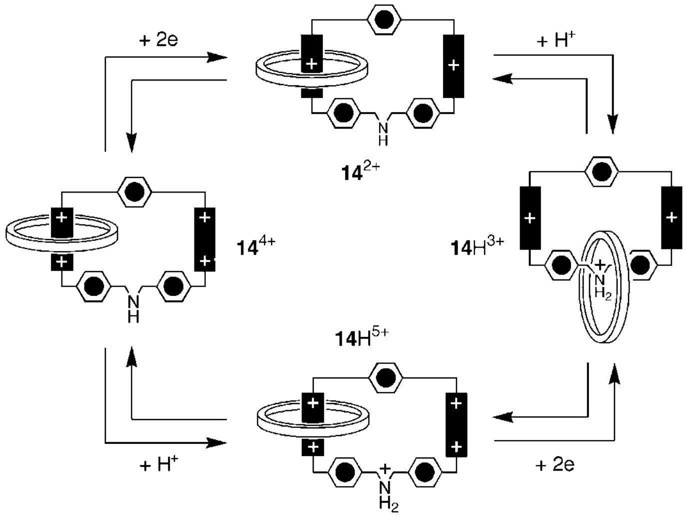


Figure 7. Schematic representation of the AND logic behavior exhibited by the deprotonated [2]catenane $\mathbf{14}^{4+}$. The input signals correspond to the injection of two electrons and the addition of a proton, respectively, while the output manifests itself in the change in the position of the macrocyclic polyether.

Catenanes containing 1/5DN38C10 (6): The absorption and redox properties of the [2]catenane **9**H_2^{6+} and the [3]catenanes **8**H^{5+} and **10**H_2^{6+} are summarized in Table 4, in which the properties of the previously studied macrocyclic polyether 1/5DN38C10 (**6**),[13] the [2]catenane $\mathbf{23}^{4+}$,[4g] the cyclophane $\mathbf{24}^{4+}$,[13] and the [3]catenane $\mathbf{26}^{4+}$[13] are also displayed for comparison. Unfortunately, the cyclophane components of [2]catenane **9**H_2^{6+} and [3]catenane **10**H_2^{6+}, and [3]catenane **8**H^{5+} could not be prepared. Although their redox behavior and potential values should be reasonably very similar to those of **13**H^{5+}, which, in turn, are not too distant from those exhibited by cyclophane $\mathbf{24}^{4+}$, their availability would have helped considerably in the interpretation of the electrochemical results.

The [2]catenane **9**H_2^{6+} has a CT absorption band sligthly displaced to higher energies compared to that of [2]catenane $\mathbf{23}^{4+}$. The molar absorption coefficient, however, is less than half that of $\mathbf{23}^{4+}$, and even smaller than that exhibited by a closely related rotaxane.[20] This observation suggests that in **9**H_2^{6+} macrocycle **6** surrounds a bipyridinium unit but—contrary to what happens in the case of $\mathbf{23}^{4+}$, which has a much smaller cyclophane—it does not interact with the second (alongside) bipyridinium unit. Accordingly, the [3]catenanes **8**H^{5+} and **10**H_2^{6+} exhibit a molar absorption coefficient twice that of **9**H_2^{6+}. In all cases, deprotonation does not cause substantial changes[21] in the absorption spectra, showing that **6** prefers to stay on the bipyridinium recognition site even in the protonated species. None of the catenanes exhibits the fluorescence of the free macrocycle **6**, because of the quenching effect of the low energy CT levels.

On electrochemical reduction, the [2]catenane **9**H_2^{6+} exhibits two distinct one-electron processes, followed by a two-electron process (Table 4 and Figure 8). This behavior shows that the two bipyridinium units of **9**H_2^{6+} are not equivalent. The potential of the first reduction process is about the same as that shown by the bipyridinium units in the free cyclophane $\mathbf{24}^{4+}$, while the value for the second reduction process is not far from that observed for the same process in the [2]catenane $\mathbf{23}^{4+}$, and similar to that of the first (two-electron) reduction process observed in

Table 4. Absorption and electrochemical data (MeCN, 298 K) of the macrocyclic polyether **6**, the reference [2]catenane $\mathbf{23}^{4+}$, the reference [3]catenane $\mathbf{26}^{4+}$, the [2]catenane **9**H_2^{6+}, and the [3]catenanes **10**H_2^{6+} and **8**H^{5+}.

Compound	Absorption[a] λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	Electrochemical reduction[b] $E_{1/2}$ [V] (vs SCE)
6[c]	295	17600	–
$\mathbf{24}^{4+}$[d]	260, 340	83000, 3000	–0.31 (2); –0.72 (2)
$\mathbf{23}^{4+}$[c]	529	1100	–0.35 (1); –0.56 (1); –0.81 (1); –0.89 (1)
$\mathbf{26}^{4+}$[d]	558	1300	–0.55 (2); –0.90 (2)
9H_2^{6+}	504	350	–0.33 (1); –0.47 (1); –0.76 (2)
$\mathbf{9}^{4+}$[e]	487	430	–0.35 (1); –0.49 (1); –0.78 (2)
10H_2^{6+}	510	930	–0.50 (2); –0.75 (2)
$\mathbf{10}^{4+}$[e]	493	1060	–0.51 (2); –0.75 (2)
8H^{5+}	519	1400	–0.51 (2); –0.90 (2)
$\mathbf{8}^{4+}$[f]	521	1300	–0.52 (2); –0.91 (2)

[a] For the catenanes, only the data regarding the CT absorption bands are reported. [b] Argon purged solution, $TBAPF_6$ as supporting electrolyte, glassy carbon as working electrode; all processes are reversible; halfwave potential values in V vs SCE; the number of exchanged electrons is indicated in parentheses. [c] Data from Ref. [4g]. [d] Data from Ref. [13]. [e] Obtained by addition of two equivalents of n-Bu_3N. [f] Obtained by addition of one equivalents of n-Bu_3N.

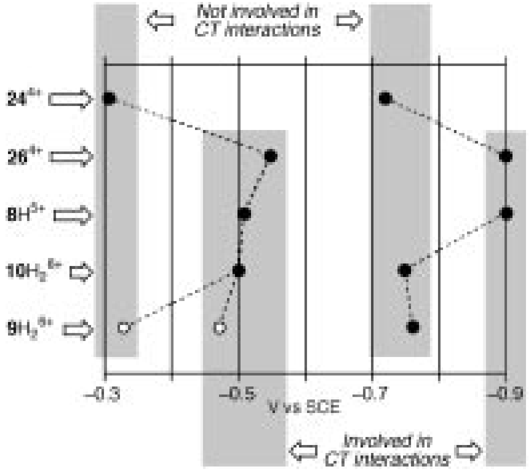


Figure 8. Correlation diagram for the reduction processes (MeCN, 298 K) of the [2]catenanes **8**H^{5+} and **10**H_2^{6+}, and the [2]catenane **9**H_2^{6+}. Their deprotonated forms, obtained by addition of one (or two) equivalents of n-Bu_3N, exhibit the same behavior (see text). The reduction processes relating to the cyclophane $\mathbf{24}^{4+}$ and its [3]catenane $\mathbf{26}^{4+}$ are also shown for comparison. ○: monoelectronic processes; ●: bielectronic processes..

the [3]catenanes $\mathbf{8H}^{5+}$ and $\mathbf{10H}_2^{6+}$. These results demonstrate that, in $\mathbf{9H}_2^{6+}$, the macrocyclic polyether **6** surrounds one of the two bipyridinium units and does not perturb the other one, while, in the [3]catenanes, both the bipyridinium units are surrounded by a molecule of **6**. In $\mathbf{9H}_2^{6+}$, the second reduction of the two bipyridinium units occurs at the same potential, and at a value not distant from that of $\mathbf{13H}^{5+}$ and $\mathbf{24}^{4+}$. This observation shows that **6** is no longer preferentially engaged with one bipyridinium unit when the first reduction of each unit has occurred. In addition, deprotonation does not cause any splitting in the two-electron process; this corresponds to the second reduction of the two bipyridinium units, contrary to what happens for $\mathbf{14H}^{5+}$ (vide supra). The different behaviors of $\mathbf{9H}_2^{6+}$ and $\mathbf{14H}^{5+}$ upon deprotonation are related presumably to the larger size and much greater flexibility of the cyclophane component of the former catenane relative to that of $\mathbf{13H}^{5+}$.[22] As a matter of fact, inspection of CPK space-filling molecular models shows that while $\mathbf{24}^{4+}$ is a very rigid square-shaped "box", $\mathbf{13H}^{5+}$ can be viewed (Figure 1) as a trapezoid with considerable flexibility on one of its sides and so the cyclophane component of $\mathbf{9H}_2^{6+}$ is quite floppy. Apparently, the catenane $\mathbf{9H}_2^{6+}$, after one-electron reduction of its two bipyridinium units, is capable of adopting "co-conformations" in which macrocycle **6** (which also has a larger cavity than its counterpart **5** in catenane $\mathbf{14H}^{5+}$) remains well away from such units, regardless of the protonation state of the system (redox switching, Figure 9, top). We recall that the [3]catenane $\mathbf{10H}_2^{6+}$ has a bielectronic reduction wave at a potential much more negative than that corresponding to unperturbed bipyridinium units and close to that of the other [3]catenane $\mathbf{8H}^{5+}$ (Table 4 and Figure 8). This behavior demonstrates that the two macrocycle polyethers surround the two bipyridinium units. The second reduction of the two bipyridinium units of $\mathbf{10H}_2^{6+}$ occurs once again at the same potential, which is, however, much less negative than that exhibited by $\mathbf{8H}^{5+}$ and $\mathbf{26}^{4+}$. This behavior suggests that, after the two-electron reduction of $\mathbf{10H}_2^{6+}$, the two macrocycle polyethers are free to move away from the one-electron reduced bipyridinium units (redox switching, Figure 9 bottom), whereas this possibility does not exist in the case of the [3]catenanes $\mathbf{8H}^{5+}$ and $\mathbf{26}^{4+}$, whose cyclophane components do not possess enough recognition sites to receive the two macrocycle polyethers after reduction of the bipyridinium units (vide supra). As in the case of the [2]catenane $\mathbf{9H}_2^{6+}$—and probably for the same reasons—the redox switching of $\mathbf{10H}_2^{6+}$ is not affected by the protonation state of the [3]catenane. Not surprisingly, the electrochemical behavior of the [3]catenane $\mathbf{8H}^{5+}$ is also independent on its protonation state.

Conclusion

Either one or two dialkylammonium and two bipyridinium recognition sites have been introduced into a π-electron-deficient ring component of three [2]catenanes and of three [3]catenanes incorporating π-electron-rich macrocyclic polyethers (BPP34C10 or 1/5DN38C10) as their other ring component(s). The template-directed syntheses of these catenanes were realized by reacting the acyclic precursors of the π-electron-deficient cyclophanes in the presence of a preformed 1,4-dioxybenzene- or 1,5-dioxynaphthalene-based macrocyclic polyether. These self-assembly processes are assisted by a combination of i) π···π stacking interactions between the complementary aromatic units, ii) C–H···O hydrogen bonds between some of the bipyridinium hydrogen atoms and some of the polyether oxygen atoms, and iii) C–H···π interactions between some of the dioxyarene hydrogen atoms and the aromatic spacers separating the bipyridinium units within the π-electron-deficient cyclophanes.

The novel catenanes have been studied by absorption spectroscopy and voltammetric techniques, and their behavior has been compared with that exhibited by the component macrocyclic polyethers and by related known cyclophanes and catenanes. These investigations have shown that, in these novel catenanes, the macrocyclic polyether(s) reside(s) initially around the bipyridinium unit(s), but move to the ammonium recognition site(s) upon one-electron reduction of the two bipyridinium units. One of the [2]catenanes, which can also be switched by acid/base stimulation in its two-electron reduced form, behaves according to the AND logic operation. The "co-conformational" switching exhibited by these catenanes is of interest for the development of new prototypes of molecular-level machines, particularly with reference to the controlled unidirectional ring circumrotation in catenanes.[23]

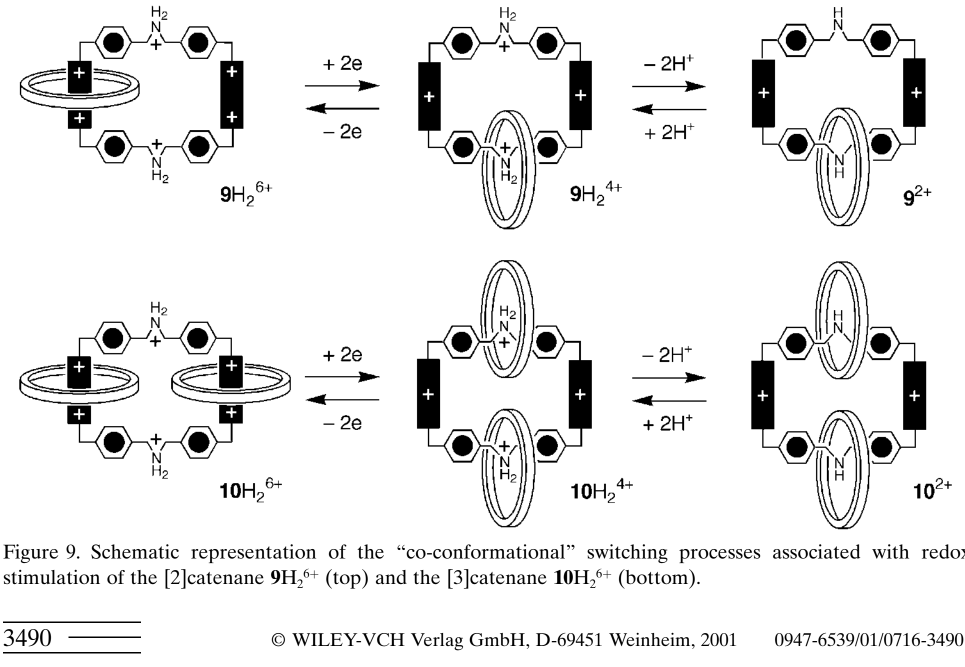


Figure 9. Schematic representation of the "co-conformational" switching processes associated with redox stimulation of the [2]catenane $\mathbf{9H}_2^{6+}$ (top) and the [3]catenane $\mathbf{10H}_2^{6+}$ (bottom).

Experimental Section

General methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried according to literature procedures.[24] The compounds **1**,[25] **4**$\cdot 2PF_6$,[26] **5**,[27] **6**,[28] **11**$\cdot 2PF_6$,[27] and **12**[27] were prepared as described previously in the literature. Thin layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on silica gel 60 (Merck 9385, 230–400 mesh). Melting points were determined on an Electrothermal 9200 melting point apparatus and are uncorrected. Liquid secondary ion mass spectrometry (LSIMS) was performed on a VG Zabspec instrument with 3-nitrobenzyl alcohol as matrix. ^1H and ^{13}C NMR spectra were recorded on Bruker AC300 or AMX400 spectrometers. Elemental analyses were performed by Quantitative Technologies. Apparatus and methods for the absorption, luminescence, and electrochemical measurements have been described previously.[4g,13] Experimental errors are estimated to be: wavelength values, ±2 nm; molar absorption coefficients, ±10%; potential values, ±10 mV.

Bis(4-bromomethylbenzyl)ammonium hexafluorophosphate (2H$\cdot$PF$_6$): A suspension of **1** (0.21 g, 0.59 mmol) in HBr/$MeCO_2H$ (33%, 10 mL) was stirred mechanically for 5 d at ambient temperature. The solvent was distilled off under reduced pressure and the residue was dissolved in H_2O (200 mL). The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, Et_2O, and *n*-hexane, and dried to afford **2**H$\cdot PF_6$ (0.24 g, 75%) as a white solid. M.p. 192–193 °C; UV (CD_3CN): λ_{max} (ε) = 231 nm (23000); LSIMS: *m*/*z*: 384 [$M-PF_6$]$^+$; ^1H NMR (CD_3CN, 298 K): δ = 7.53 (d, J = 8.3 Hz, 4H), 7.48 (d, J = 8.3 Hz, 4H), 4.61 (s, 4H), 4.24 (brs, 4H); ^{13}C NMR (CD_3CN, 298 K): δ = 140.9, 131.6, 131.2, 130.5, 52.0, 33.6; elemental analysis calcd (%) for $C_{16}H_{18}Br_2NPF_6$ (529.3): C 36.31, H 3.43, N 2.65; found C 36.13, H 3.69, N 2.58.

Bis(4-(4,4′-pyridylpyridiniummethyl)phenylmethyl)ammonium tris(hexafluorophosphate) (3H$\cdot$3PF$_6$): The dibromide **2**H$\cdot PF_6$ (0.30 g, 0.60 mmol) was added in small portions to a solution of 4,4′-bipyridine (2.00 g, 12.80 mmol) in MeCN (45 mL) maintained at 70 °C and under an atmosphere of N_2. The mixture was heated at 70 °C for a further 24 h. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, MeOH/2 M NH_4Cl (aq)/$MeNO_2$ (7:2:1)] to yield a product that was dissolved in H_2O. The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, and dried to afford **3**H$\cdot 3PF_6$ (0.31 g, 53%) as a white solid. M.p. 215 °C (decomp); UV (CD_3CN): λ_{max} (ε) = 264 nm (31900); LSIMS: *m*/*z*: 972 [M]$^+$, 826 [$M-PF_6$]$^+$, 680 [$M-2PF_6$]$^+$; ^1H NMR (CD_3CN, 298 K): δ = 8.82 (d, J = 6.7 Hz, 8H), 8.32 (d, J = 6.6 Hz, 4H), 7.96 (brs, 4H), 7.80 (brs, 4H), 7.63 (d, J = 8.0 Hz, 4H), 7.50 (d, J = 8.0 Hz, 4H), 5.76 (s, 4H), 4.23 (s, 4H); ^{13}C NMR (CD_3CN, 298 K): δ = 154.9, 150.4, 146.0, 143.5, 135.3, 132.8, 132.1, 130.5, 127.4, 123.6, 64.4, 51.8.

[3]Catenane 7H$\cdot$5PF$_6$: A solution of **2**H$\cdot PF_6$ (68.0 mg, 0.12 mmol), **4**$\cdot 2PF_6$ (100.0 mg, 0.12 mmol), and **5** (300.0 mg, 0.56 mmol) in MeCN (30 mL) was stirred for 15 d at ambient temperature. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, CH_2Cl_2/MeOH (9:1)] to yield a product that was dissolved in H_2O. The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, and dried to afford **7**H$\cdot 5PF_6$ (18.0 mg, 6%) as an orange solid. M.p. 175 °C (decomp); UV (CD_3CN): λ_{max} (ε) = 264 (53000), 459 nm (840); LSIMS: *m*/*z*: 2369 [$M-PF_6$]$^+$, 2224 [$M-2PF_6$]$^+$, 2079 [$M-3PF_6$]$^+$, 1933 [$M-4PF_6$]$^+$; ^1H NMR (CD_3COCD_3, 304 K): δ = 9.28 (d, J = 6.9 Hz, 4H), 9.13 (d, J = 6.9 Hz, 4H), 8.09 (d, J = 7.0 Hz, 4H), 8.07 (d, J = 6.9 Hz, 4H), 7.89 (d, J = 8.4 Hz, 4H), 7.83 (d, J = 8.5 Hz, 4H), 7.72–7.70 (m, 4H), 7.56–7.53 (m, 4H), 6.06 (s, 4H), 5.99 (s, 4H), 5.61 (s, 16H), 3.80–3.79 (m, 32H), 3.60–3.59 (m, 16H), 3.28–3.27 (m, 16H).

[3]Catenane 8H$\cdot$5PF$_6$: A solution of **2**H$\cdot PF_6$ (68.0 mg, 0.13 mmol), **4**$\cdot 2PF_6$ (100.0 mg, 0.12 mmol), and **6** (356.0 mg, 0.54 mmol) in MeCN (30 mL) was stirred for 15 d at ambient temperature. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, CH_2Cl_2/MeOH (9:1–5:1)] to yield a product that was dissolved in H_2O. The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, and dried to afford **8**H$\cdot 5PF_6$ (133.0 mg, 38%) as a purple solid. M.p. 195 °C (decomp); UV (CD_3CN): λ_{max} (ε) = 267 (53500), 521 nm (1100); LSIMS: *m*/*z*: 2570 [$M-PF_6$]$^+$, 2424 [$M-2PF_6$]$^+$, 2279 [$M-3PF_6$]$^+$, 2134 [$M-4PF_6$]$^+$; ^1H NMR [$(CD_3)_2CO$, 304 K]: δ = 8.85 (d, J = 6.4 Hz, 4H), 8.74 (d, J = 6.4 Hz, 4H), 8.01 (d, J = 8.5 Hz, 4H), 7.97 (d, J = 8.6 Hz, 4H), 7.76 (d, J = 8.1 Hz, 4H), 7.71 (d, J = 8.1 Hz, 4H), 7.03 (d, J = 6.7 Hz, 4H), 7.00 (d, J = 6.8 Hz, 4H), 6.30–6.25 (m, 8H), 6.11–6.07 (m, 16H), 6.03 (s, 4H), 5.91 (s, 4H), 4.03 (s, 4H), 3.91–3.83 (m, 32H), 3.80–3.79 (m, 16H), 3.70–3.69 (m, 16H); ^{13}C NMR ($(CD_3)_2CO$, 304 K): δ = 153.5, 145.2, 144.8, 144.7, 144.4, 142.3, 134.9, 131.1, 130.8, 130.5, 129.1, 125.9, 125.2, 124.8, 113.7, 105.4, 72.1, 71.7, 71.0, 68.4, 65.8, 65.2, 52.4.

[2]Catenane 9H$_2\cdot$6PF$_6$ and [3]Catenane 10H$_2\cdot$6PF$_6$: A solution of **2**H$\cdot PF_6$ (60.5 mg, 0.11 mmol), **3**H$\cdot 3PF_6$ (84.4 mg, 0.09 mmol), and **6** (220.0 mg, 0.35 mmol) in MeCN (15 mL) was stirred for 21 d at ambient temperature. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO_2, MeOH/2 M NH_4Cl (aq)/$MeNO_2$ (7:2:1)] to yield two products which were dissolved in H_2O. The precipitates obtained after the addition of NH_4PF_6 were filtered off, washed with H_2O, and dried to afford **9**$H_2\cdot 6PF_6$ (9.0 mg, 5%) and **10**$H_2\cdot 6PF_6$ (9.3 mg, 4%) as purple solids.

*[2]Catenane **9**$H_2\cdot 6PF_6$*: UV (CD_3CN): λ_{max} (ε) = 266 (22000), 504 nm (330); LSIMS: *m*/*z*: 1829 [$M-3PF_6$]$^+$, 1685 [$M-4PF_6$]$^+$, 1540 [$M-5PF_6$]$^+$; ^1H NMR (CD_3CN, 344 K): δ = 8.76 (d, J = 7.0 Hz, 8H), 7.59 (m, 16H), 7.53 (d, J = 6.2 Hz, 8H), 6.60 (pt, J = 7.7 Hz, 4H), 6.53 (d, J = 8.5 Hz, 4H), 6.39 (d, J = 7.4 Hz, 4H), 5.79 (s, 8H), 3.97–3.95 (m, 8H), 3.88–3.85 (m, 32H).

*[3]Catenane **10**$H_2\cdot 6PF_6$*: UV (CD_3CN): λ_{max} (ε) = 271 (30000), 510 nm (930); LSIMS: *m*/*z*: 2613 [$M-2PF_6$]$^+$, 2467 [$M-3PF_6$]$^+$, 2322 [$M-4PF_6$]$^+$, 2176 [$M-5PF_6$]$^+$; ^1H NMR ($(CD_3)_2CO$, 304 K): δ = 8.84 (d, J = 7.4 Hz, 8H), 7.80 (d, J = 8.3 Hz, 8H), 7.62 (d, J = 8.3 Hz, 8H), 7.15 (d, J = 7.4 Hz, 8H), 6.44 (pt, J = 8.7 Hz, 8H), 6.32 (d, J = 8.7 Hz, 8H), 6.27 (d, J = 8.5 Hz, 8H), 5.98 (s, 8H), 3.94–3.90 (m, 8H), 3.82–3.76 (m, 64H).

Cyclophane 13H$\cdot$5PF$_6$: A solution of **2**H$\cdot PF_6$ (116.0 mg, 0.22 mmol), **11**$\cdot 2PF_6$ (146.0 mg, 0.21 mmol), and **12** (125.3 mg, 0.44 mmol) in MeCN (15 mL) was stirred for 21 d at ambient temperature. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, MeOH/2 M NH_4Cl (aq)/$MeNO_2$ (7:2:1)] to yield a product that was dissolved in H_2O. The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, and dried to afford **13**H$\cdot 5PF_6$ (90.0 mg, 32%) as a white solid. UV (CD_3CN): λ_{max} (ε) = 258 nm (10700); ^1H NMR ($(CD_3)_2CO$, 298 K): δ = 9.37 (brs, 8H), 8.62 (d, J = 6.3 Hz, 4H), 8.59 (d, J = 5.9 Hz, 4H), 7.85 (s, 4H), 7.76 (d, J = 8.1 Hz, 4H), 7.67 (d, J = 8.1 Hz, 4H), 6.13 (s, 4H), 6.12 (s, 4H), 4.65 (s, 4H).

[2]Catenane 14H$\cdot$5PF$_6$: A solution of **2**H$\cdot PF_6$ (88.0 mg, 0.17 mmol), **11**$\cdot 2PF_6$ (112.0 mg, 0.16 mmol), and **5** (162.6 mg, 0.30 mmol) in MeCN (10 mL) was stirred for 21 d at ambient temperature. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, MeOH/2 M NH_4Cl (aq)/$MeNO_2$ (7:2:1)] to yield a product that was dissolved in H_2O. The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, and dried to afford **14**H$\cdot 5PF_6$ (36.8 mg, 12%) as an orange solid. UV (CD_3CN): λ_{max} (ε) = 260 (31000), 455 nm (370); LSIMS: *m*/*z*: 1611 [$M-2PF_6$]$^+$, 1466 [$M-3PF_6$]$^+$, 1320 [$M-4PF_6$]$^+$; ^1H NMR (CD_3CN, 298 K): δ = 8.91 (d, J = 6.9 Hz, 4H), 8.84 (d, J = 7.1 Hz, 4H), 7.91 (d, J = 7.0 Hz, 4H), 7.88 (d, J = 7.0 Hz, 4H), 7.77 (s, 4H), 7.52 (d, J = 8.8 Hz, 4H), 7.44 (d, J = 8.6 Hz, 4H), 5.85 (s, 8H), 5.80 (s, 8H), 4.16 (s, 4H), 3.67–3.48 (m, 32H).

1,6-Bis(4-carbomethoxyphenylimino)hexane (15): A mixture of 1,6-diaminohexane (11.5 g, 99.0 mmol) and methyl 4-formylbenzoate (33.3 g, 202.8 mmol) in PhMe (150 mL) was heated under reflux for 1 d and the H_2O formed was distilled off using a Dean–Stark apparatus. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure to afford **15** (38.4 g, 95%) as a yellowish solid. M.p. 115–116 °C; UV (CD_3CN): λ_{max} (ε) = 260 nm (51000); EIMS: *m*/*z*: 409 [M+H]$^+$; ^1H NMR ($CDCl_3$, 298 K): δ = 8.25 (s, 2H), 8.02 (d, J = 8.4 Hz, 4H), 7.73 (d, J = 8.4 Hz, 4H), 3.87 (s, 6H), 3.59 (dt, J = 6.9, 0.9 Hz, 4H), 1.71–1.66 (m, 4H), 1.41–1.36 (m, 4H); ^{13}C NMR ($CDCl_3$, 298 K): δ = 166.5, 159.7, 140.1, 131.5, 129.7, 127.8, 61.7, 52.1, 30.6, 27.0; elemental analysis calcd (%) for $C_{24}H_{28}O_4N_2$ (408.5): C 70.57, H 6.91, N 6.86; found C 70.64, H 7.34, N 6.72.

1,6-Bis(4-carbomethoxybenzylamino)hexane (16): A solution of **15** (10.42 g, 25.5 mmol), $NaBH_4$ (3.14 g, 83.0 mmol) in a mixture of THF (250 mL) and MeOH (250 mL) was stirred for 1 d at ambient temperature. After the addition of a 2 M aqueous solution of HCl, the solvent was distilled off under reduced pressure and the residue was dissolved with an 8 M aqueous solution of NaOH (400 mL). The solution was extracted with CH_2Cl_2 (3 × 250 mL), and the organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to afford **16** (7.50 g, 71%) as a yellow solid. M.p. 102–103 °C; UV (CD_3CN): λ_{max} (ε) = 234 nm (27 000); EIMS: m/z: 412 [M]$^+$; ^1H NMR ($CDCl_3$, 298 K): δ = 7.94 (d, J = 8.2 Hz, 4 H), 7.33 (d, J = 8.2 Hz, 4 H), 3.85 (s, 6 H), 3.78 (s, 4 H), 2.55 (t, J = 7.1 Hz, 4 H), 1.48–1.43 (m, 4 H), 1.37 (br s, 2 H), 1.32–1.28 (m, 4 H); ^{13}C NMR ($CDCl_3$, 298 K): δ = 166.9, 145.8, 129.6, 128.6, 127.8, 53.6, 51.9, 49.3, 29.9, 27.1; elemental analysis calcd (%) for $C_{24}H_{32}O_4N_2$ (412.5): C 69.88, H 7.82, N 6.79; found C 69.11, H 8.69, N 6.60.

1,6-Bis(4-carbomethoxybenzylamino-*N,N'*-*tert*-butoxycarbonyl)hexane (17): A solution of **16** (2.70 g, 6.6 mmol), di-*tert*-butyloxycarbonylanhydride (2.95 g, 13.5 mmol), and 4-dimethylaminopyridine (5 mg) in $CHCl_3$ (400 mL) was stirred for 24 h at ambient temperature. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, EtOAc/hexane (3:7)] to afford **17** (3.60 g, 90 %) as a white solid. M.p. 88–89 °C; UV (CD_3CN): λ_{max} (ε) = 234 nm (25 500); EIMS: m/z: 612 [M]$^+$; ^1H NMR ($CDCl_3$, 298 K): δ = 7.96 (d, J = 8.2 Hz, 4 H), 7.24 (d, J = 6.6 Hz, 4 H), 4.43–4.40 (m, 4 H), 3.88 (s, 6 H), 3.18–3.17 (m, 2 H), 3.07–3.06 (m, 2 H), 1.45–1.36 (m, 22 H), 1.23–1.19 (m, 4 H); ^{13}C NMR ($CDCl_3$, 298 K): δ = 166.9, 144.3, 144.0, 129.8, 129.0, 127.3, 126.7, 79.8, 52.1, 50.4, 49.8, 47.0, 28.4, 28.0, 26.5; elemental analysis calcd (%) for $C_{34}H_{48}O_8N_2$ (612.8): C 66.64, H 7.90, N 4.57; found C 66.63, H 8.73, N 4.56.

1,6-Bis(4-hydroxymethylbenzylamino-*N,N'*-*tert*-butoxycarbonyl)hexane (18): A solution of **17** (3.20 g, 5.2 mmol) in dry THF (50 mL) was added dropwise to a suspension of $LiAlH_4$ (0.50 g, 13.1 mmol) in THF (250 mL) maintained at 0 °C. After the addition, the mixture was allowed to warm up to ambient temperature and then it was stirred for 1 d. After the addition of H_2O (150 mL), the mixture was concentrated under reduced pressure and extracted with CH_2Cl_2 (3 × 150 mL). The organic phase was dried ($MgSO_4$), and the solvent was distilled off under reduced pressure to afford **18** (2.40 g, 83 %) as a white solid. M.p. 83–84 °C; UV (CD_3CN): λ_{max} (ε) = 263 nm (550); LSIMS: m/z: 558 [M]$^+$; ^1H NMR ($CDCl_3$, 298 K): δ = 7.28 (d, J = 7.6 Hz, 4 H), 7.18 (br s, 4 H), 4.63 (s, 4 H), 4.36 (s, 4 H), 3.11–3.05 (m, 4 H), 1.44–1.41 (m, 22 H), 1.14 (br s, 4 H); ^{13}C NMR ($CDCl_3$, 298 K): δ = 141.9, 138.9, 128.3, 127.8, 80.0, 64.5, 50.4, 50.3, 47.4, 28.7, 27.2; elemental analysis calcd (%) for $C_{32}H_{48}O_6N_2$ (556.7): C 69.04, H 8.69, N 5.03; found C 68.85, H 9.51, N 5.01.

1,6-Bis(4-bromomethylbenzylammonium)hexane dihexafluorophosphate ($19H_2 \cdot 2PF_6$): A solution of **18** (0.59 g, 1.1 mmol) in HBr/$MeCO_2H$ (45 %, 15 mL) was stirred for 3 d at ambient temperature. The solvent was distilled off under reduced pressure, and the residue was dissolved in H_2O (200 mL). The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, Et_2O, and pentane, and dried to afford **19**$H_2 \cdot 2PF_6$ (0.74 g, 90 %) as a white solid. M.p. 190–192 °C; UV (CD_3CN): λ_{max} (ε) = 228 nm (19 000); LSIMS: m/z: 629 [$M - PF_6$]$^+$, 483 [$M - 2PF_6$]$^+$; ^1H NMR ($(CD_3)_2CO$, 298 K): δ = 8.15 (br s, 4 H), 7.58 (d, J = 7.4 Hz, 4 H), 7.53 (d, J = 7.5 Hz, 4 H), 4.66 (s, 4 H), 4.52 (s, 4 H), 3.40 (t, J = 7.6 Hz, 4 H), 1.91–1.88 (m, 4 H), 1.51 (br s, 4 H); ^{13}C NMR ($(CD_3)_2CO$, 298 K): δ = 140.8, 132.2, 131.4, 130.7, 52.3, 49.1, 33.4, 26.4, 26.3; elemental analysis calcd (%) for $C_{22}H_{32}N_2Br_2P_2F_{12}$ (774.4): C 34.12, H 4.17, N 3.62; found C 34.22, H 4.33, N 3.62.

[2]Catenane $20H_2 \cdot 6PF_6$: A solution of **11** $\cdot 2PF_6$ (91.0 mg, 0.13 mmol), **19**$H_2 \cdot 2PF_6$ (105.0 mg, 0.14 mmol), and **5** (138.0 mg, 0.26 mmol) in MeCN (15 mL) was stirred for 21 d at ambient temperature. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO_2, MeOH/2 M NH_4Cl (aq)/$MeNO_2$ (7:2:1)] to yield a product that was dissolved in H_2O. The precipitate obtained after the addition of NH_4PF_6 was filtered off, washed with H_2O, and dried to afford **20**$H_2 \cdot 6PF_6$ (52.5 mg, 19 %) as an orange solid. UV (CD_3CN): λ_{max} (ε) = 261 (17 500), 434 nm (295); LSIMS: m/z: 1712 [$M - 3PF_6$]$^+$, 1567 [$M - 4PF_6$]$^+$, 1422 [$M - 5PF_6$]$^+$; ^1H NMR ($(CD_3)_2CO$, 298 K): δ = 9.32 (d, J = 7.0 Hz, 4 H), 9.26 (d, J = 7.0 Hz, 4 H), 8.46 (d, J = 6.6 Hz, 4 H), 8.44 (d, J = 5.5 Hz, 4 H), 7.90 (s, 4 H), 7.78–7.60 (m, 8 H), 6.20 (s, 4 H), 6.14 (s, 4 H), 6.05 (s, 8 H), 4.45 (br s, 4 H), 3.75–3.71 (m, 16 H), 3.64–3.62 (m, 8 H), 3.58–3.56 (m, 8 H), 3.24 (t, J = 8.5 Hz, 4 H), 2.65–2.60 (m, 4 H).

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