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Self-Complementary [2]Catenanes and Their Related [3]Catenanes

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Abstract: Three [3]catenanes with cavities large enough to accommodate aromatic guests have been designed and synthesized (yields = 5–20%) by means of kinetically controlled self-assembly processes. The X-ray structural analysis of one of three [3]catenanes confirmed the presence of a rectangular cavity (dimensions = 7×11 Å) lined by π-electron-rich recognition sites and hydrogen-bond acceptor groups. In spite of their apparently ideal recognition features, none of these [3]catenanes bind guests incorporating a π-electron-deficient bipyridinium unit. However, the template-directed syntheses of the [3]catenanes also produce, in yields of 2–23%, [2]catenanes incorporating a 1,5-dioxynaphtho[38]crown-10 interlocked with a bipyridinium-based tetracationic cyclophane. The X-ray structural analyses of two of these [2]catenanes revealed that a combination of [π···π] and [C–H···π] interactions is responsible for the formation of supramolecular homodimers in the solid state. ^{1}H NMR spectroscopic investigations of the four [2]catenanes demonstrated that supramolecular homodimers are also formed ($K_a = 17-31\,\text{M}^{-1}$, $T = 185$ K) in $(CD_3)_2CO$ solutions. Dynamic ^{1}H NMR spectroscopy revealed that the 1,5-dioxynaphtho[38]crown-10 and tetracationic cyclophane components in the four [2]catenanes and in the three [3]catenanes circumrotate ($\Delta G_c^{\neq} = 9-14$ kcal mol^{-1}) through each other's cavity in $(CD_3)_2CO$. Similarly, the 1,5-dioxynaphthalene and the bipyridinium ring systems rotate ($\Delta G_c^{\neq} = 10-14$ kcal mol^{-1}) about their [O···O] and [N···N] axes, respectively, in solution.

Keywords: catenanes · crystal engineering · molecular recognition · supramolecular chemistry · template synthesis

Introduction

Recently, we have demonstrated[1, 2] that appropriately designed [2]catenanes[3] are capable of binding[4] π-electron rich guests. These novel [2]catenane receptors incorporate the tetracationic cyclophane, cyclobis(paraquat-4,4′-biphenylene),[5] interlocked with a macrocyclic polyether containing either two or three 1,5-dioxynaphthalene ring systems. In addition to a mechanical bond, the two interlocked rings are held together by a combination of noncovalent bonds including 1) [C–H···O] hydrogen bonds[6] between the α-bipyridinium hydrogen atoms of the encircled bipyridinium unit and the polyether oxygen atoms of the crown ether, 2) [π···π] stacking[7] between the π-electron rich 1,5-dioxynaphthalene ring systems and the π-electron deficient bipyridinium units, and 3) [C–H···π] interactions[8] between the *peri* hydrogen atoms on C-4 and C-8 of the encircled 1,5-dioxynaphthalene ring system and the 4,4′-bitolyl spacers in the tetracationic cyclophane. Noncovalent bonds of these kinds are also responsible for the binding, within the vacant receptor site in these [2]catenanes, of guests containing π-electron-rich aromatic rings inserted in the middle of acyclic polyether chains. The ability to design and self-assemble [2]catenanes with an internal recognition pocket has led[2] recently to (Figure 1) the template-directed synthesis of a so-called [3]rotacatenane in which the [2]catenane comprises 1,5-

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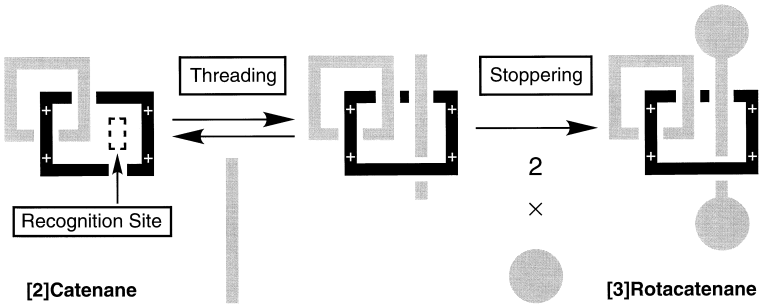


Figure 1. The threading of a π-electron-rich guest inside the π-electron-deficient cavity of a [2]catenane host and the stoppering of the guest to afford a [3]rotacatenane.

dioxynaphtho[38]crown-10 interlocked with cyclobis(paraquat-4,4′-biphenylene). Following threading of the [2]catenane by a 1,5-dioxynaphthalene-based polyether, stoppering was achieved by the introduction[9] of large triisopropylsilyl groups onto the primary hydroxy functions at the ends of the threaded unit. The template-directed synthesis of this rather exotic interlocked molecular compound provides an interesting example of alternating supramolecular assistance and covalent modification[10] through two successive cycles.

In a parallel line of research in our laboratories, the 4,4′-bitolyl spacers in the cyclobis(paraquat-4,4′-biphenylene) component in these [2]catenane receptors had been elongated[11] by inserting between their tolyl units either another phenylene ring or an acetylenic linkage. These expanded tetracationic cyclophanes were mechanically interlocked with two 1,5-dioxynaphtho[38]crown-10 macrocycles, affording [3]catenanes with π-electron-rich cavities apparently large enough, in principle, to act as recognition sites for π-electron-deficient guests. Surprisingly, however, binding (Figure 2) of

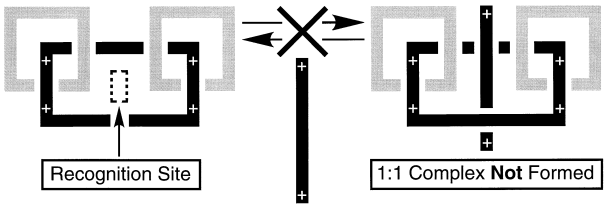
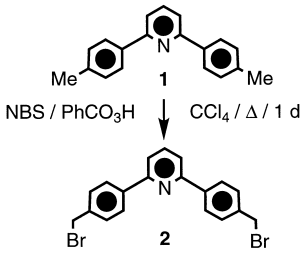


Figure 2. The attempted binding of a π-electron-deficient guest inside the π-electron-rich cavity of a [3]catenane host.

π-electron-deficient guests by these potential [3]catenane receptors was not observed.[11] A detailed computational investigation indicated[11] that the inability of these [3]catenanes to host bipyridinium-based guests might be a result of their lack of hydrogen-bond acceptors (X) in the vicinity of the potential recognition sites that are capable of sustaining [C−H···X] interactions. Thus, in an 'attempt' to activate the potential recognition sites in these [3]catenanes, both disubstituted heteroaromatic rings and polyether chains were inserted into the regions between the two tolyl units in the 4,4′-bitotlyl spacers of the cyclobis(paraquat-4,4′-biphenylene) component. While all our attempts at 'activating' the potential recognition sites in [3]catenanes have so far been unsuccessful, some of the [2]catenated by-products of the catenations showed interesting recognition behavior. We discovered that they form homodimers and in so doing behave as self-complementary [2]catenanes.[12, 13] Here, we report 1) the template-directed syntheses of four self-complementary [2]catenanes and of three [3]catenanes related to them, 2) the X-ray crystallographic analyses of two of the four self-complementary [2]catenanes and of one of the three [3]catenanes, 3) ^{1}H NMR spectroscopic evidence for the homodimerization of the four [2]catenanes in solution, and 4) variable-temperature ^{1}H NMR spectroscopic investigations of the dynamic processes involving the ring components of all these catenanes in solution. It is in the context of self-assembling capsules,[14] supramolecular polymers,[15] and self-replicating systems[16] that this new family of self-complementary interlocked molecules should be viewed as important and worthy of investigation.

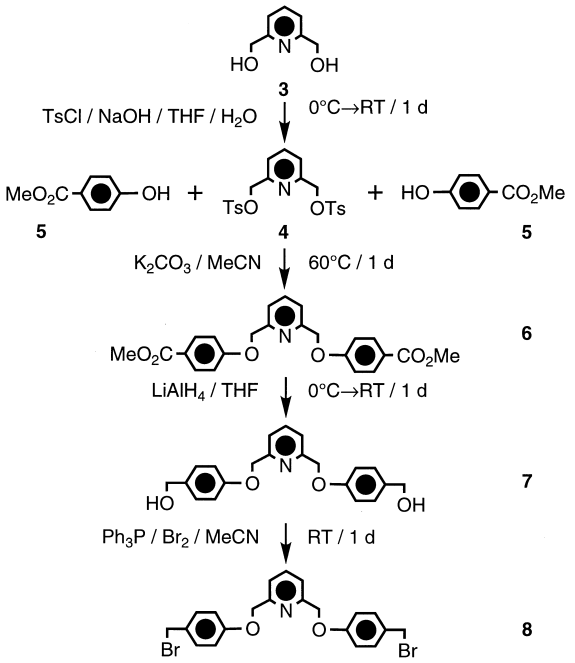
Results and Discussion

Synthesis: Bromination of **1** gave (Scheme 1) the dibromide **2** in which a pyridine ring is 2,6-disubstituted by two phenylene rings. Tosylation of **3**, followed by the coupling of the resulting

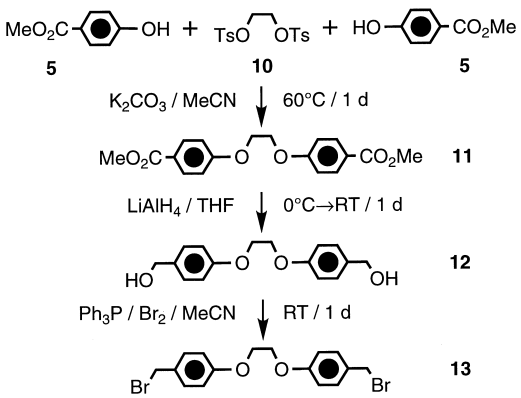


Scheme 1. The synthesis of the dibromide **2**.

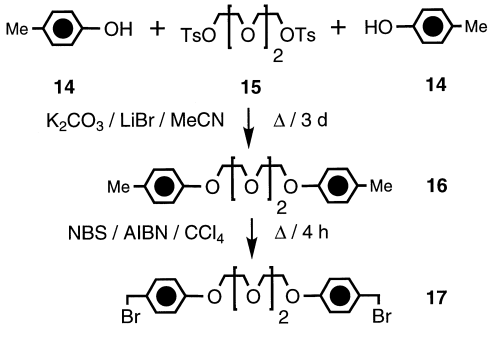
tosylate **4** with **5**, afforded (Scheme 2) the diester **6**. Reduction of **6**, followed by bromination of the diol **7**, yielded the dibromide **8** in which a 2,6-bis(oxymethyl)pyridine unit bridges the two phenylene rings. Reaction of **5** with **10** gave (Scheme 3) the diester **11**. Reduction of **11**, followed by bromination of the diol **12**, afforded the dibromide **13** in which a bismethylenedioxy unit bridges the two phenylene rings. Reaction of **14** with **15** yielded (Scheme 4) **16** which was brominated to give the dibromide **17** in which a polyether chain bridges the two phenylene rings. Alkylation of 4,4′-bipyridine with, in turn, one of the dibromides **2**, **9**, **13**, and **17** yielded (Scheme 5) the corresponding bis(hexafluorophosphate) salts **18**·2PF$_6$, **19**·2PF$_6$, **20**·2PF$_6$, and **21**·2PF$_6$, respectively, after counterion exchange. Reaction of these dibromides **2**, **9**, **13**, and **17**, respectively, with the bis(hexafluorophosphate) salts **18**·2PF$_6$, **19**·2PF$_6$, **20**·2PF$_6$, and **21**·2PF$_6$ in turn, in the presence of the macrocyclic polyether



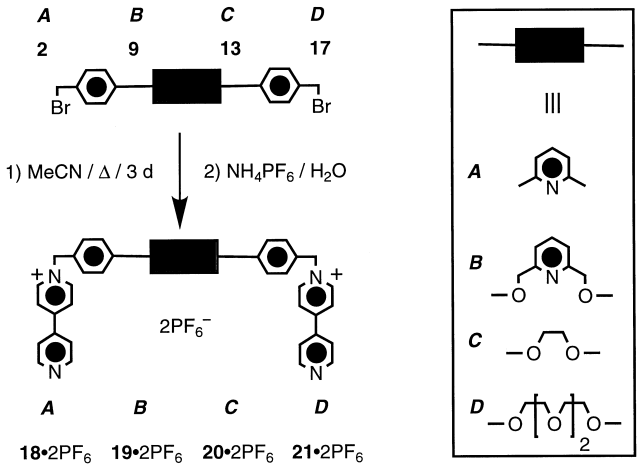
Scheme 2. The synthesis of the dibromide **8**.



Scheme 3. The synthesis of the dibromide **13**.



Scheme 4. The synthesis of the dibromide **17**.



Scheme 5. The syntheses of the bis(hexafluorophosphate) salts **18**·2PF$_6$, **19**·2PF$_6$, **20**·2PF$_6$, and **21**·2PF$_6$.

22, afforded[12] (Scheme 6) the corresponding [2]catenanes **23**·4PF$_6$, **24**·4PF$_6$, **25**·4PF$_6$, and **26**·4PF$_6$ in yields ranging from 2 to 23%. In addition, the [3]catenanes **27**·4PF$_6$, **28**·4PF$_6$, and **29**·4PF$_6$ were also isolated in yields of 20, 7, and 5%, respectively, when the precursors containing pyridine- or the bismethylene-dioxy-based spacers were employed. However, no [3]catenane was obtained when the dibromide **17** and the bis(hexafluorophosphate) salt **21**·2PF$_6$ were employed as substrates under otherwise identical conditions.

Variable-temperature ^{1}H NMR spectroscopic investigation of the [3]catenanes: The dynamic processes illustrated in Figures 3 and 4 are associated with the [3]catenanes **27**·4PF$_6$–**29**·4PF$_6$ in solution. Process I involves the circumrotation of the macrocyclic polyether through the cavity of the tetracationic cyclophane. Process II involves 1) the dislodgment of an 'inside' 1,5-dioxynaphthalene ring system from the cavity of the tetracationic cyclophane, 2) its 180° rotation around its [O···O] axis, and 3) its reinsertion inside the cavity. Process III involves 1) the dislodgment of an 'inside' 1,5-dioxynaphthalene ring system from the cavity of the tetracationic cyclophane, 2) the rotation of the adjacent bipyridinium unit around its [N···N] axis, and 3) the reinsertion of the 1,5-dioxynaphthalene ring system inside the cavity. When process I is slow on the ^{1}H NMR time scale, the 'alongside' and 'inside' 1,5-dioxynaphthalene ring systems can be distinguished. For example, the ^{1}H NMR spectrum [$(CD_3)_2CO$, 193 K] of **28**·4PF$_6$ shows (Figure 5a) two signals for the 2,6-protons ^{a}H-2/6 and ^{i}H-2/6 of the 'alongside' and 'inside' 1,5-dioxynaphthalene ring system, respectively. When the solution is allowed to warm up, process I becomes fast and the two signals coalesce (Figures 5b and 5c) into one. By employing the coalescence treatment,[17] the free energies of activation ($\Delta G_c^{\ddagger}$) associated with process I were determined (Table 1) for the [3]catenanes **27**·4PF$_6$–**29**·4PF$_6$ using ^{a}H-2/6 and ^{i}H-2/6 as the probe protons. The small differences between the $\Delta G_c^{\ddagger}$ values indicate that the nature of the spacers separating the two bipyridinium units in the tetracationic cyclophane does not affect significantly the barriers associated with process I. The local C_{2h} symmetry associated with the 'inside' 1,5-dioxynaphthalene ring systems requires that the protons H$_\alpha$ of the bipyridinium units reside (Figure 4) in one of two different sites (**A** or **B**). Thus, two sets of signals are observed[18] for H$_\alpha$ when processes II and III are slow. For example, the ^{1}H NMR spectrum [$(CD_3)_2CO$, 193 K] of **28**·

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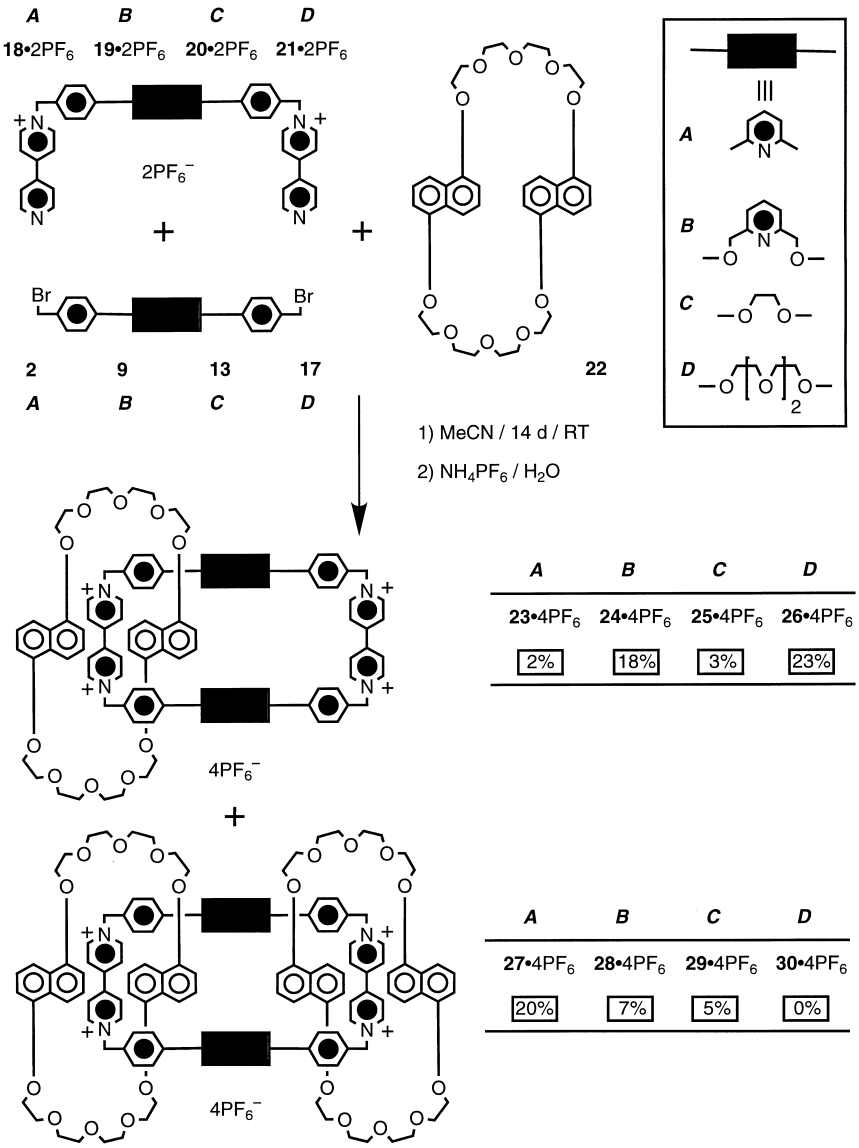

Scheme 6. The template-directed syntheses of the [2]catenanes **23** · 4 PF_6, **24** · 4 PF_6, **25** · 4 PF_6, and **26** · 4 PF_6, and of the [3]catenanes **27** · 4 PF_6, **28** · 4 PF_6, and **29** · 4 PF_6.

4 PF_6 shows two sets of signals for H_α which coalesce into one upon warming the solution up, as processes II and/or III become fast. By employing the coalescence treatment,[17] the $\Delta G_c^{\neq}$ values associated with either processes II or III, or with a combination of both, were determined (Table 1) for the [3]catenanes **28** · 4 PF_6 and **29** · 4 PF_6 using H_α as the probe protons. The small differences between the $\Delta G_c^{\neq}$ values indicate that the nature of the spacers separating the two bipyridinium units in the tetracationic cyclophane does not affect significantly the barriers associated with processes II and III.

X-ray structural analysis of one [3]catenane: X-ray structural analysis of the [3]catenane **29** · 4 PF_6 reveals (Figure 6) the crystals to contain two crystallographically independent C_i symmetric molecules, each having very similar co-conformations.[19] The interplanar separations between the 'inside' bipyridinium unit and the 'inside' and 'alongside' 1,5-dioxynaphthalene ring systems range between 3.30 and 3.41 Å in the two crystallographically independent molecules. The interplanar separations between the pair of 'inside' 1,5-dioxynaphthalene ring systems are essentially the same (7.19 and 7.22 Å). The [3]catenanes are also stabilized by additional [C–H···O] and [C–H···π] interactions which have not been analyzed in detail as a result of the poor resolution of the data. The crystallographically independent [3]catenanes stack end-to-end with adjacent 1,5-dioxynaphthalene ring systems aligned parallel, but offset, such that there is no [π···π] overlap.

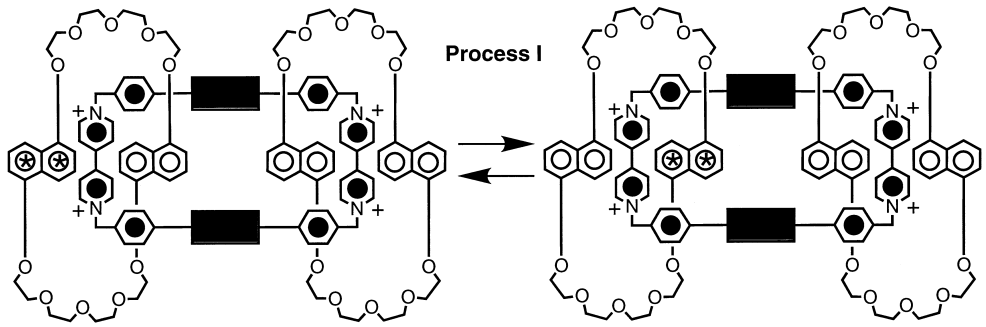

Figure 3. The dynamic process I involving the circumrotation of one of the two 1,5-dioxynaphtho[38]crown-10 through the cavity of the tetracationic cyclophane component of a [3]catenane (the symbol * is used in order to differentiate the two 1,5-dioxynaphthalene ring systems of this macrocyclic polyether).

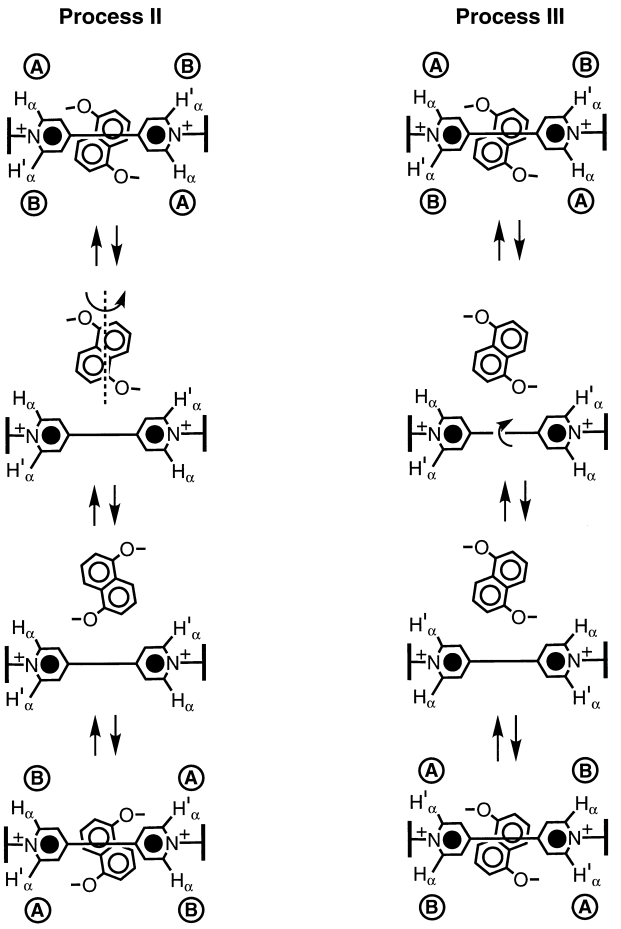

Figure 4. The dynamic processes II and III exchanging the bipyridinium protons H_α and H'_α between the sites **A** and **B** imposed by the local C_{2h} symmetry associated with the 'inside' 1,5-dioxynaphthalene ring system.

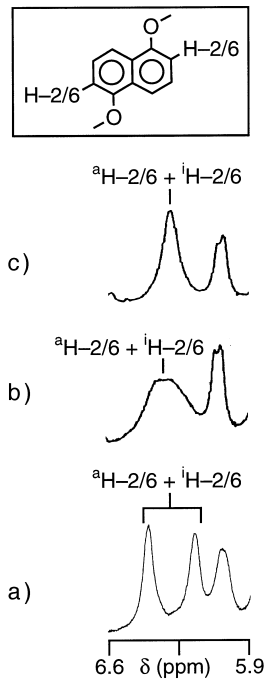

Figure 5. Partial ^{1}H NMR spectra of the [3]catenane **28** · 4 PF_6 recorded in $(CD_3)_2CO$ at (a) 193, (b) 213, and (c) 223 K (the superscripts 'a' and 'i' stand for 'alongside' and 'inside', respectively).

Table 1. Kinetic parameters[a] for the dynamic processes associated with the [3]catenanes **27** · 4 PF_6 – **29** · 4 PF_6 in $(CD_3)_2CO$.

Compound	Probe protons	$\Delta\nu$[b] [Hz]	k_c[c] [s^{-1}]	T_c[d] [K]	$\Delta G_c^{\neq}$[e] [kcal mol^{-1}]	Process
27 · 4 PF_6	H-2/6	125.7	279.3	233	10.9	I
28 · 4 PF_6	H-2/6	73.1	162.5	213	10.2	I
	H_α	74.1	164.7	213	10.2	II/III
29 · 4 PF_6	H-2/6	106.4	236.4	232	10.9	I
	H_α	109.9	244.0	233	11.0	II/III

[a] Determined by variable-temperature ^{1}H NMR spectroscopy (400 MHz) in $(CD_3)_2CO$. [b] Limiting frequency separation (error = ± 1 Hz). [c] Rate constant at the coalescence temperature (error = ± 5 Hz). [d] Coalescence temperature (error = ± 1 K). [d] Free energy barrier at the coalescence temperature (error = ± 0.2 kcal mol^{-1}).

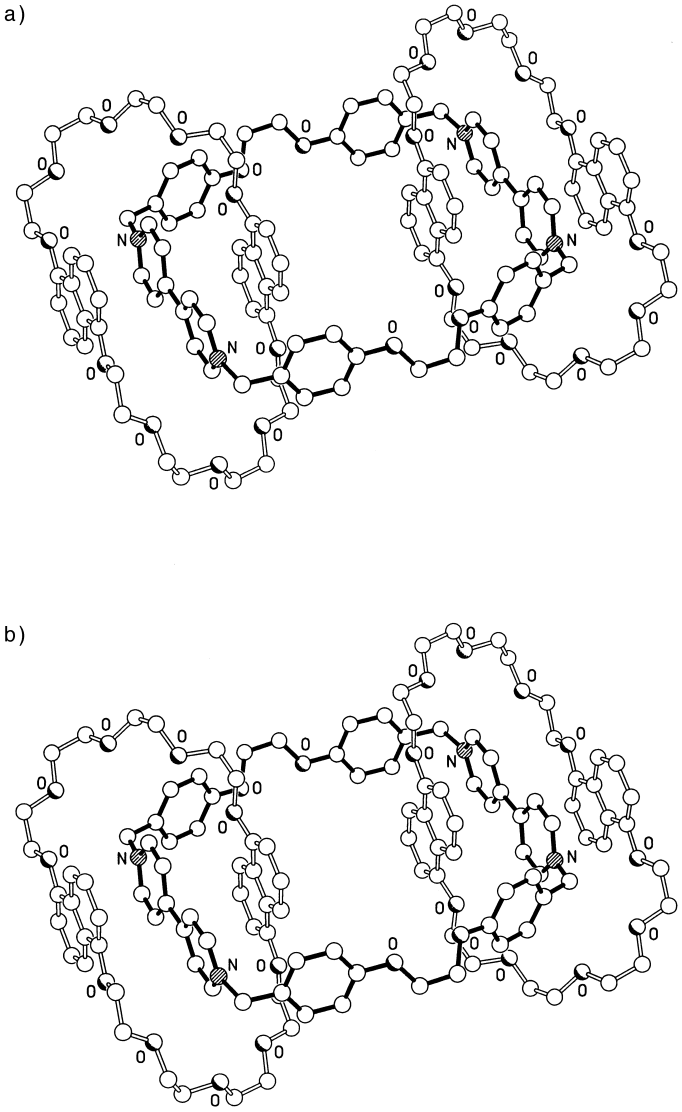

Figure 6. Ball-and-stick representations of the two crystallographically independent molecules of the [3]catenane **29**$^{4+}$ present in the crystals.

Investigation of the potential binding properties of the [3]catenanes: In order to explore the possible binding properties (Figure 2) of **27** · 4 PF_6 – **29** · 4 PF_6, 1,1′-bismethyl-4,4′-bipyridinium bis(hexafluorophosphate) was mixed with each of the [3]catenanes in $(CD_3)_2CO$. However, no chemical

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shift change was observed in a range of temperatures (185–300 K) using host:guest ratios of 5:1–1:5. These observations indicate that the π-electron-deficient bipyridinium salt is not bound by these [3]catenanes.

X-ray structural analyses of two [2]catenanes: X-ray structural analysis of the [2]catenane **24**·4PF_6 reveals (Figure 7) [π···π] stacking interactions between the 'inside' bipyridinium unit and the sandwiching 1,5-dioxynaphthalene ring systems (the mean interplanar separations between the 'inside' and the 'alongside' 1,5-dioxynaphthalene ring systems and the 'inside' bipyridinium unit are 3.37 and 3.32 Å, respectively). There are also a pair of [C–H···O] hydrogen bonds between one of the methylene hydrogen atoms

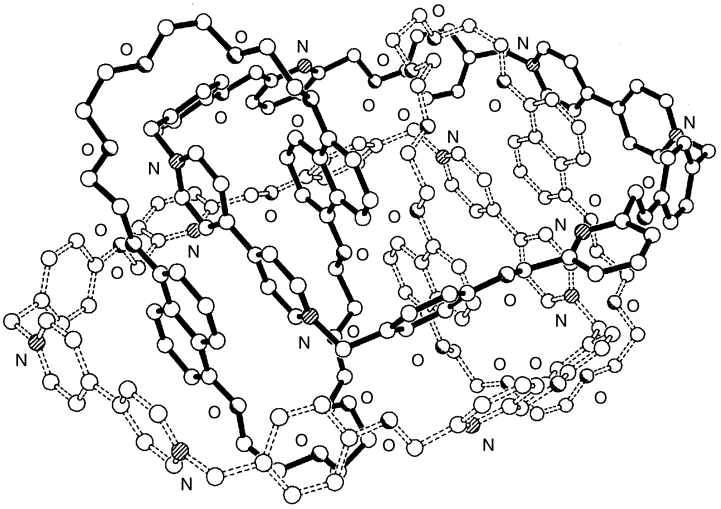

Figure 7. Ball-and-stick representation of the supramolecular homodimer formed by the [2]catenane **24**$^{4+}$ in the solid state.

adjacent to the 'inside' bipyridinium unit and some of the polyether oxygen atoms (the [C···O] and [H···O] distances and the [C–H···O] angles are 3.29, 2.38 Å, 158° and 3.30, 2.44 Å, 148°, respectively). No significant [C–H···π] interactions are observed (the shortest [H···π] separation is greater than 3 Å). The tetracationic cyclophane adopts an open conformation with a large central void between the 'inside' 1,5-dioxynaphthalene ring system and the 'alongside' bipyridinium unit (the interplanar separation is about 14 Å). As a result, mutual interpenetration of centrosymmetrically related pairs of [2]catenanes becomes possible, thus enabling the formation of a supramolecular homodimer which is stabilized by [π···π] stacking interactions between 1) the 'alongside' 1,5-dioxynaphthalene ring system of one [2]catenane and the 'alongside' bipyridinium unit of the other (the mean interplanar separation is 3.42 Å) and between 2) one of the phenoxy rings adjacent to the 'inside' bipyridinium unit in one [2]catenane and one of the pyridyl spacers in the other and vice versa (the [centroid···centroid] and the interplanar separation are 3.82 and 3.67 Å, respectively). There is also a [C–H···π] interaction between one of the *peri* hydrogen atoms of the 'alongside' 1,5-dioxynaphthalene ring system in one [2]catenane and one of the phenoxy rings adjacent to the 'alongside' bipyridinium unit of the other (the [H···π] distance and the [C–H···π] angle are 2.95 Å and 139°, respectively). The 'inside' pair of 1,5-dioxynaphthalene ring systems are aligned parallel, but offset, there being no [π···π] overlap. There are, however, a pair of [C–H···π] interactions between one of the β-methylene hydrogen atoms associated with the 'inside' 1,5-dioxynaphthalene ring system of one [2]catenane and the 'inside' 1,5-dioxynaphthalene ring system of the other and vice versa (the [H···π] distance and the [C–H···π] angle are 2.77 Å and 132°, respectively). Pairs of dimers form stepped stacks with the 'alongside' bipyridinium unit of one dimer positioned parallel, but offset, to its counterpart in the next. The area of overlap is small but the interplanar separation short (ca. 3.4 Å).

In the solid state, the tetracationic cyclophane component of the [2]catenane **25**$^{4+}$ adopts (Figure 8) a distinctly twisted conformation with approximate C_2 symmetry about an axis passing through the ring center and normal to its mean plane (the [N···N] axes of the two bipyridinium units are inclined by 42°). The 'alongside' bipyridinium unit has a distinctly twisted and bowed conformation, the mean twist angle about the bond linking the two pyridinium rings being 29°, while the two [N–CH_2] bonds are inclined by 26° (the equivalent parameters in the 'inside' bipyridinium unit are 4 and 16°, respectively). The interplanar separation between the 'inside' and 'alongside' 1,5-dioxynaphthalene ring systems and the 'inside' bipyridinium unit are 3.41 and 3.36 Å, respectively. A feature of this structure is a disorder in the polyether chains adjacent to the 'alongside' 1,5-dioxynaphthalene ring system which results in two in-plane, but slightly offset, positions of this unit. In addition to the [π···π] stacking interactions between the 'inside' bipyridinium unit and the two 1,5-dioxynaphthalene ring systems, there is a [C–H···π] inter-

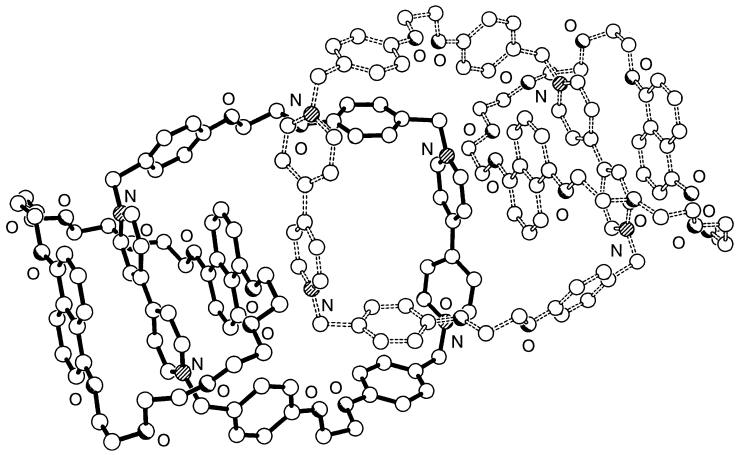

Figure 8. Ball-and-stick representation of the supramolecular homodimer formed by the [2]catenane **25**$^{4+}$ in the solid state.

action between one of the *peri* 1,5-dioxynaphthalene hydrogen atoms and the adjacent *p*-phenylene ring in the tetracationic cyclophane (the [H···π] distance is 2.77 Å and the [C–H···π] angle is 151°). The disorder in the polyether linkages precludes any analysis of probable [C–H···O] hydrogen bonding interactions. Centrosymmetrically related pairs of [2]catenanes mutually interpenetrate with one of the pyridinium rings of the 'alongside' bipyridinium unit of one [2]catenane inserted into the cavity of the other and vice versa. The resulting supramolecular homodimer is stabilized by [π···π] stacking interactions between the 'inside' 1,5-dioxynaphthalene ring systems and the facing pyridinium rings (the interplanar separation is 3.34 Å). There is also a [π···π] stacking interaction between one of the phenoxy rings in one [2]catenane and one of its counterparts in the other (the interplanar separation is 3.47 Å), supplemented by a [C–H···π] interaction between one of the hydrogen atoms *ortho* to the oxygen atom on the same phenoxy ring and the adjacent pyridinium ring (the [H···π] distance is 2.76 Å and the [C–H···π] angle is 153°). The separation between the pair of 'alongside' bipyridinium units is about 7.75 Å and the central void between them is filled by MeCN solvent molecules. The homodimeric superstructure extends in the crystal as a result of interdimer [π···π] stacking between the 'alongside' 1,5-dioxynaphthalene ring systems (the interplanar separation between the 1,5-dioxynaphthalene ring systems of adjacent dimers is 3.20 Å).

Investigation of the supramolecular homodimerization of the [2]catenanes in solution: In order to establish if the [2]catenanes **23**·4PF$_6$–**26**·4PF$_6$ form supramolecular homodimers also in solution, they were investigated by ^{1}H NMR spectroscopy. They were dissolved individually in $(CD_3)_2CO$ and the resulting solutions were diluted from a concentration (c) of about 10^{-2} to about 10^{-3} M. The ^{1}H NMR spectra recorded upon dilution at 185 K showed upfield shifts in all instances, indicating that the [2]catenanes self-associate in solution. Chemical shift changes ($\Delta\delta_o$) are evident for the signals associated with protons of both macrocyclic components of each [2]catenane. However, since the protons $^aH_\alpha$ of the 'alongside' bipyridinium unit give rise to a sharp and well-resolved doublet in the case of all [2]catenanes, they were selected as the probe protons for the determination of the association constants (K_a) for the dimerization processes. Nonlinear curve-fitting of the plots of $\Delta\delta_o$ against c gave[20] (Table 2) K_a values ranging from 17 to 31 M^{-1}. The relatively small differences between the K_a values for the dimerization of the [2]catenanes indicate that the nature of the spacers separating the two bipyridinium units in the tetracationic cyclophane does not affect significantly their self-association.

Table 2. Association constants[a] K_a and derived free energies of association ($-\Delta G^\circ$) for the dimerization of the [2]catenanes **23**·4PF$_6$–**26**·4PF$_6$ in $(CD_3)_2CO$.

Compound	K_a[b] [M^{-1}]	ΔG°[c] [kcal mol^{-1}]
23·4PF$_6$	26	1.2
24·4PF$_6$	20	1.1
25·4PF$_6$	31	1.3
26·4PF$_6$	17	1.0

[a] Determined by variable-temperature ^{1}H NMR spectroscopy (400 MHz) in $(CD_3)_2CO$ at 185 K using $^aH_\alpha$ as the probe protons. [b] Error = ± 2 M^{-1}. [c] Error = ± 0.2 kcal mol^{-1}.

Variable-temperature ^{1}H NMR spectroscopic investigation of the [2]catenanes: In addition to the dynamic processes illustrated in Figures 3 and 4, the circumrotation (process IV) of the tetracationic cyclophane through the cavity of the macrocyclic polyether is also a possibility (Figure 9) in the case of [2]catenanes **23**·4PF$_6$–**26**·4PF$_6$ in solution. When

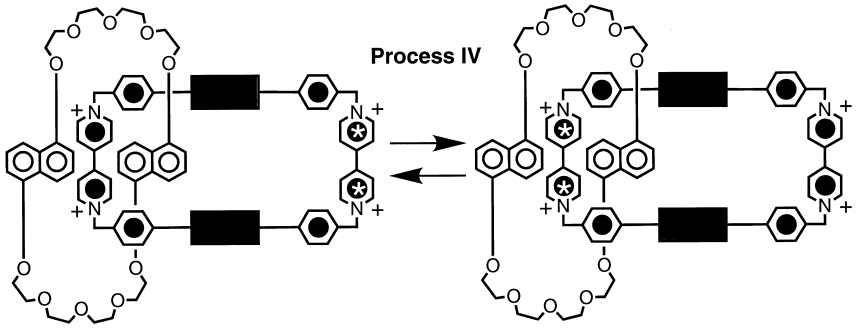

Figure 9. The dynamic process IV involving the circumrotation of the tetracationic cyclophane component through the cavity of the 1,5-dioxynaphtho[38]crown-10 of a [2]catenane (the symbol * is used in order to differentiate the two bipyridinium units of the tetracationic cyclophane).

process I is slow on the ^{1}H NMR time scale, the 'alongside' and 'inside' 1,5-dioxynaphthalene ring systems can be distinguished. For example, the ^{1}H NMR spectrum [$(CD_3)_2CO$, 185 K] of **24**·4PF$_6$ shows two signals for the 2,6-protons ^aH-2/6 and ^iH-2/6 of the 'alongside' and 'inside' 1,5-dioxynaphthalene ring system, respectively. When the solution is allowed to warm up, process I becomes fast and the two signals coalesce into one. By employing the coalescence treatment, the $\Delta G_c^{\neq}$ values associated with process I were determined (Table 3) for the [2]catenanes **23**·4PF$_6$–**26**·4PF$_6$ using ^aH-2/6 and ^iH-2/6 as the probe protons. Interestingly, the $\Delta G_c^{\neq}$ values for **24**·4PF$_6$–**26**·4PF$_6$ are very similar, while that for **23**·4PF$_6$ is higher, presumably, as a result of it containing a more rigid cyclophane component. When process IV is slow, the 'alongside' and 'inside' bipyridinium units can be distinguished. For example, the ^{1}H NMR spectrum [$(CD_3)_2CO$, 252 K] of **24**·4PF$_6$ shows (Figure 10d) two sets of signals for the α-protons $^aH_\alpha$ and $^iH_\alpha$ of the 'alongside' and 'inside' bipyridinium units, respectively. When the solution is allowed to warm up, process IV becomes fast and the two sets of signals coalesce (Figures 10e–g) into one. By employing the coalescence treatment,[17] the $\Delta G_c^{\neq}$ values associated with process IV were determined (Table 3) for the [2]catenanes **23**·4PF$_6$–**26**·4PF$_6$ using $^aH_\alpha$ and $^iH_\alpha$ as the probe protons.

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Table 3. Kinetic parameters[a] for the dynamic processes associated with the [2]catenanes **23**·4PF$_6$–**26**·4PF$_6$ in $(CD_3)_2CO$.

Compound	Probe protons	$\Delta\nu$[b] [Hz]	k_c[c] [s^{-1}]	T_c[d] [K]	$\Delta G_c^{\neq}$[e] [kcal mol^{-1}]	Process
23·4PF$_6$	H-2/6	95.6	212.4	219	10.4	I
	$^iH_\alpha$	71.4	158.6	219	10.5	II/III
	$^aH_\alpha$/$^iH_\alpha$	125.9	279.7	288	13.6	IV
24·4PF$_6$	H-2/6	36.8	81.7	188	9.2	I
	$^iH_\alpha$	61.8	137.3	195	9.3	II/III
	$^aH_\alpha$/$^iH_\alpha$	142.8	317.1	288	13.5	IV
25·4PF$_6$	H-2/6	52.7	117.1	199	9.6	I
	$^iH_\alpha$	67.4	149.7	204	9.8	II/III
	$^aH_\alpha$/$^iH_\alpha$	120.6	267.9	280	13.2	IV
26·4PF$_6$	H-2/6	52.2	116.0	184	8.9	I
	$^iH_\alpha$	156.3	347.2	291	13.6	II/III
	$^aH_\alpha$/$^iH_\alpha$	36.4	80.1	186	8.9	IV

[a] Determined by variable-temperature ^{1}H NMR spectroscopy (400 MHz) in $(CD_3)_2CO$. [b] Limiting frequency separation (error = ± 1 Hz). [c] Rate constant at the coalescence temperature (error = ± 5 Hz). [d] Coalescence temperature (error = ± 1 K). [e] Free energy barrier at the coalescence temperature (error = ± 0.2 kcal mol^{-1}).

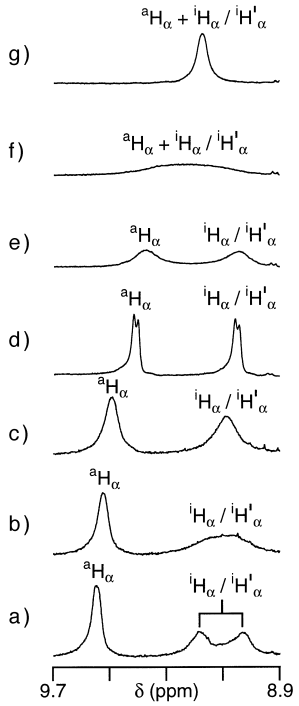

Figure 10. Partial ^{1}H NMR spectra of the [2]catenane **24**·4PF$_6$ recorded in $(CD_3)_2CO$ at (a) 185, (b) 195, (c) 208, (d) 252, (e) 274, (f) 288, and (g) 309 K (the superscripts 'a' and 'i' stand for 'alongside' and 'inside', respectively).

Interestingly, the $\Delta G_c^{\neq}$ values for **23**·4PF$_6$–**25**·4PF$_6$ are very similar, while that for **26**·4PF$_6$ is lower, presumably, as a result of it containing a more flexible cyclophane component. The local C_{2h} symmetry associated with the 'inside' 1,5-dioxynaphthalene ring system requires that the protons $^iH_\alpha$ of the 'inside' bipyridinium unit reside (Figure 3) in one of two different sites (**A** or **B**). Thus, two sets of signals are observed for $^iH_\alpha$ when process II and process III are slow. For example, the ^{1}H NMR spectrum [$(CD_3)_2CO$, 185 K] of **24**·4PF$_6$ shows (Figure 10a) two sets of signals for $^iH_\alpha$ which coalesce (Figures 10b–e) into one upon warming the solution up, as process II and/or process III become fast. By employing the coalescence treatment, the $\Delta G_c^{\neq}$ values associated with either process II or process III, or with a combination of both, were determined (Table 3) for the [2]catenanes **23**·4PF$_6$–**26**·4PF$_6$ using $^iH_\alpha$ as the probe protons. These $\Delta G_c^{\neq}$ values range from 9.3 to 13.6 kcal mol^{-1} indicating that the nature of the spacers separating the bipyridinium units in the tetracationic cyclophane component influences the energy barriers associated with these dynamic processes.

Conclusion

[3]Catenanes having large central voids with π-electron-rich recognition sites and hydrogen-bond acceptor groups can be prepared efficiently by interlocking two 1,5-dioxynaphtho[38]crown-10 macrocycles with a bipyridinium-based tetracationic cyclophane. Despite their potential recognition properties, these mechanically interlocked molecules cannot bind π-electron-deficient guests in solution. Related [2]catenanes, incorporating one 1,5-dioxynaphtho[38]crown-10 macrocycle and one bipyridinium-based tetracationic cyclophane, self-assemble into supramolecular homodimers both in solution and in the solid state. Their self-association is a result of a combination of [π···π] and [C–H···π] interactions between some of the aromatic rings that comprise their macrocyclic components. The association constants, determined in $(CD_3)_2CO$ at 185 K, for the dimerization processes are not affected significantly by the nature of the spacers separating the two bipyridinium units in the tetracationic cyclophane and range from 17 to 31 M^{-1}. The macrocyclic components of the [2]catenanes and of the [3]catenanes circumrotate through each other's cavity in $(CD_3)_2CO$. The 'inside' 1,5-dioxynaphthalene and the 'inside' bipyridinium ring systems of these catenanes rotate about their [O···O] and [N···N] axes, respectively, in $(CD_3)_2CO$. In the three [3]catenanes, the energy barriers (10.2–11.0 kcal mol^{-1}) associated with these dynamic processes are similar. In the four [2]catenanes, the energy barrier (8.9–10.4 kcal mol^{-1}) for the circumrotation of the neutral through the cavity of the charged macrocyclic component increases with the rigidity of the tetracationic cyclophane. The energy barrier (8.9–13.6 kcal mol^{-1}) for the circumrotation of the charged through the cavity of the neutral macrocyclic component shows the opposite trend. The energy barriers (9.3–13.6 kcal mol^{-1}) for the rotations of the 'inside' 1,5-dioxynaphthalene and the 'inside' bipyridinium ring systems change with the distance between the two bipyridinium units and with the rigidity of the spacers separating them.

Experimental Section

General methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried according to literature procedures.[21] The compounds **1**[22] and **22**[23] 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. Electron impact mass spectra (EIMS) were performed

using a Kratos Profile spectrometer. Liquid secondary ion mass spectrometry (LSIMS), in conjunction with a 3-nitrobenzyl alcohol or 2-nitrophenyloctyl ether matrix, was performed on a VG Zabspec instrument. For high-resolution LSIMS (HRLSIMS), the instrument was operated at a resolution of about 6000 by employing narrow-range voltage scanning along with polyethylene glycol or CsI as reference compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX400 (400 and 100.6 Mhz, respectively) spectrometer. Elemental analyses were performed by Quantitative Technologies Inc.

2,6-Di(*p*-bromomethylphenyl)pyridine (2): A suspension of **1** (478 mg, 1.74 mmol), *N*-bromosuccinimide (NBS) (774 mg, 1.35 mmol) and catalytic amounts of $PhCO_3H$ in CCl_4 (25 mL) was heated under reflux and an atmosphere of Ar for 1 d. After cooling down to ambient temperature, the mixture was filtered off and the solid residue was washed with CH_2Cl_2 and CCl_4. The filtrate was concentrated under reduced pressure and the solid residue was crystallized (CH_2Cl_2/hexane (1:2.5)) to afford **2** (490 mg, 67 %) as a white powder. M.p. 120 °C (decomp); EIMS: *m/z*: 417 $[M]^+$, 338 $[M-Br]^+$, 258 $[M-2Br]^+$; ^{1}H NMR ($CDCl_3$, 25° C): $\delta = 8.12-7.52$ (m, 8H), 7.80 (t, $J = 7.2$ Hz, 1H), 7.70 (d, $J = 7.2$ Hz, 2H), 4.57 (s, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25° C): $\delta = 156.0$, 139.4, 138.5, 137.6, 129.4, 127.3, 118.8, 33.2; anal. calcd for $C_{19}H_{15}Br_2N$ (417.144): C 54.71, H 3.62, N 3.36; found: C 54.25, H 3.39, N 3.37.

2,6-Pyridinedimethanol di-*p*-tosylate (4): A solution of *p*-toluensulfonyl chloride (68.5 g, 0.36 mol) in THF (150 mL) was added dropwise to a solution of **3** (25.0 g, 0.18 mol) and NaOH (21.6 g, 0.54 mol) in a mixture of THF (90 mL) and H_2O (90 mL) maintained at 0 °C. After 12 h, H_2O (300 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 200 mL). The organic layer was washed with H_2O (3 × 250 mL) and dried (Na_2SO_4). The solvent was distilled off under reduced pressure to afford **4** (74.8 g, 93 %) as a white solid. M.p. 107 °C; EIMS: *m/z*: 447 $[M]^+$, 276 $[M-OTs]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.80$ (d, $J = 4.6$ Hz, 4H), 7.69 (t, $J = 4.3$ Hz, 1H), 7.43–7.33 (m, 6H), 5.05 (s, 4H), 2.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 153.3$, 145.0, 137.7, 132.5, 129.8, 127.8, 121.3, 71.2, 22.4; anal. calcd for $C_{21}H_{21}NO_6S_2$ (447.532): C 56.36, H 4.73, N 3.13; found: C 56.19, H 4.41. N 2.96.

2,6-Di(*p*-methoxycarbonylphenoxymethyl)pyridine (6): A suspension of **4** (20.0 g, 0.045 mol), **5** (20.4 g, 0.134 mol) and K_2CO_3 (37.0 g, 0.268 mol) in MeCN (300 mL) was heated for 1 d at 60 °C under an atmosphere of Ar. After cooling down to ambient temperature, the mixture was filtered and the solid residue was washed with MeCN. The filtrate was concentrated under reduced pressure and the solid residue was washed with H_2O (1 L) and dried to yield **6** (18.0 g, 98 %) as a white solid. M.p. 180 °C; EIMS: *m/z*: 407 $[M]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 8.00$ (d, $J = 8.8$ Hz, 4H), 7.77 (t, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.7$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 4H), 5.27 (s, 4H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 166.7$, 162.0, 156.2, 137.8, 131.7, 123.3, 120.5, 114.5, 70.6, 51.9; anal. calcd for $C_{18}H_{18}O_6$ (330.336): C 67.80, H 5.20, N 3.44; found: C 67.43, H 4.92, N 3.29.

2,6-Di(*p*-hydroxymethylphenoxymethyl)pyridine (7): A solution of **6** (2.0 g, 5.0 mmol) in THF (28 mL) was added dropwise to a supension of $LiAlH_4$ (0.56 g, 15.0 mmol) in THF (112 mL) maintained at 0 °C and under an atmosphere Ar. After the mixture was allowed to warm up to ambient temperature and maintained at this temperature for a further 1 d, H_2O (500 mL) was added and the mixture was concentrated under reduced pressure. The resulting precipitate was filtered off, washed with H_2O (100 mL) and MeOH (100 mL), and extracted in a Soxhlet apparatus with $CHCl_3$ for 2 d. The solvent was distilled off under reduced pressure to yield **7** (1.13 g, 90 %) as a white solid. M.p. 152 °C; EIMS: *m/z*: 351 $[M]^+$, 333 $[M-H_2O]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.79$ (t, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.7$ Hz, 2H), 7.30 (d, $J = 8.6$ Hz, 4H), 7.00 (d, $J = 8.6$ Hz, 4H), 5.22 (s, 4H), 4.62 (br s, 4H); anal. calcd for $C_{21}H_{21}NO_4$ (351.402): C 71.78, H 6.02, N 3.99; found: C 71.52, H 5.98, N 4.00.

2,6-Di(*p*-bromomethylphenoxymethyl)pyridine (9): Br_2 (1.02 g, 6.40 mmol) was added slowly to a solution of Ph_3P (1.68 g, 6.40 mmol) in MeCN (200 mL) maintained at 0 °C. After the mixture was allowed to warm up to ambient temperature, **7** (1.13 g, 3.20 mmol) was added as a solid in three portions. After 1 d, the solvent was distilled off under reduced pressure and the solid residue was dissolved in CH_2Cl_2 (500 mL). The solution was washed with a 2 M aqueous solution of K_2CO_3 (2 × 250 mL), H_2O (2 × 250 mL) and a saturated aqueous solution of NaCl (250 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to yield **9** (0.66 g, 43 %) as a white solid. M.p. 139 °C; EIMS: *m/z*: 477 $[M]^+$, 398 $[M-Br]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.76$ (t, $J = 7.5$ Hz, 1H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 8.7$ Hz, 4H), 6.95 (d, $J = 8.7$ Hz, 8H), 5.21 (s, 4H), 4.50 (s, 4H); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 158.4$, 156.5, 137.9, 130.5, 120.3, 115.1, 70.5, 33.7; anal. cald for $C_{21}H_{19}Br_2NO_2$ (477.196): C 52.86, H 4.01, N 2.94; found: C 52.91, H 4.03, N 2.95.

1,2-Di(*p*-methoxycarbonylphenoxy)ethane (11): A suspension of **5** (16.60 g, 109.3 mmol), **10** (13.50 g, 36.4 mmol), and K_2CO_3 (30.20 g, 218.6 mmol) in MeCN (300 mL) was heated for 1 d at 60 °C under an atmosphere of Ar. After cooling down to ambient temperature, the mixture was filtered and the solid residue was washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by column cromatography (SiO_2, CH_2Cl_2/CH_3OH (100:1)) to yield **11** (5.20 g, 43 %) as a white solid. M.p. 156 °C; EIMS: *m/z*: 330 $[M]^+$, 299 $[M-OMe]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 8.00$ (d, $J = 8.7$ Hz, 4H), 6.95 (d, $J = 8.7$ Hz, 4H), 4.39 (s, 4H), 3.88 (s, 6H); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 166.7$, 162.2, 131.4, 114.2, 66.4, 51.8; anal.: calc. for $C_{18}H_{18}O_6$ (330.336): C 65.45, H 5.49; found: C 65.25, H 5.32.

1,2-Di(*p*-hydroxymethylphenoxy)ethane (12): A solution of **11** (5.10 g, 15.43 mmol) in THF (100 mL) was added dropwise to a supension of $LiAlH_4$ (1.74 g, 46.29 mmol) in THF (280 mL) maintained at 0 °C under an atmosphere of Ar. After the mixture was allowed to warm up to ambient temperature and maintained at this temperature for a further 1 d, H_2O (500 mL) was added. The mixture was concentrated under reduced pressure and the resulting precipitate was filtered off and washed with H_2O (100 mL), MeOH (100 mL), and CH_2Cl_2 (100 mL) to yield **12** (3.81 g, 90 %) as a white solid. M.p. 298 °C (decomp); EIMS: *m/z*: 274 $[M]^+$, 256 $[M-H_2O]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.31$ (d, $J = 8.7$ Hz, 4H), 6.95 (d, $J = 8.7$ Hz, 4H), 4.65 (d, 4H), 4.34 (s, 4H), 3.50 (d, 2H); anal. calcd for $C_{16}H_{18}O_4$ (274.316): C 70.06, H 6.61; found: C 69.43, H 6.62.

1,2-Di(*p*-bromomethylphenoxy)ethane (13): Br_2 (3.40 g, 21.4 mmol) was added slowly to a solution of Ph_3P (5.61 g, 21.4 mmol) in MeCN (150 mL) maintained at 0 °C. After the mixture was allowed to warm up to ambient temperature, a suspension of **12** (3.00 g, 10.7 mmol) in MeCN (500 mL) was added dropwise. After 1 d, the mixture was filtered and the solid residue was washed with Et_2O and crystallized (CH_2Cl_2/hexane (1:2.5)) to afford **13** (2.88 g, 67 %) as a white solid. M.p. 170 °C; EIMS: *m/z*: 400 $[M]^+$, 321 $[M-Br]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.34$ (d, $J = 8.6$ Hz, 4H), 6.90 (d, $J = 8.6$ Hz, 8H), 4.50 (s, 4H), 4.32 (s, 4H); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 158.6$, 130.5, 114.4, 66.5, 73.8; anal. calcd for $C_{16}H_{16}Br_2O_2$ (400.116): C 48.03, H 4.03; found: C 47.61, H 4.07.

1,11-Di(*p*-methylphenoxy)-3,6,9-trioxaundecane (16): A solution of **15** (12.6 g, 25 mmol) in MeCN (200 mL) was added dropwise to a suspension of **14** (5.4 g, 50 mmol), and K_2CO_3 (27 g, 200 mmol), and LiBr (0.2 g, 2 mmol) in MeCN (200 mL) maintained at reflux. Heating was continued for a further 3 d and, after the mixture had been allowed to cool down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was purified by column chromatography (SiO_2, $MeCO_2Et$/hexane (2:3)) to yield **16** (7.3 g, 78 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.05$ (d, $J = 8.8$ Hz, 4H), 6.81–6.79 (m, 4H), 4.09–4.06 (m, 4H), 3.84–3.81 (m, 4H), 3.73–3.71 (m, 4H), 3.70–3.66 (m, 4H), 2.27 (s, 6H); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 156.6$, 130.0, 129.8, 114.4, 70.8, 70.6, 69.8, 67.4, 20. 4.

1,2-Di(*p*-bromomethylphenoxy)-3,6,9-trioxaundecane (17): A solution of **16** (2.0 g, 5.3 mmol), NBS (2.4 g, 13.4 mmol), and AIBN (0.1 g, 0.6 mmol) in CCl_4 (250 mL) was heated for 4 h under reflux. After cooling down to ambient temperature, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, $MeCO_2Et$/hexane (1:1)) to yield **17** (1.5 g, 53 %) as a yellow oil. EIMS: *m/z*: 532 $[M]^+$; ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.29-7.26$ (m, 4H), 6.84 (d, $J = 8.4$ Hz, 4H), 4.47 (s, 4H), 4.11–4.08 (m, 4H), 3.84–3.81 (m, 4H), 3.79–3.61 (m, 4H), 3.68–3.66 (m, 4H); ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 158.8$, 130.3, 130.0, 129.8, 114.8, 114.4, 70.8, 70.6, 69.8, 67.4, 33.9.

Bis(hexafluorophosphate) salts 18·2PF$_6$, 19·2PF$_6$, 20·2PF$_6$, and 21·2PF$_6$: A solution of **2**, **9**, **16**, or **17** (6.59 mmol) in MeCN (450 mL) was added dropwise to a solution of 4,4′-bipyridine (6.18 g, 39.54 mmol) in MeCN (40 mL) heated under reflux. The mixture was heated under reflux for a further 3 d and, after cooling down to ambient temperature, filtered. The solid residue was washed with Et_2O and CH_2Cl_2 and dissolved in MeOH/H_2O (1:20, 500 mL). After the addition of NH_4PF_6, a white solid

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precipitated out. It was filtered off and washed with H_2O (500 mL) to afford **18**·2PF$_6$, **19**·2PF$_6$, **20**·2PF$_6$, or **21**·2PF$_6$ as a white powder.

18·2PF$_6$ (35%): M.p. 120°C (decomp); LSIMS: *m/z*:714 $[M-PF_6]^+$, 569 $[M-2PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.90–8.85 (m, 8H), 8.36–8.26 (m, 8H), 7.97–7.88 (m, 3H), 7.81–7.75 (m, 4H), 7.61 (d, J = 8.3 Hz, 4H), 5.82 (s, 4H); ^{13}C NMR (CD_3CN, 25°C): δ = 156.3, 155.5, 152.1, 145.9, 142.1, 141.4, 139.4, 134.7, 130.6, 128.8, 127.2, 123.0, 120.7, 64.8; anal. calcd for $C_{39}H_{31}N_5P_2F_{12}\cdot H_2O$ (877.651): C 53.37, H 3.79, N 7.98; found: C 53.58, H 3.66, N 7.45.

19·2PF$_6$ (67%): M.p. 120°C (decomp); LSIMS: *m/z*: 774 $[M-PF_6]^+$, 629 $[M-2PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.83 (d, J = 7.0 Hz, 8H), 8.29 (d, J = 7.0 Hz, 4H), 7.82–7.75 (m, 7H), 7.46 (d, J = 8.8 Hz, 4H), 7.10 (d, J = 8.8 Hz, 4H), 5.69 (s, 4H), 5.18 (s, 4H); ^{13}C NMR (CD_3CN, 25°C): δ = 160.4, 157.2, 155.1, 151.9, 145.5, 141.9, 138.7, 131.9, 126.9, 126.0, 122.6, 121.7, 116.5, 71.4, 64.5; anal. calcd for $C_{41}H_{35}N_5O_2P_2F_{12}\cdot H_2O$ (937.703): C 52.52, H 3.98, N 7.47; found: C 52.30, H 3.61, N 7.19.

20·2PF$_6$ (48%): M.p. 119°C (decomp); LSIMS: *m/z*: 697 $[M-PF_6]^+$, 552 $[M-2PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.86–8.77 (m, 8H), 8.28 (m, 4H), 7.77 (m, 4H), 7.45 (d, J = 8.7 Hz, 4H), 7.05 (d, J = 8.7 Hz, 4H), 5.67 (s, 4H), 4.35 (s, 4H); ^{13}C NMR (CD_3CN, 25°C): δ = 160.9, 155.3, 152.0, 145.7, 142.3, 132.2, 127.1, 126.1, 122.9, 116.4, 67.7, 64.7; anal. calcd for $C_{36}H_{32}N_4O_2P_2F_{12}\cdot 1.5H_2O$ (869.625): C 49.72, H 4.06, N 6.44; found: C 49.87, H 3.72, N 6.05.

21·2PF$_6$ (56%): M.p. 82°C; LSIMS: *m/z*: 830 $[M-PF_6]^+$, 685 $[M-2PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.84–8.78 (m, 8H), 8.29 (d, J = 6.9 Hz, 4H), 7.85 (d, J = 6.9 Hz, 4H), 7.43 (d, J = 8.8 Hz, 4H), 6.97 (d, J = 8.8 Hz, 4H), 5.67 (s, 4H), 4.09–4.07 (m, 4H), 3.76–3.74 (m, 4H), 3.61–3.59 (m, 4H), 3.57–3.55 (m, 4H); ^{13}C NMR (CD_3CN, 25°C): δ = 160.8, 154.5, 150.5, 145.5, 143.6, 131.9, 127.1, 125.5, 123.4, 116.1, 71.0, 70.9, 69.9, 68.4, 64.6.

[2]Catenanes 23·4PF$_6$, 24·4PF$_6$, 25·4PF$_6$, and 26·4PF$_6$ and [3]catenanes 27·4PF$_6$, 28·4PF$_6$, and 29·4PF$_6$: A solution of **2**, **9**, **16**, or **17** (0.31 mmol) and **18**·2PF$_6$, **19**·2PF$_6$, **20**·2PF$_6$, and **21**·2PF$_6$ (0.31 mmol), respectively, and **22** (0.59 g, 0.93 mmol) in MeCN (25 mL) was stirred for 14 d at ambient temperature. The solvent was distilled off under reduced pressure and the solid residue was purified by column cromatography (SiO_2, 2M $NH_4Cl_{(aq)}$/MeOH/$MeNO_2$ (7:2:1)) to yield two different products which were dissolved in H_2O. In both instances, the addition of NH_4PF_6 afforded a red/purple precipitate which was filtered off and washed with H_2O to give, in order of elution, a [3]catenane and a [2]catenane.

23·4PF$_6$ (2%): M.p. 210°C (decomp); LSIMS: *m/z*: 1866 $[M-PF_6]^+$, 1721 $[M-2PF_6]^+$, 1576 $[M-3PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.78 (d, J = 6.6 Hz, 8H), 8.30 (d, J = 7.9 Hz, 8H), 8.15–7.40 (m, 22H), 6.58 (pt, J = 8.0 Hz, 4H), 6.43 (d, J = 8.0 Hz, 4H), 6.36 (d, J = 8.0 Hz, 4H), 5.85 (s, 8H), 4.00–3.78 (m, 32H); ^{13}C NMR (125.7 MHz, CD_3CN, 25°C): δ = 155.1, 153.0, 147.8, 144.9, 138.7, 133.9, 129.9, 127.9, 125.7, 125.2, 119.9, 112.9, 105.1, 71.0, 70.8, 69.9, 68.0, 64.4; anal. calcd for $C_{92}H_{82}N_6O_{10}P_4F_{24}$ (2011.548): C 54.93, H 4.11, N 4.18; found: C 54.63, H 4.32, N 4.15.

24·4PF$_6$ (18%): M.p. 200°C (decomp); LSIMS: *m/z*: 2018 $[M-PF_6]^+$, 1872 $[M-2PF_6]^+$, 1728 $[M-3PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.76 (br s, 8H), 7.80–7.40 (m, 16H), 7.24 (d, J = 7.7 Hz, 4H), 7.10 (br s, 8H), 6.59 (pt, J = 7.9 Hz, 4H), 6.37 (d, J = 7.9 Hz, 8H), 5.72 (s, 8H), 5.09 (s, 8H), 3.90–3.70 (m, 32H); ^{13}C NMR (CD_3CN, 25°C): δ = 160.6, 157.1, 154.0, 145.5, 132.9, 132.2, 130.1, 126.7, 126.2, 121.8, 116.7, 113.8, 106.1, 72.0, 71.7, 71.6, 70.9, 68.9, 65.3; anal. calcd for $C_{98}H_{98}N_6O_{14}P_4F_{24}$ (2163.738): C 54.40, H 4.57, N 3.88; found: C 54.53, H 4.42, N 3.91; crystal data: $[C_{98}H_{98}N_6O_{14}][PF_6]_4\cdot 4MeCN\cdot 2H_2O$, M_r = 2373.0, triclinic, space group $P\bar{1}$ (no. 2), a = 13.567(1), b = 17.762(2), c = 24.924(3) Å, α = 74.41(1), β = 87.72(1), γ = 73.23(1)°, V = 5534.5(9) Å^3, Z = 2, ρ_{calcd} = 1.424 g cm^{-3}, $\mu(Cu_{K\alpha})$ = 15.8 cm^{-1}, $F(000)$ = 2458, T = 193 K; red rhombs, 0.56 × 0.35 × 0.32 mm, Siemens P4 rotating anode diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, ω scans, 16246 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms of the [2]catenane and of the hexafluorophosphate counterions, as well as the full occupancy non-hydrogen atoms of the included solvent molecules, were refined anisotropically (the others isotropically) using full-matrix least-squares based on F^2 to give R_1 = 0.096, wR_2 = 0.243 for 9537 independent observed reflections ($|F_0| > 4\sigma(|F_0|)$, $2\theta \le 120°$) and 1507 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132674. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

25·4PF$_6$ (3%): M.p. 190°C (decomp); LSIMS: *m/z*: 1865 $[M-PF_6]^+$, 1720 $[M-2PF_6]^+$, 1574 $[M-3PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.70 (d, J = 6.3 Hz, 8H), 7.70–7.30 (m, 16H), 7.05 (d, J = 8.2 Hz, 8H), 6.57 (pt, J = 7.9 Hz, 4H), 6.45–6.40 (m, 8H), 5.70 (s, 8H), 4.34 (s, 8H), 3.90–3.70 (m, 32H); ^{13}C NMR (CD_3CN, 25°C): δ = 160.9, 153.8, 145.4, 132.0, 129.9, 126.5, 126.4, 126.0, 116.5, 113.8, 105.9, 721.9, 71.6, 70.7, 68.7, 67.9, 65.2; anal. calcd for $C_{88}H_{92}N_4O_{14}P_4F_{24}$ (2009.566): C 52.60, H 4.61, N 2.79; found: C 52.41, H 4.53, N 2.77; crystal data: $[C_{88}H_{92}N_4O_{14}][PF_6]_4\cdot 4MeCN\cdot 2H_2O$, M_r = 2209.8, triclinic, space group $P\bar{1}$ (no. 2), a = 13.839(1), b = 17.918(1), c = 24.238(3) Å, α = 86.05(1), β = 79.40(1), γ = 85.66(1)°, V = 5881(1) Å^3, Z = 2, ρ_{calcd} = 1.248 g cm^{-3}, $\mu(Cu_{K\alpha})$ = 14.4 cm^{-1}, $F(000)$ = 2288, T = 183 K; red blocks, 0.63 × 0.40 × 0.33 mm, Siemens P4 rotating anode diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, ω scans, 17039 independent reflections. The structure was solved by direct methods and the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 to give R_1 = 0.176, wR_2 = 0.445 for 7330 independent observed reflections ($|F_0| > 4\sigma(|F_0|)$, $2\theta \le 120°$) and 1477 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137355. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

26·4PF$_6$ (23%): LSIMS: *m/z*: 2129 $[M-PF_6]^+$, 1984 $[M-2PF_6]^+$, 1839 $[M-3PF_6]^+$; HRLSIMS: *m/z* calcd. for $[M-2PF_6]^+$ ($C_{100}H_{106}N_4O_{20}P_2F_{12}$) = 1983.9640, *m/z* found = 1983.9280; ^{1}H NMR (CD_3CN, 75°C): δ = 8.91–8.70 (m, 8H), 8.31–8.27 (m, 4H), 7.76–7.40 (m, 16H), 7.08–7.04 (m, 10H), 6.68–6.67 (m, 2H), 6.46–6.41 (m, 2H), 5.76–5.71 (m, 10H), 4.13–3.51 (m, 64H).

27·4PF$_6$ (20%): M.p. 280°C (decomp); LSIMS: *m/z*: 2536 $[M-PF_6]^+$, 2390 $[M-2PF_6]^+$, 2246 $[M-3PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.64 (d, J = 6.5 Hz, 8H), 8.39 (d, J = 8.2 Hz, 8H), 8.05–7.90 (m, 14H), 6.75 (d, J = 6.5 Hz, 8H), 6.49 (pt, J = 7.9 Hz, 8H), 6.27 (d, J = 7.9 Hz, 8H), 6.12 (d, J = 7.9 Hz, 8H), 5.83 (s, 8H), 3.90–3.60 (m, 64H); ^{13}C NMR (CD_3CN, 25°C): δ = 154.9, 152.7, 144.1, 143.3, 140.6, 138.4, 134.0, 130.2, 127.7, 125.5, 125.0, 123.9, 119.6, 112.7, 104.8, 71.0, 70.8, 69.7, 67.7, 64.4; anal. calcd for $C_{130}H_{134}N_6O_{20}P_4F_{24}\cdot H_2O$ (2698.387): C 57.86, H 5.08, N 3.11; found: C 57.53, H 4.82, N 2.95.

28·4PF$_6$ (7%): M.p. 220°C (decomp); LSIMS: *m/z*: 2507 $[M-2PF_6]^+$, 2364 $[M-3PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.57 (d, J = 6.7 Hz, 8H), 7.67 (d, J = 8.8 Hz, 8H), 7.06 (d, J = 8.8 Hz, 8H), 6.95–6.85 (m, 6H), 6.71 (d, J = 6.9 Hz, 8H), 6.44 (pt, J = 8.0 Hz, 8H), 6.24 (d, J = 8.0 Hz, 8H), 6.15 (d, J = 8.0 Hz, 8H), 5.67 (s, 8H), 5.03 (s, 8H), 3.90–3.70 (m, 64H); ^{13}C NMR (CD_3CN, 25°C): δ = 160.4, 156.9, 153.8, 144.8, 144.0, 138.6, 132.2, 127.0, 126.5, 126.0, 124.7, 121.4, 116.7, 113.7, 105.8, 71.9, 71.6, 71.1, 70.7, 68.7, 65.3; anal. calcd for $C_{134}H_{142}N_6O_{24}P_4F_{24}$ (2800.476): C 57.47, H 5.11, N 3.00; found: C 57.77, H 4.98, N 2.91.

29·4PF$_6$ (5%): M.p. 266°C (decomposition); LSIMS: *m/z*: 2648 $[M]^+$, 2503 $[M-PF_6]^+$, 2358 $[M-2PF_6]^+$, 2213 $[M-3PF_6]^+$; ^{1}H NMR (CD_3CN, 25°C): δ = 8.53 (d, J = 6.6 Hz, 8H), 7.63 (d, J = 8.7 Hz, 8H), 7.09 (d, J = 8.7 Hz, 8H), 6.70 (d, J = 6.6 Hz, 8H), 6.44 (br s, 8H), 6.42–6.00 (m, 8H), 5.68 (s, 8H), 4.26 (s, 8H), 3.90–3.69 (m, 64H); ^{13}C NMR (CD_3CN, 25°C): δ = 161.2, 153.8, 144.8, 132.2, 127.1, 126.5, 126.0, 124.8, 116.8, 113.7, 105.8, 72.0, 71.7, 70.8, 68.7, 68.2, 65.4; anal. calcd for $C_{124}H_{136}N_4O_{24}P_4F_{24}$ (2710.300): C 56.28, H 5.18, N 2.12; found: C 56.40, H 4.31, N 1.74; crystal data: $[C_{124}H_{136}N_4O_{24}][PF_6]_4\cdot 2.5MeCN\cdot 2.5H_2O$, M_r = 2793.9, triclinic, space group $P\bar{1}$ (no. 2), a = 14.692(3), b = 23.769(8), c = 26.634(6) Å, α = 63.83(2), β = 81.76(2), γ = 79.20(3)°, V = 8180(4) Å^3, Z = 2 (there are two crystallographically independent C_i symmetric molecules in the asymmetric unit), ρ_{calcd} = 1.134 g cm^{-3}, $\mu(Cu_{K\alpha})$ = 11.8 cm^{-1}, $F(000)$ = 2912, T = 183 K; red rhombs, 0.90 × 0.87 × 0.17 mm, Siemens P4 rotating anode diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, ω scans, 16470 independent reflections. The structure was solved by direct methods and, on account of a shortage of observed data, only the hexafluorophosphate counterions and the heteroatoms of the [3]catenane were refined anisotropically (the others isotropically) using full-matrix least-squares based on

F^2 to give $R_1 = 0.288$, $wR_2 = 0.636$ for 4935 independent observed reflections ($|F_0| > 4\sigma(|F_0|)$, 2θ 110°) and 870 parameters. The very high value of R_1 is a result of a combination of very weak data from a partially crazed crystal (less than 30% observed), the enforced isotropic refinement of all but the heteroatoms of the [3]catenane (as a consequence of the severe shortage of observed data), the significant disorder associated with the hexafluorophosphate counterions and to a lesser with the included solvent molecules (discrete alternate orientations of these units could not be resolved) and the generally high thermal motion present in the macrocyclic polyether components. The structure is, however, definitive. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137356. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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$$k_c = \frac{\pi \Delta \nu}{\sqrt{2}} \quad (1)$$

$$\Delta G_c^{\neq} = RT_c \ln \frac{kT_c}{hk_c} \quad (2)$$

respectively. $\Delta\nu$ is the limiting frequency separation and R, k and h are the gas, Boltzmann, and Planck constants, respectively. For Equations (1) and (2), see: I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, **1971**, *4*, 71 – 235.

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Equation (3), see: K. A. Connors, *Binding Constants*, Wiley, New York, **1987**.

$$\Delta\delta_o = \frac{\Delta_m + 4cK_a\Delta\delta_m - \sqrt{\Delta\delta_m^2 + 8cK_a\Delta\delta_m^2}}{8cK_a} \quad (3)$$

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