Bis[2]catenanes and a Bis[2]rotaxane—Model Compounds for Polymers with Mechanically Interlocked Components**

Peter R. Ashton, Jürgen Huff, Stephan Menzer, Ian W. Parsons, Jon A. Preece, J. Fraser Stoddart,* Malcolm S. Tolley, Andrew J. P. White, and David J. Williams

Abstract: The self-assembly of three bis[2]catenanes and a bis[2]rotaxane, by two complementary strategies, is reported. A synthetic route to derivatives of bis-*para*-phenylene[34]crown-10 (BPP34C10) and 1,5-naphtho-*para*-phenylene[36]-crown-10 (1/5NPP36C10) containing a fused five-membered ring with a secondary amine function is described. These intermediate *N*-allylimido macrocyclic polyethers undergo template-directed reactions with 1,1′-[1,4-phenylenebis-(methylene)]bis-4,4′-bipyridinium bis-(hexafluorophosphate) and 1,4-bis(bromomethyl)benzene to produce [2]catenanes containing an *N*-allyl functionality. The *N*-allylimido macrocyclic polyethers have also been reduced and deprotected to afford macrocycles possessing a free NH group, which are then linked through a 4,4′-biphenyldicarbonyl spacer to produce bis(crown ether)s, in which each crown ether moiety has two recognition sites. These ditopic BPP34C10 and 1/5NPP36C10 derivatives are capable of sustaining self-assembly reactions at both recognition sites to yield bis[2]catenanes. The self-assembly of a complementary bis[2]catenane, in which two tetracationic cyclophanes are linked together with a flexible hexyl chain, has also been achieved by treating 1,1′-[1,4-phenylenebis(methylene)]bis-4,4′-bipyridinium bis-(hexafluorophosphate) with a compound containing two linked 1,4-bis(bromomethyl)benzene units in the presence of BPP34C10. Replacing BPP34C10 with a dumbbell-shaped compound containing a linear polyether unit intercepted by a naphthalene residue and terminated by two bulky adamantoyl groups has led to the self-assembly of a bis[2]rotaxane. The X-ray crystal structures of one of the catenanes and its associated crown ether component are reported, together with solution state dynamic ^{1}H NMR spectroscopic studies, showing that there is substantial degree of order characterizing the molecular structure of the catenanes.

Keywords
catenanes · polycatenanes · polyrotaxanes · rotaxanes · self-assembly

Introduction

The development of methods for the efficient synthesis of catenanes and rotaxanes[1] offers exciting prospects in the field of molecular electronics.[2] Nanometer-scale architectures and information storage devices,[3] based on molecules containing noncovalently bound, mechanically interlocked components, are amongst the most challenging targets that confront supramolecular chemists. Furthermore, polymers containing mechanically interlocked components, for example polycatenanes[4] and polyrotaxanes,[5, 6] are expected to exhibit interesting physical properties,[5] in addition to offering possibilities for the introduction of an even higher level of sophistication into nanoscale molecular structures. The realization of large molecular arrays, based upon mechanically interlocked components, depends upon the ability to design and synthesize starting materials for self-assembly reactions which will lead to the formation of higher [*n*]catenanes and/or [*n*]rotaxanes. The improvements already achieved in the self-assembly of catenanes, based on π-electron-rich crown ethers and π-electron-deficient tetracationic cyclophanes, have allowed the progression to take place from [2]catenanes[7] and [3]catenanes,[8] via [4]catenanes,[9] to [5]catenanes[9]—the most prominent example is the recently described[9b] two-step self-assembly of olympiadane. In recent years, systems based on π-electron-rich linear threads have also made [2]rotaxanes accessible[10] through self-assembly processes.

Figure 1 illustrates in cartoon form some of the currently unknown polymeric structures (**I**, **II**, and **III**), which can be disconnected to the low-molecular weight model systems **IV**–**VIII**. The research described in this paper, namely, the preparation and properties of **VI**, **VII**, and **VIII**, represents an early contribution towards the synthesis of such polymeric structures. In principle, the π-electron-rich crown ether components can be interlocked by tetracationic cyclophanes with an extended cavity (**V**)[8] or by a building block based on a covalently linked pair (**VI**) of π-electron-deficient cyclophanes.[11] In

[*] Prof. J. F. Stoddart, P. R. Ashton, Dr. J. Huff, Dr. I. W. Parsons, Dr. J. A. Preece, M. S. Tolley
School of Chemistry, University of Birmingham
Edgbaston, Birmingham B15 2TT (UK)
Telefax: Int. code + (121) 414-3531
Dr. D. J. Williams, Dr. S. Menzer, Dr. A. J. P. White
Department of Chemistry, Imperial College
South Kensington, London SW7 2AY (UK)
Telefax: Int. code + (171) 594-5804

[**] "Molecular Meccano", Part 5: for Part 4, see P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, S. Menzer, L. Pérez-Garcia, L. Prodi, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 11171–11197.

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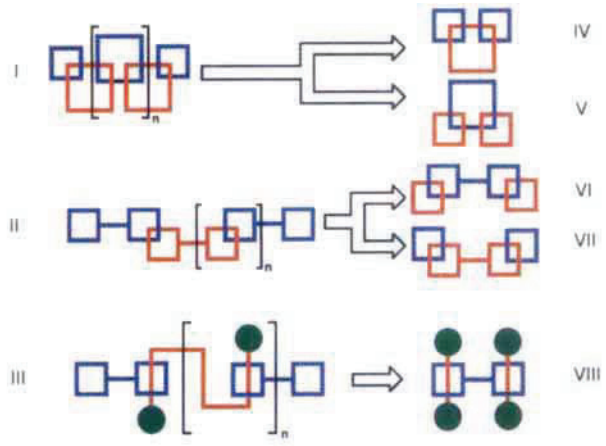


Fig. 1. Cartoon representations of some polymers containing mechanically interlocked components and their disconnections to low molecular weight model compounds. The blue forms represent components containing π-electron-deficient tetracationic cyclophanes, and the red forms represent components containing π-electron-rich crown ethers.

a previous communication,[12] we reported that π-electron-deficient tetracationic cyclophanes can be interlocked by crown ethers (**IV**) with larger rings and more binding sites than in the parent bis-*para*-phenylene[34]crown-10. An alternative way of creating a π-electron-rich host with more than one binding site for π-electron-deficient cyclophanes is to covalently link two macrocycles (**VII**), such as bis-*para*-phenylene-[34]crown-10. The latter approach is complementary in an electronic sense to the use of the covalently linked π-electron-deficient cyclophanes (**VI**). Together, model compounds **VI** and **VII** represent a significant step towards the self-assembly of mechanically interlocked polymers, since they establish the efficacy of the general chemical pathways used to assemble the corresponding polymers. They are also useful as representative model compounds to study the thermodynamics and kinetics of the polymerization steps, and of the various dynamic processes associated with these interlocked multicomponent molecules.

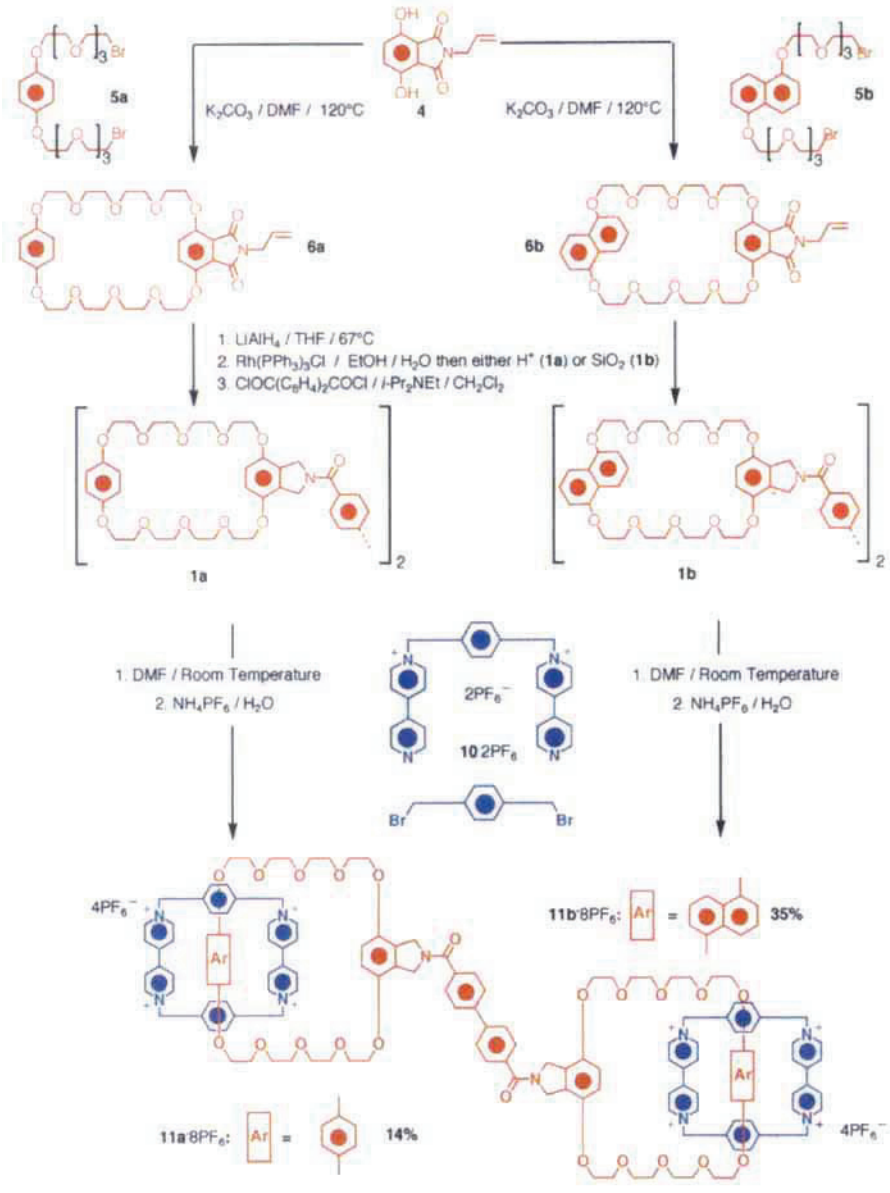
The cartoons **III** and **VIII** show how macrocycles can be linked by dumbbell-shaped components. Possible synthetic pathways to these compounds, which have been shown to be feasible in other cases,[13] are the stoppering at both ends of precomplexed threads[13a] and the slippage of suitably stoppered threads into rings.[13b–d] These methods have not as yet been exploited in the self-assembly of polymers containing repeating units of linked [3]rotaxanes.

This paper describes the synthesis and properties of three new bis[2]catenanes of types **VI** and **VII**, all of which contain [2]catenane links that could be inserted into polymer backbones. Furthermore, we report the synthesis of a bis[2]rotaxane of type **VIII**. These new mechanically interlocked model compounds, which belong to polymer types **II** and **III**, have been characterized by (dynamic) NMR spectroscopy and mass spectrometry. Two of them have been the subject of a preliminary communication.[11]

Results and Discussion

Synthesis: The target compounds, chosen as the first ditopic biscrown hosts, and the synthetic routes employed to prepare them, are depicted in Scheme 1 (the self-assembly steps shown in Scheme 1 will be discussed later).

The binding sites of the host compounds **1a** and **1b** are linked through a rigid 4,4′-dicarbonylbiphenyl spacer unit, which is connected to the two crown ether macrocycles through an isoindoline unit as one of the two aromatic building blocks. The dimerization of the crown ethers could thus be achieved, whilst



Scheme 1. The synthesis of the ditopic crown ethers **1a** and **1b** and the self-assembly of the bis[2]catenanes **11a**·8 PF_6 and **11b**·8 PF_6.

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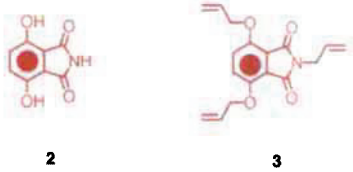
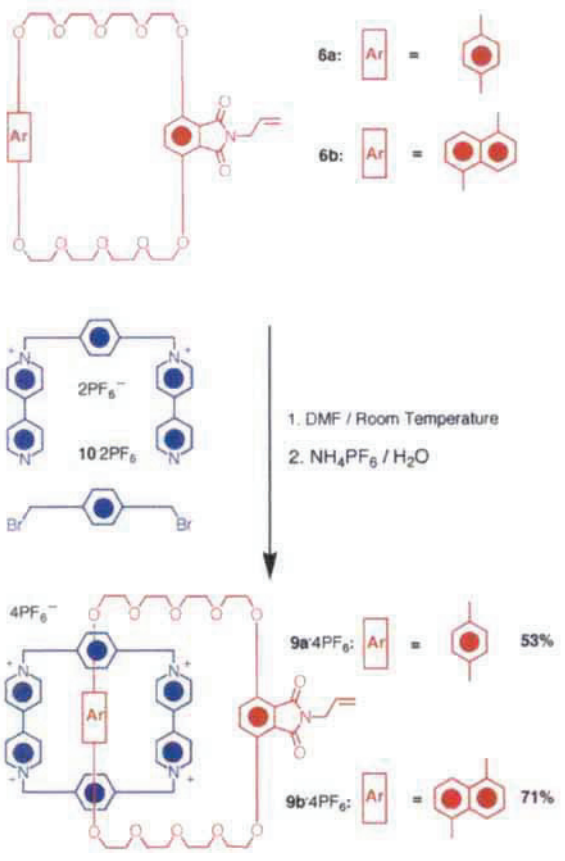
avoiding 1) a decrease in the electron density of the aromatic π donors in the target macrocyclic receptors and 2) the introduction of additional flexibility into the ditopic host molecules. It has been observed earlier[14] that π-electron-rich crown ethers containing a 1,5-dioxynaphthalene residue are more efficient in self-assembly reactions than their 1,4-dioxybenzene counterparts. Therefore, these π-electron-rich moieties were each incorporated into ditopic receptor compounds **1b** and **1a**, respectively. For the functionalized aromatic component of the receptors, *N*-allyl-1,4-dihydroxyphthalimide (**4**) was chosen as a suitable precursor, and its synthesis was accomplished by using a variation of a known procedure[15] to obtain 1,4-dihydroxyphthalimide (**2**) from 2,3-dicyanohydroquinone in a yield of 46%. This compound was then converted into 1,4-diallyloxy-*N*-allylphthalimide (**3**) (99%). Deprotection of **3** with BBr_3 afforded the *N*-allyl derivative **4** in quantitative yield.



2 **3**

The macrocyclizations (Scheme 1) leading to crown ethers **6a** (yield 40%) and **6b** (yield 25%) were performed in DMF at 120 °C with K_2CO_3 as the base. In the case of **6a**, employing Cs_2CO_3 as the base and potential template decreased the yield of the crown ether to 18%. Dibromides **5a** and **5b** were used in the base-promoted macrocyclizations, since dibromides are reported to be superior to bistosylates in macrocyclizations.[16] Indeed, the bistosylate corresponding to **5a** (base: Cs_2CO_3) gave the macrocycle **6a** in only 15% yield. The dibromides **5a** and **5b** were prepared in good overall yields (**5a**: 63%, **5b**: 59%) by alkylating the appropriate aromatic dihydroxy compounds with tetraethylene glycol monotosylate with LiBr as a catalyst, followed by tosylation of the resulting diols and subsequent substitution of the two tosyl groups by bromide ions. Starting from the *N*-allylimidocrown ethers **6a** and **6b**, the ditopic macrocycles **1a** and **1b** were prepared by 1) reduction of **6a** and **6b** with $LiAlH_4$, 2) deallylation with $Rh(PPh_3)_3Cl$, and 3) *N*-acylation with 4,4′-biphenyl dicarboxylic acid dichloride in overall yields (3 steps) of 11% and 6%, respectively. The *N*-allylamino-substituted crown ethers, resulting from the reduction of *N*-allylimido precursors **6a** and **6b**, and the deallylated secondary aminocrowns turned out to be unstable on exposure to air, presumably as a result of their rapid oxidation.[17] For this reason, they were employed in the final reactions without extensive purification to limit loss of products.

The ability of the *N*-allylimidocrown ethers **6a** and **6b** to take part in template-directed reactions with **10**·$2PF_6$ and 1,4-bis(bromomethyl)benzene was examined (Scheme 2), because the products **9a**·$4PF_6$ and **9b**·$4PF_6$ are examples of [2]catenanes containing a reactive allyl residue, which can be further elaborated. It was also of interest to establish whether crown ethers such as **6a** and **6b**, containing aryl unit with reduced π-electron density (i.e., the *N*-allylimido aryl moiety), would fail to act as efficient templates in self-assembly reactions or whether the presence of only one π-electron-rich aryl residue (1,4-dioxybenzene or 1,5-dioxynaphthalene) would be sufficient to template the formation of [2]catenanes. The question can be answered unambiguously: reaction of **10**·$2PF_6$ and 1,4-bis(bromomethyl)benzene in the presence of crown ether **6a** yielded the [2]catenane **9a**·$4PF_6$ in a 53% yield, while the corresponding reaction in the presence of **6b**, which contains a 1,5-dioxynaphthalene unit, yielded the [2]catenane **9b**·$4PF_6$ in 71% yield. Furthermore, the crown ether **1c** (prepared from **6b** by the reduction/deallylation/*N*-acylation route shown in Scheme 1, except that benzoyl chloride was employed in the *N*-acylation step), which contains the more π-electron-rich isoindoline functionality, undergoes catenation with even greater efficiency, affording the [2]catenane **11c**·$4PF_6$ in 88% yield (Scheme 3).

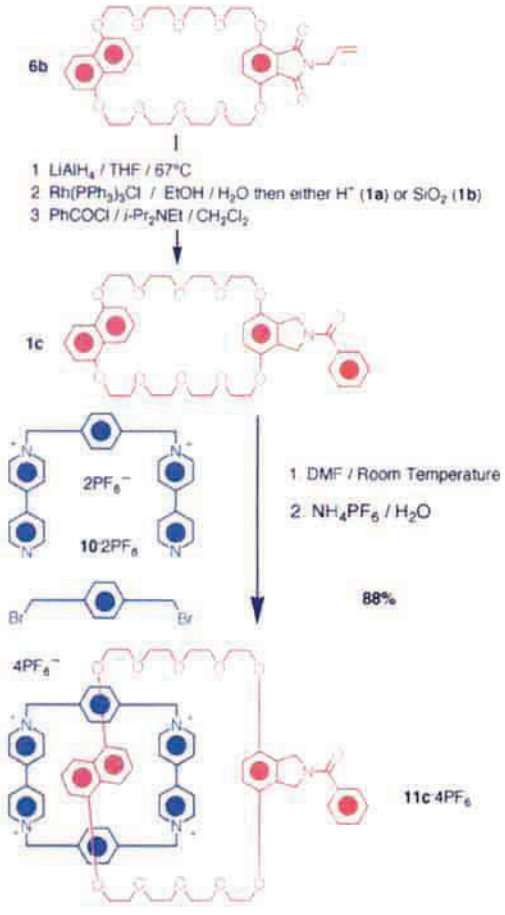


Scheme 2. The self-assembly of the [2]catenanes **9a**·$4PF_6$ and **9b**·$4PF_6$.

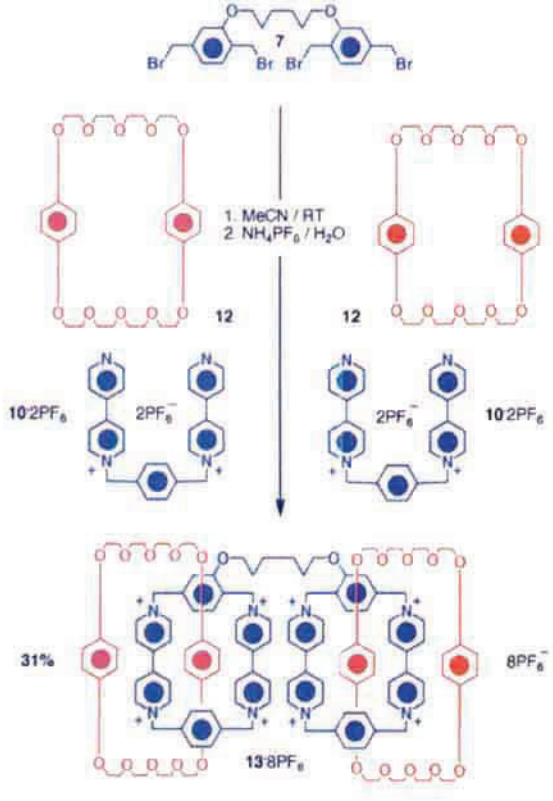
The facile self-assembly of these [2]catenanes indicates that the decrease in the π-electron density in one of the aromatic residues of **6a** or **6b** does not inhibit their properties as templates. This observation is important in relation to the future application of these crown ether components in synthesis and to post-catenation reactions (e.g., polymerizations) utilizing the *N*-allyl residue as a site for further elaboration.

With bis(crown ether)s **1a** and **1b**, we found that catenations occur (Scheme 1) at both recognition sites simply by stirring at room temperature and ambient pressure with **10**·$2PF_6$ (1.7 mol equiv) and *para*-xylylene dibromide (1.2 mol equiv) in DMF. The bis[2]catenane **11a**·$8PF_6$, containing a *para*-phenylene moiety, self-assembles in a yield of 14%. When the 1,4-dioxybenzene residue was replaced with a 1,5-dioxynaphthalene moiety (**1a** vs. **1b**), the yield of the bis[2]catenane (**11b**·$8PF_6$) rose to 35%. This increase in yield reflects the greater π-electron donating ability of the dioxynaphthalene moiety compared to the hydroquinone unit and demonstrates that these building blocks can be employed in a predictable manner in the self-assembly of bis[2]catenanes. The fact that no monocatenated products were isolated in either case is an interesting and important observation. It appears that the intermediate monocatenated products are not present in significant concentrations in the reaction mixtures during the molecular self-assembly processes.

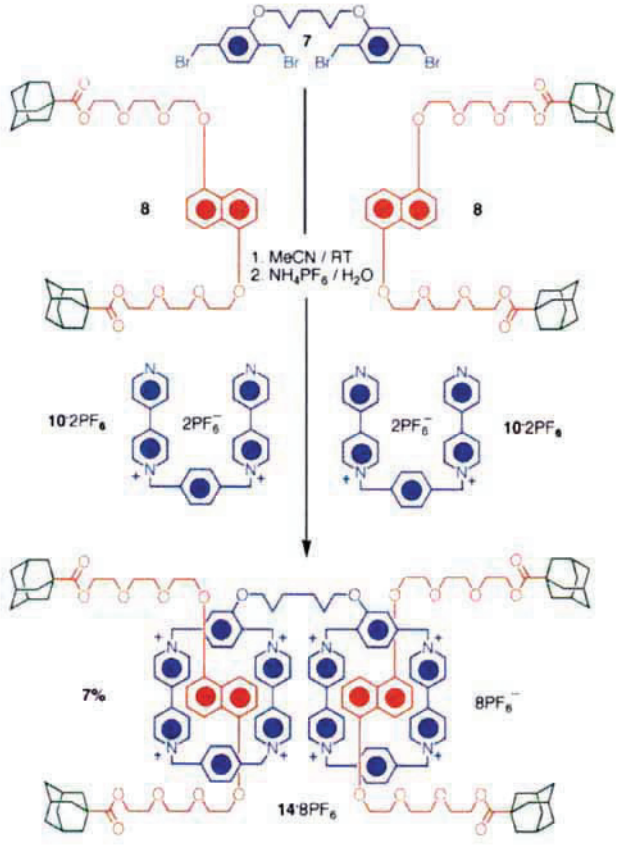
The routes to the complementary bis[2]catenane (Scheme 4) and bis[2]rotaxane (Scheme 5) were equally productive. 1,6-Bis(2,5-dimethylphenoxy)hexane, obtained in 74% yield from



Scheme 3. The self-assembly of the [2]catenane **11c**·4PF$_6$.



Scheme 4. The self-assembly of the bis[2]catenane **13**·8PF$_6$.



Scheme 5. The self-assembly of the bis[2]rotaxane **14**·8PF$_6$.

the reaction of 2,5-dimethylphenol (2 mol equiv) with 1,6-dibromohexane in MeCN using K_2CO_3 as the base, was subjected to radical bromination in CCl_4 with *N*-bromosuccinimide in the presence of AIBN as the initiator. After removal of the succinimide by filtration and precipitation by addition of hexane, the tetrabromide **7** was isolated in 36%. Reaction of **7** (1.2 mol equiv) with **10**·2PF$_6$ (2 mol equiv) in MeCN for 14 days at room temperature in the presence of crown ether **12** (6 mol equiv)[18] afforded the bis[2]catenane **13**·8PF$_6$ in 31% yield (Scheme 4).

1,5-Bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}naphthalene was esterified (CH_2Cl_2/C_5H_5N) with adamantoyl chloride (2.2 mol equiv) to afford the dumbbell-shaped diester **8** in 65% yield (Scheme 5). Reaction of **7** (1.2 mol equiv) with **10**·2PF$_6$ (2 mol equiv) in MeCN for 14 days at room temperature in the presence of **8** (6 mol equiv) afforded the bis[2]rotaxane **14**·8PF$_6$ in 7% yield. Similarly, reaction of **7** (1.2 mol equiv) with **10**·2PF$_6$ (2 mol equiv) in MeCN for 14 days at room temperature in the presence of **16** (6 mol equiv) afforded the bis(tetracationic cyclophane) **15**·8PF$_6$ in 22% yield (Scheme 6), after continuous extraction of the template from an aqueous solution of the bispseudorotaxane with $CHCl_3$.

X-Ray Crystallography: The X-ray structural analysis of the crown ether **6b** shows (Fig. 2) that the macrocycle has a self-filling folded geometry with the planes of the 1,5-dioxynaphthalene and the 1,4-dioxyphthalimido units oriented essentially orthogonal with respect to one another (82° between their mean planes). The plane of the *N*-allyl group is inclined by 84° with respect to the phthalimido ring plane. As expected, the coplanarity of the *O*-methylene groups attached to the naphthalene ring is retained, though the angles at both C(14) and C(23) show

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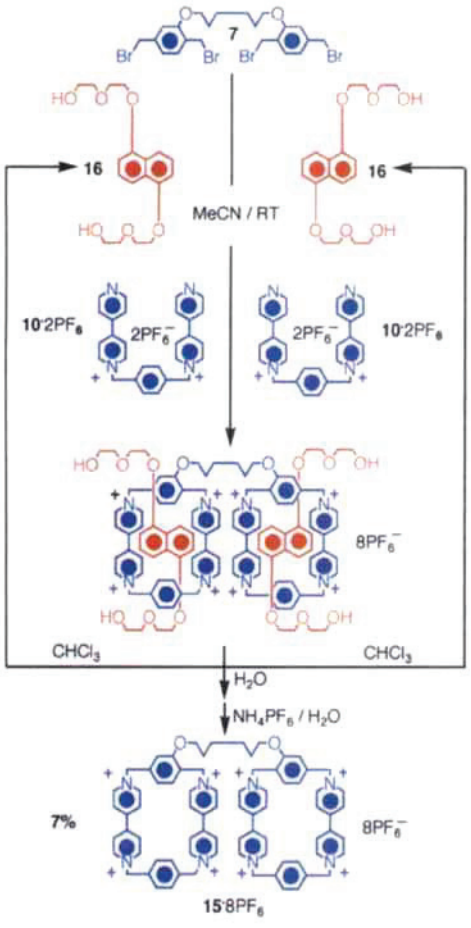

Scheme 6. The self-assembly of the bistetracationic cyclophane **15**·8 PF_6.

marked departures from the normal trigonal geometries. In both instances, planarity is maintained, but the "exterior" angles O(13)–C(14)–C(15) and C(22)–C(23)–O(24) are significantly enlarged by approximately 6° from 120°. Although one of the *O*-methylene groups attached to the phthalimido unit is coplanar with the aromatic ring plane, the other [O(1)–C(2)] is rotated by 59° out of the plane. The orthogonal relationship of the two aromatic units is accompanied by a T-type[19] edge-to-face interaction involving the C(15)–C(16) edge of the naphthalene ring and the six-membered ring of the phthalimido unit. The ring centroid/ring centroid distance is 5.0 Å, and the hydrogen atom attached to C(15) is 3.0 Å away from the center of the phthalimido six-membered ring—this H ··· ring centroid vector is inclined by 85° relative to the phthalimido ring plane.

There are two notable intermolecular packing interactions (Fig. 3). Centrosymmetrically related pairs of molecules (Fig. 3 top) are oriented with the phthalimido rings parallel and

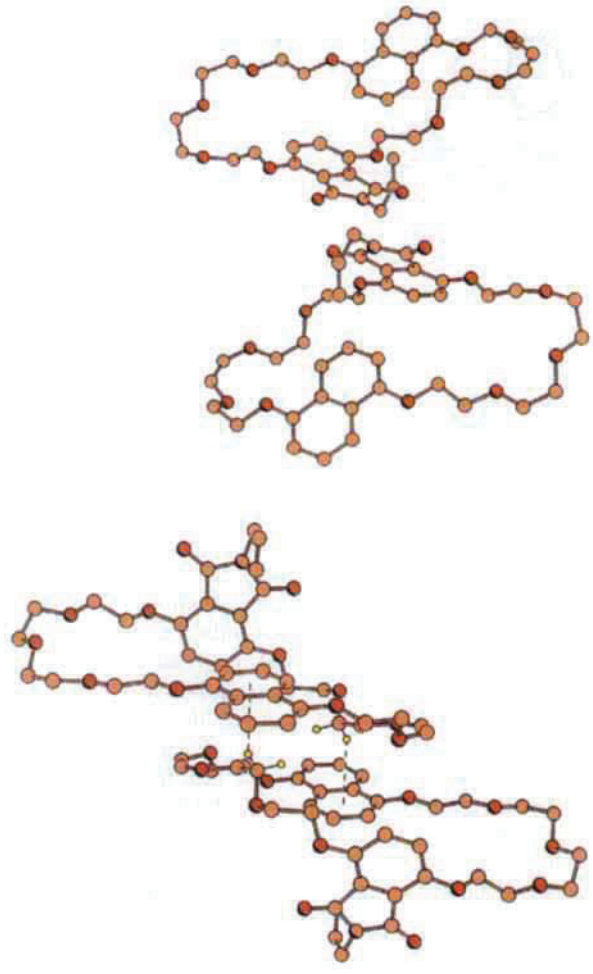

Fig. 3. The solid-state structure of the crown ether **6b** illustrating the "dimeric" nature of pairs of the molecules as a result of the overlapping of the phthalimido units (top), and the C–H ··· π intermolecular interactions between the "dimeric pairs" (bottom).

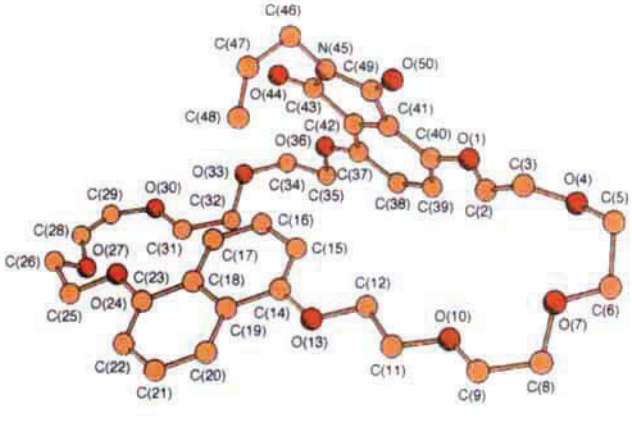

Fig. 2. A ball-and-stick representation of the X-ray crystal structure of the crown ether **6b**.

partially overlapping. The mean interplanar separation is 3.25 Å and the shortest intermolecular atom–atom contact [between C(43) and its symmetry related counterpart] is 3.22 Å. The other principal intermolecular interaction (Fig. 3, bottom) occurs between molecules arranged about a different crystallographic symmetry center and involves a pair of C–H ··· π hydrogen bonds between one of the methylene hydrogen atoms attached to C(32) in one molecule and the C(14)–C(19) portion of the naphthalene ring in another and vice versa. The H ··· ring centroid distances are 2.68 Å, and the H ··· ring centroid vector is inclined by 82° with respect to the naphthalene ring plane.

The [2]catenane **9b**·4 PF_6 crystallizes with seven included molecules of acetonitrile and one water molecule, which is disordered between three different sites in the unit cell. The X-ray structural analysis reveals (Fig. 4) the 1,5-naphtho unit of the macrocyclic polyether to be positioned within the center of the tetracationic cyclophane, which adopts a conventional barrel-

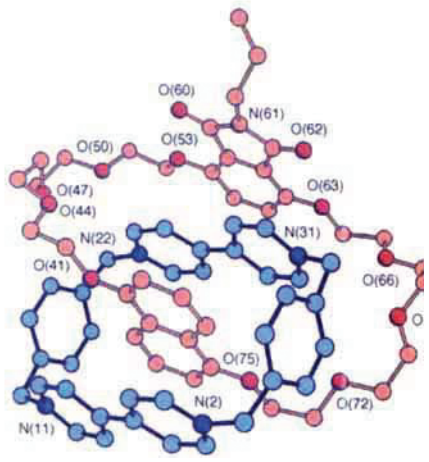

Fig. 4. A ball-and-stick representation of the X-ray crystal structure of the [2]catenane **9b**·4PF_6.

like geometry with almost symmetric bowing and twisting distortions. The bipyridinium units have torsional twists of 5.0° (outside) and 6.3° (inside) about the C–C bonds linking the two pyridinium rings in each case. Both units are folded with angles subtending their N–CH_2 bonds of 19.5 and 19.7° (outside and inside), respectively. The *para*-xylyl residues also exhibit similar folding with angles subtended by the C(Ar)–CH_2 bonds of 16.4° in both instances. The overall dimensions of the cyclophane are 10.49 Å (*para*-xylyl/*para*-xylyl centroid/centroid separation) and 6.66 Å between the centers of the C–C bonds linking the pairs of pyridinium units. The 1,5-naphtho ring of the macrocyclic polyether is sandwiched almost centrally between the two bipyridinium units of the cyclophane at distances of 3.34 Å (outside) and 3.32 Å (inside), respectively. The O–Np–O vector [O(41)···O(75)] is inclined by 53° to the plane of the cyclophane (as defined by the best plane through the four corner methylene carbon atoms), and both *peri* protons on the naphthalene rings are directed toward the centers of the *para*-xylyl rings of the cyclophane at distances of 2.57 and 2.59 Å between the hydrogen atoms and the respective *para*-xylyl ring centroids—the associated C–H···ring centroid angles are both 147°. These C–H···π interactions are significantly stronger than those we have observed[20] previously in related catenanes where these contacts are usually of 2.8–2.9 Å. The polyether linkages between the naphthalene ring and the phthalimido unit are weakly bound to the cyclophane through a series of C–H···O hydrogen bonds involving α-bipyridinium, *para*-xylyl, and methylene protons. These interactions have C···O distances in the range of 3.20 to 3.34 Å, H···O distances between 2.35 and 2.51 Å, and C–H···O angles in the range 138 to 151°. The phthalimido ring is oriented approximately parallel to its adjacent inside bipyridinium unit at an interplanar distance of 3.33 Å. The catenane molecules are arranged within the crystal as centrosymmetrically related "dimer pairs" (Fig. 5, top) with the phthalimido ring in one molecule aligned parallel and overlapping (mean interplanar separation 3.38 Å) with that in the next molecule (Fig. 5, bottom). The "dimer pairs" are arranged centrosymmetrically with respect to each other to form stepped stacks (Fig. 5, right) with the outside bipyridinium units arranged proximal and parallel but offset in a direction normal to the mean plane of the cyclophane by approximately 3.8 Å.

Mass Spectrometry: This technique has proven to be a valuable tool for the characterization of catenanes. Schill et al.[21] were among the first researchers to use this method to characterize

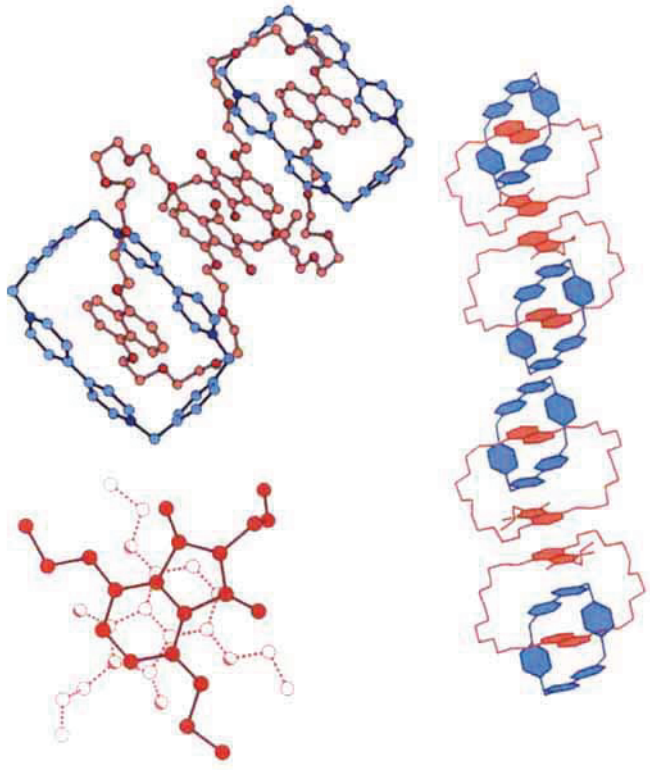

Fig. 5. The solid-state structure of the [2]catenane **9b**·4PF_6 illustrating the "dimeric" nature of pairs of molecules (top), the alignment and overlapping of the phthalimido units (bottom), and the "dimer pairs" forming stepped stacks (right).

catenanes[21a,b] and rotaxanes[21c] and to emphasize its importance in elucidating the structures of these interlocked molecules.[21d] In order to reduce fragmentation and obtain peaks for the molecular ions of the mechanically linked molecules, modern soft ionization methods, such as fast atom bombardment (FAB), liquid secondary ion (LSI), and electrospray (ES) mass spectrometry are particularly useful. Figure 6 shows—as an example—the fragmentation pattern observed in the FAB mass spectrum of bis[2]catenane **11a**·8PF_6. The peak at $m/z = 3418$ can be assigned to the molecular ion of the bis[2]catenane after the loss of one PF_6^- counterion. The signals at $m/z = 3272$, 3128, and 2982 are caused by the loss of two, three, and four PF_6^- counterions, respectively. The group of signals at $m/z = 2317$, 2171, and 2043 arise from the loss of one of the two tetracationic cyclophanes and one, two, and three PF_6^- counterions, respectively. The FAB mass spectrum of the analogous bis[2]catenane

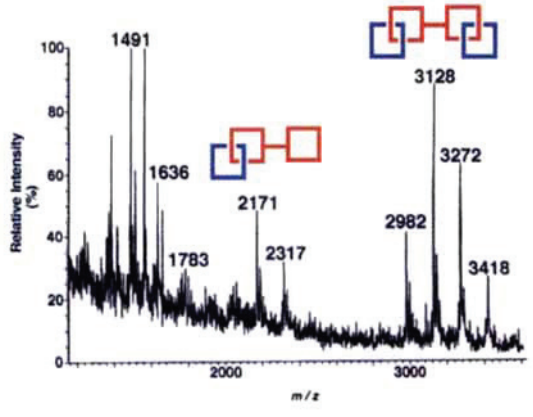

Fig. 6. Mass spectrum of the bis[2]catenane **11b**·4PF_6.

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11b·8PF_6 exhibits peaks corresponding to $[M - PF_6]^+$, $[M - 2PF_6]^+$, and $[M-3PF_6]^+$. In this case, a second group of signals caused by the loss of one tetracationic cyclophane from the bis[2]catenane are hardly distinguishable from the noise. The electronically complementary bis[2]catenane **13**·8PF_6 gives a group of peaks in the FAB mass spectrum at $m/z = 3245$ $[M - PF_6]^+$, 3097 $[M - 2PF_6]^+$, and 2953 $[M - 3PF_6]^+$. The bis[2]rotaxane **14**·8PF_6 exhibits a group of peaks for the molecular ions at $m/z = 3665$ $[M - PF_6]^+$, 3522 $[M - 2PF_6]^+$, and 3377 $[M - 3PF_6]^+$. The loss of one of the π-electron-rich threads accounts for peaks at $m/z = 2774$ $(-PF_6)$ and 2629 $(-2PF_6)$. The peak expected for the linked tetracationic cyclophanes, as a result of the loss of both threads, appears at $m/z = 2024$ $(-2PF_6)$.

These results show that the FAB mass spectrometric methods are suitable for the analysis and identification of even higher catenanes and rotaxanes—this development augurs well for the identification of polycatenanes and polyrotaxanes by means of these modern soft ionization methods.

^{1}H NMR Spectroscopy: The ^{1}H NMR spectra of the [2]catenanes reveal a lot about the structural characteristics and dynamic behavior of these compounds. The chemical shift differences observed in the ^{1}H NMR spectra of the free macrocycles (**1a**/**1b**/**1c**/**6a**/**6b**) compared with those of the catenated compounds **9a**·4PF_6/**9b**·4PF_6/**11a**·8PF_6/**11b**·8PF_6/**11c**·4PF_6) confirm that, in all cases, the phthalimido unit or the isoindoline is positioned alongside the tetracationic cyclophane. This arrangement would be expected for a residue having reduced π-electron density (phthalimido) and being sterically demanding (phthalimido and isoindoline). The hydroquinone unit (**9a**·4PF_6/**11a**·8PF_6) and the 1,5-dioxynaphthalene moiety (**9b**·4PF_6/**11b**·8PF_6/**11c**·4PF_6) reside inside the π-electron-deficient cyclophane (Table 1). An analysis of the spectroscopic data for the [2]catenanes **9b**·4PF_6 and **11c**·4PF_6, and the bis[2]catenane **11b**·8PF_6 is given in Table 1.

Dynamic ^{1}H NMR spectroscopy has been employed to investigate and determine the rates of various dynamic processes that occur in the catenanes described in this paper.[22] Some of the processes have been discussed in previous papers for other [2]catenanes.[7–9] These processes include the circumrotation of one macrocycle through the other. However, additional temperature-dependent processes are evident from variable-temperature ^{1}H NMR spectroscopy carried out on some of the new [2]catenanes and bis[2]catenanes reported in this paper. The high-temperature ^{1}H NMR spectra recorded for the bis[2]catenane **13**·8PF_6 in CD_3CN reveal high energies of activation for the circumrotations of the crown ether rings through the cavities of the tethered tetracationic cyclophanes. At room temperature, two well-separated resonances are observed at $\delta = 6.14$ and 3.31 for the hydroquinone ring protons of the crown ether component. These proton resonances can be assigned to the "inside" and "outside" hydroquinone rings, respectively, with respect to the two tethered tetracationic cyclophane components. These observations mean that the circumrotation of the crown ether rings through the tetracationic cyclophane components is slow on the ^{1}H NMR timescale at room temperature. On warming up the CD_3CN solution of the [2]catenane, the resonances for the hydroquinone ring protons coalesce; this indicates much faster rates of circumrotation of the crown ether rings. The kinetic and thermodynamic data for this process are summarized in Table 2. The main conclusion we can draw from comparing the free energies of activation is that replacing one of the *para*-phenylene rings in the tetracationic cyclophane by monosubstituted phenylene rings, as in **13**·8PF_6, has little or no influence upon the circumrotation of the crown ether ring through the tetracationic cyclophane component. The corresponding free-energy barrier for the system comprised of bis-*para*-phenylene[34]crown-10 and the tetracationic cyclophane is 15.7 kcal mol^{-1}.

Table 2. Kinetic and thermodynamic data [a] for the circumrotation of the crown ether through the cavity of the tetracationic cyclophane in the bis[2]catenane **13**·8PF_6 (T_{ex} = temperatrure of line broadening, $\Delta\nu$ = half-line width, k_{ex} = rate constant).

Probe H	T_{ex}/K	$\Delta\nu$/Hz	k_{ex}/s^{-1}	$\Delta G^{\ddagger}_{ex}$/kcal mol^{-1}
"outside" hydroquinone	352	124	276	15.5

[a] ^{1}H NMR spectra recorded at 400 MHz in CD_3CN solution.

The low-temperature ^{1}H NMR spectra (Fig. 7) recorded in CD_3COCD_3 for **9b**·4PF_6 allows us to investigate the rate of circumrotation of the tetracationic cyclophane through the cavity of the crown ether component. This circumrotation is asso-

Table 1. ^{1}H NMR chemical shift data (400 MHz) [δ ($\Delta\delta$)] [a] for the [2]catenanes **9b**·4PF_6 and **11c**·4PF_6, and the bis[2]catenane **11b**·8PF_6 in CD_3CN at ambient temperature.

Catenane	Tetracationic cyclophane [b]				Crown ether			
	Bipyridinium		Xylyl		Phthalimido/	Naphthalene		
	α-CH	β-CH	C_6H_4	NCH_2	isoindoline	H-2 H-6	H-3 H-7	H-4 H-8
9b·4PF_6	9.05 (+ 0.19) 8.68 (− 0.18)	7.20–7.29 (− 0.92)	8.19 (+ 0.67) 8.07 (+ 0.55)	5.93 (+ 0.19) 5.81 (+ 0.07)	6.68 [c] (− 0.05)	6.30 [c] (− 0.39)	6.03 [c] (−1.24)	2.49 [c] (− 5.33)
11c·4PF_6	8.96 (+ 0.10) 8.91 (+ 0.05) 8.60 (− 0.26) 8.55 (− 0.31)	7.01–7.16 (−1.08)	7.89–8.11 (+ 0.48)	5.61–6.05 (+ 0.09)	5.61–6.05 [d] (− 0.97)	5.61–6.05 [d] (− 0.88)	5.61–6.05 [d] (−1.37)	2.38–2.43 [d] (− 5.41)
11b·8PF_6	8.96 (+ 0.10) 8.93 (+ 0.07) 8.60 (− 0.26) 8.58 (−0.28)	7.08–7.14 (−1.00)	7.95–8.08 (+ 0.50)	5.64–5.87 (+ 0.02)	5.91–6.00 [e] (− 0.39)	6.22 [e] (− 0.48)	5.95 [e] (−1.28)	2.38–2.43 [e] (− 5.43)

[a] The $\Delta\delta$ values in parentheses beside or under the respective δ values relate to the changes in chemical shift exhibited by the particular probe proton upon catenane formation. Positive and negative values indicate movements of the resonances to low and high fields, respectively. [b] For the free tetracationic cyclophane (CD_3CN, 300 MHz), $\delta = 8.86$ (d, bipyridinium α-*CH*), 8.16 (d, bipyridinium β-*CH*), 7.52 (s, xylyl C_6H_4), 5.74 (s, NCH_2). [c] For the **6b** ($CDCl_3$, 300 MHz), $\delta = 6.63$ (s, phthalimido Ar-*H*), 6.75 (d, naphthalene, H-2,6), 7.27 (t, naphthalene H-3,7), 7.82, (d, naphthalene H-4,8). [d] For **1c** ($CDCl_3$, 300 MHz), $\delta = 6.30$ (s, isoindoline Ar-*H*), 6.71 (m, naphthalene, H-2,6), 7.20 (t, naphthalene H-3,7), 7.82 (d, naphthalene H-4,8). [e] For **1b** ($CDCl_3$, 300 MHz), $\delta = 6.28–6.41$ (m, isoindoline Ar-*H*), 6.63–6.76 (m, naphthalene, H-2,6), 7.14–7.31 (m, naphthalene H-3,7), 7.76–7.91 (m, naphthalene H-4,8).

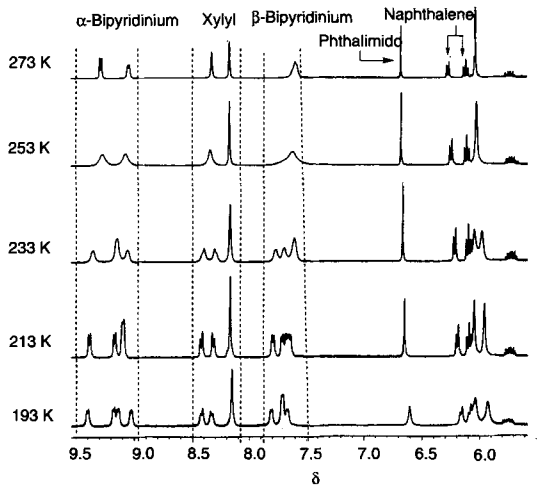

Fig. 7. ^{1}H NMR spectra of the [2]catenane **9b**·4PF$_6$ recorded at temperatures below room temperature in CD_3COCD_3.

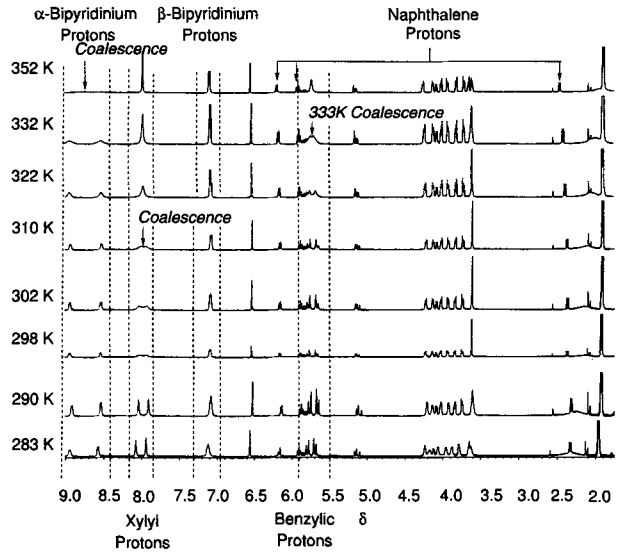

Fig. 8. ^{1}H NMR spectra of the [2]catenane **9b**·4PF$_6$ recorded in the temperature range from 283 K to 352 K in CD_3CN.

ciated with a relatively low free energy barrier, as is revealed by the temperature-dependent behavior of the signals for the α-bipyridinium ring protons and the xylyl ring protons in the tetracationic cyclophane of **9b**·4PF$_6$. For example, on cooling the CD_3COCD_3 solution down to 193 K, one of the two doublets observed at $\delta = 9.32$ for one set of α-bipyridinium protons at 273 K separates into two doublets centered at $\delta = 9.40$ and 9.18 (Fig. 7). This temperature-dependent behavior equates with the fact that, when the circumrotation of the tetracationic cyclophane through the crown ether cavity is slowed down on the ^{1}H NMR timescale, the protons on the two bipyridinium units become anisochronous, since one bipyridinium unit lies "inside" and the other "alongside" the cavity of the crown ether. Similarly, one of the two the xylyl singlet resonances, centered on $\delta = 8.38$ at 273 K, resonates as an AB system ($\delta_A = 8.42$, $\delta_B = 8.32$) when the CD_3COCD_3 solution of **9b**·4PF$_6$ is cooled down to 213 K; this indicates that the adjacent xylyl protons become anisochronous when the circumrotation of the tetracationic cyclophane through the crown ether becomes slow on the ^{1}H NMR timescale. These temperature dependencies have been employed to calculate the kinetic and thermodynamic data for this process. They are listed in Table 3.

Table 3. Kinetic and thermodynamic data [a] for the circumrotation of the tetracationic cyclophane component through the cavity of the crown ether in the [2]catenane **9b**·4PF$_6$ (T_c = coalescence temperature, $\Delta\nu$ = limiting chemical shift difference, k_c = rate constant).

Probe H	T_c/K	$\Delta\nu$/Hz	k_c/s^{-1}	ΔG_c^*/kcal mol^{-1}
bipyridinium α-CH [b]	352	124	276	11.5
xyly C_6H_4 [c]	240	41	101	11.8

[a] ^{1}H NMR spectra recorded at 400 MHz in CD_3COCD_3 solutions. [b] Exchanging set of doublets at $\delta = 9.40$ and 9.18 ($J = 6.1$ Hz). [c] Exchanging AB system at $\delta = 8.42$ and 8.31 ($J_{AB} = 8.1$ Hz)

The high-temperature ^{1}H NMR spectra (Fig. 8) of **9b**·4PF$_6$ reveal that some additional dynamic processes are occurring in this catenane. On warming up a solution of **9b**·4PF$_6$ in CD_3CN, all the indications are that the naphthalene residue is located "inside" the cavity of the tetracationic cyclophane; for example, the doublet at $\delta = 2.35$ for the H-4 and H-8 protons does not broaden at all on heating the CD_3CN solution up to 352 K. Similarly, the resonances for the H-2 and H-6, and H-3 and H-7 protons of naphthalene remain well resolved. Thus, by inspection of the variable-temperature ^{1}H NMR spectra (Fig. 7 and 8), we can draw several conclusions about the molecular structure of the [2]catenane. The introduction of the sterically demanding phthalimido aromatic unit as one of the recognition sites in the crown ether results in a large preference for the naphthalene residue to be located "inside" the tetracationic cyclophane. Indeed, the only observable translational isomer is the one in which the naphthalene residue is located "inside" the cavity of the tetracationic cyclophane. This conclusion is supported by the chemical shift data (Table 1) and by the fact that the resonances for the naphthalene protons remain sharp over a wide range of temperatures (Fig. 7 and 8). However, several other signals in the ^{1}H NMR spectrum do coalesce. The α-bipyridinium protons, which resonate as two doublets at room temperature, coalesce to one doublet at 352 K. In addition, the xylyl protons resonate as two singlets, which coalesce at 310 K, while the benzylic methylene protons resonate as an AB system at room temperature, which coalesces to a singlet at 333 K. Thus, the C_2 symmetry imposed on the [2]catenane by the naphthalene residue located "inside" the cavity of the tetracationic cyclophane (Illustration in Fig. 9) is destroyed on warming up a CD_3CN solution of **9b**·4PF$_6$.

The kinetic and thermodynamic data for these processes are shown in Table 4. It is evident that at least two dynamic processes are occurring—one with an activation barrier of 15.2 kcal mol^{-1} and the other with a free energy of activation of 16.6 kcal mol^{-1}. From a CPK space-filling molecular model of **9b**·4PF$_6$, it is clear that there are three ways of destroying the

Table 4. Kinetic and thermodynamic data [a] relating to the proposed processes 1–3 (Fig. 9) in the [2]catenane **9b**·4PF$_6$ calculated by bandshape analysis (sh) and/or coalescence methods (c) ($\Delta\nu$ = limiting chemical shift difference).

Probe H	T_{ex} or T_c/K	$\Delta\nu$/Hz	k_{ex} or k_c (sh/c)/s^{-1}	ΔG_{ex}^* or ΔG_c^* (sh/c)/kcal mol^{-1}
α-bipyridinium	352	168	374	–/16.6
NCH_2^+	333	39	116	–/16.6
xylyl	310	–/53	115/118	15.2/15.2
xylyl	303	–	72/–	15.2/–
xylyl	293	–	32/–	15.1/–

[a] ^{1}H NMR spectra recorded at 400 MHz in CD_3CN solution.

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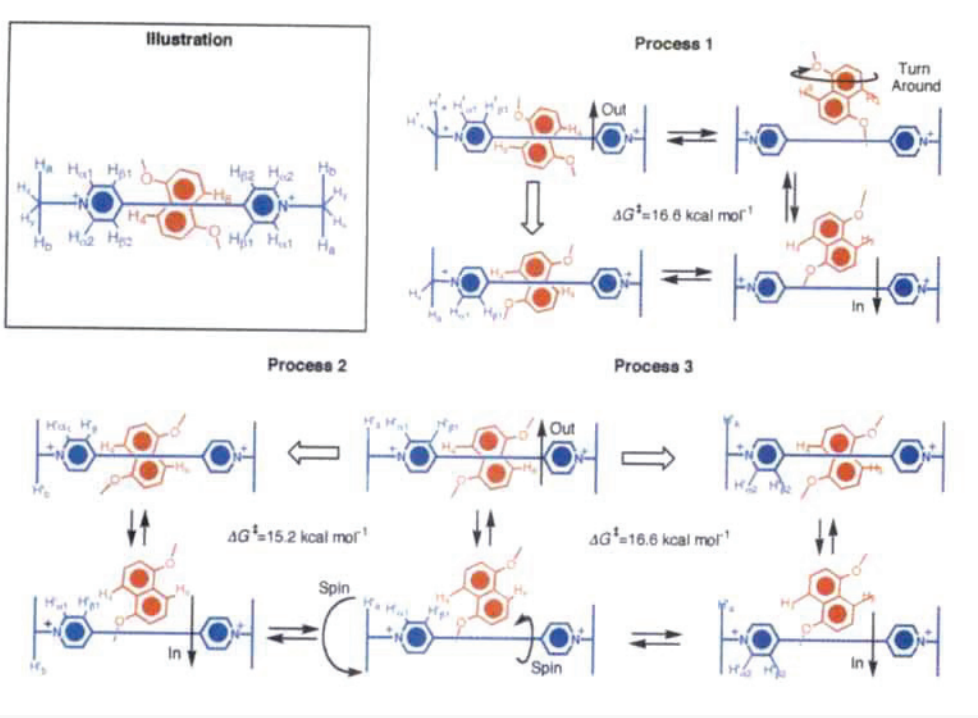

Fig. 9. The three proposed dynamic processes (1–3) that might occur in solutions of the [2]catenane **9b**·4PF_6 at and above room temperature on the ^{1}H NMR timescale: Process 1: naphthalene out/turn around/naphthalene in, Process 2: naphthalene out/xylyl spin/naphthalene in, and Process 3: naphthalene out/bipyridinium spin/naphthalene in. H_a and H_b are the *para*-phenylene protons and H_x and H_y the benzylic methylene protons on opposite sides of the *para*-xylyl units in the tetracationic cyclophane component of the [2]catenane. The alphabetical/numerical subscripts (a/b, x/y, α1/α2, β1/β2) define the magnetic environments of pairs of protons that can undergo chemical or site exchange in the molecule.

C_2 symmetry imposed by the "inside" naphthalene residue. Firstly, it can dislodge itself from the tetracationic cyclophane's cavity and turn around before reentering the cavity (Process 1 in Fig. 9). Secondly, while the naphthalene residue is dislodged from the cavity, the *para*-xylyl group can spin through 180° (Process 2 in Fig. 9). And thirdly, while the naphthalene residue is dislodged from the cavity, the bipyridinium units can also spin through 180° (Process 3 in Fig. 9). Since the use of the xylyl aromatic resonances as the probe gives the lowest value for the activation energy (Table 4), we must conclude that it is the spinning of the *para*-xylyl residues (Process 2 in Fig. 9) that is responsible for the coalescence of the xylyl aromatic resonances. Thus, Process 1 or 3 must give rise to the higher energy activation barrier. As both these processes would result in the same coalescence behavior for the α-bipyridinium and benzylic methylene proton resonances, we cannot say which is responsible for the coalescence of these signals in the high-temperature ^{1}H NMR spectrum.

Conclusions and Reflections

The present investigations demonstrate that the use of covalently linked recognition sites containing either two π-electron-deficient tetracationic cyclophanes or two π-electron-rich crown ether residues in self-assembly reactions leads to biscatenanes and bisrotaxanes—key mechanically interlocked molecules, which are valuable model compounds for the synthesis and for the characterization of polycatenanes and polyrotaxanes. Since we have been able to demonstrate that the "dimerization" of the components does not affect their abilities to undergo self-assembly processes, our approach to self-assembling polymers employing electronically complementary bifunctional monomeric building blocks receives some vindication at this early stage of research. The logical extension of this research is to employ these ditopic substrates in polymerizations. Indeed, these experiments are already being conducted. Preliminary results indicate that a low molecular weight polymer of type **II** (Fig. 1) begins to self-assemble when either **1a** or **1b**, along with **7** and two molar equivalents of **10**·2PF_6, are reacted together in DMF at room temperature.[23] However, it is unlikely that the self-assembly steps—which proceed under kinetic control in the reactions described in this paper[29]—can be induced to occur with sufficiently high efficiency to lead to high molecular weight polymers. Thus, it seems prudent at this time to consider an approach to the synthesis of polymers containing bis[2]catenane units that relies upon more traditional ways of synthesizing polymers. Figure 10 illustrates—in cartoon form—the general approach which we are proposing to adopt using suitably functionalized bis[2]catenanes as "monomers" in an appropriate block copolymerization procedure.

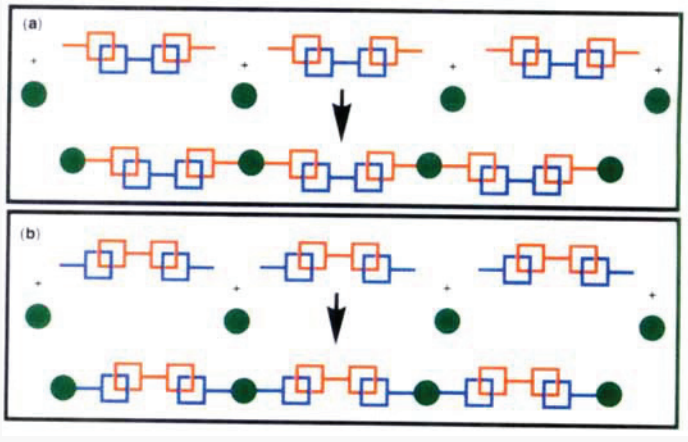

Fig. 10. Cartoon representations of how suitably functionalized bis[2]catenanes could be employed as "monomers" to form block copolymers by some well-established methodology. In a) and b) the complementary "monomers" are employed along with a suitable linking unit (represented by a green circle) to form the corresponding block copolymers. In the bis[2]catenane monomers, the blue forms represent components containing π-electron-deficient tetracationic cyclophanes, and the red forms represent components containing π-electron-rich crown ethers.

Experimental Section

Materials and Methods: Solvents were purified and dried by literature methods [24]. Reagents were employed as purchased from Aldrich. Thin layer chromatography (TLC) was carried out on aluminium sheets, precoated with silica gel 60F (Merck 5554) or aluminium oxide 60F neutral (Merck 5550). The plates were inspected by UV light prior to development with iodine vapor or by treatment with ceric ammo-

nium molybdate reagent and subsequent heating. Preparative thin layer chromatography (PTLC) was carried out using TLC plates precoated with silica gel $60F_{254}$ (Merck 5717) having a layer thickness of 2 mm. Column chromatography was performed using silica gel 60 (Merck 7734, 0.063–0.200 mm) or aluminium oxide 90 (neutral, act. II–III, Merck 1097, 0.063–0.200 mm). Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. Elemental analyses were performed either by the University of Sheffield or by the University of Birmingham Microanalytical Laboratories. Mass spectra were recorded on a Kratos Profile spectrometer (EIMS and CIMS) or on a Kratos MS80RF spectrometer, equipped with a saddle-field source (Ion Tech Limited) operating at 8 keV using a krypton primary atom beam (FABMS). High resolution mass spectra (LSIMS) were obtained from a VG Zabspec triple focusing mass spectrometer operating at a resolution of 5000 and using voltage scanning with polyethylene glycol or CsI as a reference. ^{1}H NMR Spectra were recorded on a Bruker AC 300 (300 MHz) or on a Bruker AMX 400 (400 MHz). ^{13}C NMR spectra were recorded on a Bruker AC 300 (75.5 MHz) using the JMOD pulse sequence. All chemical shifts are quoted on the δ scale with TMS or the solvent as an internal standard. Coupling constants are expressed in Hz. X-Ray crystallographic analyses were carried out as described in the appropriate compound characterisation sections. Further details of the X-ray crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB Cambridge CB2 1EZ (UK), on quoting the full journal citation.

2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethanol 1-(4-methylbenzenesulfonate) (tetraethyleneglycol monotosylate) [25]: A solution of NaOH (5.47 g, 137 mmol) in water (30 mL) was added to a mixture of tetraethyleneglycol (175.6 g, 904 mmol) and THF (25 mL). After the mixture had cooled down to 5 °C, a solution of toluene-*p*-sulfonyl chloride (16.7 g, 87.5 mmol) in THF (100 mL) was added with stirring over 1 h. After stirring at 5 °C for 2 h, the reaction mixture was poured onto ice water (500 mL). The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed twice with water (50 mL). Drying of the organic layer and evaporation of the solvent under reduced pressure afforded 27.48 g (90% yield with reference to toluene-*p*-sulfonyl chloride) of a clear oil, which was characterized as tetraethylenglycol monotosylate. The ^{1}H NMR spectrum was in accordance with that already reported in the literature [25].

4,7-Dihydroxy-1*H*-isoindole-1,3(2*H*)-dione·3 H_2O (1,4-dihydroxyphthalimide · 3 H_2O) (**2**) [15]: In a variation of the procedure described by Thiele et al. [15], 2,3-dicyanohydroquinone (20.00 g, 124.9 mmol) was suspended in a mixture of conc. sulfuric acid (75 mL, $d = 1.84\,g\,cm^{-3}$) and water (10 mL). The flask was placed in a cold water bath and then heated with stirring to 100 °C. After the starting material had completely dissolved, heating was continued for 20 min. The reaction mixture was poured into ice water (200 mL) and left at room temperature for 6 h. The precipitated solid was filtered off and washed thoroughly with cold water. Drying in vacuo for 14 h yielded 13.47 g (46%) of the desired product **2** as a yellow solid. An analytical sample of **2** was obtained by drying the material in vacuo to constant weight. ^{1}H NMR (300 MHz, CD_3SOCD_3, 25 °C): δ = 10.71 (bs, 1H; N*H*), 10.02 (bs, 2H; Ar-O*H*), 7.04 (s, 2H; Ar-*H*); ^{13}C NMR (75.5 MHz, CD_3SOCD_3, 25 °C): δ = 168.0, 147.9, 125.7, 115.3; MS (70 eV, EI): *m/z* (%): 179 (100) [M^+].

4,7-Diallyloxy-2-allyl-1*H*-isoindole-1,3(2*H*)-dione (**3**): 4,7-Dihydroxy-1*H*-isoindole-1,3(2*H*)-dione·3 H_2O (3.40 g, 14.6 mmol) was heated under reflux with K_2CO_3 (13.60 g, 98.4 mmol) in allyl bromide (40 mL) for 48 h. The excess allyl bromide was removed in vacuo, and the solid residue partitioned between Et_2O (400 mL) and water (200 mL). After separation of the layers, the aqueous layer was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to yield 4.34 g (99%) of **3** as an off-white solid. M.p. 68–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.13 (s, 2H; Ar-*H*), 5.99–6.12 (m, 2H; 2 × OCH_2CH=CH_2), 5.79–5.92 (m, 1H; NCH_2CH=CH_2), 5.46–5.50 (m, 2H; N-CH_2CH=CH_2), 5.14–5.36 (m, 4H; 2 × OCH_2CH=CH_2), 4.68–4.75 (m, 4H; 2 × OCH_2CH=CH_2), 4.21–4.62 (m, 2H; NCH_2CH=CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 165.9, 149.9, 132.4, 131.8, 122.0, 119.2, 118.2, 117.7, 70.5, 39.8; MS (70 eV, EI): *m/z* (%): 299 (79) [M^+], 41 (100) [$C_3H_5^+$]; $C_{17}H_{17}NO_4$ (299.3): calcd C 68.22, H 5.72, N 4.68; found C 68.35, H 5.50, N 4.84.

4,7-Dihydroxy-2-allyl-1*H*-isoindole-1,3(2*H*)-dione (1,4-dihydroxy-*N*-allylphthalimide) (**4**): Phthalimide **3** (4.33 g, 14.5 mmol) was dissolved in CH_2Cl_2 (10 mL). The solution was cooled in an ice bath and a 1 M solution of BBr_3 in CH_2Cl_2 (35 mL, 35 mmol of BBr_3) was added rapidly and dropwise with vigorous stirring. A yellow precipitate formed and the reaction mixture was stirred at room temperature for 9 h. Subsequent hydrolysis was accomplished by careful addition of MeOH (10 mL). The resulting solution was concentrated in vacuo, redissolved in MeOH (2 × 50 mL) and concentrated again. The residue was partitioned between EtOAc (400 mL) and water (100 mL). After separation of the layers, the aqueous one was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to obtain 3.17 g (100%) of the desired product **4** as a greenish-yellow solid. M.p. 189–191 °C (subl.). ^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C): δ = 8.54 (s, 2H; Ar-O*H*), 7.15 (s, 2H; Ar-*H*), 5.83–5.96 (m, 1H; N-CH_2CH=CH_2), 5.10–5.22 (m, 2H; N-CH_2CH=CH_2), 4.15–4.20 (dt, ^3J = 5.0, ^5J = 1.5 Hz, 2H; N-CH_2CH=CH_2); ^{13}C NMR (75.5 MHz, CD_3COCD_3, 25 °C): δ = 168.2, 149.1, 133.3, 126.7, 116.8, 114.5, 39.9; MS (70 eV, EI): *m/z* (%): 219 (100) [M^+]; $C_{11}H_9NO_4$ (219.2): calcd C 60.28, H 4.14, N 6.39; found C 58.87, H 4.12, N 6.14.

1,4-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]benzene [8c]: Hydroquinone (4.11 g, 37.3 mmol) was added to a degassed mixture of tetraethyleneglycol monotosylate (26.00 g, 74.7 mmol), K_2CO_3 (20.65 g, 149.4 mmol), and a catalytic amount of LiBr in dry MeCN (250 mL). The reaction mixture was heated under reflux for 24 h and filtered after cooling. The residue was dissolved in water (200 mL) and the resulting solution was extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was combined with the previously obtained filtrate and concentrated in vacuo. The resulting brown oil was dissolved in CH_2Cl_2 (200 mL) and the solution was washed carefully with a mixture of brine and 10% aq. NaOH (3:1, 3 × 100 mL). Drying of the organic layer ($MgSO_4$) and removal of the solvent under reduced pressure afforded 14.49 g (84%) of the title compound as a light brown oil, which was used in subsequent reactions without further purification. The ^{1}H NMR spectrum was in accordance with that reported in the literature [8c].

1,4-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]benzene bis(methylbenzenesulfonate) [26]: Following a procedure similar to that described by Ouchi et al. [27], 1,4-bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]benzene (14.00 g, 30.3 mmol) was dissolved in THF (50 mL). A solution of NaOH (3.43 g, 85.8 mmol) in water (18 mL) was added. The mixture was cooled in an ice bath down to 5 °C and a solution of toluene-*p*-sulfonyl chloride (10.85 g, 56.9 mmol) in THF (25 mL) was added with stirring over 1 h. The internal temperature during the addition was maintained below 5 °C. After the addition was completed, stirring was continued at room temperature for 2 h. The reaction mixture was poured into ice water (50 mL) and extracted with CH_2Cl_2 (3 × 100 mL). Drying of the combined organic layers ($MgSO_4$) and removal of the solvent in vacuo afforded 19.83 g (85%) of the title compound as a colorless oil. The ^{1}H NMR spectrum was in accordance with that reported in the literature [26].

1,4-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]benzene dibromide (5a): 1,4-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]benzene bis(4-methylbenzenesulfonate) (15.36 g, 19.9 mmol) and LiBr (9.20 g, 106.3 mmol) were dissolved in dry Me_2CO (100 mL), and the reaction mixture heated under reflux for 30 h. After cooling down to room temperature, the solution was filtered and the residue washed with Me_2CO. After evaporation of the combined filtrates in vacuo, the residue was purified by filtration over silica gel (eluent EtOAc) to afford 10.32 g (88%) of **5a** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.83 (s, 4H; Ar-*H*), 4.03–4.11 (m, 4H; $ArOCH_2$), 3.63–3.93 (m, 24H; OCH_2), 3.47 (t, ^3J = 6.5 Hz, 4H; 2 × CH_2Br); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 153.2, 115.6, 71.2, 70.8, 70.7, 70.7, 70.6, 69.9, 68.1, 30.3; MS (8 keV, FAB): *m/z* : 588 [M^+]; $C_{22}H_{36}Br_2O_8$ (588.3): calcd C 44.91, H 6.17; found C 44.63, H 6.23.

1,5-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]naphthalene: 1,5-Bishydroxynaphthalene (5.23 g, 32.7 mmol) was added to a degassed mixture of tetraethyleneglycol monotosylate (22.75 g, 65.3 mmol), K_2CO_3 (17.85 g, 129.2 mmol), and a catalytic amount of LiBr in dry MeCN (250 mL). The reaction mixture was heated under reflux for 24 h and filtered after cooling. The residue was dissolved in water (200 mL), and the resulting solution extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was combined with the previously obtained filtrate and evaporated in vacuo. The resulting brown oil was dissolved in CH_2Cl_2 (200 mL), and the solution washed carefully with a mixture of brine and 10% aq. NaOH (3:1, 3 × 100 mL). The organic layer was dried ($MgSO_4$), and the solvent removed under reduced pressure to afford 15.68 g (94%) of the title compound as a brown oil, which was used in subsequent reactions without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.86 (d, ^3J = 9 Hz, 2H; naphthalene *H*-4,8), 7.35 (t, ^3J = 9 Hz, 2H; naphthalene H-3,7), 6.84 (d, ^3J = 9 Hz, 2H; naphthalene *H*-2,6), 4.30 (t, ^3J = 5 Hz, 4H; 2 × $ArOCH_2$), 4.01 (t, ^3J = 5 Hz, 4H; 2 × $ArOCH_2CH_2$), 3.56–3.87 (m, 24H; OCH_2), 2.51 (bt, ^3J = 6 Hz, 2H; 2 × O*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 154.4, 126.8, 125.10, 114.7, 105.8, 72.5, 71.0, 70.7, 70.3, 69.9, 68.0, 61.7; HRMS (LSIMS) $C_{26}H_{40}O_{10}$: [*M* + H]$^+$ calcd 513.2700, found 513.2687.

1,5-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]naphthalene bis(4-methylbenzenesulfonate): The title compound was prepared following a similar procedure to that described in the literature [27]. 1,5-Bis[2-[2-[2-(2-hydroxyethoxy)-ethoxy]ethoxy]ethoxy]naphthalene (15.67 g, 30.6 mmol) was dissolved in THF (40 mL). A solution of NaOH (3.65 g, 91.2 mmol) in water (25 mL) was added. The mixture was cooled in an ice bath down to 5 °C. A solution of toluene-*p*-sulfonyl chloride (13.12 g, 68.8 mmol) in THF (100 mL) was added with stirring over 2 h; the internal temperature was kept below 5 °C. After the addition was completed, stirring was continued at room temperature for 2 h. The reaction mixture was poured into ice water (200 mL) and extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed in vacuo to afford 23.09 g (92%) of title compound as a light brown oil. The ^{1}H NMR spectrum was in accordance with that reported in the literature [27].

1,5-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]naphthalene dibromide (5b): 1,5-Bis[2-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]ethoxy]naphthalene bis(4-methyl-

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benzenesulfonate) (23.07 g, 28.1 mmol) and LiBr (13.80 g, 159.5 mmol) were dissolved in dry Me_2CO (150 mL), and the reaction mixture was heated under reflux for 24 h. After cooling down to room temperature, the solution was filtered and the residue washed with Me_2CO. The combined filtrates were evaporated in vacuo, and the residue was purified by filtration through silica gel (eluent: EtOAc) to afford 12.19 g (68%) of **5b** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.85 (d, ^3J = 8 Hz, 2H; naphthalene *H*-4,8), 7.34 (t, ^3J = 8 Hz, 2H; naphthalene *H*-3,7), 6.83 (d, ^3J = 8 Hz, 2H; naphthalene H-2,6), 4.28 (t, ^3J = 4 Hz, 4H; ArOCH_2), 3.99 (t, ^3J = 4 Hz, 4H; ArOCH$_2CH_2$), 3.59–3.88 (m, 20H; OCH_2), 3.43 (t, ^3J = 7 Hz, 4H; BrCH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 154.4, 126.8, 125.1, 114.7, 105.8, 71.2, 71.0, 70.8, 70.7, 70.6, 69.9, 68.0, 30.4; MS (8 keV, FAB): *m/z* : 638 [M^+]; $C_{26}H_{38}Br_2O_8$ (638.4): calcd C 48.92, H 6.00; found C 48.94, H 6.14.

***N*-Allylphthalylimido-*para*-phenylene[34]crown-10 (6a)**: Phthalimide **4** (1.85 g, 8.4 mmol) was added to a degassed suspension of K_2CO_3 (4.65 g, 33.6 mmol) in dry DMF (200 mL). A solution of dibromide **5a** (4.95 g, 8.4 mmol) in dry DMF (200 mL) was added with stirring over 5 h at a bath temperature of 120 °C. Heating at 120 °C was continued for 24 h. The reaction mixture was filtered, the residue washed with MeCN, and the combined filtrates evaporated in vacuo. The resulting brown oil was purified by column chromatography (SiO_2, gradient CH_2Cl_2/MeOH/Et_2O 30:2:17 to 30:2:7) to afford 2.173 g (40%) of **6a** as a colorless oil which crystallized on standing overnight. M.p. 68–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.07 (s, 2H; phthalimido protons), 6.76 (s, 4H; hydroquinone protons), 5.77–5.90 (m, 1H; C*H*=CH$_2$), 5.12–5.26 (m, 2H; CH=CH_2), 4.17–4.23 (m, 4H; 2 × OCH_2), 3.98–4.07 (m, 4H; 2 × OCH_2), 3.65–3.93 (m, 26H; OCH_2 and NCH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 165.9, 153.2, 150.4, 131.8, 122.8, 118.9, 117.6, 115.6, 70.9, 70.8, 70.8, 70.0, 69.8, 69.6, 63.3, 39.7; HRMS (LSIMS) $C_{33}H_{43}NO_{12}$: [*M* + Na]$^+$ calcd 668.2683, found 668.2658.

***N*-Allylphthalylimido-1,5-naphthyl[34]crown-10 (6b)**: Phthalimide **4** (3.660 g, 16.70 mmol) was added to a degassed suspension of K_2CO_3 (10.530 g, 76.19 mmol) in dry DMF (400 mL). A solution of **5b** (10.650 g, 16.68 mmol) in dry DMF (400 mL) was added with stirring over 9 h at a bath temperature of 120 °C. Heating at 120 °C was continued for 30 h. The reaction mixture was filtered, the residue washed with MeCN, and the combined filtrates evaporated in vacuo. The resulting brown oil was filtered through a short column (SiO_2, Me_2CO/MeOH 8:2, R_f of product: 0.33) and then purified by column chromatography (SiO_2, EtOAc/EtOH 10:1) to afford 2.87 g (25%) of **6b** as a white solid. Crystals suitable for X-ray crystallography were grown by recrystallization from Me_2CO. M.p. 99–101 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.82 (d, ^3J = 6 Hz, 2H; naphthalene *H*-4,8), 7.27 (t, ^3J = 6 Hz, 2H, naphthalene *H*-3,7), 6.75 (d, ^3J = 6 Hz, 2H; naphthalene *H*-2,6), 6.63 (s, 2H; phthalimido Ar-*H*), 5.73–5.90 (m, 1H; C*H*=CH$_2$), 5.07–5.26 (m, 2H; CH=CH_2), 4.25 (t, ^3J = 5 Hz, 4H; 2 × ArOCH_2), 4.10–4.15 (m, 2H; NCH_2), 3.93–4.07 (m, 8H; OCH_2), 3.62–3.85 (m, 20H; OCH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 165.8, 154.4, 150.1, 131.9, 126.7, 125.1, 122.3, 118.6, 117.6, 114.65, 105.9, 70.9, 70.8, 69.8, 69.7, 69.5, 68.2, 39.7; MS (8 keV, FAB): *m/z* : 696 [*M* + H]$^+$; $C_{37}H_{45}NO_{12}$ (695.7): calcd C 63.87, H 6.52, N 2.01; found C 64.14; H, 6.74, N 2.03. X-Ray data: $C_{37}H_{45}NO_{12}$, M_r = 695.7, triclinic, space group $P\bar{1}$, a = 9.954(6), b = 13.774(7), c = 14.656(8) Å, α = 67.51(4), β = 70.58(5), γ = 82.09(5)°, V = 1751(2) Å^3, Z = 2, $\mu(Cu_{K\alpha})$ = 8 cm^{-1}, ρ_{calc} = 1.32 g cm^{-3}, crystal dimensions = 0.10 × 0.20 × 0.33 mm. Data collected at room temperature on a Siemens P4/PC diffractometer, graphite monochromator, $Cu_{K\alpha}$ radiation with ω scans. 5590 Independent measured reflections, 3085 with [$|F_0| > 4\sigma(|F_0|)$, 2θ = 3–125°] corrected for Lorentz and polarization factors but not for absorption. Structure solved by direct methods and non-hydrogen atoms refined anisotropically; H atoms included in calculated positions, assigned isotropic thermal parameters $U(H) = 1.2\,U_{eq}(C)$, and allowed to ride on parent carbon atoms. Refinement by full matrix least squares based on F to give R = 0.082, R_w = 0.084 [$w^{-1} = \sigma^2(F) + 0.0005F^2$]; 452 refined parameters; residual electron density in the range −0.50 to 0.44 e Å^{-3}. Computations carried out with the SHELXTL version 4.2 program system [30].

1,6-Bis(2,5-dimethylphenoxy)hexane: 2,5-Dimethylphenol (9.46 g, 77 mmol) was added to a suspension of K_2CO_3 (56 g, 410 mmol) in MeCN (250 mL). The reaction mixture was heated under reflux for 1 h in an atmosphere of N_2. 1,6-Dibromohexane (9.1 g, 37 mmol) was added, and refluxing continued for a further 2 d. The reaction mixture was cooled, and the inorganic residues were filtered off and washed with MeCN and CH_2Cl_2. The filtrate was concentrated in vacuo. The resulting residue was taken up in CH_2Cl_2 (250 mL), and washed with 10% aqueous NaOH (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo and the residue recrystallized from light petroleum, affording 1,6-bis(2,5-dimethylphenoxy)hexane as a white crystalline material (10.5 g, 86%). M.p. 94 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.08 (d, ^3J = 7 Hz, 2H; Ar-*H*-3), 6.74 (d, ^3J = 7 Hz, 2H; Ar-*H*-4), 6.71 (s, 2H; Ar-*H*-6), 4.02 (t, ^3J = 6 Hz, 4H; Ar-O-CH_2), 2.39 (s, 6H; Ar-CH_3), 2.26 (s, 6H; Ar-CH_3), 1.86–1.95 (m, 4H; Ar-O-CH$_2$-CH_2), 1.61–1.67 (m, 4H; Ar-O-CH$_2$-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.2, 136.5, 130.4, 123.7, 120.7, 112.1, 67.8, 29.5, 26.1, 21.5, 15.9. MS (70 eV, EI): *m/z* (%): 326 (20) [M^+].

1,6-Bis(2,5-bis(bromomethyl)phenoxy)hexane (7): NBS (9.4 g, 67.5 mmol) and AIBN (20 mg) were added to a solution of 1,6-bis(2,5-dimethylphenoxy)hexane (3.91 g, 12.0 mmol) in CCl_4 (150 mL). The reaction mixture was refluxed gently under N_2 for 4 h. It was then cooled, and the succinimide filtered off. The filtrate was concentrated to approximately half its volume. Hexane was added and a white precipitate formed. The precipitate was filtered off and washed with hexane, affording **7** as a white powder (3.1 g, 41%). M.p. 151 °C; ^{1}H NMR (300M Hz, $CDCl_3$, 25 °C, TMS): δ = 7.29 (d, ^3J = 7 Hz, 2H; Ar-*H*-2), 6.93, (dd, ^3J = 7 Hz, ^4J = 1 Hz, 2H; Ar-*H*-3), 6.89 (d, ^4J = 1 Hz, 2H; Ar-*H*-6), 4.54 (s, 4H; Ar-CH_2-Br), 4.45 (s, 4H; Ar-CH_2-Br), 4.08 (t, ^3J = 6 Hz, 4H; Ar-O-CH_2), 1.87–1.98 (m, 4H; Ar-O-CH$_2$-CH_2), 1.62–1.69 (m, 4H; Ar-O-CH$_2$-CH$_2$-CH_2); ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ = 157.0, 140.0, 131.1, 126.0, 121.0, 112.3, 68.1, 33.3, 29.1, 28.5, 25.7. MS (70 eV, EI): *m/z* (%): 642 (5) [M^+]; $C_{22}H_{26}O_2Br_4$ (642.1) calcd C 41.16, H 4.08; found C 41.45, H 3.93.

1,5-Bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene: 1,5-Dihydroxynaphthalene (16 g, 100 mmol) was added to a suspension of K_2CO_3 (60 g, 434 mmol) in DMF (250 mL). The suspension was heated to 80 °C under N_2 and stirred for a further 30 min. A solution of 2-(2-(2-chloroethoxy)-ethoxy)ethoxyethanol (26.5 g, 330 mmol) in DMF (50 mL) was added dropwise during 1 h. Heating was continued for a further 4 d. The reaction mixture was cooled, and the solid inorganic residues were filtered off in vacuo and washed with DMF. The DMF was removed in vacuo, and the resulting brown solid taken up into CH_2Cl_2 (100 mL) and washed with saturated Na_2CO_3 (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried ($MgSO_4$), filtered under gravity, and the CH_2Cl_2 removed in vacuo. The resulting solid was recrystallized from EtOH (500 mL) affording the title compound as a yellow crystalline solid (13 g, 52%). M.p. 66 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.87 (d, ^3J = 8 Hz, 2H; naphthalene *H*-4,8), 7.38 (t, ^3J = 8 Hz, 2H; naphthalene *H*-3,7), 6.84 (d, ^3J = 8 Hz, 2H; naphthalene *H*-2,6), 4.36 (t, ^3J = 5 Hz, 4H; Ar-OCH_2), 4.04 (t, ^3J = 5 Hz, 4H; OCH_2), 3.82 (m, 4H; OCH_2), 3.71 (m, 8H; OCH_2), 3.62 (m, 4H; OCH_2), 1.95–2.20 (bs, 2H; O*H*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.4, 126.8 125.1, 114.6, 105.8, 72.5, 70.9, 70.4, 69.8, 68.0, 61.7; MS (70 eV, EI): *m/z* (%): 424 (10) [M^+].

1,5-Bis[2-(2-(2-(1-adamantoyl)ethoxy)ethoxy)ethoxy]naphthalene (8): 1-Adamantoyl chloride (4.21 g, 21.2 mmol) in CH_2Cl_2 (50 mL) was added dropwise to a solution of 1,5-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene (1.5 g, 3.5 mmol) in pyridine-$CHCl_3$ (150 mL of 1:2 v/v), under nitrogen. The solution was warmed to 60 °C with stirring for 2 h. It was then cooled and washed with 10% aqueous hydrochloric acid (2 × 100 mL), and water (2 × 100 mL). The organic layer was dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. The resulting residue was subjected to silica gel column chromatography with EtOAc/light petroleum (1:1) as the eluent. The fractions containing the product were combined and the eluent removed in vacuo, affording **8** as a white solid (1.38 g, 88%). M.p. 108 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.86 (d, ^3J = 8 Hz, 2H; naphthalene *H*-4,8), 7.34 (t, ^3J = 8 Hz, 2H; naphthalene *H*-3,7), 6.84 (d, ^3J = 8 Hz, 2H; naphthalene *H*-2,6), 4.31 (t, ^3J = 8 Hz, 4H; Ar-OCH_2), 4.22 (m, 4H; OCH_2), 4.01 (t, J = 8 Hz, 4H; OCH_2), 3.80 (m, 4H; OCH_2), 3.68–3.74 (m, 8H; OCH_2), 1.96–2.02 (m, 6H; adamantoyl-C*H*), 1.87–1.92 (m, 12H; adamantoyl-CH_2), 1.62–1.75 (m, 12H; adamantoyl-CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 177.6, 154.4, 126.8, 125.1, 114.6, 105.7, 71.0, 70.7, 69.9, 69.3, 68.0, 63.3, 40.7, 38.8, 36.5, 27.9; MS (8 keV, FAB): *m/z* : 748 [M^+]; $C_{44}H_{60}O_{10}$ (748.9): calcd C 70.56, H 8.07; found C 70.28, H 7.87.

[2]Catenane 9a·4PF$_6$: A solution of **10**·2PF$_6$ [8c] (0.126 g, 0.18 mmol), 1,4-bis(bromomethyl)benzene (0.033 g, 0.12 mmol), and crown ether **6a** (0.066 g, 0.10 mmol) in dry DMF (4 mL) was stirred at room temperature for 14 d. A deep orange color developed. The reaction mixture was concentrated, and the residue purified by column chromatography (SiO_2, MeOH/2M aq. NH_4Cl/$MeNO_2$ 7:2:1). The colored fractions were combined, evaporated in vacuo, and dissolved in water (100 mL). A solution of NH_4PF_6 (5.5 g, 34 mmol) in water (10 mL) was added until no further precipitation occurred. The precipitate was filtered off, washed with water (20 mL) and redissolved in Me_2CO. The orange solution was filtered to remove a white insoluble residue and concentrated to dryness. The residue was washed thoroughly with water and dried in vacuo to afford 0.095 g (53%) of the [2]catenane **9a** as an orange solid. Crystals, which were not of sufficient quality for X-ray crystallography, were grown by vapor diffusion of iPr_2O into an MeCN solution of the compound. M.p. > 275 °C (decomp.); ^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C): δ = 9.33 (d, $^3J_{AB}$ = 8 Hz, 8H; bipyridinium α-C*H*), 8.17 (d, $^3J_{AB}$ = 8 Hz, 8H; bipyridinium β-C*H*), 8.05 (s, 8H; xylyl-H), 6.83 (s, 2H; Ar-*H* phthalimide), 6.04 (s, 8H; 4 × NCH_2), 5.80–5.94 (m, 1H; C*H*=CH$_2$), 5.10–5.19 (m, 2H; CH=CH_2), 4.08–4.13 (m, 2H; NCH_2-CH=CH$_2$), 4.02 (bs, 12H; OCH_2 and "inside" hydroquinone protons), 3.88–3.95 (m, 8H; OCH_2), 3.74–3.85 (m, 12H; OCH_2), 3.66–3.71 (m, 4H; OCH_2); ^{13}C NMR (75.5 MHz, CD_3COCD_3, 25 °C): δ = 165.2, 151.2, 150.1, 146.7, 145.9, 137.7, 133.3, 131.8, 126.2, 122.8, 118.7, 117.5, 113.9, 71.7, 71.1, 70.9, 70.7, 70.26, 70.2, 67.4, 65.7, 40.1; MS (8 keV, FAB): *m/z* : 1600 [$M - PF_6^-$]$^+$, 1456 [$M - 2PF_6$]$^+$; HRMS (LSIMS) $C_{69}H_{75}O_{12}N_5P_3F_{18}$: [$M - PF_6$]$^+$ calcd 1600.4338, found 1600.4252.

[2]Catenane 9b·4PF$_6$: A solution of **10**·2PF$_6$ [8c] (0.0900 g, 0.1274 mmol), 1,4-bis(bromomethyl)benzene (0.024 g, 0.09 mmol), and crown ether **6b** (0.052 g, 0.07 mmol) in a mixture of dry DMF (3 mL) was stirred at room temperature for 11 d. The color of the solution turned to deep purple. The reaction mixture was

concentrated to dryness, and the residue subjected to column chromatography on silica gel (eluent MeOH/2M aq. NH_4PF_6/$MeNO_2$ 7:2:1). After collection of the colored fractions and evaporation of solvent in vacuo, the residue was redissolved in water (75 mL) and the desired [2]catenane precipitated by addition of a solution of NH_4PF_6 (4.0 g, 25 mmol) in water (7 mL). The precipitate was filtered off and dried in vacuo to afford 0.096 g (71%) of the [2]catenane **9b** as a purple solid. Crystals suitable for X-ray crystallography were grown by vapor diffusion of iPr_2O into an MeCN solution of the compound. M.p. > 280 °C (decomp.); ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ = 9.05 (d, ^3J = 6 Hz, 4H; "inside" bipyridinium α-C*H*), 8.68 (d, ^3J = 6 Hz, 4H; "alongside" bipyridinium α-C*H*), 8.19 (bs, 4H; xylyl-H) 8.07 (bs, 4H; xylyl-H), 7.20–7.29 (m, 8H; "inside" bipyridinium β-C*H*), 6.68 (s, 2H; Ar-H phthalimide), 6.30 (d, ^3J = 8 Hz, 2H; naphthalene *H*-2,6), 6.03 (t, ^3J = 8 Hz, 2H; naphthalene *H*-3,7), 5.92–6.02 (m, 1H; H_2C=C*H*-CH_2N), 5.93 (d, $^2J_{AB}$ = 13 Hz, 4H; 2 × NCH_2), 5.81 (d, $^2J_{AB}$ = 13 Hz, 4H; 2 × NCH_2), 5.20–5.32 (m, 2H; H_2C=CH-CH_2N), 4.35–4.40 (m, 4H; OCH_2), 4.25–4.31 (m, 4H; OCH_2), 4.21–4.25 (m, 2H; N-CH_2CH=CH_2), 4.13–4.20 (m, 4H; OCH_2), 4.04–4.09 (m, 4H; OCH_2), 3.94–4.01 (m, 4H; OCH_2), 3.86–3.92 (m, 4H; OCH_2), 3.76 (bs, 8H; OCH_2), 2.49 (d, ^3J = 8 Hz, 2H; naphthalene H-2,6 or H-4,8); ^{13}C NMR (75.5 MHz, CD_3CN, 25 °C): δ = 165.5, 151.8, 149.9, 145.4, 145.1, 137.33, 133.2, 132.0, 129.2, 126.0, 125.1, 124.9, 122.8, 115.7, 108.9, 104.8, 72.0, 71.4, 71.3, 70.6, 70.6, 70.4, 69.8, 65.8, 40.2; MS (8 keV, FAB): *m/z* : 1651 $[M^+ - PF_6]$, 1506 $[M^+ - 2PF_6]$, 1361 $[M^+ - 3PF_6]$; HRMS (LSIMS) $C_{73}H_{77}N_5O_{12}P_3F_{18}$: $[M - PF_6]^+$ calcd 1650.4494, found 1650.4531. X-Ray data: **9b**·4PF_6·7MeCN·H_2O, $C_{87}H_{100}F_{24}N_{12}O_{13}P_4$, M_r = 2101.7, triclinic, space group $P\bar{1}$, a = 13.590(3), b = 14.203(3), c = 27.031(5) Å, α = 101.70(3), β = 99.28(3), γ = 105.63(3)°, V = 4789(2) Å^3. Z = 2, $\mu(Cu_{K\alpha})$ = 17 cm^{-1}, ρ_{calc} = 1.46 g cm^{-3}, crystal dimensions = 0.20 × 0.33 × 0.40 mm. Data collected at −70 °C on a Siemens P4 rotating anode diffractometer, graphite monochromator, $Cu_{K\alpha}$ radiation with ω scans. 9382 Independent measured reflections, 7053 with $[|F_o| > 4\sigma(|F_o|)$, $2\theta = 3-111°]$ corrected for Lorentz and polarisation factors but not for absorption. Structure solved by direct methods. A ΔF map revealed the presence of seven MeCN molecules, six of which were ordered; the seventh was disordered, but retained an atom in a common position for the two disordered molecules. The difference map also showed the presence of an included water molecule disordered about three different positions. Three of the PF_6^- counterions are ordered whilst the fourth is disordered about two 50/50 occupancy sites. The disordered PF_6^- counterion was refined subject to atom–atom distance constraints. The atoms of the tetracationic cyclophane were refined isotropically as were those of the naphthalene ring and the phthalimido unit of the macrocyclic polyether. The remaining non-hydrogen atoms were refined anisotropically. H atoms were included in calculated positions, assigned isotropic thermal parameters $U(H) = 1.2\,U_{eq}(C)$ and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares based on F^2 to give R_1 = 0.1112, wR_2 = 0.2909; 1007 refined parameters; residual electron density in the range −0.45 to 1.03 e Å^{-3}. Computations were carried out using the SHELXTL version 5.0 program system.

Biscrown ether 1a: **Reduction** of the imido crown ether **6a** was achieved by dissolving **6a** (0.987 g, 1.53 mmol) under N_2 in dry THF (20 mL). $LiAlH_4$ (0.189 g, 4.98 mmol) was added, and the reaction mixture heated under reflux with stirring for 3 h. After the mixture had cooled down to room temperature, water was added until no more H_2 evolved. The mixture was filtered under suction, and the residue washed with Et_2O (10 mL). Et_2O was added to the filtrate until two layers appeared. The layers were separated, and the aqueous layer was washed with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated in vacuo. **Deallylation** [28] of the intermediate allylamino crown ether was achieved by immediately dissolving the remaining 0.761 g of a light brown oil under N_2 in a degassed mixture (10 mL) of EtOH/water (9:1). $Rh(PPh_3)_3Cl$ (0.080 g, 0.09 mmol) and DABCO (0.029 g, 0.26 mmol) were added. The mixture was heated under reflux with stirring for 6 h and then allowed to cool down to room temperature. Aqueous HCl (10%, 1.5 mL) was added, and stirring was continued for 30 min at room temperature. Aqueous NaOH (10%, 7 mL) and water (10 mL) were added. The mixture was extracted with CH_2Cl_2 (4 × 20 mL), and, after drying ($MgSO_4$), the combined organic layers were evaporated in vacuo. The dark brown oil was immediately filtered through a short column (SiO_2, eluent EtOAc/MeOH/NEt_3 10:1:1, R_f of the desired product: 0.14). **Dimerization** of the amino crown ether obtained was accomplished by dissolving the oily product (0.194 g, 0.336 mmol) under N_2 in a mixture of dry CH_2Cl_2 (10 mL) and dry iPr_2NEt (2 mL). A solution of 4,4′-biphenyl dicarboxylic acid dichloride (0.047 g, 0.165 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise with stirring over 30 min. Stirring was continued at room temperature for 48 h and the reaction mixture was washed with water (2 × 10 mL). The organic layer was dried ($MgSO_4$) and the solvent was evaporated in vacuo. Purification by column chromatography (Al_2O_3, eluent EtOAc/EtOH 100:5) afforded 0.117 g (11% with reference to **6a**) of **1a** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.71 (d, $^3J_{AB}$ = 9 Hz, 4H; biphenyl-*H*), 7.65 (d, $^3J_{AB}$ = 9 Hz, 4H; biphenyl-*H*), 6.71 (s, 4H; Ar-*H* hydroquinone protons), 6.63 (d, $^3J_{AB}$ = 8.0 Hz, 2H; Ar-*H* isoindoline), 6.58 (d, $^3J_{AB}$ = 8 Hz, 2H; Ar-*H* isoindoline), 4.94 and 4.72 (2 × bs, 2 × 4H, CH_2N *cis*/*trans* amide), 3.57–4.10 (m, 64H; OCH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 169.8, 153.2, 153.0, 148.4, 148.0, 141.8, 135.99, 127.8, 127.2, 126.6, 115.5, 115.5, 111.7, 111.2, 70.9, 70.9, 70.8, 70.6, 69.80, 69.7, 68.5, 68.2, 53.4, 51.3; MS (8 keV, FAB): *m/z*: 1361 $[M + H^+]$; HRMS (LSIMS) $C_{70}H_{93}N_2O_{22}$: $[M + H]^+$ calcd 1361.6220, found 1361.6259.

Bis[2]catenane 11a·8PF_6: A solution of **10**·2PF_6 [8c] (0.054 g, 0.008 mmol), 1,4-bis(bromomethyl)benzene (0.014 g, 0.05 mmol), and biscrown ether **1a** (0.031 g, 0.02 mmol) in dry DMF (2 mL) was stirred at room temperature for 6 d. The solution turned orange. The reaction mixture was evaporated, and the residue purified by column chromatography (SiO_2, gradient MeOH/2M aq. NH_4Cl/$MeNO_2$ 7:2:1 to 2M aq. NH_4Cl/DMF/MeOH/$MeNO_2$ 12:10:7:1). The fractions containing a colored compound (R_f = 0.05, eluent: MeOH/2M aq. NH_4Cl/$MeNO_2$ 7:2:1) were concentrated to dryness, and the residue redissolved in water. Precipitation with saturated aqueous NH_4PF_6 yielded an orange solid, which was further purified by two subsequent recrystallizations. Vapor diffusion of iPr_2O into an CH_3CN solution of the compound afforded 0.0082 g of the bis[2]catenane **11a**. Evaporation of the mother liquor and purification of the residue by PTLC (eluent: DMF/MeOH/2M aqueous NH_4Cl/$MeNO_2$ 10:7:2:1) afforded further 0.0034 g of the bis[2]catenane **11a**, total yield: 0.0116 g (14%) of an orange solid. M.p. > 270 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 8.91 (d, $^3J_{AB}$ = 7 Hz, 16H; bipyridinium α-C*H*), 7.92 (d, $^3J_{AB}$ = 8 Hz, 4H; biphenyl-H), 7.80 (s, 16H; xylyl-H), 7.78 (d, $^3J_{AB}$ = 8 Hz, 4H; biphenyl-H), 7.67 (d, $^3J_{AB}$ = 7 Hz, 16H; bipyridinium β-C*H*), 6.11 (d, $^3J_{AB}$ = 9 Hz, 2H; Ar-*H* isoindoline), 6.06 (d, $^3J_{AB}$ = 9 Hz, 2H; Ar-*H* isoindoline), 5.70 (s, 16H; NCH_2), 4.52 and 4.39 (2 × s, 2 × 4H; CH_2N *cis*/*trans* amide), 3.38–4.01 (m, 72H; OCH_2 and Ar-*H* inside hydroquinone protons); MS (8 keV, FAB): *m/z*: 3418 $[M - PF_6]^+$, 3272 $[M - 2PF_6]^+$, 3128 $[M - 3PF_6]^+$, 2982 $[M - 4PF_6]^+$; HRMS (LSIMS) $C_{146}H_{156}N_{10}O_{22}P_5F_{30}$: $[M - 3PF_6]^+$ calcd 3126.9638, found 3126.9733.

Biscrown ether 1b: **Reduction** of imido crown ether **6b** was achieved by dissolving **6b** (1.000 g, 1.44 mmol) under N_2 in dry THF (20 mL). $LiAlH_4$ (0.218 g, 5.74 mmol) was added, and the reaction mixture heated under reflux with stirring for 6 h. After the mixture had cooled down to room temperature, water was added until no more H_2 evolved. The mixture was filtered under suction and the residue washed with Et_2O (15 mL). Et_2O was added to the filtrate until two layers appeared. The layers were separated, and the aqueous layer was washed with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated in vacuo. **Deallylation** [28] of the intermediate allylamino crown ether was accomplished by dissolving immediately the remaining 0.812 g of a light brown solid under N_2 in a degassed mixture (10 mL) of EtOH/water (9:1). $Rh(PPh_3)_3Cl$ (0.079 g, 0.09 mmol) and DABCO (0.029 g, 0.26 mmol) were added. The mixture was heated under reflux with stirring for 4 h and subsequently evaporated in vacuo. The dark brown oil was immediately filtered down a short column (SiO_2, eluent EtOAc/MeOH/NEt_3 10:1:1, R_f of the product: 0.16) without prior treatment with HCl. To accomplish the **dimerization** of the resultant amino crown ether, the oily product obtained in the last step (0.190 g, 0.30 mmol) was dissolved under N_2 in a mixture of dry CH_2Cl_2 (20 mL) and dry iPr_2NEt (4 mL). A solution of 4,4′-biphenyl dicarboxylic acid dichloride (0.042 g, 0.15 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise with stirring over 45 min. Stirring was continued at room temperature for 48 h, and the reaction mixture evaporated in vacuo. Purification by column chromatography (SiO_2, eluent CH_2Cl_2/MeOH 30:1, R_f of the product = 0.34 in CH_2Cl_2/MeOH 10:1) and subsequent recrystallization from Me_2CO/iPr_2O afforded 0.067 g (6% with reference to **6b**) of the desired product as an off-white solid. M.p. 183–185 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.76–7.91 (m, 4H; 2 × naphthalene *H*-4,8), 7.66 (d, $^3J_{AB}$ = 8 Hz, 4H; biphenyl-H), 7.55 (d, $^3J_{AB}$ = 8 Hz, 4H; biphenyl-H), 7.14–7.31 (m, 4H; 2 × naphthalene *H*-3,7), 6.63–6.76 (m, 4H; 2 × naphthalene *H*-2,6), 6.28–6.41 (m, 4H; 2 × isoindolino-H), 4.83, 4.53 (2 × bs, 2 × 4H, CH_2N *cis*/*trans* amide), 4.15–4.27 (m, 8H; OCH_2), 3.55–4.08 (m, 56H; OCH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 169.7, 154.4, 154.3, 148.2, 147.7, 141.8, 135.9, 127.7, 127.1, 126.7, 126.4, 125.1, 114.7, 114.4, 111.4, 110.9, 105.6, 105.5, 71.0, 70.9, 70.6, 69.7, 69.6, 68.3, 68.0, 53.3, 51.2; MS (8 keV, FAB): *m/z* : 1462 $[M + H]^+$; HRMS (LSIMS) $C_{82}H_{96}N_2O_{22}$: $[M + H]^+$ calcd 1461.6533, found 1461.6607.

Bis[2]catenane 11b·8PF_6: A mixture of **10**·2PF_6 [8c] (0.0297 g, 0.004 mmol), 1,4-bis(bromomethyl)benzene (0.0078 g, 0.030 mmol), and biscrown ether **1b** (0.0181 g, 0.012 mmol) in dry DMF (1 mL) was stirred at room temperature for 10 d. The color of the solution turned to purple. The reaction mixture was evaporated and the residue was purified by column chromatography (SiO_2, eluent MeOH/2M aq. NH_4Cl/$MeNO_2$ 7:2:1). The fractions containing a colored compound (R_f = 0.05) were concentrated to dryness, and the residue was redissolved in water. Precipitation with saturated aqueous NH_4PF_6 yielded a purple solid, which was further purified by suspending the solid in Me_2CO. Precipitation of the desired product was completed by vapor diffusion of iPr_2O into the Me_2CO suspension to afford 0.0158 g of the bis[2]catenane **11b**·8PF_6 (35%) as a purple solid. M.p. > 270 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 8.96 (d, ^3J = 6 Hz, 4H; "inside" bipyridinium α-C*H*), 8.93 (d, ^3J = 6 Hz, 4H; "inside" bipyridinium α-C*H*), 8.60 (d, ^3J = 8 Hz, 4H; "alongside" bipyridinium α-C*H*), 8.58 (d, ^3J = 8 Hz, 4H; "alongside" bipyridinium α-C*H*); 7.95–8.08 (m, 16H; xylyl-H), 7.91 (d, $^3J_{AB}$ = 8 Hz, 4H; biphenyl-H), 7.74 (d, $^3J_{AB}$ = 8 Hz, 4H; biphenyl-H), 7.08–7.14 (bm, 16H; bipyridinium β-C*H*), 6.22 (d, ^3J = 8 Hz, 4H; naphthalene *H*-2,6), 5.91–6.00 (m, 4H; aryl-*H* isoindoline), 5.95 (m, ^3J = 8 Hz, 4H; naphthalene *H*-3,7), 5.64–5.87 (m, 16H; NCH_2), 4.45 (bs, 4H; NCH_2 *cis*/*trans* amide), 4.28 (bs, 12H; OCH_2 and NCH_2 *cis*/*trans* amide), 4.12–4.20 (m, 8H; OCH_2), 4.03–4.09 (m, 4H; OCH_2), 3.94–4.02 (m, 8H; OCH_2), 3.82–3.88 (m, 8H; OCH_2), 3.73–3.77 (m, 8H; OCH_2), 3.60–3.66 (m, 8H; OCH_2), 3.48–3.55 (m, 4H; OCH_2), 3.42–3.46 (m, 4H;

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OCH_2), 3.33–3.41 (m, 4H; OCH_2), 2.38–2.43 (m, 4H; naphthalene H-4,8); MS (8 keV, FAB): *m/z*: 3517 $[M-PF_6]^+$, 3372 $[M-2PF_6]^+$, 3228 $[M-3PF_6]^+$. HRMS (LSIMS) $C_{154}H_{160}F_{36}N_{10}O_{22}P_6$: $[M-2PF_6]^+$ calcd 3372.9627, found 3372.9825.

Benzoylated crown ether 1c: The reduction of imido crown ether **6b** and the subsequent deallylation affording the NH-substituted intermediate was achieved as described in the synthesis of **1b**. To accomplish the benzoylation of the amino crown ether, the oily product obtained in the last step (0.103 g, 0.16 mmol) was dissolved under N_2 in a mixture of dry CH_2Cl_2 (5 mL) and dry iPr_2NEt (2 mL). Benzoyl chloride (2 mL, 1.6 g, 11 mmol) in dry CH_2Cl_2 (10 mL) was added. Stirring was continued at room temperature for 48 h, and the reaction mixture was evaporated in vacuo. Purification by column chromatography (R_f of product = 0.29 in EtOAc/EtOH 10:1, two subsequent SiO_2 columns; first eluent: gradient EtOAc to EtOAc/EtOH 10:1, second eluent: toluene/acetone 6:3) yielded 0.053 g of **1c** as an oily brown product (>90% pure, 36% yield referring back to **6b**). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.82 (d, ^3J = 8 Hz, 1H; naphthalene *H*-4,8), 7.80 (d, ^3J = 8 Hz, 1H; naphthalene *H*-4,8), 7.41–7.50 (m, 5H; phenyl), 7.21 (t, ^3J = 8 Hz, 1H; naphthalene *H*-3,7), 7.20 (t, ^3J = 8 Hz, 1H; naphthalene *H*-3,7), 6.71 (d, ^3J = 8 Hz, 1H; naphthalene *H*-2,6), 6.69 (d, ^3J = 8 Hz, 1H; naphthalene *H*-2,6), 6.30 (AB system, $^3J_{AB}$, *J* = 7 Hz, 2H; 1,2,3,4-tetrasubstituted Ar-*H*), 4.80 (s, 2H; N-CH_2), 4.48 (s, 2H; N-CH_2), 4.16–4.26 (m, 4H; OCH_2); 4.00–4.05 (m, 2H; OCH_2), 3.95–4.05 (m, 2H; OCH_2), 3.85–3.90 (m, 2H; OCH_2), 3.58–3.85 (m, 22H; OCH_2);^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 170.1, 154.4, 154.3, 148.2, 147.7, 136.8, 132.2, 132.1, 131.9, 129.8, 129.0, 128.6, 128.4, 128.2, 127.0, 126.8, 126.7, 126.4, 126.3, 125.3, 125.1, 125.0, 114.7, 114.4, 111.4, 110.9, 105.6, 77.2, 71.0, 70.9, 70.8, 70.6, 69.8, 69.6, 68.3, 68.0, 64.3, 53.2, 51.1; MS (8 keV, FAB): *m/z* : 732 $[M+H]^+$; HRMS (LSIMS) $C_{41}H_{49}NO_{11}$: $[M+H]^+$ calcd 732.3384, found 732.3318.

[2]Catenane 11c·4PF$_6$: A mixture of **10**·2PF$_6$ [8c] (0.0404 g, 0.057 mmol), 1,4-bis(bromomethyl)benzene (0.0106 g, 0.040 mmol), and biscrown ether **1c** (0.0246 g, 0.034 mmol) in dry DMF (1.5 mL) was stirred at room temperature for 6 d. The color of the solution turned to purple. The reaction mixture was evaporated, and the residue purified by PTLC (eluent: MeOH/2 M aq. NH_4Cl/$MeNO_2$ 7:2:1). The fraction containing a colored compound was treated with a concentrated solution of NH_4PF_6 in MeCN to dissolve the [2]catenane. The resulting solution was evaporated and the residue treated with water (4 × 15 mL) to extract the excess of NH_4PF_6. Drying of the residue in vacuo afforded 0.0395 g of the bis[2]catenane **11c**·4PF$_6$ (88%) as a purple solid. M.p. > 270 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 8.96 (d, ^3J = 6 Hz, 2H; "inside" bipyridinium α-*CH*), 8.91 (d, ^3J = 6 Hz, 2H; "inside" bipyridinium α-*CH*), 8.60 (d, ^3J = 7 Hz, 2H; "alongside" bipyridinium α-*CH*), 8.55 (d, ^3J = 7 Hz, 2H; "alongside" bipyridinium α-*CH*); 7.89–8.11 (m, 8H; xylyl-H), 7.52–7.60 (m, 5H; phenyl group), 7.01–7.16 (bm, 8H; bipyridinium β-*CH*), 6.19 (d, ^3J = 8 Hz, 2H; naphthalene *H*-2,6), 5.61–6.05 (m, 14H; 4H from aryl-*H* isoindoline and 2H from naphthalene *H*-3,7 and 8H from NCH_2), 4.40 (bs, 2H; NCH_2 *cis/trans* amide), 4.22–4.31 (m, 4H; OCH_2), 4.11–4.21 (m, 6H; OCH_2 and NCH_2 *cis/trans* amide), 4.04–4.09 (m, 2H; OCH_2), 3.99–4.03 (m, 2H; OCH_2), 3.93–3.98 (m, 2H; OCH_2), 3.88–3.79 (m, 4H; OCH_2), 3.71–3.78 (m, 4H; OCH_2), 3.58–3.68 (m, 4H; OCH_2), 3.47–3.52 (m, 2H; OCH_2), 3.41–3.47 (m, 2H; OCH_2), 3.29–3.36 (m, 2H; OCH_2), 2.38–2.43 (m, 4H; naphthalene *H*-4,8); MS (8 keV, FAB): *m/z*: 1687 $[M-PF_6]^+$, 1542 $[M-2PF_6]^+$, 1397 $[M-PF_6]^+$; HRMS (LSIMS) $C_{77}H_{81}O_{11}N_5P_5F_{18}$: $[M-PF_6]^+$ calcd 1686.4858, found 1686.4964.

Bis[2]catenane 13·8PF$_6$: A solution of the tetrabromide **7** (66 mg, 0.10 mmol), **10**·2PF$_6$ [8c] (132 mg, 0.19 mmol), and the crown ether **12** [18] (300 mg, 0.56 mmol) in MeCN (10 mL) were stirred for 14 d, after which time the solution had turned red and a red solid had begun to appear. The addition of Et_2O precipitated the salt. The resulting red solid was filtered off and chromatographed on a silica gel column (eluent: initially MeOH/2 M aq. NH_4Cl/$MeNO_2$ 7:2:1, and then original eluent/DMF/2 M aqueous NH_4Cl 1:0.5:0.5 and finally 1:1:1). The fractions containing the red band were combined and concentrated in vacuo. The addition of water (50 mL) dissolved the solid residue. Saturated aqueous NH_4PF_6 was added to the red solution. A red solid precipitated out, which was filtered off and washed with water, CH_2Cl_2, and Et_2O. The solid was dried in vacuo, affording a red powder **13**·8PF$_6$ (73 mg, 31%). M.p. > 270 °C. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ = 8.95 (d, ^3J = 7 Hz, 4H; bipyridinium α-*CH*), 8.808.92 (m, 12H; bipyridinium α-*CH*), 7.82 (d, ^3J = 8 Hz, 2H; Ar-*H*-3), 7.81 (s, 8H; xylyl-H), 7.62–7.75 (bm, 16H; bipyridinium β-*CH*), 7.46 (dd, ^3J = 8, ^4J = 1 Hz, 2H; Ar-*H*-4), 7.34 (d, ^4J = 1 Hz, 2H; Ar-*H*-3), 6.18 (s, 8H; "inside" hydroquinone protons), 5.72 (s, 12H; NCH_2), 5.67 (s, 4H; NCH_2), 4.35 (m, 4H; Ar-O-CH_2-alkyl), 3.88–4.02 (m, 34H; OCH_2), 3.75–3.88 (m, 10H; OCH_2), 3.55–3.70 (m, 16H; OCH_2), 3.46–3.31 (m, 12H; OCH_2), 2.16 (m, 4H; Ar-OCH_2-CH_2-alkyl), 1.81 (m, 4H; Ar-OCH_2CH_2-CH_2-alkyl); ^{13}C NMR (75.5 MHz, CD_3CN, 25 °C): δ = 158.42, 153.15, 147.32, 147.13, 139.85, 137.89, 137.79, 134.3, 131.9, 126.6, 125.8, 123.7, 116.0, 113.6, 71.7, 71.6, 71.0, 70.9, 70.7, 70.4, 70.1, 68.6, 67.5, 65.7, 60.8, 30.6, 26.5; MS (8keV, FAB): *m/z*: 3245 $[M-PF_6]^+$; $C_{134}H_{154}O_{22}N_8P_8F_{48}$ (3388.4); calcd C 44.64, H 4.03, N 3.93; found C 44.65, H 4.22, N 3.68.

Bis[2]rotaxane 14·8PF$_6$: A solution of the tetrabromide **7** (85.8 mg, 0.13 mmol), **10**·2PF$_6$ [8c] (158 mg, 0.22 mmol), and the dumbbell-shaped component **8** (500 mg, 0.67 mmol) in MeCN (10 mL) were stirred for 14 d, after which time the solution had turned purple and a purple solid began to appear. The addition of Et_2O (50 mL) precipitated all the salt. The resulting purple solid was filtered off and chromatographed on a silica gel column (eluent: initially MeOH/2 M aq. NH_4Cl/$MeNO_2$ 7:2:1, and then original eluent/DMF/2 M aqueous NH_4Cl 1:0.5:0.5 and finally 1:1:1). The fractions containing the purple band were combined and concentrated in vacuo. The addition of water (50 mL) dissolved the solid residue. Saturated aqueous NH_4PF_6 was added to the purple solution. A purple solid precipitated out, which was filtered off and washed with water, CH_2Cl_2, and Et_2O. The solid was dried in vacuo, affording a purple powder **14**·8PF$_6$ (31 mg, 7%). M.p. > 270 °C. ^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ = 8.90–9.11 (m, 8H; bipyridinium α-*CH*), 8.84–8.90 (m, 4H; bipyridinium α-*CH*), 8.56–8.84 (m, 4H; bipyridinium α-*CH*), 8.08 (m, 8H; bipyridinium β-*CH*), 7.99 (d, ^3J = 7 Hz, 2H; Ar-H-3), 7.15–7.68 (m, 20H; bipyridinium β-*CH* and xylyl-H), 6.32 (d, 2H; naphthalene *H*-2 or *H*-6), 6.07 (m, 4H; naphthalene *H*-3,7), 5.75 (s, 12H; N-CH_2), 5.71 (s, 4H; N-CH_2), 5.54 (d, ^3J = 8 Hz, 2H; naphthalene *H*-2 or *H*-6), 4.72 (m, 4H; Ar-O-CH_2-alkyl), 4.33 (m, 8H; OCH_2), 4.21 (m, 8H; OCH_2), 4.15 (m, 8H; OCH_2), 4.02 (m, 8H; OCH_2), 3.92 (m, 8H; OCH_2), 3.78 (m, 8H; OCH_2), 2.69 (m, 2H; naphthalene *H*-4 or *H*-8), 2.47 (m, 2H; naphthalene *H*-4 or *H*-8), 2.24 (m, 4H; Ar-OCH_2-CH_2-alkyl), 1.87 (m, 12H; adamantoyl-CH), 1.83 (m, 4H; Ar-OCH_2CH_2-CH_2-alkyl), 1.74 (m, 24H; adamantoyl-CH_2), 1.57–1.72 (m, 24H; adamantoyl-CH_2); MS (8 keV, FAB): *m/z*: : 3665 $[M-PF_6]^+$, 3522 $[M-2PF_6]^+$, 3377 $[M-3PF_6]^+$; HRMS (LSIMS) $C_{166}H_{194}O_{22}N_8P_7F_{42}$: $[M-PF_6]^+$ calcd 3667.1834, found 3667.1820.

Bis(tetracationic cyclophane) 15·8PF$_6$: A solution of the tetrabromide **7** (66.0 mg, 0.10 mmol), **10**·2PF$_6$ [8c] (132 mg, 0.19 mmol), and the template **16** (300 mg, 0.56 mmol) in MeCN (10 mL) were stirred for 14 d, after which time the solution turned purple and a purple solid began to appear. The addition of Et_2O (50 mL) precipitated all the salt. The resulting purple solid was filtered off and dissolved in H_2O (100 mL). The purple aqueous layer was extracted continuously for 2 d with $CHCl_3$ to remove the template from the bispseudorotaxane. To the resulting yellow turbid aqueous phase was added saturated aqueous NH_4PF_6; this resulted in the precipitation of the cationic material, which was filtered off and chromatographed on a silica gel column (eluent: initially MeOH/2 M aq. NH_4Cl/$MeNO_2$ 7:2:1, and then original eluent/DMF/2 M aq. NH_4Cl 1:0.5:0.5 and finally 1:1:1). The fractions containing the bistetracationic cyclophane were combined and concentrated in vacuo. The addition of water (50 mL) dissolved the solid residue. Saturated aqueous NH_4PF_6 was added to the aqueous solution. A solid precipitated out, which was filtered off and washed with water, CH_2Cl_2, and Et_2O. The solid was dried in vacuo, affording a white powder **14**·8PF$_6$ (73 mg, 22%). M.p. > 270 °C. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ = 8.89 (m, 12H; bipyridinium α-*CH*), 8.83 (d, ^3J = 6 Hz, 4H; bipyridinium α-*CH*), 8.20 (m, 12H; bipyridinium β-*CH*), 8.16 (d, ^3J = 6 Hz, 4H; bipyridinium β-*CH*), 7.62 (d, ^3J = 8 Hz, 2H; Ar-*H*-3), 7.54 (s, 8H; *para*-xylyl-H), 7.27 (dd, ^3J = 8 Hz, ^4J = 1 Hz, 2H; Ar-*H*-4), 7.00 (d, ^4J = 1 Hz, 2H; Ar-*H*-5), 5.77 (s, 8H; NCH_2), 5.75, (s, 4H; NCH_2), 5.72 (s, 4H; NCH_2), 3.98 (t, ^3J = 8 Hz, 4H; OCH_2), 1.96 (m, 4H; OCH_2-CH_2), 1.62 (m, 4H; OCH_2CH_2-CH_2); ^{13}C NMR (75.5 MHz, CD_3COCD_3, 25 °C): δ = 158.6, 150.7, 150.6, 150.4, 150.3, 146.7, 139.0, 133.2, 131.4, 131.3, 128.3, 127.6, 125.3, 122.9, 113.9, 69.9, 66.1, 65.7, 61.5, 29.6, 26.4; HRMS (LSIMS) $C_{78}H_{74}N_8P_7F_{42}O_2$: $[M-PF_6]^+$ calcd 2169.3428, found 2169.3543.

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