

Cyclobis(paraquat-4,4'-biphenylene)—An Organic Molecular Square**

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Abstract: Template-directed syntheses of cyclobis(paraquat-4,4'-biphenylene) (**1**)—a *molecular square*—have been achieved by use of π -electron-rich macrocyclic hydroquinone-based and acyclic ferrocene-based templates. In particular, the use of a polyether-disubstituted ferrocene derivative as a template permits synthesis of **1** (which is accessible only in very low yields without templates) on a preparative scale. Furthermore, the use of a macrocyclic hydroquinone-based polyether template incorporating an ester function in one polyether chain—an “oriented” macrocycle—affords a 1:1 mixture of two topologically stereoisomeric [3]catenanes. Ester hydrolysis of the π -electron-rich

macrocyclic components mechanically interlocked with **1** within the catenated structures releases the tetracationic cyclophane in quantitative yield as a result of the degradation of the [3]catenanes. The molecular square has been characterized by X-ray crystallography, FAB mass spectrometry, ^1H NMR and ^{13}C NMR spectroscopies, and elemental analysis. The binding properties of **1** and of the smaller cyclophane cyclobis(paraquat-*p*-

phenylene) toward a series of π -electron-rich guests have also been investigated with the above techniques and UV/VIS spectroscopy. The self-assembly of the resulting supramolecular complexes in solution and in the solid state is driven mainly by π - π stacking interactions and hydrogen-bonding interactions, as well as by edge-to-face T-type interactions. In particular, the complexation of ferrocene or a ferrocene-based derivative within the cavity of **1** suggests the possibility of constructing functioning ferrocene-based molecular and supramolecular devices that can be controlled electrochemically in the form of catenanes, rotaxanes, and pseudorotaxanes.

Keywords

catenanes • second-sphere coordination • self-assembly • template syntheses • topological stereoisomerism

Introduction

Self-assembly^[1] processes are widely used in the biological world for the construction of large and complex molecular and supramolecular architectures. Striking illustrations of the beauty and efficiency of self-assembly are provided by the building up of thermodynamically stable structures such as the tobacco mosaic virus,^[2] DNA,^[3] and the enzyme ribonuclease.^[4] As a result of a so-called nucleation step, an initial structure (seed) is generated by the combination of simple complementary subunits through either covalent or noncovalent bonding interactions. The seed has built into it all the necessary information for the subsequent growth of the entire assembly by a series of cooperative phenomena. The virtues of these genealogically directed syntheses^[5] include i) overall high efficiency, ii) built-in error checking and recovery, and consequently iii) a high degree of control over the self-assembly of such complex structures.

These features and properties of biological self-assembly processes have won the attention of synthetic chemists in recent years to the extent that an increasing number of examples of abiotic self-assembling systems, based on covalent and noncovalent bonding interactions, have been reported in the literature since the mid-1980s. A wide variety of synthetic molecular and supramolecular architectures, such as double-stranded helicates,^[6] interlocked systems,^[7] liquid crystals,^[8] molecular crystals,^[9] hydrogen-bonded aggregates,^[10] receptor–substrate complexes,^[11] and Langmuir–Blodgett films^[12] have been generated, demonstrating the versatility and applicability of self-assembly processes. Particular interest has focused on the use of templates in order to promote the assembly of wholly synthetic complex molecular architectures—otherwise accessible only in very low yields—by so-called template-directed syntheses.^[13]

Recently, we have developed^[14] a synthetic methodology for the template-directed syntheses of mechanically interlocked molecular structures, such as catenanes^[15] and rotaxanes^[16] via precatenanes and pseudorotaxanes.^[17] These molecular and supramolecular architectures (Fig. 1) are comprised of two or more complementary subunits held together by a series of noncovalent bonding interactions and, in the case of catenanes and rotaxanes, by a *mechanical bond*. Their self-assembly in solution is driven mainly by i) π - π stacking interactions between the π -electron-deficient bipyridinium units and the π -electron-rich hydroquinone rings,^[18] ii) hydrogen-bonding interactions between the acidic hydrogen atoms in the α positions with respect to the nitrogen atoms of the bipyridinium units and the

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[**] “Molecular Meccano”, Part 8: for Part 7, see P. R. Ashton, P. T. Glink, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 729–736.

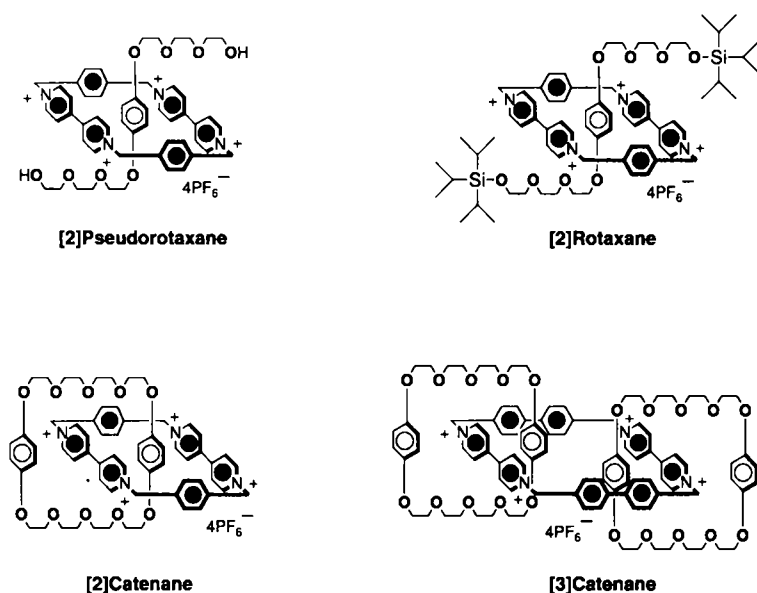


Fig. 1. Mechanically interlocked structures and superstructures incorporating π -electron-deficient bipyridinium-based cyclophanes and π -electron-rich hydroquinone-based polyether derivatives.

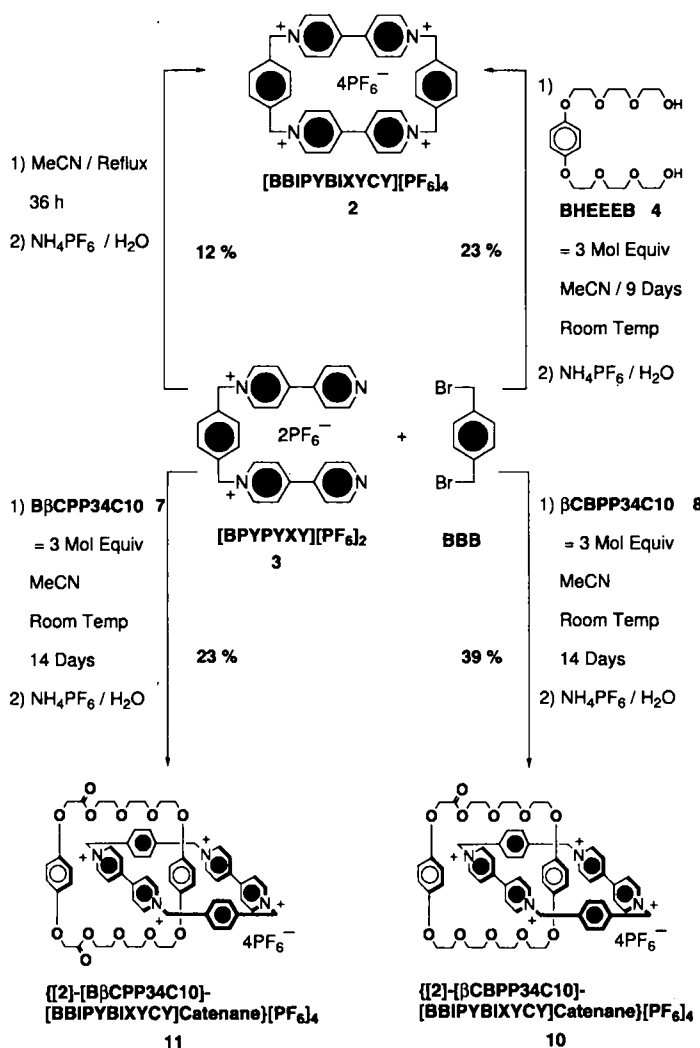
polyether oxygen atoms,^[19] and iii) edge-to-face T-type interactions between the hydrogen atoms attached to the hydroquinone ring and the π systems of the aromatic spacers separating the bipyridinium units.^[20] Thus, the single components possess the necessary stereoelectronic *information* required to produce an initial structure (nucleation), which is then converted by covalent bonding (growth) into the targeted interlocked molecular compound. The careful design of the matching subunits is therefore extremely important. The entire self-assembly process is driven by their information content expressed through their stereoelectronic properties. In the last few years,^[14, 21, 22] we have demonstrated how versatile this self-assembling approach is by the synthesis of a wide range of molecular compounds and supramolecular arrays, and also how reminiscent of the more complex processes occurring in nature it is. Against this background we have exploited the possibility of employing the self-assembly principle to template the formation of the rigid tetracationic cyclophane cyclobis(paraquat-4,4'-biphenylene) ([BBIPYBIBTCY][PF₆]₄, **1**) having approximately 90° bond angles and so constituting an organic molecular square.^[23] Recently, numerous rigid tetranuclear cationic macrocycles—the members of a new family of hosts—have been synthesized.^[23] However, iodine atoms or transition metals have usually been incorporated at the corners of the squares. In contrast, **1** is the first example of a rigid *organic* molecular square.

Results and Discussion

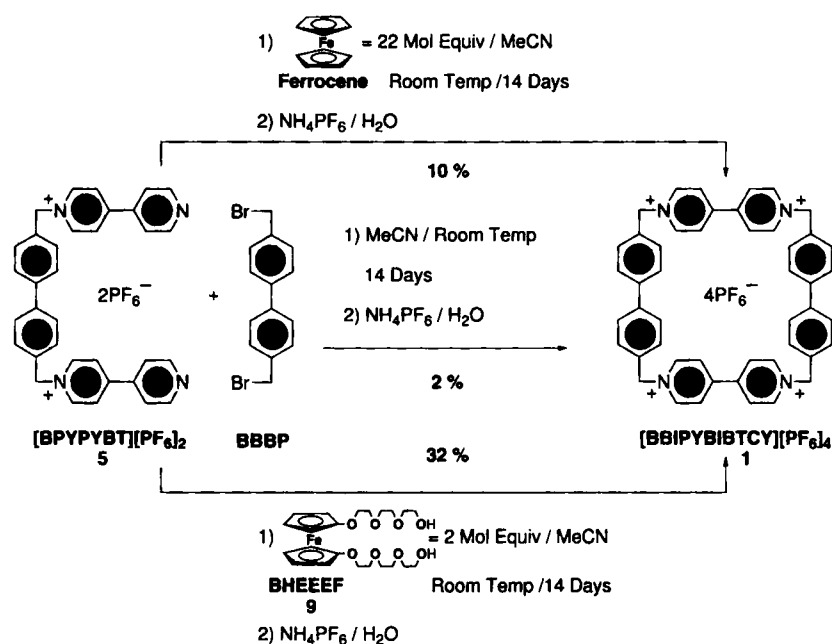
Names: It is convenient at this point to explain the abbreviations used throughout the text and in the illustrations. Compounds 1,4-dihydroxybenzene, 4-benzyloxyphenol, 1,4-(bisbromomethyl)benzene, 4,4'-(bisbromomethyl)-1,1'-biphenyl and bis-*p*-phenylene-34-crown-10 are abbreviated to **1/4DHB**, **4BNP**, **BBB**, **BBBP**, and **BPP34C10**, respectively. The salt 4,4'-dimethylbipyridinium hexafluorophosphate—commonly known as paraquat—is abbreviated to [PQT][PF₆]₂. The other acronyms can be understood by applying the following rules. **B** stands for benzene when present at the end of a name and for bis

when present in other parts of the name. **A**, **BN**, **C**, **E**, **H**, and **M** stand for acetoxy, benzyloxy, carbonyl, ethoxy, hydroxy, and methoxy groups, respectively. **CY**, **XY**, **BT**, **BIXY**, **BIBT**, **BIPY**, and **PYPY** stand for cyclophane, xylene, bitolyl, bisxylene, bis-bitolyl, bipyridinium, and pyridylpyridinium units, respectively. β indicates the position of the carbonyl groups in the polyether chains, starting from the carbon atom directly attached to the hydroquinone ring.

Synthesis: The cyclophane [BBIPYBIXCY][PF₆]₄ (**2**) can be synthesized in a 12% yield^[14b] (Scheme 1) by reacting **BBB** with [BPYPYXY][PF₆]₂ (**3**) in MeCN under reflux over 36 h. The yield can be increased^[14b] to 23% by performing the reaction at room temperature in the presence of 3.0 molar equivalents of the templating agent **BHEEBB** (**4**). The larger cyclophane [BBIPYBIBTCY][PF₆]₄ (**1**), in which the two bipyridinium units are separated by biphenylene spacers, is able to accommodate two hydroquinone rings in its cavity, as proven by the template-directed synthesis of the [3]catenane depicted in Figure 1.^[14c, 21b] Unfortunately, the direct synthesis (Scheme 2) of the cyclophane itself is extremely low-



Scheme 1. Synthesis of the cyclophane [BBIPYBIXCY][PF₆]₄ (**2**) with and without the templating agent **BHEEBB** (**4**), and of the [2]catenanes [2]-[BBP34C10]-[BBIPYBIXCY]catenane[PF₆]₄ (**10**) and [2]-[BBP34C10]-[BBIPYBIXCY]catenane[PF₆]₄ (**11**).



Scheme 2. Synthesis of the cyclophane [BBIPYBiBTCY][PF₆]₄ (**1**) with and without the templating agents ferrocene or BHEEEF (**9**).

yielding. The reaction of [BPYPYBT][PF₆]₂ (**5**) with an equimolar amount of BBBP in MeCN at room temperature over 14 days gave the tetracationic cyclophane in only a 2% yield!^[14c] Changes to the reaction conditions—namely reagent concentration, temperature, and time—only caused the yield of **1** to decrease (Table 1). By analogy with the synthesis of the smaller cyclophane **2**, we envisaged the possibility of employing a templating agent such as BHEEEB in order to increase the yield above 2%.

Table 1. Reaction conditions and yields for the formation of [BBIPYBiBTCY][PF₆]₄ (**1**) from MeCN solutions containing equimolar amounts of [BPYPYBT][PF₆]₂ (**5**) and BBBP.

Concentration (M) [a]	Temperature (°C)	Time (d)	Yield (%)
8.5 · 10 ⁻³	25	14	2.0
6.0 · 10 ⁻³	0	28	0.6
6.0 · 10 ⁻³	80	2	0.5
4.0 · 10 ⁻⁴	25	14	traces
4.0 · 10 ⁻⁴	50	7	traces

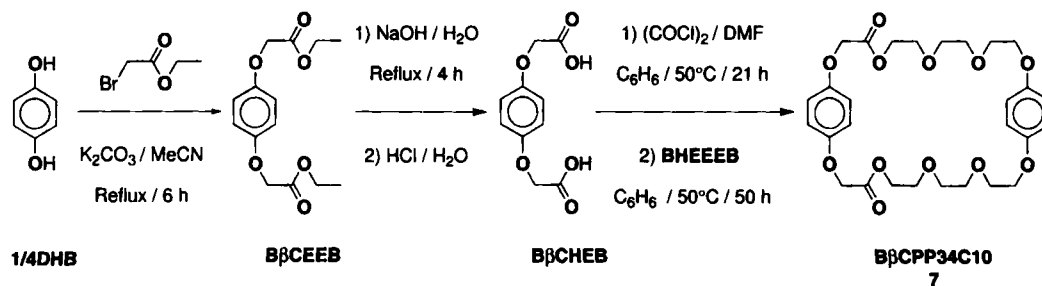
[a] Concentration of [BPYPYBT][PF₆]₂ or BBBP.

The reaction of [BPYPYBT][PF₆]₂ (**5**) and BBBP in equimolar amounts in the presence of 6.0 molar equivalents of BHEEEB (**4**) in MeCN at room temperature over 14 days afforded the cyclophane **1** in 5% yield. Although the presence of this templating agent, under otherwise identical conditions, increases the yield by a factor of two and a half, the outcome is still far from satisfactory. By contrast, when the crown ether BPP34C10 (**6**) is present in the reaction mixture as

3.0 molar equivalents instead of the acyclic BHEEEB, the yield of the resulting [3]catenane^[14c, 21b] (Fig. 1) is 22%. Indeed, the self-assembly of the [3]catenane seems to be a lot more easily achieved than the synthesis of one of its components! Nevertheless, since the three macrocyclic units are mechanically linked in the catenated structure, the release of the intact cyclophane **1** from the [3]catenane would only be possible after the cleavage of one of the covalent (C–O) bonds in both the macrocyclic polyethers. Several unsuccessful attempts were made to cleave an ether bond within the two crown ether components of the [3]catenane. Degradation of the bipyridinium-based cyclophane occurs under the severe reaction conditions necessary to cleave the ether bonds (for example, 60% HPF₆ at 50 °C or 95–98% H₂SO₄ at room temperature), preventing a successful outcome to this approach. We therefore reasoned that, by introducing into the polyether chains of the two crown ethers a functionality such as a carboxylic ester that could be hydrolyzed under relatively mild acidic conditions, it should be possible to cleave such macrocyclic polyether lactones and

release the intact cyclophane from the [3]catenane. We chose the macrocyclic polyether bislactone BβCPP34C10 (**7**) as a candidate for the proposed experiment.

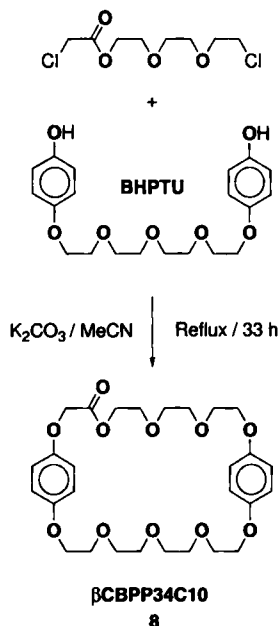
The synthesis of **7** was achieved following the route shown in Scheme 3. The reaction of 1/4DHB with ethyl bromoacetate afforded the dicarboxylic diester BβCEEB. The hydrolysis of BβCEEB under basic conditions afforded the corresponding salt, which was precipitated, on acidification, as the dicarboxylic acid BβCHEB. Reaction of this dicarboxylic acid with oxalyl chloride produced the diacid chloride, which was used immediately in the next step of the reaction sequence. A solution of the crude diacid chloride in dry benzene and an approximately equimolar benzene solution of BHEEEB (**4**) were added simultaneously, from separate dropping funnels, to a large volume of dry benzene. The reaction gave **7** in a yield of 23% relative to **4**. In order to assess the ability of this macrocyclic polyether bislactone to form catenates by the familiar self-assembly approach, we treated [BPYPYXY][PF₆]₂ (**3**) with BBB (Scheme 1) in MeCN at room temperature for 14 days in the presence of **7**. The reaction afforded the corresponding [2]catenane in 23% yield, whereas, in contrast, the [2]catenane incorporating BPP34C10 is formed^[14b, 21a] in 70% yield under otherwise identical conditions. When we attempted to self-assemble a [3]catenane by reacting [BPYPYBT][PF₆]₂ (**5**) with BBBP in either MeCN or DMF in the presence of BβCPP34C10 (**7**), no catenated compounds could be isolated or indeed detected by thin-layer chromatography. Surprisingly, the introduction with-



Scheme 3. Synthesis of the π-electron-rich macrocyclic bislactone BβCPP34C10 (**7**).

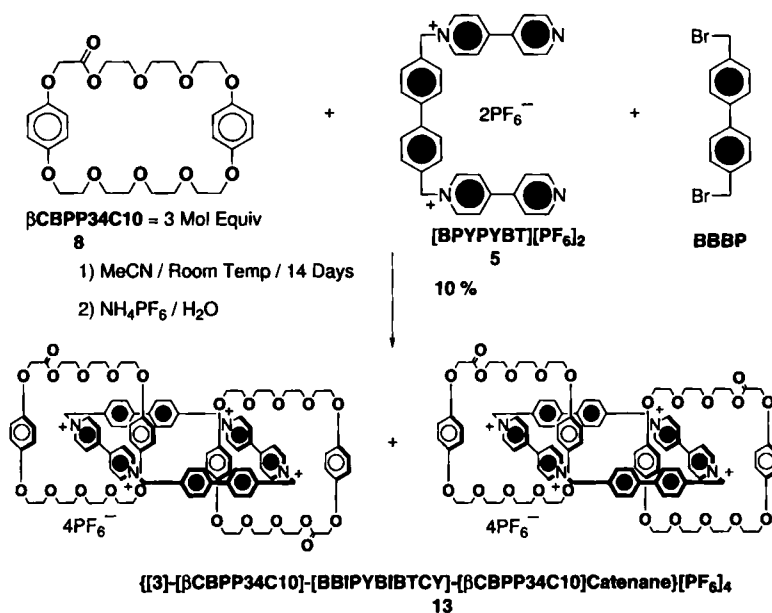
in each polyether chain of a carbonyl group in place of a methylene group has a dramatic effect upon the recognition characteristics of the macrocycle during the attempted catenation, to the extent that the self-assembly process is inhibited completely.

On the basis of these negative results, we decided to synthesize the macrocyclic polyether lactone **β CBPP34C10** (**8**), which, having only one carbonyl



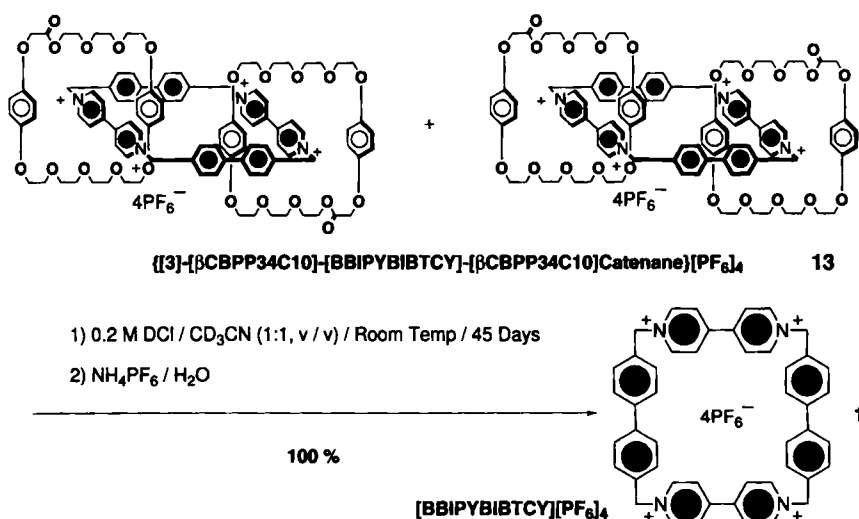
Scheme 4. Synthesis of the π -electron-rich macrocyclic lactone **β CBPP34C10** (**8**).

group in one of the two polyether chains, should be stereoelectronically more similar to **6**. The synthesis of **8** was carried out by the route shown in Scheme 4. The high-dilution reaction of **BHPTU** with 2-[2-(2-chloroethoxy)ethoxy]ethyl chloroacetate in the presence of excess potassium carbonate afforded **8** in a yield of only 4% relative to **BHPTU**. Treatment of **[BPYPYXY][PF₆]₂** (**3**) with **BBB** in MeCN in the presence of **8** (Scheme 1) afforded the corresponding [2]catenane in a 39% yield. As expected, the yield of the [2]catenane was lower than the 70% yield of the **BPP34C10**-containing [2]catenane, but it was significantly higher than the 23% yield of the **B β CPP34C10**-containing [2]catenane. By treating **[BPYPYBT][PF₆]₂** (**5**) with **BBBP** in MeCN in the presence of **8** (Scheme 5), a mixture of two topologically stereoisomeric [3]catenanes was obtained in an overall yield of 10%. The *oriented* topology of the π -electron-rich macrocyclic lactone **8** results in the formation of two isomeric [3]catenanes, differing in the relative orientations of the two π -electron-rich components within the interlocked structure. The presence of two isomers was confirmed by the ¹H NMR spectrum recorded at room temperature in CD₃CN. As a result of the asymmetry of the π -electron-rich components caused by the presence of the carbonyl group on one of the polyether chains, the hydrogen atoms of the methylene groups incorporated within the tetracationic cyclophane are diastereotopic. Furthermore, since the rotation of the π -electron-rich macrocycles through the cavity of the tetracationic cyclophane is fast on the ¹H NMR timescale at room temperature, the methylene protons incorporated within the π -electron-deficient macrocycle resonate as a single AB system for each topologically stereoisomeric [3]catenane. The ¹H NMR spectrum shows two partially overlapping AB systems for the CH₂-N hydrogen atoms, indicating the presence of two distinct species in solution, the two topologically isomeric [3]catenanes. Several attempts to separate this isomeric mixture



Scheme 5. Synthesis of the two topological stereoisomers of the [3]catenane {[3]- **β CBPP34C10**-[**BBIPYBIBTCY**]- **β CBPP34C10**catenane}[PF₆]₄ (**13**).

by HPLC were unsuccessful: the two isomers were eluted with exactly the same retention times under all the many different conditions that were attempted. The mixture of the two isomeric [3]catenanes was hydrolyzed (Scheme 6) in 0.2 M DCl/CD₃CN at room temperature over 45 days to yield the cyclophane **[BBIPYBIBTCY][PF₆]₄** (**1**) in 100% yield. The reaction was followed by ¹H NMR spectroscopy; the partial spectra, recorded at different intervals, are reproduced in Figure 2. The spectrum of the starting reaction mixture (Fig. 2a) shows a doublet corresponding to the α protons of the bipyridinium units incorporated within the [3]catenane structures. After 1 day, a second doublet starts to emerge at lower field (Fig. 2b). This resonance corresponds to the α protons of the bipyridinium units incorporated within the [2]catenane derived from the [3]catenane following hydrolysis of the first ester bond. After 6 days, the signal for the α protons of the bipyridinium units in the free cyclophane begin to appear at even lower field (Fig. 2c). The last two spectra show the disappearance of the resonances for the



Scheme 6. Synthesis of the cyclophane **[BBIPYBIBTCY][PF₆]₄** (**1**) by acid hydrolysis of the two topological stereoisomers of the [3]catenane {[3]- **β CBPP34C10**-[**BBIPYBIBTCY**]- **β CBPP34C10**catenane}[PF₆]₄ (**13**).

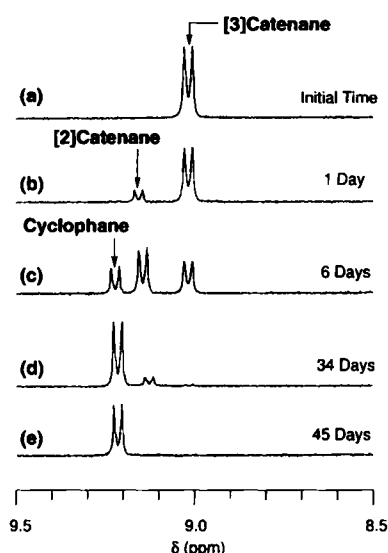
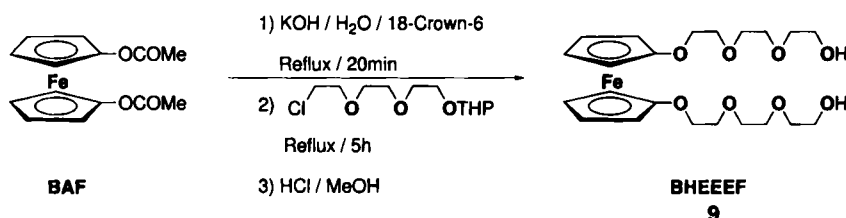


Fig. 2. Partial ^1H NMR spectra of $\{[3]-[\beta\text{CBPP}34\text{C}10]-[\text{BBIPYBIBTCY}]-[\beta\text{CBPP}34\text{C}10]\text{catenane}\}[\text{PF}_6]_4$ (**13**) in 0.2M DCl/ CD_3CN recorded at room temperature a) at the initial time and after b) 1 d; c) 6 d; d) 34 d; e) 45 d.

[3]catenanes and finally of those for the [2]catenane (Figs. 2d and 2e), demonstrating that the reaction has finally gone to completion.

Although the reaction described in Scheme 6 is a quantitative one, the low yield (4%) of the macrocyclic polyether lactone $\beta\text{CBPP}34\text{C}10$ (**8**) and subsequently of the [3]catenanes (10%), along with the amount of effort and time required for the preparation of all the precursors, make the method a rather inconvenient and inefficient one overall. The X-ray crystal structure^[14c, 21b] of the [3]catenane **12** suggested to us a possible alternative route for templating the formation of the cyclophane **1**. Since the interplanar distance between the two hydroquinone rings residing inside the cavity of the cyclophane in the [3]catenane is 3.63 Å (Fig. 3), an ideal templating agent should incorporate in its structure two parallel π systems that are electron-rich and are able to participate in π - π stacking interactions with the bipyridinium moieties separated by a distance of about 3.6 Å. Rather conveniently, the two cyclopentadienyl rings incorporated



Scheme 7. Synthesis of the 1,1'-disubstituted ferrocene derivative **BHEEF** (**9**).

within the structure of ferrocene are separated by a distance of 3.32 Å^[24] (Fig. 3). Furthermore, many examples of charge-transfer complexes formed between ferrocene derivatives and π -electron-deficient compounds have been reported^[25] in the literature. We therefore decided to employ ferrocene as a templating agent for the synthesis of **1** and, indeed, the reaction (Scheme 2) of **5** with **BBBP** in MeCN in the presence of 22 molar equivalents of ferrocene at room temperature over 14 days yielded **1** in 10% yield.^[26] Encouraged by this result, we decided to synthesize a ferrocene-based derivative bearing polyether chains attached to the cyclopentadienyl rings in order to improve, by hydrogen-bonding interactions, the templating ability of the template. The synthesis of **BHEEF** (**9**) was achieved as outlined in Scheme 7.^[26] The base-promoted hydrolysis of **BAF** followed by alkylation with protected 2-[2-(2-chloroethoxy)ethoxy]ethanol in situ afforded **BHEEF** after the removal of the tetrahydropyran protecting groups. By reacting **5** with **BBBP** in MeCN in the presence of 2 molar equivalents of **BHEEF** at room temperature over 14 days (Scheme 2), $\{[\text{BBIPYBIBTCY}][\text{PF}_6]_4\}$ (**1**) was obtained in 32% yield,^[26] that is, some 16 times more than the original 2% yield obtained in the absence of any template at all.

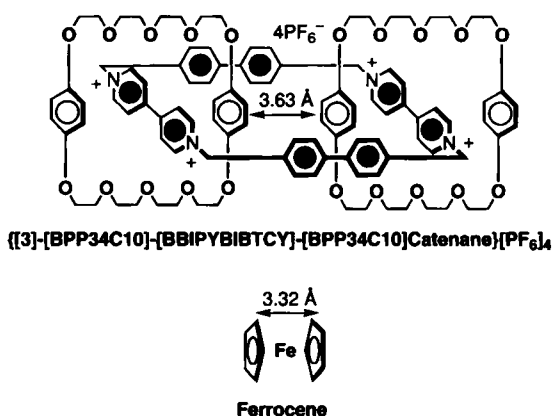


Fig. 3. Comparison between the distance separating the mean planes of the two hydroquinone rings residing inside the cavity of the tetracationic cyclophane within the [3]catenane $\{[3]-[\text{BPP}34\text{C}10]-[\text{BBIPYBIBTCY}]-[\text{BPP}34\text{C}10]\text{catenane}\}[\text{PF}_6]_4$ (**12**) and the interplanar separation between the cyclopentadienyl rings of ferrocene.

Association constants: In order to investigate the depression of the catenation yields that we observed upon introduction of one and then two carbonyl groups within the polyether chains of the π -electron-rich macrocycles, we decided to investigate the binding properties of a series of model compounds. The π -electron-rich macrocycles **BPP34C10** (**6**),^[27] **B β CPP34C10** (**7**), and **β CBPP34C10** (**8**) all form 1:1 complexes in solution with the simple bipyridinium dication $[\text{PQT}][\text{PF}_6]_2$ (Fig. 4). The association constants for these complexes in Me_2CO were evaluated (Table 2) by UV/Vis spectroscopy by probing the charge-transfer band arising from the interaction between the π -electron-rich

Table 2. Association constants for the 1:1 complexes formed at 25 °C in Me_2CO between $[\text{PQT}][\text{PF}_6]_2$ and the π -electron-rich macrocycles **BPP34C10** (**6**), **B β CPP34C10** (**7**), and **β CBPP34C10** (**8**), as well as for the 1:1 complexes formed at 25 °C in MeCN between $[\text{BBIPYBIBTCY}][\text{PF}_6]_4$ (**2**) and the π -electron-rich acyclic derivatives **BMEEB**, **β CBMEEB**, and **B β CBMEEB**.

Compound	K_a (M^{-1})	$-\Delta G^\circ$ (kcal mol^{-1})	λ_{max} [d] (nm)
BPP34C10 [a,b]	730	3.9	436
βCBPP34C10 [a]	73	2.5	427
BβCPP34C10 [a]	5	1.0	417
BMEEB [c]	3800	4.9	—
βCBMEEB [c]	680	3.9	—
BβCBMEEB [c]	520	3.7	—

[a] The association constants (K_a) were evaluated by UV/Vis spectroscopy with titration methodology (ref. [30]). [b] The values of K_a , $-\Delta G^\circ$, and λ_{max} reported for the complex $[\text{BPP}34\text{C}10][\text{PQT}][\text{PF}_6]_2$ are literature values (ref. [27]). [c] The association constants (K_a) were evaluated by ^1H NMR spectroscopy by the continuous variation method (ref. [30]). The protons attached to the hydroquinone ring of the guest were used as the probe. [d] Wavelength corresponding to the maximum of the charge-transfer band originating from the interaction between the bipyridinium unit and the hydroquinone rings.

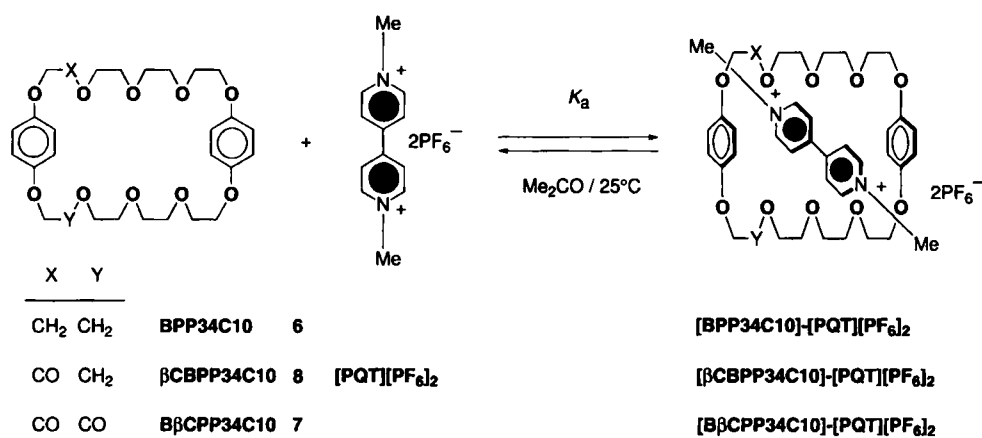


Fig. 4. Complexation of [PQT][PF₆]₂ by the π -electron-rich macrocycles BPP34C10 (6), β CBPP34C10 (8), and B β CPP34C10 (7).

hydroquinone rings and the π -electron-deficient bipyridinium unit inserted into the cavities of the macrocycles. On introduction of one carbonyl group in the β position in one of the polyether chains of the macrocycle, the association constant decreases from 730 to 73 M⁻¹. The introduction of a second carbonyl group in the β position on the other polyether chain of the macrocycle leads to a decrease in the association constant from 73 to 5 M⁻¹. The dramatic reduction of the binding ability of the π -electron-rich macrocycles upon the stepwise insertion of these two carbonyl groups is directly reflected in the yields obtained during self-assembly of the catenanes. The correlation between the binding energies for the complexation of [PQT][PF₆]₂ and the yields of the catenated products with the three different macrocycles BPP34C10 (6), β CBPP34C10 (8), and B β CPP34C10 (7) is apparently linear (Fig. 5). Similarly, the association constants for the binding of the acyclic model compounds BMEEB, β CMEEB, and B β CMEEB (Fig. 6) by the cyclophane [BBIPYBIXYCY][PF₆]₄ (2).

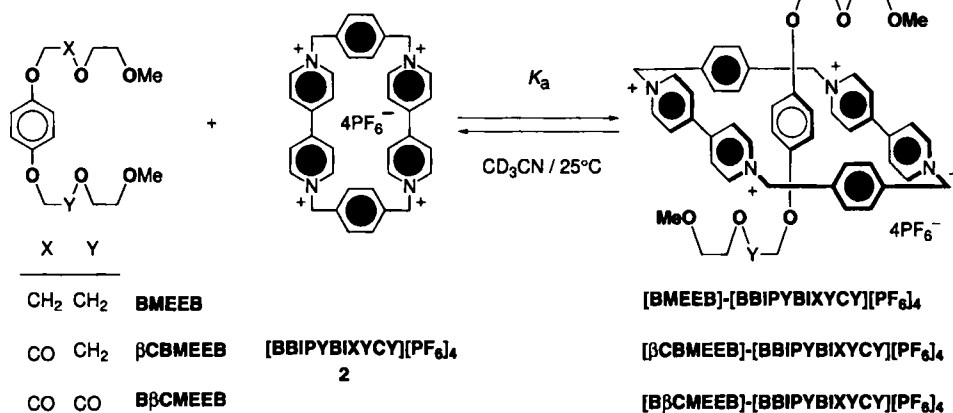


Fig. 6. Complexation of the π -electron-rich acyclic derivatives BMEEB, β CMEEB, and B β CMEEB by the cyclophane [BBIPYBIXYCY][PF₆]₄ (2).

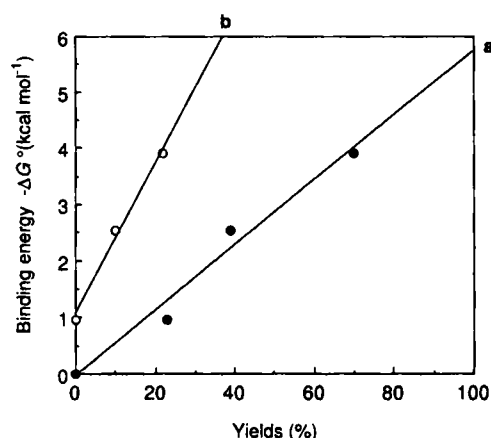
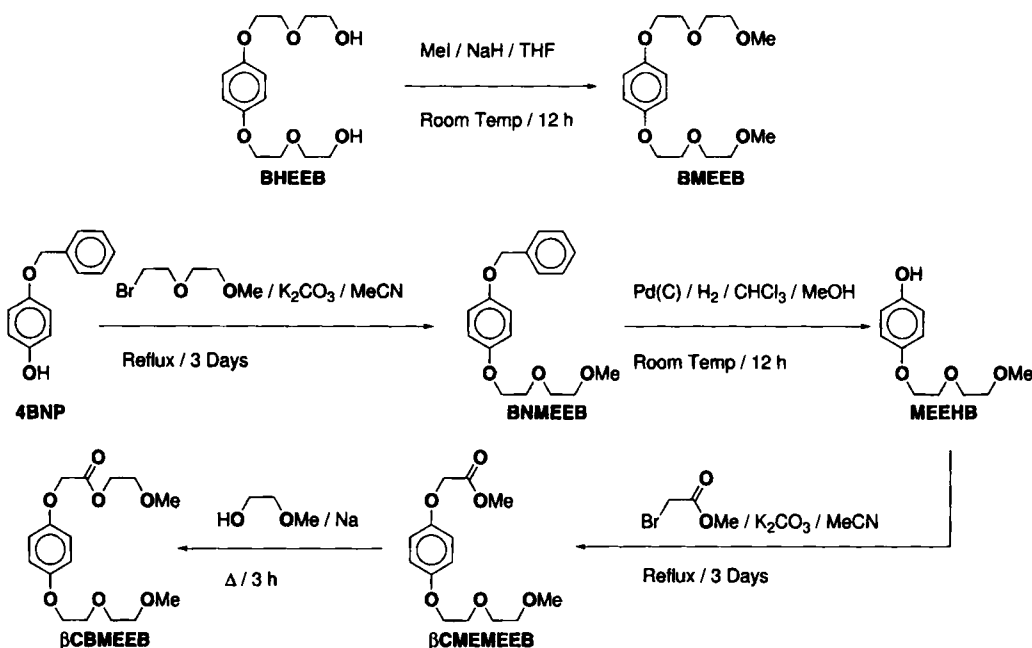
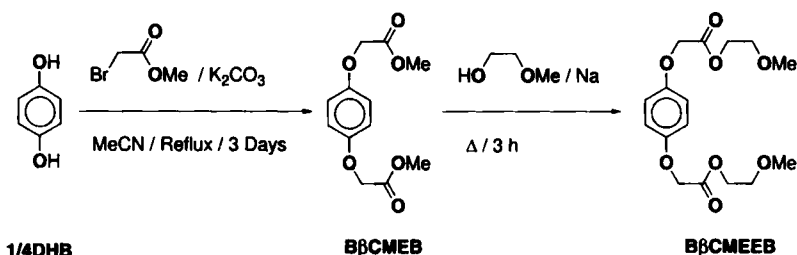


Fig. 5. Correlation between the binding energy for the complexation of [PQT][PF₆]₂ in Me₂CO at 25°C and the yields for the formation of a) the [2]catenane and b) the [3]catenane for the π -electron-rich macrocycles BPP34C10 (6), β CBPP34C10 (8), and B β CPP34C10 (7).

BIXYCY][PF₆]₄ (2) are dramatically affected by the presence of the ester functions within the polyether chains. The ether BMEEB and the esters β CMEEB and B β CMEEB were synthesized as shown in Schemes 8 and 9. Reaction (NaH/THF) of BHEEB with methyl iodide gave BMEEB. Alkylation of 4BNP with 1-bromo-2-(2-methoxyethoxy)ethane, followed by hydrogenolysis, gave the compound MEEHB. Reaction of MEEHB with methyl bromoacetate, followed by transesterification of β CMEMEEB, gave the π -electron-rich acyclic ester β CBMEEB. Alkylation (K₂CO₃/MeCN) of 1/4DHB methyl bromoacetate, followed by transesterification of B β CMEEB, afforded the π -electron-rich acyclic diester B β CMEEB. The association constants (Table 2) in MeCN for the 1:1 complexes formed by the tetracationic cyclophane and the π -electron-rich acyclic derivatives were evaluated by ¹H NMR spectroscopy with the hydroquinone protons as the probe. Introduction of one carbonyl group into one of the polyether chains of the π -electron-rich acyclic derivative brings about a decrease in the association constant from 3800 to 680 M⁻¹. On introduction of a second carbonyl group into the other polyether chain, the association constant decreases from 680 to 520 M⁻¹. Once again, the presence of the carbonyl group has a dramatic effect upon the recognition process, probably by decreasing the strength of the hydrogen-bonding interactions between the acidic α protons on the bipyridinium units and the oxygen atoms present in the two polyether chains by a combination of adverse steric and electronic effects. A continuous variation plot for the binding of BHEEB (4) by 2 shows a maximum corresponding to a 1:1



Scheme 8. Synthesis of the π -electron-rich acyclic derivatives **BMEEB** and β **CBMEEB**.



Scheme 9. Synthesis of the π -electron-rich acyclic derivative β **CBMEEB**.

stoichiometry for the complex formed in CD_3CN (Fig. 7a). When the same experiment was carried out for the binding of **4** by the larger cyclophane **[BBIPYBIBTCY][PF₆]₄** (**1**), the curve maximum no longer corresponds to 1:1 stoichiometry (Fig. 7b). Nevertheless, the FAB mass spectrum of an equimolar MeCN solution of **1** and **4** had a peak at $m/z = 1626$, corresponding to the "molecular weight" of the 1:1 complex, and two other peaks at $m/z = 1481$ and 1336 , corresponding to the loss

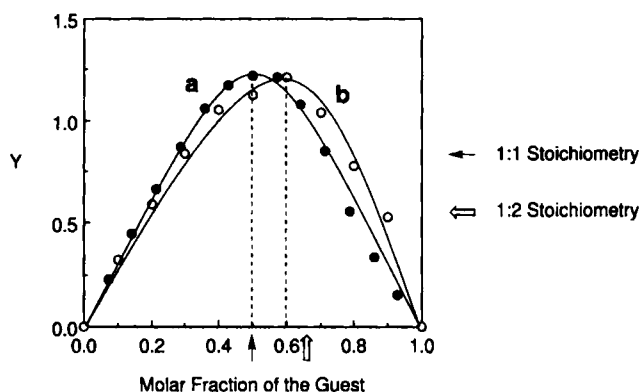


Fig. 7. Continuous variation plots for the complexation of **BHEEB** (**4**) by the cyclophane **[BBIPYBIXYCY][PF₆]₄** (**2**) in CD_3CN at 25°C . a) Y = Molar fraction of the guest \times chemical shift difference for the probe protons and **[BBIPYBIBTCY][PF₆]₄** (**1**); b) Y = Molar fraction of the guest \times chemical shift difference for the probe protons $\times 50$.

of one and two hexafluorophosphate counterions, respectively, from the complex. The determination of the association constants by ^1H NMR spectroscopy employing titration methodology^[28] revealed the presence in solution of both a 1:1 complex ($K_a = 36\text{M}^{-1}$, $\Delta G^\circ = -2.1\text{ kcal mol}^{-1}$) and a 2:1 complex ($K_a = 12\text{M}^{-1}$, $\Delta G^\circ = -1.5\text{ kcal mol}^{-1}$). As expected, **[BBIPYBIBTCY][PF₆]₄** (**1**), with a larger cavity than **[BBIPYBIXYCY][PF₆]₄** (**2**), is able to accommodate two hydroquinone units in its cavity, affording not only a 1:1

complex, but, consistently with the catenated structure represented in Figure 1, a 2:1 complex. This complex was subsequently characterized in the solid state (vide infra).

In order to probe and explain the successful template-directed syntheses (Scheme 8) of **1** by the ferrocene derivatives, we evaluated the association constants for the 1:1 complexes (Fig. 8) formed between this tetracationic cyclophane and i) ferrocene and ii) **BHEEF** (**9**). These are fascinating examples of second-sphere coordination^[29] in operation. The association constants were determined in CD_3CN by ^1H NMR spectroscopy by means of a titration methodology^[30] and by means of the protons in the β positions with respect to the nitrogen atoms on the bipyridinium units within the tetracationic cyclophane. In the case of ferrocene, the association constant was found to be 80M^{-1} ,^[26] corresponding to a binding energy of $-2.6\text{ kcal mol}^{-1}$. By contrast, the association constant for the binding of **9** by **1** was found to be 1600M^{-1} ,^[26] corresponding to a binding energy of $-4.4\text{ kcal mol}^{-1}$. The large increase in the K_a value on going from ferrocene to **BHEEF** (**9**) is caused by the presence of the polyether chains, which are able to support hydrogen-bonding interactions with the acidic protons on the bipyridinium units within the tetracationic cyclophane. The formation of the 1:1 complex between **1** and **9** was confirmed by FAB mass spectrometry. The FAB mass spectrum showed a peak at $m/z = 1735$ corresponding to the "molecular weight" of the complex, and three other peaks at $m/z = 1589$, 1443 , and 1298 originating from the loss of one, two, and three hexafluorophosphate counterions, respectively.

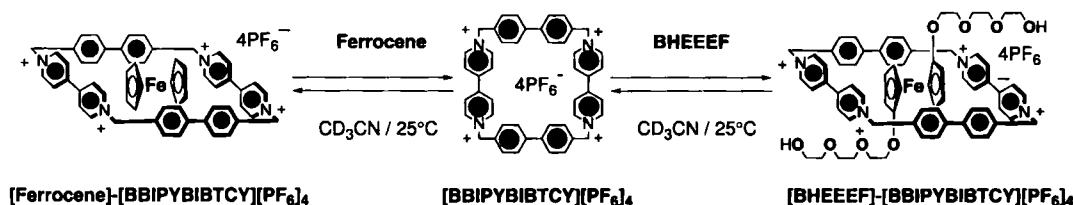


Fig. 8. Complexation of ferrocene and BHEEF (9) by the cyclophane [BBIPYBIBTCY][PF₆]₄ (1).

¹H NMR spectroscopy: The chemical shifts (δ) in the ¹H NMR spectra of the most significant resonances for a wide range of complexes in CD₃CN at room temperature are listed in Table 3. Upon mixing equimolar amounts of BPP34C10 and [PQT][PF₆]₂ in CD₃CN at room temperature, an orange color develops immediately as a result of the charge-transfer interaction between the bipyridinium unit and the hydroquinone rings.

Table 3. ¹H NMR spectroscopic data (δ values) for the complexes and reference compounds in CD₃CN at room temperature.

Compound	Polycationic Component α -CH [a] β -CH [b]	Neutral Component ArH [c] CpH [d]
[PQT][PF ₆] ₂	8.84 8.36	
BPP34C10		6.73
[BPP34C10]-[PQT][PF ₆] ₂	8.80 8.07	6.44
β CBPP34C10		6.77
[β CBPP34C10]-[PQT][PF ₆] ₂	8.83 8.32	6.71
B β CPP34C10 [e]		6.79, 6.78
[B β CPP34C10]-[PQT][PF ₆] ₂ [e]	8.84 8.36	6.77, 6.76
[BBIPYBIXYCY][PF ₆] ₄	8.89 8.17	
BMEEB		6.85
[BMEEB]-[BBIPYBIXYCY][PF ₆] ₄	8.91 7.89	4.49
β CBMEEB		6.85
[β CBMEEB]-[BBIPYBIXYCY][PF ₆] ₄	8.89 8.07	5.45
B β CMEEB		6.85
[B β CMEEB]-[BBIPYBIXYCY][PF ₆] ₄	8.89 8.13	6.36
[BBIPYBIBTCY][PF ₆] ₄	8.94 8.25	
BHEEF		6.85
[BHEEF]-[BBIPYBIBTCY][PF ₆] ₄ [f]	8.94 8.24	6.81
ferrocene		4.16
[ferrocene]-[BBIPYBIBTCY][PF ₆] ₄	8.89 8.12	4.08
BHEEF [g]		4.12, 3.94
[BHEEF]-[BBIPYBIBTCY][PF ₆] ₄ [g]	8.95 8.09	2.63, 2.41

[a] Protons attached to the bipyridinium units in the α position with respect to the nitrogen atoms. [b] Protons attached to the bipyridinium units in the β position with respect to the nitrogen atoms. [c] Protons attached to the hydroquinone rings incorporated within the π -electron-rich components. [d] Protons attached to the cyclopentadienyl rings of the ferrocene derivatives. [e] The π -electron-rich macrocycle β CBPP34C10 incorporates two hydroquinone rings, each giving rise to a singlet in the ¹H NMR spectrum. [f] Equimolar solution of BHEEF and [BBIPYBIBTCY][PF₆]₄, containing both the 1:1 and the 2:1 complexes. [g] The 1,1'-disubstituted ferrocene derivative BHEEF comprises two pairs of heterotopic protons for each of the two equivalent cyclopentadienyl rings. In the ¹H NMR spectrum at room temperature, these protons give rise to two broad resonances, each centered on the δ value reported in the table.

The ¹H NMR spectrum of the 1:1 mixture reveals significant upfield shifts for the resonances in both the host and the guest. The hydrogen atoms attached to the hydroquinone rings, as well as those α and β to the nitrogen atoms on the bipyridinium unit, are shifted upfield and associated with $\Delta\delta$ values of -0.29 , -0.04 , and -0.29 , respectively. The chemical shift differences observed for these resonances are a consequence of the close spatial proximity of the complementary aromatic units as a result of the pseudorotaxane-like geometries^[14b] (Fig. 4) possessed by these supramolecular complexes. By contrast, when the π -electron-rich macrocycles β CBPP34C10 (8) and B β CPP34C10 (7), containing ester functions within their

polyether chains, are mixed with equimolar amounts of [PQT][PF₆]₂, no significant differences in the chemical shifts are observed, presumably as a result of the weak association in the 1:1 complexes formed between host and guest. The cy-

clophane [BBIPYBIXYCY][PF₆]₄ (2) is able to form pseudorotaxane-like complexes in solution with the π -electron-rich acyclic derivatives BMEEB, β CBMEEB, and B β CMEEB (Fig. 6). The hydrogen atoms attached to the hydroquinone ring of the uncomplexed acyclic polyethers resonate at $\delta = 6.85$ in CD₃CN at room temperature in all three cases (see the partial ¹H NMR spectrum of BMEEB illustrated in Fig. 9a). When equimolar amounts of 2 and BMEEB are mixed in CD₃CN at room temperature, the resonances corresponding to the hydroquinone ring protons move to $\delta = 4.49$ ($\Delta\delta = -2.36$) (Fig. 9b). In contrast, on mixing the acyclic polyether β CBMEEB, bearing only one ester function, with an equimolar amount of the tetracationic cyclophane, the hydroquinone ring protons move to $\delta = 5.45$ ($\Delta\delta = -1.40$) (Fig. 9c). Finally,

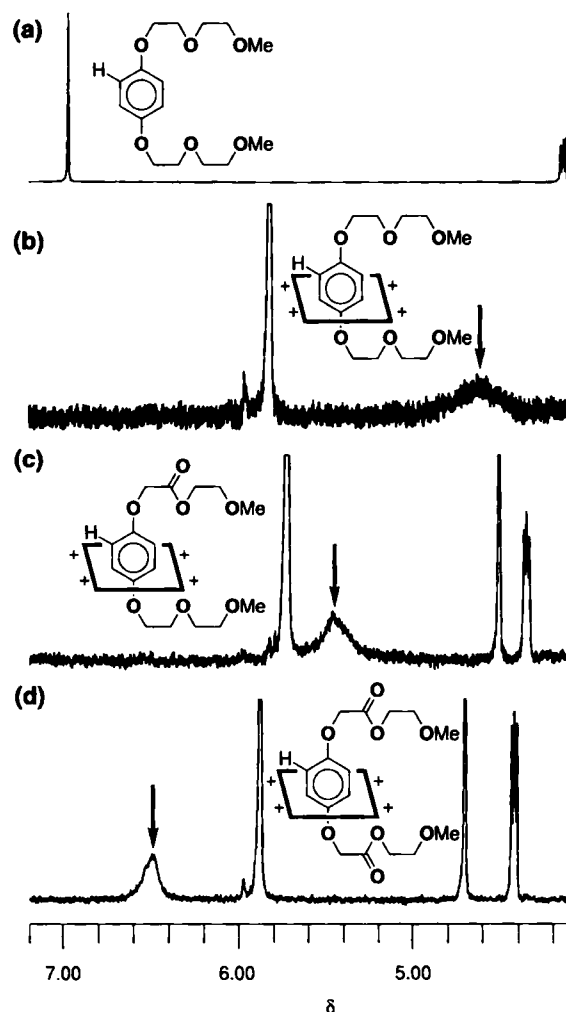


Fig. 9. Partial ¹H NMR spectra of a) the free π -electron-rich acyclic polyether BMEEB and the pseudorotaxane complexes b) [BMEEB]-[BBIPYBIXYCY][PF₆]₄, c) [β CBMEEB]-[BBIPYBIXYCY][PF₆]₄, and d) [B β CMEEB]-[BBIPYBIXYCY][PF₆]₄.

when the acyclic polyether **B β CMEEB** bearing two ester functions is added to **[BBIPYBIXYCY][PF₆]₄** (**2**) under the same conditions, the protons attached to the hydroquinone ring resonate at $\delta = 6.36$ ($\Delta\delta = -0.29$) (Fig. 9d). Thus, the presence of ester functionalities within the polyether chains of the π -electron-rich guests is directly reflected in the progressively smaller changes in chemical shift observed for the complexes when one and then two ester functions are present in the guest. This trend in $\Delta\delta$ values presumably reflects the decreasing stabilities of the 1:1 complexes.

The ¹H NMR spectrum recorded in CD₃COCD₃ at -50°C of the [2]catenane **{[2]-[β CBPP 34 C 10]-[BBIPYBIXYCY]catenane}[PF₆]₄** (**10**), which incorporates one ester function within one of its two polyether chains, provides evidence for the presence of two translational isomers in a 4:1 ratio (Fig. 10). On

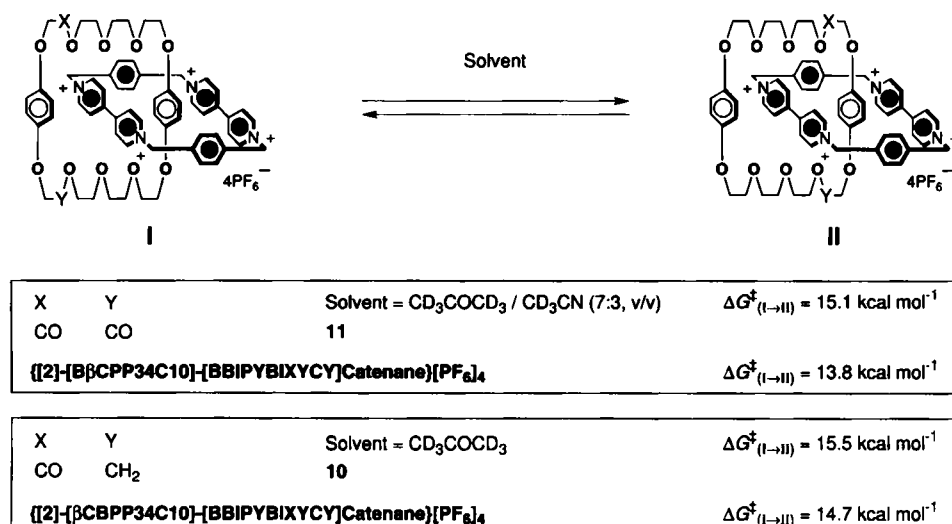


Fig. 10. Equilibration between the translational isomers of the [2]catenanes **{[2]-[β CBPP 34 C 10]-[BBIPYBIXYCY]catenane}[PF₆]₄** (**10**) and **{[2]-[β CBPP 34 C 10]-[BBIPYBIXYCY]catenane}[PF₆]₄** (**11**).

the basis of the binding studies with **[BBIPYBIXYCY][PF₆]₄** (**2**) carried out with the acyclic model compounds (Fig. 6 and Table 2), we believe that the major isomer in solution is **I** with the hydroquinone ring closer to the ester function outside the cavity of the cyclophane. Variable-temperature ¹H NMR spectroscopic studies in the range -80 – 30°C afforded the energies of activation (ΔG^\ddagger values) for the equilibration process by means of the coalescence method.^[31] The energy barrier for the circumrotation process leading from the major (**I**) to the minor (**II**) isomer corresponds to $15.5 \text{ kcal mol}^{-1}$, while the energy for the opposite process is $14.7 \text{ kcal mol}^{-1}$ at the coalescence temperature of 34°C . Interestingly, the difference between the energies of activation ($0.8 \text{ kcal mol}^{-1}$) and the difference between the binding energies for the complexation of **BMEEB** and **β CBMEEB** by **2** ($1.0 \text{ kcal mol}^{-1}$, Table 2) are approximately the same: the complexes are the acyclic analogues of the translational isomers **I** and **II**. Similarly, the ¹H NMR spectrum of the [2]catenane **{[2]-[β CBPP 34 C 10]-[BBIPYBIXYCY]catenane}[PF₆]₄** (**11**) with two ester functions, recorded in CD₃COCD₃/CD₃CN (7:3, v/v) at -50°C , shows that the two translational isomers **I** and **II** are present in a 10:1 ratio. Again, we assume that the isomer **I** is the major isomer in solution on the basis of the association constants reported in Table 2. In this case, the energy barrier for the process leading from the major (**I**) to the minor (**II**) isomer corresponds to $15.1 \text{ kcal mol}^{-1}$, while the energy for the opposite process is $13.8 \text{ kcal mol}^{-1}$ at the coales-

cence temperature of 22°C . Once more, the difference ($1.3 \text{ kcal mol}^{-1}$) between these two values corresponds well with the difference ($1.2 \text{ kcal mol}^{-1}$) between the binding energies for the complexes **[BMEEB]-[BBIPYBIXYCY][PF₆]₄** and **[β CMEEB]-[BBIPYBIXYCY][PF₆]₄**.

The tetracationic cyclophane **[BBIPYBIBTCY][PF₆]₄** (**1**) and **BHEEEB** (**4**) form both a 1:1 complex and a 2:1 complex in solution. However, by mixing equimolar amounts of **4** and **1**, the resonances of host and guest are only slightly affected in CD₃CN at room temperature (Table 3), presumably as a result of the low association constants. When ferrocene is used as the guest in CD₃CN at room temperature, the protons in the α and β positions of the tetracationic cyclophane are shifted by $\Delta\delta = -0.05$ and -0.13 , respectively, while the protons attached to the cyclopentadienyl rings of ferrocene move by $\Delta\delta = -0.08$. Upon combination in CD₃CN at room temperature of equimolar amounts of the cyclophane **1** and the strongly bound guest **BHEEEF** (**9**), a deep green color appears immediately, presumably as a result of charge-transfer interactions between the bipyridinium units and the cyclopentadienyl rings. The chemical shift for the α protons of the tetracationic cyclophane is almost unaffected upon complexation, while the chemical shift for those in the β positions is influenced ($\Delta\delta = -0.16$). More interestingly, the resonances corresponding to the protons attached to the cyclopentadienyl rings are shifted to higher fields by approximately $\Delta\delta = 1.5$.

X-ray crystal structures: The square geometry adopted in the crystal by the tetracationic cyclophane **[BBIPYBIBTCY]⁴⁺** (cation of **1**) is illustrated in Figure 11.^[26] The overall dimensions of this molecular square, as defined by the distances separating the centroids of the bonds linking the pyridinium rings and the centroids of the bonds linking phenylene rings, are 10.87 and 10.96 \AA , respectively (Table 4). These values compare with the distances of 10.75 and 11.24 \AA , respectively, observed for the tetracationic component of **{[3]-[BPP 34 C 10]-[BBIPYBIBTCY]-[BPP 34 C 10]catenane}[PF₆]₄** (**12**),^[14c, 21b] reflecting the ability of the cyclophane to adjust the internal dimensions of its cavity in order to accommodate within it the two π -electron-rich

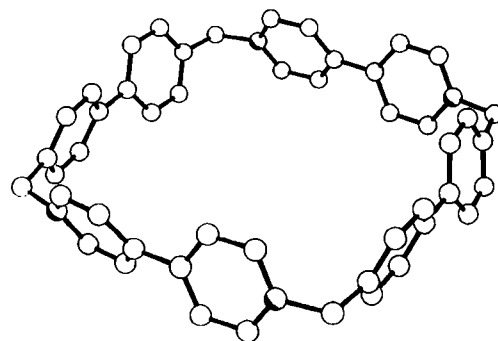
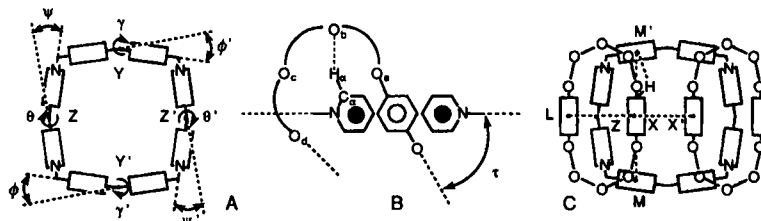


Fig. 11. Ball-and-stick representation of the molecular structure of the tetracationic cyclophane **[BBIPYBIBTCY]⁴⁺** (cation of **1**).

Table 4. Distances (Å) and angles (°) [a] characterizing the molecular and supramolecular geometries of the cyclophane [BBIPYBIBTCY][PF₆]₄ (1), the [3]catenanes {[3]-[BPP 34 C 10]-[BBIPYBIBTCY]-[BPP 34 C 10]catenane}[PF₆]₄ (12) and {[3]-[CBPP 34 C 10]-[BBIPYBIBTCY]-[CBPP 34 C 10]catenane}[PF₆]₄ (13), as well as the [3]pseudorotaxane [BHEEEB]₂-[BBIPYBIBTCY][PF₆]₄ (14).

Compound	θ	γ	ψ	ϕ	τ	Z...Z'	Y...Y'	Z...X	Z...L	X...X'	X...M	X...M'
1 [b]	27/24	31/34	20/21	19/21	—	10.87	10.96	—	—	—	—	—
12 [c,d]	18	29	17	25	49	10.75	11.24	3.56	3.52	3.82	5.93	5.03
13 [c,d]	17	32	19	21	49	10.79	11.06	3.57	3.43	3.77	5.73	5.10
14 [c,d]	29	33	18	19	51	10.84	10.83	3.57	—	3.78	5.61	5.09



[a] The distances and angles indicated in the table are illustrated in the diagrams A, B, and C. [b] As a result of the absence of a crystallographic center of symmetry in the case of the tetracationic cyclophane 1, two sets of data are observed for the twist angles between the pyridinium rings (θ , θ') and the phenylene rings (γ , γ') as well as the out-of-plane bending angles within the bipyridinium (ψ , ψ') and biphenylene (ϕ , ϕ') units. [c] C₆—H_a...O_b, C₆...O_b distances, and C₆—H_a...O_b angles: 2.46, 3.29 Å, and 145° for 12, 2.47, 3.28 Å, and 143° for 13, 2.40, 3.19 Å, and 139° for 14. [d] H...M' distances and X—H...M' angles, 2.76 Å and 166° for 12, 2.86 Å and 157° for 13, 2.84 Å and 157° for 14.

hydroquinone rings. Differences are also observed in the twist angles between the aromatic rings of the bipyridinium and biphenylene units, as well as in their out-of-plane bending angles (Table 4). The twist angles between the pyridinium rings within the two bipyridinium units are 27 and 24°, compared with 18° in the [3]catenane 12, whilst the twist angles between the phenylene rings within the two biphenylene units are 31 and 34°, compared with 29° in the [3]catenane.^[14c, 21b] The out-of-plane bending angles within the bipyridinium units are 20 and 21°, compared with 17° in the [3]catenane, whilst the bending angles subtended between the C—CH₂ bonds of the biphenylene units are 19 and 21°, compared with 25° in the [3]catenane.^[14c, 21b] The tetracationic cyclophane [BBIPYBIBTCY]⁴⁺ (cation of 1) packs to form mosaic-like layers in the crystal (Fig. 12).^[26] In one direc-

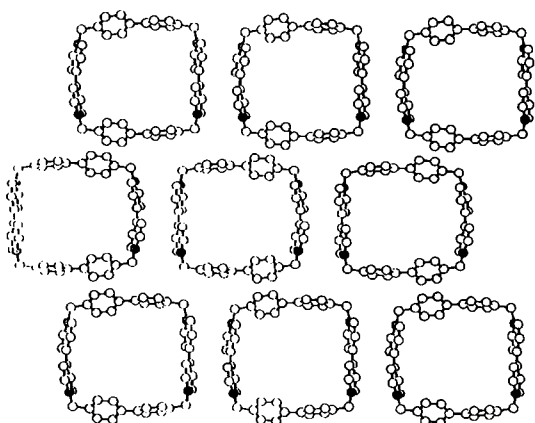


Fig. 12. Ball-and-stick representation of part of one of the mosaic-like layers of the cyclophane [BBIPYBIBTCY]⁴⁺ (cation of 1), showing the two different types of phenylene-phenylene stacking interactions.

tion, the bipyridinium units of adjacent molecules are aligned in register and separated by an interplanar distance of about 3.7 Å. In the other direction, the biphenylene units are offset such that only one of the two phenylene rings is overlapped and centrosymmetrically related with another phenylene ring in the adjacent molecule. As a result of the absence of a crystallographic

center of symmetry within each molecule, two types of phenylene-phenylene π - π stacking interactions are observed within each sheet. The parallel inter-ring plane separations are effectively the same at 3.35 and 3.36 Å, but the phenylene centroid-centroid separations differ at 3.56 and 3.69 Å, respectively, as a result of the different degrees of stagger within each sheet. Adjacent sheets are separated by 7.8 Å and are offset such that one of the methylene carbon atoms of each cyclophane within one sheet is positioned approximately over the center of a macrocycle in the next.

The X-ray crystallographic analysis of {[3]-[CBPP 34 C 10]-[BBIPYBIBTCY]-[CBPP 34 C 10]catenane}[PF₆]₄ (13) reveals a structure that appears to be little changed from that adopted by the [3]catenane 12 incorporating BPP 34 C 10 as the π -electron-rich component (Fig. 13, Table 4). Two hydroquinone rings are threaded through the center of the tetracationic cyclophane in a centrosymmetric relationship, there being an interplanar separation of 3.52 Å and a centroid-centroid distance of 3.77 Å between the slightly sheared π -electron-rich rings. The inside hydroquinone...bipyridinium centroid-centroid sepa-

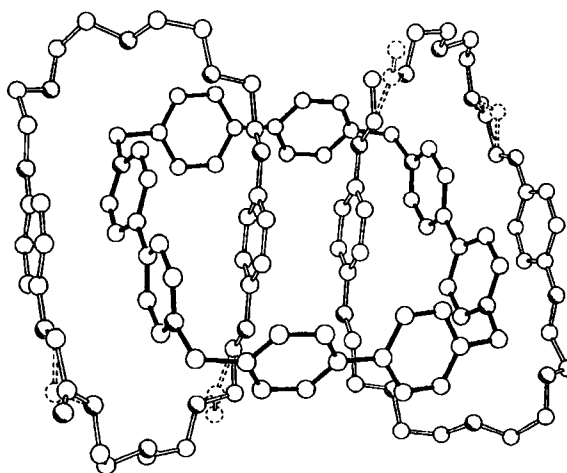


Fig. 13. Ball-and-stick representation of the molecular structure adopted in the crystal by the [3]catenane {[3]-[CBPP 34 C 10]-[BBIPYBIBTCY]-[CBPP 34 C 10]catenane}⁴⁺ (cation of 13).

ration ($Z \cdots X$) is 3.57 Å and the equivalent *outside* centroid–centroid separation ($Z \cdots L$) is 3.43 Å, compared with 3.56 and 3.52 Å, respectively, in the case of $\{[3]\text{-[BPP 34 C 10]-[BBIPYBIBTCY]-[BPP 34 C 10]catenane}\}[\text{PF}_6]_4$ (12).^[14c, 21b] In addition to the π - π stacking interactions between the π -electron-rich hydroquinone rings and the π -electron-deficient bipyridinium units in 13, there is also intercomponent stabilization by edge-to-face C–H $\cdots\pi$ T-type interactions (ring centroid–ring centroid separation 5.10 Å, H $\cdots\pi$ distance 2.86 Å, C–H $\cdots\pi$ angle 157°, compared with 5.03 and 2.76 Å and 166°, respectively, in the case of the parent [3]catenane (12)^[14c, 21b] and C–H $\cdots\pi$ O hydrogen bonding between one of the bipyridinium α carbon atoms and a polyether oxygen atom in the macrocyclic lactone (C $\cdots\pi$ O, H $\cdots\pi$ O distances 3.28 and 2.47 Å, C–H $\cdots\pi$ O angle 143°, compared with 3.29 and 2.46 Å and 145°, respectively, in the case of the [3]catenane 12^[14c, 21b]). The packing motif (Fig. 14) of the [3]catenane $\{[3]\text{-[BPP 34 C 10]-[BBIPYBIBTCY]-[BPP 34 C 10]catenane}\}[\text{PF}_6]_4$ (13) is also very similar to that of the [3]catenane incorporating BPP 34 C 10 (12).^[14c, 21b] A two-dimensional array is formed in the crystal as a result of, in one direction, π - π stacking interactions between one of the phenylene rings of each biphenylene unit in one molecule and the centrosymmetrically related counterpart in the adjacent molecule (centroid–centroid separation, 3.77 Å) and, in the other direction, partial overlap between the π system of centrosymmetrically related hydroquinone rings. However, a noticeable increase in shearing between these hydroquinone rings is observed with their centroid–centroid separation being 5.11 Å, compared with 3.66 Å in the case of $\{[3]\text{-[BPP 34 C 10]-[BBIPYBIBTCY]-[BPP 34 C 10]catenane}\}[\text{PF}_6]_4$ (12).^[14c, 21b] As regards distinguishing between different isomeric forms (Fig. 15), the X-ray crystal structure analysis definitely excludes the stereoisomers Ib, IIa, and IIc, proving the ester groups in the macrocyclic lactone components to be located on opposite sides of the mean plane defined by the tetracationic component. The space group requires an overlapped centrosymmetric distribution for the molecules in the crystal. However, there is clear evidence for the existence of two discrete sites for the ester functions within only one of the two polyether chains of each macrocyclic lactone. On the basis of occupancy refinement, relative populations of 40 and 60% have

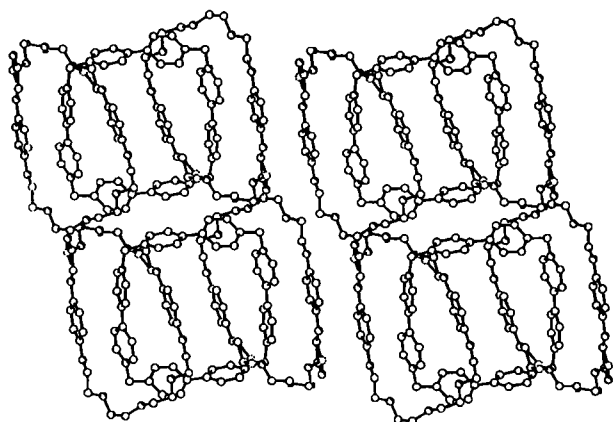


Fig. 14. Ball-and-stick representation of part of the two-dimensional array formed in the crystal by the [3]catenane $[\text{BPP 34 C 10}]\text{-}[\text{BBIPYBIBTCY}]\text{-}[\text{BPP 34 C 10}]\text{catenane}^{4+}$ (cation of 13).

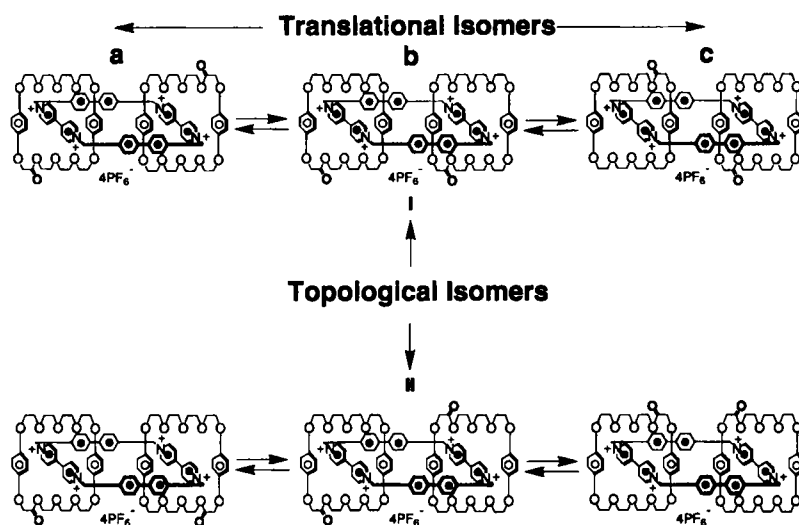


Fig. 15. Representation of the six possible isomers of the [3]catenane $[\text{BPP 34 C 10}]\text{-}[\text{BBIPYBIBTCY}]\text{-}[\text{BPP 34 C 10}]\text{catenane}^{4+}$ (cation of 13).

been determined for the *inside* and *outside* locations of the ester functions, respectively. Presumably a mixture of the translational stereoisomers Ia and Ic and their topological stereoisomer IIb is present in the crystal.

The X-ray structural analysis of the [3]pseudorotaxane $[\text{BHEEBB}]\text{-}[\text{BBIPYBIBTCY}][\text{PF}_6]_4$ (14) reveals a centrosymmetric structure in which two BHEEBB units are inserted through the cavity of the cyclophane (Fig. 16). The interplanar separation (Table 4) between the two hydroquinone rings is 3.44 Å (centroid–centroid separation $X \cdots X'$ 3.78 Å) and the distance from the centroid of the C–C bond linking the two pyridinium rings to the proximal hydroquinone ring centroid ($Z \cdots X$) is 3.57 Å. These stacking geometries are consistent with favorable π - π stabilizing interactions for the complex as a whole. Secondary stabilizing interactions include C–H $\cdots\pi$ O hydrogen bonds between one of the α -CH bipyridinium hydrogen atoms on one of each of the diametrically opposite pyridinium rings and the second oxygen atom on one of the polyether chains of each thread (C $\cdots\pi$ O and H $\cdots\pi$ O distances, C–H $\cdots\pi$ O angle, 3.19 and 2.40 Å, 139°), and aromatic edge-to-face interactions between the threaded hydroquinone substrates and one of each of the phenylene rings of the two bitolyl units in the cyclophane. These latter pairs of single edge-to-face interactions (double interactions are observed for the majority of analogous

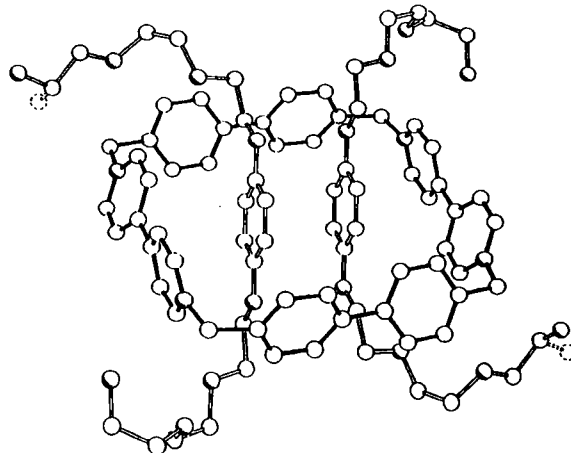


Fig. 16. Ball-and-stick representation of the supramolecular structure of the [3]pseudorotaxane $[\text{BHEEBB}]_2\text{-}[\text{BBIPYBIBTCY}]^{4+}$ (cation of 14).

[2]pseudorotaxanes, [2]rotaxanes, and [2]catenanes) are a consequence of the two hydroquinone rings being sheared with respect to each other and thus being individually asymmetrically positioned with respect to their associated pairs of facing phenylene rings (hydroquinone–phenylene centroid–centroid distances, 5.61 and 5.09 Å). The tetracationic cyclophane within the [3]pseudorotaxane **14** has a conformation little changed from that adopted in the free state, there being significant amounts of twisting and bending of the biphenylene and bipyridinium units. There is a notable absence (Fig. 17) of any inter-

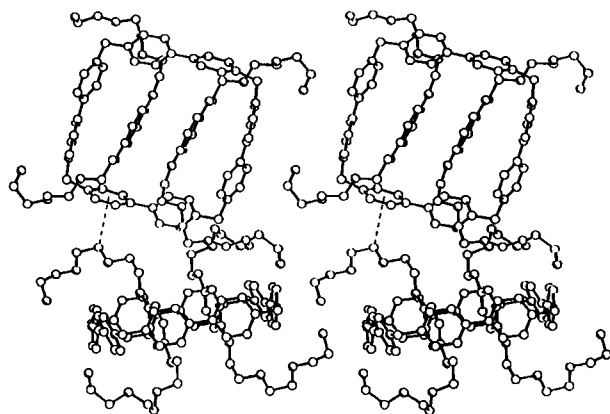


Fig. 17. Ball-and-stick representation of the supramolecular structure of the [3]pseudorotaxane [BHEEB]-[BBIPYBIBTCY]⁴⁺ (cation of **14**) showing the C–H... π interactions between adjacent complexes.

complex π – π stacking within the crystal. The complexes pack such that the pairs of BHEEB hydroxyl groups, which lie over the exterior faces of the bipyridinium units, interleave with the noticeable absence of any OH...O hydrogen bonding to form chains of complexes. Adjacent chains are oriented orthogonally with respect to each other and are crosslinked by C–H... π interactions between one of the O–CH₂ carbon atoms in one polyether arm of each BHEEB and one of the phenylene rings in the two bitolyl units of the cyclophane (H...ring-centroid distance 2.80 Å, C–H...ring-centroid angle, 169°).

The X-ray structural analysis of the [2]pseudorotaxane [B β CMEEB]-[BBIPYBIXYCY][PF₆]₄ (**15**) shows the π -electron-rich diester to be threaded through the cavity of the cyclophane in a centrosymmetric manner with the hydroquinone ring sandwiched between the two π -electron-deficient bipyridinium units (Fig. 18). The distance separating the hy-

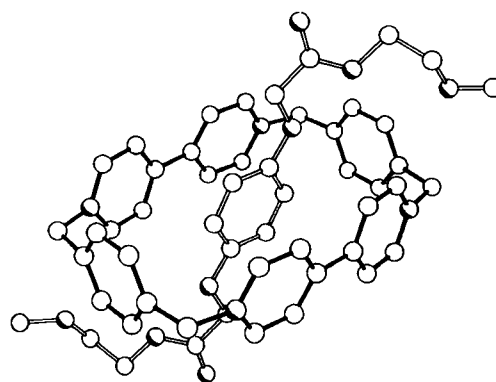
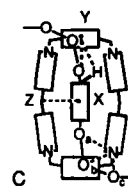
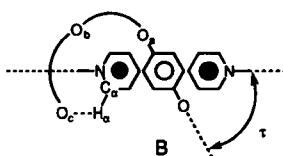
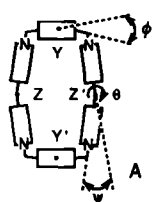


Fig. 18. Ball-and-stick representation of the supramolecular structure of the [2]pseudorotaxane [B β CMEEB]-[BBIPYBIXYCY]⁴⁺ (cation of **15**).

droquinone ring centroid and the centroid of the C–C bond linking the pyridinium rings is 3.54 Å, compared with 3.62 Å in the case of the analogous [2]pseudorotaxane [BHEEB]-[BBIPYBIXYCY][PF₆]₄ (**16**)^[14b] incorporating BHEEB as the guest. The O–C₆H₄–O axis of the hydroquinone ring is more steeply inclined to the mean plane of the cyclophane (as defined by its four methylene carbon atoms) than in the [2]pseudorotaxane **16**,^[14b] resulting in increased separations between one nitrogen atom in each bipyridinium unit and the oxygen atoms of the two chains. Relatively strong C–H...O hydrogen-bonding interactions are observed between the oxygen atoms of the terminal methoxy groups and one of the α -CH hydrogen atoms of each bipyridinium unit. The C...O and H...O distances in **15** are 3.19 and 2.25 Å, respectively (Table 5), compared with 3.18 and 2.28 Å in the case of the [2]pseudorotaxane **16**,^[14b] whilst the C–H...O angle is 165°, compared with 173° in the case of the BHEEB-containing [2]pseudorotaxane **16**. Edge-to-face T-type interactions C–H... π between the hydrogen atoms attached to the hydroquinone rings and the *p*-xylene spacers are observed in both [2]pseudorotaxanes. The C–H...ring-centroid distance (H...Y) and the C–H...ring-centroid angle are 2.79 Å and 173° in the case of the [2]pseudorotaxane [B β CMEEB]-[BBIPYBIXYCY][PF₆]₄ (**15**) (Table 5), compared with 2.76 Å and 165° in the case of **16**.^[14b] The cyclophane component of the [2]pseudorotaxane **15** adopts an open-box geometry remarkably similar to that observed in the free state and in the [2]pseudorotaxane **16**, and exhibits the characteristic bowing and twisting deformations summarized in Table 5. Significant differences are observed in the twist angles between the pyridinium rings within the bipyridinium units, presumably as a result

Table 5. Distances (Å) and angles (°) [a] characterizing the molecular and supramolecular geometries of the cyclophane [BBIPYBIXYCY][PF₆]₄ (**2**) and the [2]pseudorotaxanes [BHEEB]-[BBIPYBIXYCY][PF₆]₄ (**16**) and [B β CMEEB]-[BBIPYBIXYCY][PF₆]₄ (**15**).

Compound	θ	ψ	ϕ	τ	O _a ...N	O _b ...N	O _c ...N	C ₂ ...O _c	H _a ...O _c	C ₆ H ₄ O _c	Z...Z'	Y...Y'	H...Y	XHY
2	19	23	14	–	–	–	–	–	–	–	6.82	10.31	–	–
16	20	30	8	52	4.07	4.39	3.79	3.18	2.28	173	7.25	10.08	2.76	165
15	7	26	12	56	4.33	4.72	3.91	3.19	2.25	165	7.08	10.22	2.79	173



[a] The distances and angles indicated in the table are illustrated in the diagrams A, B, and C.

of the C–H···O hydrogen-bonding interactions linking adjacent complexes in the crystal, *vide infra*. Thus, the twist angle is reduced to 7° in the case of the [2]pseudorotaxane [B β CMEEB]-[BBIPYBIXYCY][PF₆]₄ (15), compared with 19° in the case^[14b] of the free cyclophane (2). The 1:1 complex packs to form (Fig. 19) offset chains of molecules that extend in the crystallographic *c* direction with the *p*-xylyl rings of the cyclophane

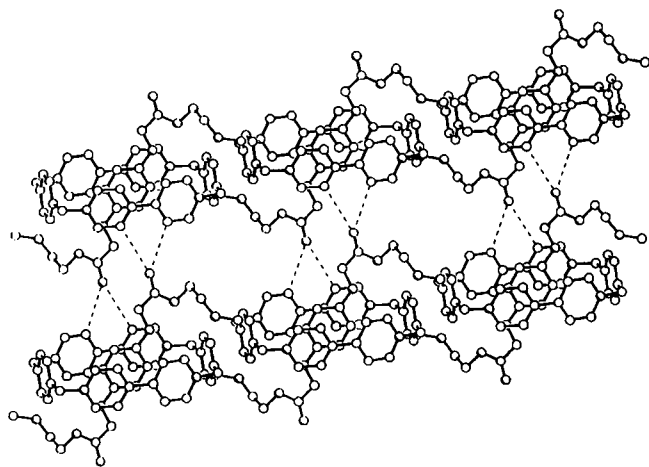


Fig. 19. Ball-and-stick representation of the supramolecular structure of the [2]pseudorotaxane [B β CMEEB]-[BBIPYBIXYCY]⁴⁺ (cation of 15) showing the pairs of C–H···O hydrogen-bonding interactions between complexes in adjacent layers.

component of one complex oriented parallel to those in another with an interplanar separation of 3.38 Å and a centroid–centroid separation of 4.59 Å. In the crystallographic *a* direction, the cyclophane components stack in register to form continuous channels through which the diester units are threaded. Adjacent complexes along this direction are cross-linked by pairs of C–H···O hydrogen bonds each involving two β -CH bipyridinium hydrogen atoms within one complex and the ester carbonyl oxygen atom of the neighboring complex. The C–H···O and H···O distances and C–H···O angles are 3.37, 2.45 Å, 161°, and 3.27, 2.32 Å, and 170°.

Conclusions

The template-directed synthesis of cyclobis(paraquat-4,4'-biphenylene) [BBIPYBIBTCY][PF₆]₄ (1) has been achieved by employing π -electron-rich acyclic and macrocyclic templates (Fig. 20). In particular, the use of the acyclic 1,1'-disubstituted ferrocene polyether derivative BHEEEF (9) as the template provides the possibility of synthesizing 1—accessible only in very

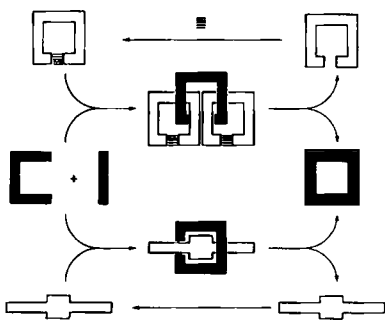


Fig. 20. Schematic representation of the use of acyclic and degradable macrocyclic templates.

low yields without the use of a template—on a preparative scale. By employing the hydroquinone-based macrocyclic polyether β CBPP 34C 10 (8), which has an ester function within one of its two polyether chains, the template-directed synthesis of two topologically stereoisomeric [3]catenanes has been achieved. As a result of the *oriented* topology of 8, two relative orientations for the π -electron-rich macrocyclic components are possible within the catenated structure, thus affording two topologically stereoisomeric [3]catenanes. Ester hydrolysis of the macrocyclic lactones incorporated within these isomeric catenanes (which have not been separated) releases the tetracationic cyclophane component—namely 1—in a quantitative yield after the degradation of the [3]catenanes. Cyclobis(paraquat-4,4'-biphenylene) is the first example of a rigid *organic* tetracationic *molecular square* incorporating carbon atoms at the corner of the square. This molecular square is able to accommodate two substrates containing hydroquinone rings within its cavity, affording pseudorotaxane-like complexes with 2:1 stoichiometry both in solution and in the solid state. Furthermore, [BBIPYBIBTCY][PF₆]₄ (1) binds ferrocene-based derivatives as a result of second-sphere coordination^[29] of the metallocene unit. This result suggests strongly the possibility of synthesizing electrochemically active^[32] molecular and supramolecular devices^[33] in the form of catenanes, rotaxanes, and pseudorotaxanes.^[34]

Experimental Section

General methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried (benzene with CaH₂, CH₂Cl₂ with CaH₂, DMF with CaH₂, MeCN with P₂O₅, and THF with Na/Ph₃CO) according to procedures described in the literature [35]. [BPYPYXY][PF₆]₂ (3) [14b], BHEEEF (4) [14b], [BPYPYBT][PF₆]₂ (5) [14e], BBBP [14e], BHPTU [14b], BAF [36], [PQT][PF₆]₂ [14b], and BHEEB [14b] were prepared according to literature procedures. The reagent 2-[2-(2-chloroethoxy)ethoxy]ethyl chloroacetate was synthesized by the reaction of chloroacetyl chloride with 2-[2-(chloroethoxy)ethoxy]ethanol in the presence of triethylamine in CH₂Cl₂ at 0°C. The protection of 2-[2-(chloroethoxy)ethoxy]ethanol was carried out by treatment with 3,4-dihydro-2H-pyran in the presence of *p*-toluenesulfonic acid at 0°C in CH₂Cl₂. Thin-layer chromatography (TLC) was carried out with aluminum sheets precoated with silica gel 60F (Merck 5554). The plates were inspected by UV light and developed with iodine vapour. Column chromatography was carried out with silica gel 60F (Merck 9385, 230–400 mesh). High performance liquid chromatography (HPLC) was performed with a Gilson 714 system fitted with a UV detector. Melting points were determined on an Electrothermal 9200 apparatus and are not corrected. Microanalyses were performed by either the University of Birmingham Microanalytical Service or by the University of Sheffield Microanalytical Service. Low resolution mass spectra were recorded on a Kratos profile spectrometer operating in electron impact (EIMS) mode. Fast atom bombardment mass spectra (FABMS) were recorded on a Kratos MS80 spectrometer operating at 8 keV with a xenon primary atom beam. The matrix used was 3-nitrobenzyl alcohol. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 2 with HPLC-quality solvents. ¹H NMR spectra were recorded on either a Bruker AC 300 (300 MHz) spectrometer or a Bruker AMX 400 (400 MHz) spectrometer with either the solvent or TMS used as internal standards. ¹³C NMR spectra were recorded on either a Bruker AC 300 (75.5 MHz) spectrometer or a Bruker AMX 400 (100.6 MHz) spectrometer with either the solvent or TMS as internal standards. All chemical shift differences are quoted in ppm on the δ scale and the coupling constants are expressed in Hertz (Hz). X-ray crystallographic analyses were carried out as described in the appropriate compound characterization sections.

15,24,41,50-Tetraazonia[1.0.1.0.1.0.1.0]paracyclophane tetrakis(hexafluorophosphate) ([BBIPYBIBTCY][PF₆]₄, 1):

Method A: A solution of BBBP (43.0 mg, 0.13 mmol) and [BBIPYBT][PF₆]₂ (100.0 mg, 0.13 mmol) in dry MeCN (15 mL) was stirred at room temperature for 14 d. The solvent was evaporated under reduced pressure and the resulting solid was suspended in MeNO₂ (30 mL). The mixture was filtered and the resulting clear solution was concentrated under reduced pressure and purified by column chromatography (SiO₂, MeOH/2M NH₄Cl/MeNO₂, 7:2:1) to afford, after counterion exchange (NH₄PF₆/H₂O), [BBIPYBIBTCY][PF₆]₄ (1) as a white solid (3.2 mg, 2%); m.p. 194°C (decomp.); FABMS: m/z = 1107 [M – PF₆]⁺, 962 [M – 2PF₆]⁺, 817 [M – 3PF₆]⁺; ¹H NMR (CD₃CN): δ = 8.95 (d, J = 7 Hz, 8H), 8.25 (d, J = 7 Hz, 8H), 7.66 (d, J = 7 Hz, 8H), 7.54 (d, J = 8 Hz, 8H), 5.82 (s, 8H); ¹³C NMR (CD₃CN): δ = 150.8, 146.3, 141.6, 134.8, 130.8, 128.9, 128.5, 65.8; Anal.

calcd for $C_{46}H_{40}F_{24}N_4P_4$: C 46.02, H 3.22, N 4.47; found C 46.02, H 3.49, N 4.37. Single crystals suitable for X-ray crystallography were grown by vapor diffusion of iPr_2O into a MeCN solution of $[BBIPYBIBTCY][PF_6]_4$. X-ray data: $C_{46}H_{40}F_{24}N_4P_4 \cdot 4MeCN$, $M = 1416.9$, triclinic, $a = 12.778(3)$, $b = 14.548(3)$, $c = 16.667(3)$ Å, $\alpha = 89.80(3)$, $\beta = 98.47(3)$, $\gamma = 91.79(3)^\circ$, $V = 3063(1)$ Å³, $T = 213$ K, space group = $P\bar{1}$, $Z = 2$, $\rho_{\text{calcd}} = 1.54$ g cm⁻³, $\mu(Cu_K\alpha) = 22.2$ cm⁻¹, $F(000) = 1440$. Data for a crystal of dimensions $0.33 \times 0.17 \times 0.10$ mm collected on a Siemens P4/RA diffractometer ($2\theta \leq 110^\circ$), ω scans, $Cu_K\alpha$ radiation (graphite monochromator). 7700 independent reflections were measured; of these 5832 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods and refined anisotropically. Three of the hexafluorophosphate anions are in general positions, whilst two are positioned on independent symmetry centers. Hydrogen atom positions were determined from ΔF maps and optimized. The refinement was by full-matrix least squares based on F^2 to give $R_1 = 0.083$, $wR_2 = 0.208$ for 837 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.72 and -0.45 e Å⁻³.

Method B: A solution of BBBP (22.0 mg, 0.06 mmol) and $[BBIPYBT][PF_6]_2$ (50.0 mg, 0.06 mmol) in dry MeCN (10 mL) was stirred at 0 °C for 28 d. The reaction mixture was purified as described for method A to yield $[BBIPYBIBTCY][PF_6]_4$ (0.5 mg, 0.6%).

Method C: A solution of BBBP (22.0 mg, 0.06 mmol) and $[BBIPYBT][PF_6]_2$ (50.0 mg, 0.06 mmol) in dry MeCN (10 mL) was stirred at 80 °C for 48 h. The reaction mixture was purified as described for method A to yield $[BBIPYBIBTCY][PF_6]_4$ (0.4 mg, 0.5%).

Method D: A solution of BBBP (22.0 mg, 0.06 mmol) and $[BBIPYBT][PF_6]_2$ (50.0 mg, 0.06 mmol) in dry MeCN (150 mL) was stirred at 25 °C for 14 d. The reaction mixture was purified as described for method A to yield $[BBIPYBIBTCY][PF_6]_4$ (traces).

Method E: A solution of BBBP (22.0 mg, 0.06 mmol) and $[BBIPYBT][PF_6]_2$ (50.0 mg, 0.06 mmol) in dry MeCN (150 mL) was stirred at 50 °C for 7 d. The reaction mixture was purified as described for method A to yield $[BBIPYBIBTCY][PF_6]_4$ (traces).

Method F: A solution of BBBP (43.0 mg, 0.13 mmol), $[BBIPYBT][PF_6]_2$ (100.0 mg, 0.13 mmol) and BHEEB (287 mg, 0.77 mmol) in dry MeCN (15 mL) was stirred at room temperature for 14 d. The reaction mixture was purified as described for method A to yield $[BBIPYBIBTCY][PF_6]_4$ as a white solid (7.9 mg, 5%).

Method G: A solution of $\{[3]-[CBPP34C10]-[BBIPYBIBTCY]-[CBPP34C10]catenane\}[PF_6]_4$ (13 (11.0 mg, 0.005 mmol) in CD_3CN (0.5 mL) and DCI (0.2 M in D_2O , 0.5 mL), maintained at room temperature, was periodically checked by 1H NMR until the reaction was observed to be complete (45 d). The solution was concentrated in vacuo and then diluted with H_2O (25 mL). The addition of a saturated aqueous solution of NH_4PF_6 afforded a white precipitate, which was filtered and washed with H_2O (10 mL) to yield $[BBIPYBIBTCY][PF_6]_4$ (6.3 mg, 100%).

Method H: A solution of BBBP (43.0 mg, 0.13 mmol), $[BBIPYBT][PF_6]_2$ (100.0 mg, 0.13 mmol), and ferrocene (530 mg, 2.85 mmol) in dry MeCN (20 mL) was stirred at room temperature for 14 d. The solvent was evaporated and the residue was suspended in Et_2O (50 mL). The mixture was filtered and the residue was purified by column chromatography (SiO_2 , $MeOH/2M NH_4Cl/MeNO_2$, 7:2:1) to afford, after counterion exchange (NH_4PF_6/H_2O), $[BBIPYBIBTCY][PF_6]_4$ as a white solid (16.0 mg, 10%).

Method I: A solution of BBBP (239 mg, 0.71 mmol), $[BBIPYBT][PF_6]_2$ (548 mg, 0.70 mmol), and BHEEF (9 (629 mg, 1.31 mmol) in dry MeCN (25 mL) was stirred at room temperature for 14 d. The solvent was evaporated and the residue was suspended in $CHCl_3$ (25 mL). The mixture was filtered and the resulting solid was purified by column chromatography (SiO_2 , $MeOH/2M NH_4Cl/MeNO_2$, 7:2:1) to afford, after counterion exchange (NH_4PF_6/H_2O), $[BBIPYBIBTCY][PF_6]_4$ as a white solid (278 mg, 32%).

1,4-Bis(ethyloxycarbonylmethylenoxy)benzene (BCEEB): 1/4 DHB (5.50 g, 50.0 mmol) was added to a suspension of K_2CO_3 (73.00 g, 529 mmol) in dry MeCN (300 mL) under N_2 . The suspension was stirred vigorously for 30 min at 50 °C, and then ethyl bromoacetate (18.40 g, 110 mmol) was added over 30 min. The reaction mixture was heated under reflux for 6 h. After cooling to room temperature, the suspension was filtered, and the residue washed with $MeCO_2Et$ (300 mL). The combined organic solutions were concentrated in vacuo, and the residue was dissolved in CH_2Cl_2 (400 mL) and washed with H_2O (3×200 mL). The organic phase was dried ($MgSO_4$), and the solvent was evaporated off under vacuum. Purification of the residue by column chromatography (SiO_2 , $PhCH_3$) gave BCEEB as a white crystalline solid (11.90 g, 84%); m.p. 72 °C; EIMS 282 $[M]^+$; 1H NMR ($CDCl_3$): $\delta = 6.86$ (s, 4H), 4.57 (s, 4H), 4.26 (q, $J = 7$ Hz, 4H), 1.30 (t, $J = 7$ Hz, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 169.1$, 152.9, 115.9, 66.3, 61.32, 14.2; Anal. calcd for $C_{14}H_{18}O_6$: C 59.57, H 6.38; found C 59.39, H 6.55.

1,4-Bis(carboxymethylenoxy)benzene (BCEEB): BCEEB (1.00 g, 3.6 mmol) was added to a solution of NaOH (430 mg, 10.6 mmol) in H_2O (100 mL) and the solution was heated under reflux for 4 h. After cooling to room temperature, acidification with dilute HCl gave BCEEB as a white crystalline solid (760 mg, 94%); m.p. 253 °C; EIMS: $m/z = 226$ $[M]^+$; 1H NMR (CD_3SOCD_3): $\delta = 12.96$ (brs, 2H), 6.84 (s, 4H), 4.59 (s, 4H); ^{13}C NMR (CD_3SOCD_3): $\delta = 170.4$, 152.2, 115.4, 65.1; Anal. calcd for $C_{10}H_{10}O_6$: C 53.10, H 4.42; found C 53.40, H 4.43.

1, 4, 7, 10, 13, 18, 21, 24, 27, 30 - Decaoxa - 3, 28 - dioxo [13, 13] paracyclophane (BCPP34C10, (6): BCBCEB (4.00 g, 17.7 mmol) was suspended in a mixture of dry benzene (300 mL) and dry DMF (5 drops). Oxalyl chloride (18.00 g, 142 mmol) was added at room temperature and under N_2 to the suspension. The temperature was raised to 50 °C and stirring was maintained for 21 h. After cooling to room temperature, the solution was concentrated to give a yellow solid, which was redissolved in dry benzene (250 mL). The benzene solution of the bisacid chloride and a solution of BHEEB (3.98 g, 10.6 mmol) in dry benzene (250 mL) were added over 2 h and 40 min from two separate dropping funnels, to vigorously stirred dry benzene (500 mL) maintained at 50 °C under N_2 . The stirring was continued for 48 h, and then the solution was concentrated in vacuo. Purification of the residue by column chromatography (SiO_2 , hexane/ Me_2CO , 6:4) gave a solid, which was recrystallized from hexane/ Me_2CO (6:4) to give BCPP34C10 as a crystalline white solid (1.377 g, 23%); m.p. 90 °C; FABMS: $m/z = 564$ $[M]^+$; 1H NMR ($CDCl_3$): $\delta = 6.79$ (s, 4H), 6.77 (s, 4H), 4.52 (s, 4H), 4.39–4.34 (m, 4H), 4.06–4.01 (m, 4H), 3.86–3.80 (m, 4H), 3.76–3.63 (m, 12H); ^{13}C NMR ($CDCl_3$): $\delta = 169.0$, 153.2, 152.8, 115.9, 115.7, 70.9, 70.7, 69.9, 68.8, 68.8, 66.1, 64.2; Anal. calcd for $C_{28}H_{36}O_{12}$: C 59.57, H 6.43; found C 59.84, H 6.44.

$\{[2]-[BCPP34C10]-[BBIPYBIXYCY]catenane\}[PF_6]_4$ (11): A solution of BCPP34C10 (7, 293 mg, 0.52 mmol), $[BBIPYXY][PF_6]_2$ (149 mg, 0.20 mmol) and 1,4-bis(bromomethyl)benzene (56 mg, 0.20 mmol) in dry MeCN (15 mL) was stirred at room temperature for 14 d. The solvent was removed in vacuo and the resulting solid residue was purified by column chromatography (SiO_2 , $MeOH/2M NH_4Cl/MeNO_2$, 7:2:1) to afford $\{[2]-[BCPP34C10]-[BBIPYBIXYCY]catenane\}[PF_6]_4$, after counterion exchange (NH_4PF_6/H_2O), as a red crystalline solid (75 mg, 23%); m.p. 297 °C (decomp.); FABMS: $m/z = 1519$ $[M - PF_6]^+$, 1374 $[M - 2PF_6]^+$, 1229 $[M - 3PF_6]^+$; 1H NMR (CD_3CN): $\delta = 8.87$ (d, $J = 7$ Hz, 8H), 7.79 (s, 8H), 7.72 (d, $J = 7$ Hz, 8H), 6.34 (brs, 4H), 5.68 (s, 8H), 4.46 (brs, 4H), 4.07–3.81 (m, 20H), 3.57 (brs, 8H); ^{13}C NMR (CD_3COCD_3/CD_3CN , 7:3, v/v): $\delta = 168.9$, 152.7, 151.0, 147.2, 145.6, 137.6, 131.7, 126.7, 116.4, 113.9, 71.5, 71.4, 70.9, 70.3, 67.4, 66.5, 65.7, 63.9; Anal. calcd for $C_{64}H_{68}F_{24}N_4O_{12}P_4$: C 46.16, H 4.12, N 3.36; found C 46.46, H 4.40, N 3.64.

1,4,7,10,13,18,21,24,27,30-Decaoxa-3-oxo[13,13]paracyclophane (BCBPP34C10, 8): A solution of BHPTU (555 mg, 1.5 mmol) and 2-[2-(2-chloroethoxy)-ethoxy]ethyl chloroacetate (358 mg, 1.5 mmol) in dry MeCN (400 mL) was added over 19 h to a refluxing suspension of K_2CO_3 (1.01 g, 7.3 mmol). The reaction mixture was heated under reflux for a further 24 h. After cooling to room temperature, the suspension was filtered, and the solid residue was washed with CH_2Cl_2 (200 mL). The combined organic layers were concentrated in vacuo, the residue was dissolved in CH_2Cl_2 (200 mL) and washed with H_2O (3×150 mL). The organic phase was dried ($MgSO_4$), and the solvent was evaporated off under vacuum. Purification of the residue by column chromatography (SiO_2 , $MeCO_2Et$ /hexane, 6:4) gave a solid, which was recrystallized from Me_2CO /hexane to give BCBPP34C10 as a white crystalline solid (34 mg, 4%); m.p. 82 °C, FABMS: $m/z = 550$ $[M]^+$; 1H NMR ($CDCl_3$): $\delta = 6.77$ (s, 4H), 6.76 (s, 4H), 4.53 (s, 2H), 4.40–4.34 (m, 2H), 4.47–3.95 (m, 6H), 3.87–3.80 (m, 6H), 3.77–3.64 (m, 14H); ^{13}C NMR ($CDCl_3$): $\delta = 169.1$, 153.8, 153.2, 153.1, 152.1, 115.8, 115.7, 115.6, 70.9, 70.9, 70.8, 70.7, 69.9, 69.8, 69.8, 68.8, 68.3, 68.1, 66.3, 64.2; Anal. calcd for $C_{28}H_{36}O_{11}$: C 61.08, H 6.95; found C 60.98, H 7.17.

$\{[2]-[BCPP34C10]-[BBIPYBIXYCY]catenane\}[PF_6]_4$ (10): A solution of BCBPP34C10 (100 mg, 0.18 mmol), $[BBIPYXY][PF_6]_2$ (50 mg, 0.07 mmol), and 1,4-bis(bromomethyl)benzene (BBB) (19 mg, 0.07 mmol) in dry MeCN (3 mL) was stirred at room temperature for 14 d. The solvent was removed in vacuo and the resulting solid residue was purified by column chromatography (SiO_2 , $MeOH/2M NH_4Cl/MeNO_2$, 7:2:1) to afford, after counterion exchange (NH_4PF_6/H_2O), a red solid. The solid was recrystallized twice by vapor diffusion of iPr_2O into a MeCN solution to give $\{[2]-[BCPP34C10]-[BBIPYBIXYCY]catenane\}[PF_6]_4$ as a red crystalline solid (45 mg, 39%); m.p. 298 °C (decomp.); FABMS: $m/z = 1506$ $[M - PF_6]^+$, 1360 $[M - 2PF_6]^+$, 1215 $[M - 3PF_6]^+$; 1H NMR (CD_3CN): $\delta = 8.86$ (d, $J = 7$ Hz, 8H), 7.79 (s, 8H), 7.69 (d, $J = 7$ Hz, 8H), 6.27 (brs, 4H), 5.77–5.60 (m, 8H), 4.47 (brs, 2H), 4.02–3.44 (m, 32H); ^{13}C NMR (CD_3COCD_3): $\delta = 168.8$, 153.9, 152.1, 151.2, 147.2, 145.7, 137.8, 131.9, 126.7, 116.6, 115.9, 114.1, 71.1, 70.4, 68.6, 67.4, 66.4, 65.8, 63.7; Anal. calcd for $C_{64}H_{70}F_{24}N_4O_{10}P_4 \cdot 4H_2O$: C 44.61, H 4.56, N 3.25; found C 44.49, H 4.29, N 3.27.

$\{[3]-[CBPP34C10]-[BBIPYBIBTCY]-[CBPP34C10]catenane\}[PF_6]_4$ (13): A solution of BCBPP34C10 (200 mg, 0.36 mmol), $[BBIPYBIBT][PF_6]_2$ (95 mg, 0.12 mmol) and BBBP (49 mg, 0.14 mmol) in dry MeCN (7 mL) was stirred at room temperature for 14 d. The solvent was removed in vacuo to afford a red solid, which was suspended in $MeNO_2$ and filtered. The red solution was concentrated under reduced pressure and the resulting red solid was purified by column chromatography (SiO_2 , $MeOH/2M NH_4Cl/MeNO_2$, 7:2:1) to afford, after counterion exchange (NH_4PF_6/H_2O) and crystallization from MeCN/ iPr_2O , a mixture of the two topological stereoisomers of $\{[3]-[CBPP34C10]-[BBIPYBIBTCY]-[CBPP34C10]catenane\}[PF_6]_4$ as a red crystalline solid (27 mg, 10%); m.p. 280 °C (decomp.); FABMS: $m/z = 2353$ $[M]^+$, 2208 $[M - PF_6]^+$, 2063 $[M - 2PF_6]^+$, 1917 $[M - 3PF_6]^+$; 1H NMR (CD_3CN): $\delta = 8.84$ (d, $J = 7$ Hz, 8H), 7.74 (d, $J = 8$ Hz, 8H), 7.68 (d, $J = 8$ Hz, 8H), 7.59 (d, $J = 7$ Hz, 8H), 5.80–5.65

(m, 8H), 5.64–5.57 (m, 4H), 5.36–5.20 (m, 8H), 5.02–4.90 (m, 4H), 4.51–4.47 (m, 4H), 3.95–3.87 (m, 4H), 3.85–3.70 (m, 28H), 3.67–3.61 (m, 4H), 3.52–3.39 (m, 8H), 3.30–3.21 (m, 4H), 3.04–2.93 (m, 4H), 2.87–2.76 (m, 4H); ^{13}C NMR (CD_3CN): δ = 169.5, 153.1, 152.4, 152.0, 151.7, 147.3, 145.7, 141.7, 135.2, 131.0, 128.9, 126.9, 115.8, 115.0, 114.6, 71.4, 71.3, 71.1, 70.7, 70.5, 70.3, 70.0, 68.1, 67.8, 66.6, 65.8, 65.1; Anal. calcd for $\text{C}_{104}\text{H}_{116}\text{F}_{24}\text{N}_4\text{O}_{22}\text{P}_4 \cdot 2\text{H}_2\text{O}$: C 52.27, H 5.06, N 2.34; found C 52.45, H 5.25, N 2.46. Single crystals suitable for X-ray crystallography were grown by vapor diffusion of $i\text{Pr}_2\text{O}$ into a MeCN solution of $\{[\text{3}]\text{-}\beta\text{CBPP34C10}\}\text{-}[\text{BBIPYBIBTCY}]\text{-}[\beta\text{CBPP34C10}]\text{-catenane}\}\text{[PF}_6\text{]}_4$. X-ray data: $\text{C}_{104}\text{H}_{116}\text{F}_{24}\text{N}_4\text{O}_{22}\text{P}_4 \cdot 4\text{MeCN}$, $M = 2518.1$, triclinic, $a = 12.949(2)$, $b = 14.946(3)$, $c = 16.665(1)$ Å, $\alpha = 96.45(1)^\circ$, $\beta = 91.76(1)^\circ$, $\gamma = 108.77(1)^\circ$, $V = 3027(1)$ Å 3 , $T = 203$ K, space group = $P\bar{1}$, $Z = 1$ (the molecule has crystallographic C_2 symmetry), $\rho_{\text{calcd}} = 1.38$ g cm $^{-3}$, $\mu(\text{CuK}\alpha) = 15.1$ cm $^{-1}$, $F(000) = 1308$. Data for a crystal of dimensions $0.33 \times 0.20 \times 0.13$ mm were collected on a Siemens P4/RA diffractometer ($2\theta \leq 110^\circ$), ω scans, $\text{CuK}\alpha$ radiation (graphite monochromator). 7585 independent reflections were measured and of these, 5522 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods. The outside hydroquinone rings and substantial portions of their associated polyether linkages are disordered; in each case, two partial occupancy orientations were identified. Two partial occupancy sites were also identified for the ester group within one of the polyether linkages. Their relative occupancies were determined by an occupancy refinement. The major occupancy portions of the crown ether, the whole of the tetracationic cyclophane and the major component of the disordered hexafluorophosphate anions were refined anisotropically. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent atoms. The refinement was by full-matrix least squares based on F^2 to give $R_1 = 0.082$, $wR_2 = 0.216$ for 872 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.75 and -0.45 e Å $^{-3}$.

1,1'-Bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]ferrocene (BHEEF, 9): A solution of BAF (207 mg, 0.68 mmol) and 18-crown-6 (5.0 mg, 0.02 mmol) in KOH (1.8 M in H_2O , 10 mL) was stirred under reflux for 20 min. 2-[2-(2-(Tetrahydropyranyloxy)ethoxy)ethoxy]ethyl chloride (690 mg, 2.7 mmol) was added to the reaction mixture and refluxed for a further 5 h. The reaction mixture was washed with Et_2O (3×20 mL) and the resulting organic solution was washed with H_2O (3×10 mL). The organic phase was dried (MgSO_4), and the solvent evaporated in vacuo. The resulting oil was dissolved in MeOH (10 mL) and 1 M HCl (1 mL) and the solution was stirred at room temperature for 2 h. The solution was then diluted with 1 M HCl (150 mL) and washed with CH_2Cl_2 (3×70 mL); the organic layer was dried (MgSO_4), and the solvent evaporated off under vacuum. The resulting oil was purified by column chromatography (SiO_2 , $\text{CHCl}_3/\text{Me}_2\text{CO}$, 6:4) to yield BHEEF (66 mg, 20%) as yellow oil: EIMS: $m/z = 482$ [M] $^+$; ^1H NMR (CD_3COCD_3): δ = 4.22 (brs, 4H), 4.05–3.88 (m, 8H), 3.78–3.49 (m, 22H); ^{13}C NMR (CD_3COCD_3): δ = 73.5, 71.3, 71.1, 70.6, 70.6, 63.1, 62.0, 61.8, 56.5; Anal. calcd for $\text{C}_{22}\text{H}_{34}\text{FeO}_8 \cdot \text{H}_2\text{O}$: C 52.80, H 6.85; found C 52.72, H 7.16.

1,4-Bis[2-(2-methoxyethoxy)ethoxy]benzene (BMEEB): BHEEB (5.0 g, 18 mmol) was added to a suspension of NaH (4.9 g, 204 mmol) in dry THF (200 mL) under N_2 . The suspension was stirred vigorously for 40 min at room temperature, and then methyl iodide (19.8 g, 139 mmol) was added. The reaction mixture was stirred for 24 h before the excess of NaH was quenched by the addition of H_2O (150 mL). The solution was concentrated to 100 mL in vacuo, and extracted with MeCO_2Et (3×100 mL). The organic phase was washed with H_2O (200 mL) and dried (Na_2SO_4). The solvent was evaporated in vacuo to give an oil. Crystallization of the residue from $\text{CH}_2\text{Cl}_2/\text{hexane}$ at low temperatures, with liquid nitrogen as a coolant, afforded BMEEB as a white powder (4.5 g, 82%), which turned into a yellow oil at room temperature: EIMS: $m/z = 314$ [M] $^+$; ^1H NMR (CDCl_3): δ = 6.79 (s, 4H), 4.06–4.02 (m, 4H), 3.80–3.77 (m, 4H), 3.65–3.68 (m, 4H), 3.54–3.52 (m, 4H), 3.35 (s, 6H); ^{13}C NMR (CD_3CN): δ = 153.1, 115.6, 71.9, 70.7, 69.9, 68.1, 59.0; Anal. calcd for $\text{C}_{16}\text{H}_{24}\text{O}_6$: C 61.13, H 8.34; found C 61.26, H 8.51.

1-Benzyloxy-4-[2-(2-methoxyethoxy)ethoxy]benzene (BNMEEB): 4BNP (26.8 g, 134 mmol) was added to a suspension of K_2CO_3 (92.5 g, 670 mmol) in dry MeCN (500 mL) under N_2 . The suspension was stirred vigorously for 30 min at 70°C , and then a solution of 1-bromo-2-(2-methoxyethoxy)ethane (25.0 g, 134 mmol) in dry MeCN (100 mL) was added over 40 min. The resulting reaction mixture was heated under reflux for 16 h. After cooling to room temperature, the suspension was filtered, and the solid was washed with MeCN (200 mL). The combined organic solutions were concentrated in vacuo, and the residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (3×100 mL). The organic phase was dried (MgSO_4) and the solvent was evaporated in vacuo to afford BNMEEB as a brown oil (43.9 g, 90%); EIMS: $m/z = 302$ [M] $^+$; ^1H NMR (CDCl_3): δ = 7.44–7.31 (m, 5H), 6.91–6.82 (m, 4H), 5.00 (s, 2H), 4.10–4.06 (m, 2H), 3.84–3.81 (m, 2H), 3.73–3.70 (m, 2H), 3.58–3.55 (m, 2H), 3.38 (s, 3H); ^{13}C NMR (CDCl_3): δ = 153.1, 115.6, 71.7, 69.9, 68.1, 59.0; Anal. calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4$: C 71.50, H 7.33; found C 70.99, H 7.48.

4-[2-(2-Methoxyethoxy)ethoxy]phenol (MEEHB): A solution of BNMEEB (10.0 g, 33 mmol) in $\text{CHCl}_3/\text{MeOH}$ (1:1, v/v, 300 mL) was subjected to hydrogenolysis over

10% palladium on charcoal (500 mg) at room temperature for 24 h. After removal of the catalyst by filtration, the solvent was evaporated off under vacuum to give MEEHB as a pale yellow oil (7.0 g, 99%), which was employed in the following step without further purification: EIMS: $m/z = 212$ [M] $^+$; ^1H NMR (CDCl_3): δ = 6.76–6.68 (m, 4H), 5.90 (brs, 1H), 4.01–3.98 (m, 2H), 3.84–3.80 (m, 2H), 3.75–3.71 (m, 2H), 3.64–3.60 (m, 2H), 3.40 (s, 3H); ^{13}C NMR (CDCl_3): δ = 153.5, 150.2, 116.1, 115.8, 71.9, 70.6, 69.9, 68.0, 59.0.

1-[2-(2-Methoxyethoxy)ethoxy]-4-methyloxycarbonylmethylenoxy-benzene (βCMEEB): MEEHB (7.0 g, 33 mmol) was added to a suspension of K_2CO_3 (22.9 g, 166 mmol) in dry MeCN (150 mL) under N_2 . The suspension was stirred vigorously for 30 min at 70°C , and then a solution of methyl bromoacetate (7.6 g, 49.7 mmol) in dry MeCN (100 mL) was added over 45 min. The resulting reaction mixture was heated under reflux for 3 d. After cooling to room temperature, the suspension was filtered, and the solid was washed with MeCN (200 mL). The combined organic solutions were concentrated in vacuo, and the residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (3×100 mL). The organic phase was dried with Na_2SO_4 and the solvent was evaporated off under vacuum. Purification of the residue by column chromatography (SiO_2 , $\text{MeCO}_2\text{Et}/\text{CH}_2\text{Cl}_2$, 1:20) gave βCMEEB as a pale yellow oil (8.0 g, 85%); EIMS: $m/z = 284$ [M] $^+$; ^1H NMR (CDCl_3): δ = 6.82 (s, 4H), 4.56 (s, 2H), 4.08–4.05 (m, 2H), 3.82–3.79 (m, 2H), 3.77 (s, 3H), 3.70–3.67 (m, 2H), 3.55–3.52 (m, 2H), 3.36 (s, 3H); ^{13}C NMR (CDCl_3): δ = 169.6, 153.8, 152.2, 115.8, 115.7, 72.0, 70.7, 69.8, 68.1, 66.2, 59.0, 52.1.

1-[2-(2-Methoxyethoxy)ethoxy]-4-(2-methoxyethyloxycarbonyl)-methylenoxybenzene (βCMEEB): βCMEEB (7.0 g, 25 mmol) was added to a solution of Na (10 mg, 0.4 mmol) in 2-methoxyethanol (150 mL) and the solution was heated under reflux for 2 h. After cooling to room temperature, the solvent was evaporated off under vacuum. Purification of the residue by column chromatography (SiO_2 , CH_2Cl_2) gave βCMEEB as a pale yellow oil (5.0 g, 46%); EIMS: $m/z = 328$ [M] $^+$; ^1H NMR (CDCl_3): δ = 6.85 (s, 4H), 4.62 (s, 2H), 4.29–4.26 (m, 2H), 4.04–4.01 (m, 2H), 3.74–3.71 (m, 2H), 3.62–3.59 (s, 2H), 3.57–3.54 (m, 2H), 3.50–3.47 (m, 2H), 3.30 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (CDCl_3): δ = 170.1, 154.7, 153.2, 116.7, 116.5, 72.7, 71.2, 71.0, 70.4, 69.0, 66.7, 64.9, 59.0; Anal. calcd for $\text{C}_{18}\text{H}_{24}\text{O}_7$: C 58.53, H 7.37; found C 57.55, H 7.37.

1,4-Bis(methyloxycarbonylmethylenoxy)benzene ($\beta\beta\text{CMEB}$): 1/4DMB (5.0 g, 46 mmol) was added to a suspension of K_2CO_3 (62.7 g, 454 mmol) in dry MeCN (150 mL) under N_2 . The suspension was stirred vigorously for 30 min at 70°C and then a solution of methyl bromoacetate (20.8 g, 137 mmol) in dry MeCN (50 mL) was added over 40 min. The reaction mixture was heated under reflux for 3 d. After cooling to room temperature, the suspension was filtered, and the solid was washed with MeCN (200 mL). The combined organic solutions were concentrated in vacuo, and the residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (3×100 mL). The organic phase was dried (Na_2SO_4) and the solvent was evaporated off under vacuum. Purification of the residue by column chromatography (SiO_2 , $\text{MeCO}_2\text{Et}/\text{CH}_2\text{Cl}_2$, 1:20) gave $\beta\beta\text{CMEB}$ as a white solid (11.0 g, 95%); m.p. 97°C ; FABMS: $m/z = 254$ [M] $^+$; ^1H NMR (CDCl_3): δ = 6.86 (s, 4H), 4.59 (s, 4H), 3.80 (s, 6H); ^{13}C NMR (CDCl_3): δ = 169.5, 152.9, 115.9, 66.2, 52.2; Anal. calcd for $\text{C}_{12}\text{H}_{14}\text{O}_6$: C 56.69, H 5.55; found C 56.29, H 5.36.

1,4-Bis(2-methoxyethyloxycarbonyl)methylenoxybenzene ($\beta\beta\text{CMEB}$): $\beta\beta\text{CMEB}$ (9.62 g, 39 mmol) was added to a solution of Na (40 mg, 1.7 mmol) in 2-methoxyethanol (150 mL) and the solution was heated under reflux for 2 h. After cooling to room temperature, the solvent was evaporated off under vacuum. Purification of the residue by column chromatography (SiO_2 , $\text{MeCO}_2\text{Et}/\text{CH}_2\text{Cl}_2$, 1:20) gave a solid, which was recrystallized from hexane/ CH_2Cl_2 to give $\beta\beta\text{CMEB}$ as a white solid (9.46 g, 71%); m.p. 44°C ; FABMS: $m/z = 342$ [M] $^+$; ^1H NMR (CDCl_3): δ = 6.86 (s, 4H), 4.62 (s, 4H), 4.38–4.35 (m, 4H), 3.64–3.60 (m, 4H), 3.38 (s, 6H); ^{13}C NMR (CDCl_3): δ = 169.1, 152.8, 116.0, 70.2, 66.1, 64.1, 59.0; Anal. calcd for $\text{C}_{16}\text{H}_{22}\text{O}_8$: C 56.14, H 6.47; found C 55.91, H 6.34.

[3]Pseudorotaxane $[\text{BHEEB}]_2\text{-}[\text{BBIPYBIBTCY}]\text{[PF}_6\text{]}_4$ (14): Single crystals suitable for X-ray crystallography were grown by vapor diffusion of $i\text{Pr}_2\text{O}$ into a MeCN solution of equimolar amounts of BHEEB and $[\text{BBIPYBIBTCY}]\text{[PF}_6\text{]}_4$. X-ray data: $\text{C}_{84}\text{H}_{93}\text{F}_{24}\text{N}_4\text{O}_{16}\text{P}_4 \cdot 2\text{MeCN} \cdot 0.75\text{H}_2\text{O}$, $M = 2077.4$, monoclinic, $a = 17.522(1)$, $b = 19.257(5)$, $c = 14.924(3)$ Å, $\beta = 90.17(1)^\circ$, $V = 4971(2)$ Å 3 , $T = 173$ K, space group = $P2_1/c$, $Z = 2$, $\rho_{\text{calcd}} = 1.39$ g cm $^{-3}$, $\mu(\text{CuK}\alpha) = 16.7$ cm $^{-1}$, $F(000) = 2148$. Data for a crystal of dimensions $0.33 \times 0.15 \times 0.08$ mm were collected on a Siemens P4/RA diffractometer ($2\theta \leq 122^\circ$), ω scans, $\text{CuK}\alpha$ radiation (graphite monochromator). 7522 independent reflections were measured and of these, 5939 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods. One of the terminal hydroxyl groups was found to be disordered and two discrete positions (50:50 occupancy) were identified. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent atoms. The refinement was by full-matrix least squares based on F^2 to give $R_1 = 0.103$, $wR_2 = 0.297$ for 646 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.93 and -0.59 e Å $^{-3}$.

[2]Pseudorotaxane $[B\beta CMEEB][BBIPYBIXYCY][PF_6]_4$ (15): Single crystals suitable for X-ray crystallography were grown by vapor diffusion of iPr_2O into a MeCN solution of equimolar amounts of $B\beta CMEEB$ and $[BBIPYBIXYCY][PF_6]_4$. X-ray data: $C_{32}H_{44}F_{12}N_4O_6P_4 \cdot 4MeCN \cdot 0.5H_2O$, $M = 1616.1$, triclinic, $a = 10.785(2)$, $b = 13.497(3)$, $c = 13.915(2)$ Å, $\alpha = 91.61(2)$, $\beta = 103.19(2)$, $\gamma = 110.33(2)^\circ$, $V = 1836.4(6)$ Å³, $T = 293$ K, space group = $P\bar{1}$, $Z = 1$, $\rho_{calcd} = 1.46$ g cm⁻³, $\mu(CuK\alpha) = 20.1$ cm⁻¹, $F(000) = 827$. Data for a crystal of dimensions $0.67 \times 0.60 \times 0.41$ mm were collected on a Siemens P4/RA diffractometer ($2\theta \leq 110^\circ$), ω scans, $CuK\alpha$ radiation (graphite monochromator). 4620 independent reflections were measured and of these 3648 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. The data were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods. The terminal methoxyl groups were found to be disordered and two discrete (39:61) partial occupancy sites were identified. Hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent atoms. The refinement was by full-matrix least squares based on F^2 to give $R_1 = 0.087$, $wR_2 = 0.240$ for 523 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.89 and -0.43 e Å⁻³.

General methods for the determination of the association constants by UV/Vis and ¹H NMR spectroscopy:

Method A: A series of solutions with constant concentrations ($\approx 10^{-3}$ M) of the π -electron-rich macrocycle and containing different amounts of $[PQT][PF_6]_4$ ($\approx 10^{-4}$ – 10^{-2} M) in Me₂CO were prepared. The absorbance at the wavelength (λ_{max}) corresponding to the maximum of the charge-transfer band for the 1:1 complex was measured for all the solutions. The correlation between the absorbance and the guest concentration was used [30] to evaluate the association constant (K_a) in a nonlinear curve-fitting program.

Method B: A series of solutions with constant concentrations ($\approx 10^{-3}$ M) of the cyclophane $[BBIPYBIBTCY][PF_6]_4$ (1) and containing different amounts of the guest ($\approx 10^{-2}$ – 10^{-1} M) in CD₃CN were prepared. The chemical shifts of the host protons attached to the bipyridinium units β to the nitrogen atoms were measured by ¹H NMR spectroscopy at 25 °C. The correlation between the chemical shift and the guest concentration was used to evaluate the association constant (K_a) in a nonlinear curve-fitting program.

General method for the determination of the association constants by ¹H NMR spectroscopy employing continuous variation methodology: A solution of $[BBIPYBIXYCY][PF_6]_4$ (2) and a solution of the π -electron-rich acyclic guest with identical concentrations ($\approx 10^{-3}$ M) were prepared in CD₃CN as the solvent. By employing the two stock solutions, several new solutions with the same total volumes, but differing in the ratios of the two components (from 1:9 to 9:1 host:guest), were prepared. The chemical shifts of the protons attached to the hydroquinone ring of the guest were measured by ¹H NMR spectroscopy at 25 °C. The correlation between the mole fraction of the guest and the chemical shift change for the probe protons was used to evaluate the association constant (K_a) in a nonlinear curve-fitting program [30].

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- [37] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-12. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code + (1223) 336-033; e-mail: teched@chemcrs.cam.ac.uk).