Doubly Docked Pseudorotaxanes**

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Abstract: The complexation phenomena associated with the ditopic crown ether bis-*p*-phenylene[34]crown-10 (BPP34C10) and four bisammonium salts, each endowed with two bulky 3,5-di-*tert*-butylbenzyl termini and a pair of NH_2^+ centers that are linked through a suitable spacer unit, have been studied. These studies have led to a route to the supramolecular syntheses of singly stranded, doubly docked [2]pseudorotaxanes, in which each NH_2^+ center interacts simultaneously with the crown ether's independent polyether arcs, so that one dicationic unit can interpenetrate the cavity of one BPP34C10 macroring by means of hydrogen-bonding interactions. NMR spectroscopy, mass spectrometry, and X-ray crystallography demonstrate (in solution, in the gas phase, and in the solid state, respectively) that the doubly docked [2]pseudorotaxanes are generated through the self-assembly of BPP34C10 with bisammonium dications bearing *p*-xylylene, 2,6-naphthalenebis(methylene), or hexamethylene spacer units. In contrast, X-ray crystallography shows that a supermolecule, possessing a hot-dog-like co-conformation, is synthesized noncovalently when BPP34C10 self-assembles with a bisammonium salt in which the NH_2^+ centers are separated by a shorter pentamethylene spacer unit. The double docking of one of the bisammonium dications within BPP34C10's cavity has been utilized in a prototypical chromophoric supramolecular device that operates in response to changes in its surrounding pH. A 1:1:1 solution of the hexafluorophosphate salt of this bisammonium dication with BPP34C10 and a 4,4′-bipyridinium salt is colorless, since the crown ether complexes preferentially with the bisammonium dication. Conversely, it is red in the presence of $i\mathrm{Pr_2NEt}$ because the NH_2^+ centers are deprotonated, forcing the crown ether to interact with the 4,4′-bipyridinium salt by means of, inter alia, charge-transfer interactions. This process is reversible, since the solution is decolorized upon treatment with CF_3CO_2H.

Keywords: host – guest chemistry • inclusion compounds • molecular recognition • pseudorotaxanes • supramolecular devices

Introduction

The so-called pseudorotaxanes[1] are ideal precursors for the construction[2] of interlocked molecular assemblies and interwoven superarchitectures. The search for novel protocols that can be utilized for the supramolecular synthesis[3] of new classes of pseudorotaxanes, by self-assembly,[4] has led us to develop[5] supramolecular systems that are based upon the mutual recognition between secondary dialkylammonium ions and macrocyclic polyethers of varying constitutions. We have demonstrated that the composition of the pseudorotaxane superarchitecture is dependent on the size of the macroring employed for the supramolecular synthesis (Figure 1): by way of illustration, only one NH_2^+-containing strand can be passed through the cavity of the dibenzo[24]crown-8 (DB24C8) macroring,[5a, 5c–e, 5g] whereas two such strands can be fed through its larger congener bis-*p*-phenylene[34]crown-10 (BPP34C10),[5b–e] which acts, in this instance, as a *ditopic coreceptor*.[6] In both cases, the principal recognition mechanism between the separate components involves $[N^+-H\cdots O]$ and $[C-H\cdots O]$ hydrogen bonding between the cationic NH_2^+-bearing guests and the neutral polyether receptors.

Recently, we started to explore the potential of BPP34C10 to bind two NH_2^+ centers concurrently within its macrocyclic interior, in order to prepare controllable molecular switches[7] based upon systems that are endowed with different compet-

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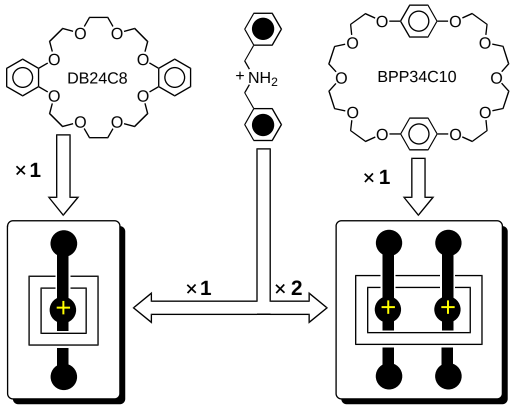


Figure 1. Schematic diagram depicting how differently sized macrorings self-assemble with the dibenzylammonium ion to generate pseudorotaxanes with diverse stoichiometries. The dibenzylammonium ion self-assembles with DB24C8 to produce a singly stranded [2]pseudorotaxane, while it forms a doubly stranded [3]pseudorotaxane with BPP34C10.

ing recognition motifs. Previously, these two cationic centers have been located on different strands,[5b–e, 8] whereas in the prototypical system, illustrated in Figure 2, they reside on the same strand. Here, we describe the consequences of employing different spacer units between the two NH$_2^+$ centers for the design of one of the two competing receptor sites of the potentially switchable system.

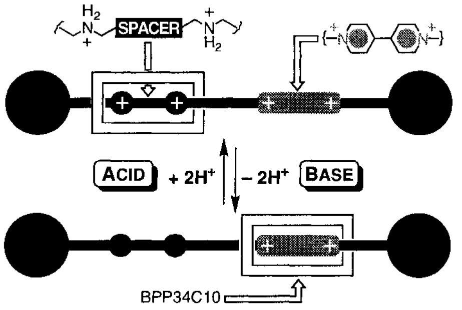


Figure 2. Schematic picture of a pH-operated [2]rotaxane switch. The BPP34C10 macrocycle is compelled to shuttle back-and-forth between the dumbbell's *α*,*ω*-bisammonium and 4,4′-bipyridinium[9] units as a result of added acid or base.

In previous investigations on the threading of the *α*,*α*′-bisbenzylammonium-*p*-xylene dication ($\mathbf{1}^{2+}$) with BPP34C10, we discovered that a doubly stranded, doubly encircled [4]pseudorotaxane complex was generated, in the solid state, with all the ingredients of the analogous 1:2 complex formed between a pair of dibenzylammonium ions and BPP34C10 (Figure 1). Recently, we analyzed the supramolecular aspects of this crystal structure in more detail and have discovered that PF$_6^-$ counterions are located in the cavities formed between 2$_1$-screw-related [4]pseudorotaxanes to create an interwoven[10] one-dimensional supramolecular array (Figure 3a). There are more than ten C–H bonds, emanating both from hydroquinone rings and benzylic methylene groups, that are directed toward the fluorine atoms of these PF$_6^-$ anions in an arrangement that is reminiscent of those which we have observed[5f–g, 8b, 10] hitherto in examples of anion-assisted self-assembly. On the other hand, in solution, the 2:2 complex disassembles (Figure 3b) to produce a complex which we believe possesses a 1:1 stoichiometry—that is, a [2]pseudorotaxane—thereby potentially fulfilling our requirements for the simultaneous binding of a covalently interconnected pair of NH$_2^+$ centers within the cavity of a single BPP34C10 molecule. Indeed, molecular modeling indicates[11] that the insertion of appropriate spacer units between the NH$_2^+$ centers should favor the formation of singly stranded, doubly docked [2]pseudorotaxanes, as opposed to their doubly stranded, doubly encircled [4]pseudorotaxane congeners.

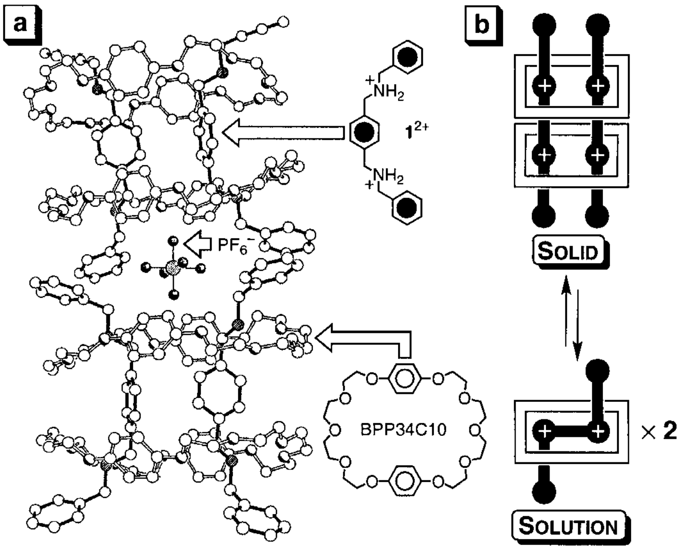
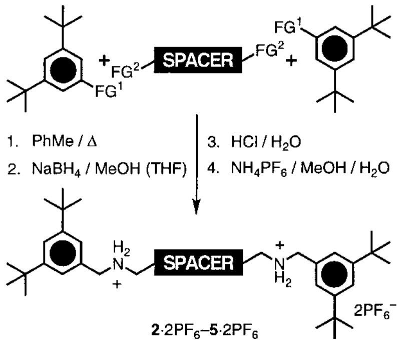


Figure 3. a) Ball-and-stick view of the one-dimensional supramolecular array generated in the solid state when the dication $\mathbf{1}^{2+}$ self-assembles, using assistance from attendant PF$_6^-$ anions, with BPP34C10. b) Schematic representation illustrating how the [4]pseudorotaxane [(BPP34C10)$_2$·($\mathbf{1}$)$_2$]$^{4+}$ disassembles in solution to create two [2]pseudorotaxanes [BPP34C10·$\mathbf{1}$]$^{2+}$.

Results and Discussion

Design logic: Initially, we speculated that the presence of bulky alkyl substituents (e.g., a pair of *m*,*m*′-disposed *tert*-butyl groups) on the dications' phenyl termini should 1) prevent the insertion of a second strand into the cavity of the BPP34C10 macroring, 2) increase the solubility of the pseudorotaxanes, and 3) inhibit solid-state, anion-assisted self-assembly (vide supra). Moreover, we conjectured that rigid aromatic spacer units—such as *p*-xylylene or 2,6-naphthalenebis(methylene)—could be sandwiched by the hydroquinone rings of BPP34C10, thus rendering further stabilization, through π–π stacking interactions, to the doubly docked [2]pseudorotaxanes. On the other hand, we believed that flexible aliphatic spacer units—such as penta- or hexamethylene—would permit the dications' NH$_2^+$ centers to adopt favorable hydrogen-bonding geometries with the polyether loops of the BPP34C10 macroring.

Synthesis: The bis(hexafluorophosphate) salts of the requisite dications $2^{2+}-5^{2+}$ were prepared by the synthetic protocol outlined in Scheme 1. Standard reductive amination procedures were employed to synthesize the dications' diamine precursors, which were then transformed into the desired salts by treatment with hydrochloric acid followed by counterion exchange.



Compound	FG¹	FG²	SPACER	Overall Yield (%)
$2\cdot2PF_6$	CHO	CH_2NH_2	p-C_6H_4	18
$3\cdot2PF_6$	CH_2NH_2	CHO	2,6-$C_{10}H_6$	62
$4\cdot2PF_6$	CHO	CH_2NH_2	$(CH_2)_3$	60
$5\cdot2PF_6$	CHO	CH_2NH_2	$(CH_2)_4$	64

Scheme 1. Synthetic method employed to prepare the salts $2\cdot2PF_6$–$5\cdot2PF_6$.

Formation and characterization of complexes: The ability of all four of the bis(hexafluorophosphate) salts $2\cdot2PF_6$–$5\cdot2PF_6$ to form 1:1 complexes with BPP34C10 was investigated in solution, gas phase, and solid state by NMR spectroscopy, mass spectrometry, and X-ray crystallography, respectively.

α,α'-Bis(3,5-di-tert-butylbenzylammonium)-p-xylene bis(hexafluorophosphate) ($2\cdot2PF_6$): The solubility of the salt $2\cdot2PF_6$ increases markedly in nonpolar halogenated solvents, such as $CHCl_3$ or CH_2Cl_2, in the presence of one or more molar equivalents of BPP34C10, thus indicating the formation of a complex. The ^1H NMR spectra of 1:1 mixtures of the two components, in CD_2Cl_2 at room temperature, display only time-averaged signals as a result of fast kinetic exchange between complexed and uncomplexed states on the ^1H NMR timescale (300.1/400.1 MHz). This observation is hardly surprising, since CPK space-filling molecular models indicate that the BPP34C10 macroring has no difficulty in traversing the dication's 3,5-di-*tert*-butylbenzyl termini. Furthermore, the spectrum of this mixture reveals significant chemical shift differences, supplemented by considerable broadening, of almost all of its resonances with respect to their uncomplexed components. To cite an instance, the resonance for the protons of the dication's *p*-xylylene unit is shifted (Table 1) dramatically upfield in the presence of an equimolar quantity of the receptor BPP34C10. In addition, the resonance associated with the protons attached to the hydroquinone units of the macrocyclic polyether experience considerable upfield shifts, giving further credence to the proposal that the *p*-xylylene unit lies inside the cavity of the BPP34C10 macrocycle.

Table 1. Selected ^1H NMR resonances[a] for 1) uncomplexed BPP34C10/$2\cdot2PF_6$, and 2) 1:1 mixtures of these constituents of the [BPP34C10·2]$(PF_6)_2$ complex.

	δ_u[h, k]	δ_c[i, l, m]	$\Delta\delta$[j]
CH_2–Xy[b]	4.07	4.08–4.16	+ (0.01–0.09)
CH_2–Tmn[c]	4.26	4.08–4.16	− (0.10–0.18)
CH–Xy[d]	7.43	6.59	− 0.84
CH–*o*-Tmn[e]	7.30	7.37	+ 0.07
CH–*p*-Tmn[f]	7.54	7.54	0.00
CH–Hq[g]	6.76	6.59	− 0.17

[a] The ^1H NMR spectra were recorded on a Bruker AC300 (300.1 MHz) spectrometer in CD_2Cl_2 at 30 °C. [b] Methylene protons on the *p*-xylylene unit of the salt. [c] Methylene protons on the 3,5-di-*tert*-butylbenzyl termini of the salt. [d] Aromatic protons of the salt's *p*-xylylene unit. [e] Aromatic protons of the salt's 3,5-di-*tert*-butylbenzyl termini that are located *ortho* with respect to the benzylic methylene moiety. [f] Aromatic protons of the salt's 3,5-di-*tert*-butylbenzyl termini that are located *para* as regards to the benzylic methylene group. [g] Aromatic protons of BPP34C10's hydroquinone units. [h] δ values for the resonances of BPP34C10 and $2\cdot2PF_6$ in their uncomplexed states (ca. 5×10^{-3} M). [i] δ values for the resonances of BPP34C10 and $2\cdot2PF_6$ in a 1:1 solution of both components (ca. 5×10^{-3} M). [j] $\Delta\delta$ values were obtained from the relationship $\Delta\delta = \delta_c - \delta_u$. [k] The resonances for both sets of benzylic methylene protons were assigned employing a selective (^1H–^1H) decoupling experiment. [l] The resonances for both groups of benzylic methylene protons were designated from a (^1H–^1H) NOE difference experiment. [m] The resonances for both sets of benzylic methylene protons appear as two broad signals that overlap partially with one another.

An analysis of the complex by liquid secondary ion (LSI) mass spectrometry revealed a peak at $m/z = 1078$, corresponding to the 1:1 complex with the loss of both PF_6^- counterions. This observation provides clear evidence that a characterizable 1:1 complex forms in the gas phase.

An analysis of the crystalline[12] 1:1 complex formed between BPP34C10 and $2\cdot2PF_6$ by X-ray crystallography shows that the dication 2^{2+} is threaded through the cavity of the BPP34C10 macroring in a C_i-symmetric fashion (Figure 4); the *p*-xylylene residue within the thread is sandwiched between the hydroquinone rings of the crown ether. The conformation of the macrocyclic polyether is such that its two hydroquinone rings are sheared sideways with respect to each other and the central *p*-xylylene residue. The interplanar (3.21 Å) and centroid–centroid distances (3.74 Å) between the *p*-xylylene and hydroquinone rings are consistent with

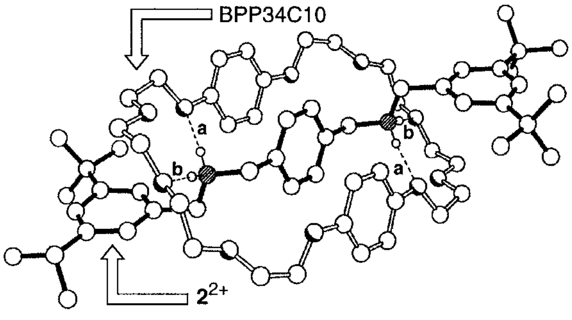


Figure 4. X-ray crystal structure of the doubly docked [2]pseudorotaxane complex formed between BPP34C10 and the dication 2^{2+}. The intracomplex hydrogen-bonding geometries are ([N⁺···O], [H···O] distances (Å), [N⁺–H···O] angles (°)) a) 2.88, 1.98, 172; b) 3.06, 2.18, 165.

strong $\pi-\pi$ stabilization.[13] These interactions are supplemented by pairs of $[N^+-H\cdots O]$ hydrogen bonds from each of the dicationic strand's NH_2^+ centers to the central oxygen atoms and one of the hydroquinone oxygen atoms, in both polyether arcs of the BPP34C10 macrocycle. The intrachain $[N^+\cdots N^+]$ separation is 7.60 Å. The $CH_2NH_2^+CH_2C_6H_4CH_2NH_2^+CH_2$ portion of the dication's backbone is folded, the $C-N^+$ bonds each being oriented approximately orthogonally to their proximal aromatic rings; the *p*-xylylene unit and the terminal 1,3,5-trisubstituted benzene rings are oriented essentially perpendicular to each other. There are no noteworthy intercomplex packing interactions.

2,6-Bis(3,5-di-tert-butylbenzylammoniummethylene)naphthalene bis(hexafluorophosphate) (**3**·$2PF_6$): The observation that, in the [BPP34C10·**2**]$^{2+}$ complex, the bisammonium dication is held within the macroring's cavity partly as a consequence of $[N^+-H\cdots O]$ bonds involving the phenolic oxygen atoms of the macrocycle's hydroquinone rings, led us to conclude that the resultant [2]pseudorotaxane was unable to maximize its stabilization, at least in a hydrogen-bonding sense, since the hydroquinone rings' phenolic oxygen atoms are less basic than their aliphatic counterparts. Accordingly, we sought a longer aromatic spacer unit, namely, 2,6-naphthalenebis(methylene), that would allow the dicationic guest to orient itself inside BPP34C10's cavity with its NH_2^+ centers held further apart from one another so as to prevent any interactions with the aromatic rings' phenolic oxygen atoms. In other words, in the ensuing pseudorotaxane, the NH_2^+ centers should interact only with the crown ether's aliphatic oxygen atoms, thus producing stronger hydrogen bonds. Furthermore, we anticipated that the naphthalene rings of the dication would enter into more efficient $\pi-\pi$ stacking interactions with the crown ether's alongside hydroquinone residues, thereby stabilizing the pseudorotaxane co-conformation[14] even more.

Not surprisingly, the ^1H NMR spectrum of an equimolar mixture of BPP34C10 and the salt **3**·$2PF_6$ (recorded in CD_2Cl_2 at ambient temperature) exhibits only time-averaged signals. Once again, the signal for the hydroquinone ring protons of the BPP34C10 macrocycle is displaced (Table 2) toward higher field in the presence of the bisammonium salt. Interestingly, in contrast with the [BPP34C10·**2**]$^{2+}$ complex, both groups of benzylic methylene protons experience substantial downfield shifts.

In order to study the complexation process further, a ($^1H-{}^1H$) NOESY experiment, performed at −30 °C in CD_2Cl_2, was carried out on an equimolar mixture of BPP34C10 and **3**·$2PF_6$. A selected row of the two-dimensional (2D) matrix, intersecting the diagonal through the hydroquinone resonance of the crown ether, shows strong cross-coupling peaks with the resonances of the naphthalene spacer unit of the dication, in addition to those of the protons of the dication's trisubstituted phenyl termini that are located in the *ortho* position with respect to the connected methylene unit. This result provides a further indication that the naphthalene spacer unit lies in close spatial proximity to the hydroquinone rings within the complex and, consequently, supports the existence of either face-to-face[15] or pseudorotaxane co-conformation[14] whose lifetime is long enough to bring about cross-coupling peaks in the 2D matrix.

Table 2. Selected ^1H NMR resonances[a] for 1) free BPP34C10/**3**·$2PF_6$, and 2) equimolar mixtures of these two components.

	δ_u[d]	δ_c[e, g]	$\Delta\delta$[f]
CH_2−Npt[b]	4.08	4.40	+0.32
CH_2−Tmn[c]	4.19	4.53	+0.34
CH−*o*-Tmn[c]	7.28	7.41	+0.13
CH−*p*-Tmn[c]	7.52	7.53	+0.01
CH−Hq[c]	6.76	6.20	−0.56

[a] The ^1H NMR spectra were recorded on a Bruker AC300 (300.1 MHz) spectrometer in CD_2Cl_2 at 30 °C. [b] Methylene protons adjacent to the naphthalene hub. [c] See Table 1 for an explanation of the descriptor. [d] δ values associated with the resonances of BPP34C10 and **3**·$2PF_6$ in their uncomplexed states (ca. 5×10^{-3} M). [e] δ values for the resonances of BPP34C10 and **3**·$2PF_6$ in an equimolar solution of both components (ca. 5×10^{-3} M). [f] $\Delta\delta$ values were acquired from the equation $\Delta\delta=\delta_c-\delta_u$. [g] The assignments of the resonances for both components were confirmed by a ($^1H-{}^1H$) NOESY experiment, recorded on a Bruker AMX400 (400.1 MHz) spectrometer in CD_2Cl_2 at −30 °C.

A 1:1 CD_2Cl_2 solution of the two components was analyzed by electrospray (ES) mass spectrometry. The spectrum's base peak, appearing at $m/z=1274$, corresponds to the mass of the 1:1 complex with the loss of one of its PF_6^- counterions (Figure 5).

The solid-state structure of the [BPP34C10·**3**]$^{2+}$ complex[12] reveals (Figure 6) that the dication is, once again, threaded centrosymmetrically through the center of the BPP34C10 macroring, with its naphthalene moiety sandwiched between the macrocycle's two hydroquinone rings in a $\pi-\pi$ stacked[13] arrangement (the mean interplanar separation is 3.67 Å). The naphthalene spacer unit increases the separation between the NH_2^+ centers ($[N^+\cdots N^+]=9.6$ Å), but prevents optimal deployment of the four N^+-H bonds for hydrogen bonding to the polyether oxygen atoms; there are only two $[N^+-H\cdots O]$ hydrogen bonds in the [2]pseudorotaxane

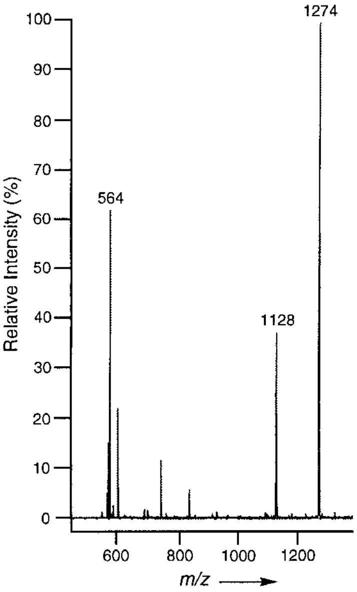


Figure 5. ES Mass spectrum of an equimolar solution of BPP34C10 and **3**·$2PF_6$. There is no indication of the creation of complexes bearing a stoichiometry greater than 1:1.

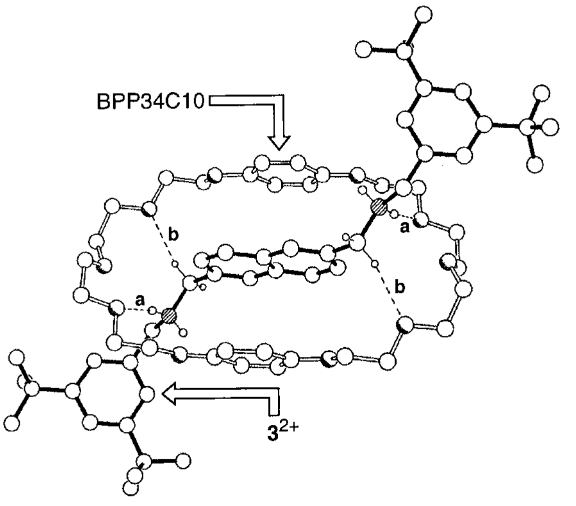


Figure 6. Solid-state structure of the doubly docked [2]pseudorotaxane supermolecule [BPP34C10 · **3**]$^{2+}$. The intrasupermolecule [N^+–H ··· O] and [C–H ··· O] hydrogen-bonding geometries are ([X ··· O], [H ··· O] distances (Å), [X–H ··· O] angles (°)) a) 3.11, 2.03, 167; b) 3.31, 2.36, 167.

Table 3. Selected ^{1}H NMR resonances[a] for 1) uncomplexed BPP34C10/**4** · 2 PF$_6$, and 2) equimolar mixtures of these constituents of the [BPP34C10 · **4**](PF$_6$)$_2$ complex.

	δ_u[d, g]	δ_c[e, h]	$\Delta\delta$[f]
CH_2–Tmn[b]	4.08	4.09	+0.01
CH_2–α[c]	2.94	2.75	−0.19
CH_2–β[c]	1.76	1.34	−0.42
CH_2–γ[c]	1.51	1.04	−0.47
CH–Hq[b]	6.76	6.85	+0.09

[a] The ^{1}H NMR spectra were recorded on a Bruker AC300 (300.1 MHz) spectrometer in CD$_2$Cl$_2$ at 30 °C. [b] Descriptor is defined in Table 1. [c] Methylene protons on the dication's polymethylene chain that are located in the α, β, and γ positions, respectively, as regards to the NH_2^+ centers. [d] δ values associated with the resonances of BPP34C10 and **4** · 2 PF$_6$ in their uncomplexed states (ca. 5×10^{-3} M). [e] δ values associated with the resonances of BPP34C10 and **4** · 2 PF$_6$ in an equimolar mixture of both components (ca. 5×10^{-3} M). [f] $\Delta\delta$ values were acquired from the equation $\Delta\delta = \delta_c - \delta_u$. [g] The resonances for the protons on the polymethylene chain were assigned from a selective (^{1}H–^{1}H) decoupling experiment. [h] The assignments for the resonances associated with the polymethylene protons were confirmed by a (^{1}H–^{1}H) COSY experiment.

superarchitecture. Nevertheless, these are supplemented by two [C–H ··· O] hydrogen bonds, which occur from one of the hydrogen atoms on each of the carbon atoms adjacent to the naphthalene spacer to another pair of oxygen atoms. The BPP34C10 macrocycle has an open boxlike conformation, wherein its CH$_2$OC$_6$H$_4$OCH$_2$ units have a *cisoid* geometry, and the transannular ring-centroid–ring-centroid separation between the two hydroquinone rings is 7.4 Å. The C–N^+ bonds within the dication are each oriented approximately orthogonally with respect to their proximal aromatic rings, the CCH$_2$NH$_2^+$CH$_2$C segments of the backbone having an all-*anti* geometry. Once again, there are no intercomplex interactions of note.

*1,5-Bis(3,5-di-tert-butylbenzylammonium)pentane bis(hexafluorophosphate) (**4** · 2 PF$_6$)*: Thus far, in our quest for bisammonium dications that are both sterically and electronically complementary to the macrocyclic polyether BPP34C10, we have only examined species in which the NH_2^+ centers are separated by aromatic spacers of different lengths and constitutions. The question we then posed ourselves was: what would be the effect of replacing the cations' rigid aromatic moieties with flexible aliphatic chains? The increased mobility of the NH_2^+ centers that would result should allow them to achieve more optimal hydrogen bonding with the polyether arcs of the BPP34C10 macroring.

Although, as expected, the dicationic salt **4** · 2 PF$_6$ is extremely soluble in polar solvents (such as Me$_2$CO, MeCN, and Me$_2$SO) that are capable of solvating its NH_2^+ centers, it is only sparingly soluble in nonpolar halogenated solvents (such as CHCl$_3$ and CH$_2$Cl$_2$). However, its solubility in nonpolar solvents increases significantly in the presence of an equimolar quantity of BPP34C10, a result that is diagnostic of complex formation. The ^{1}H NMR spectrum of an equimolar BPP34C10–**4** · 2 PF$_6$ mixture, recorded in CD$_2$Cl$_2$ at ambient temperature, displays time-averaged sets of resonances, thus implying fast kinetic exchange between the [BPP34C10 · **4**](PF$_6$)$_2$ complex and its constituents on the ^{1}H NMR timescale (300.1/400.1 MHz). Thus, once again, it appears that the dication $\mathbf{4}^{2+}$ experiences no difficulty in threading its way through the cavity of the BPP34C10 macroring. Noticeably, the resonances of the dication's central pentamethylene unit are displaced toward higher fields in the presence of an equimolar amount of the crown ether. In particular, the signal associated with the hydrocarbon chain's central methylene unit (i.e., those in the γ position) experiences a large change in its chemical shift value (Table 3), while those signals associated with the nearby α and β protons are somewhat less affected. These observations are in good agreement with the formation of an inclusion complex in which the pentamethylene spacer unit, linking the dication's NH_2^+ centers, is located in the center of the BPP34C10 macrocycle's cavity, with its median protons experiencing the strongest shielding effect from the macrocycle's hydroquinone rings.

Strong evidence for the integrity of this species in the gas phase was obtained from the LSI mass spectrum of a mixture of the two components; this showed peaks at $m/z = 1189$ and 1044 that correspond to the 1:1 complex with the loss of one or two PF_6^- counterions, respectively.

Single crystals, suitable for X-ray crystallographic analysis, were grown by liquid diffusion of nC$_5$H$_{12}$ into an equimolar solution of BPP34C10 and **4** · 2 PF$_6$ in Me$_2$CO. The X-ray analysis reveals (Figure 7) the creation of a 1:1:1 complex between BPP34C10, **4** · 2 PF$_6$, and one molecule of Me$_2$CO. The BPP34C10 macrocycle adopts an open conformation, the hydroquinone rings' centroids being separated by 6.70 Å and tilted slightly (14° between their mean planes) with respect to one another. The dication is threaded asymmetrically through the cavity of the crown ether; one of its NH_2^+ centers is positioned within one of the macrocycle's polyether loops by virtue of a pair of [N^+–H ··· O] hydrogen bonds to the second and fourth oxygen atoms of the loop. A similar interaction involving the thread's other NH_2^+ center is precluded by the inclusion of the Me$_2$CO molecule that forms an integral part of the 1:1:1 complex. This included guest molecule is involved in an [O ··· H–N^+] hydrogen bond to the NH_2^+ center and a [C–H ··· π] interaction[16] between one of its methyl hydrogen

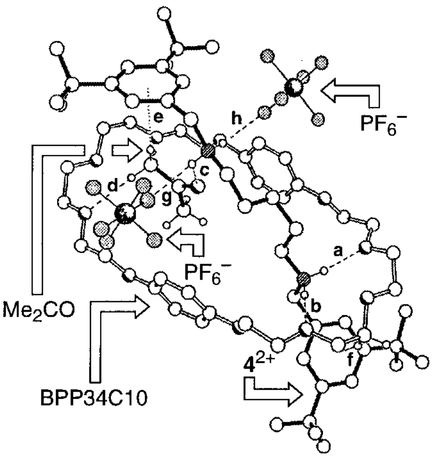


Figure 7. X-ray crystal structure of the [BPP34C10 · **4** · Me$_2$CO][PF$_6$]$_2$ complex. The intracomplex [N$^+$–H ··· O] and [C–H ··· O] hydrogen bonding geometries are ([X ··· O], [H ··· O] distances (Å), [X–H ··· O] angles (°)): a) 2.91, 2.02, 171; b) 2.95, 2.05, 178; c) 2.80, 2.17, 126; d) 3.50, 2.58, 161. The geometries for the intracomplex [C–H ··· π] interactions are ([H ··· π] distances (Å), [C–H ··· π] angles (°)): e) 2.92, 158; f) 2.84, 161, while those for the [N$^+$–H ··· F] hydrogen bonds are ([N$^+$ ··· F], [H ··· F] distances (Å), [N$^+$–H ··· F] angles (°)) g) 3.00, 2.31, 134; h) 3.00, 2.16, 155.

atoms and the 3,5-di-*tert*-butylbenzyl terminus that is located nearby. Interestingly, there is a similar [C–H ··· π] interaction between a hydrogen atom on one of the BPP34C10 macroring's methylene groups and the other 3,5-di-*tert*-butylbenzyl terminus. Additionally, there are secondary [N$^+$–H ··· F] hydrogen bonds involving one of the two NH$_2^+$ centers (the one that enters into hydrogen bonding with the Me$_2$CO molecule) and fluorine atoms of both PF$_6^-$ counterions (the [N$^+$ ··· F] distances are both 3.00 Å). The 1:1:1 [BPP34C10 · **4** · Me$_2$CO](PF$_6$)$_2$ complexes do not engage in any significant intercomplex interactions.

A dramatic change is observed in the solid-state superstructure of the complex (Figure 8) when the single crystals were obtained after an equimolar CH$_2$Cl$_2$ solution of BPP34C10 and **4** · 2PF$_6$ had been layered with nC$_6$H$_{14}$, that is, in the absence of the strong donor solvent Me$_2$CO. In this instance, threading does not occur, although the NH$_2^+$(CH$_2$)$_5$NH$_2^+$ chain of the dication lies within the convex face of the cavity of the BPP34C10 macrocycle, producing a hot-dog-like (i.e., a face-to-face[15]) co-conformation. Complex stabilization is achieved by a combination of both [N$^+$–H ··· O] and [C–H ··· π] hydrogen-bonding interactions. Notably, the dication's pentamethylene backbone does not adopt the normal all-*anti* geometry. The intrachain [N$^+$ ··· N$^+$] separation is 7.0 Å in the complex's dicationic subunit (cf., 6.78 Å in the 1:1:1 complex). Although there is no solvent included in the 1:1 complex, the folding of the dication creates, in conjunction with pairs of hydroquinone hydrogen atoms, a hydrophobic cavity, within which one of the PF$_6^-$ counterions is bound through a combination of electrostatic and [C–H ··· F] hydrogen bonds. The two hydroquinone rings are inclined by approximately 60° and have a centroid–centroid separation of 7.9 Å. The observation that a PF$_6^-$ counterion is bound by the [BPP34C10 · **4**]$^{2+}$ superstructure provides yet another example[5f–g, 8b, 10] of a novel motif that may be associated with anion recognition.[17]

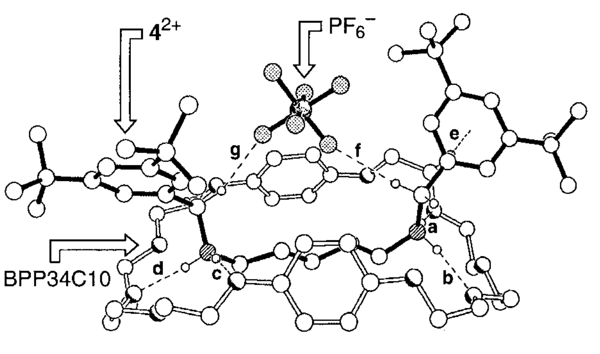


Figure 8. Ball-and-stick representation illustrating the association of a PF$_6^-$ anion with the supermolecule [BPP34C10 · **4**]$^{2+}$, which adopts a hot-dog-like co-conformation in the solid state. The intracomplex [N$^+$–H ··· O] hydrogen-bonding geometries are ([N$^+$ ··· O], [H ··· O] distances (Å), [N$^+$–H ··· O] angles (°)) a) 2.98, 2.08, 172; b) 3.01, 2.16, 159; c) 3.08, 2.18, 175; d) 2.91, 2.02, 170. The geometry for the intracomplex [C–H ··· π] interaction is ([H ··· π] distance (Å), [C–H ··· π] angle (°)) e) 2.86, 135, while the geometries for the [C–H ··· F] hydrogen bonds are ([C ··· F], [H ··· F] distances (Å), [C–H ··· F] angles (°)) f) 3.50, 2.56, 167; g) 3.23, 2.32, 158.

*1,6-Bis(3,5-di-tert-butylbenzylammonium)hexane bis(hexafluorophosphate) (**5** · 2PF$_6$)*: We have observed that, in the complex [BPP34C10 · **4**]$^{2+}$, the BPP34C10 macrocycle has to adopt an unusually distorted convex geometry, so that bisammonium dication **4**$^{2+}$ can achieve two pairs of [N$^+$–H ··· O] hydrogen bonds with its separate polyether arcs. Moreover, the guest **4**$^{2+}$ cannot interpenetrate the BPP34C10 macrocycle in a centrosymmetric fashion to generate a [2]pseudorotaxane, since its polymethylene chain forsakes an all-*anti* conformation—an outcome which forces the dication's 3,5-di-*tert*-butylbenzyl appendages to protrude out of the macrocycle's mean plane. Consequently, we believed that the bisammonium dication **5**$^{2+}$, endowed with a longer polymethylene chain, should be able to achieve both the steric and electronic complementarity obligatory for interaction, in a threading sense, with the macrocyclic polyether BPP34C10.

Unsurprisingly, the ^{1}H NMR spectra of equimolar mixtures of BPP34C10 and **5** · 2PF$_6$ in several different solvents (such as (CD$_3$)$_2$CO, CD$_3$CN, and CDCl$_3$) show that the system operates under the fast kinetic exchange regime on the ^{1}H NMR timescale (300.1/400.1 MHz), presumably as a consequence of the relatively small size of the **5**$^{2+}$ dication's termini compared with the macroring's internal void. The ^{1}H NMR spectrum of the mixture, in CD$_2$Cl$_2$ at room temperature, shows that several of its signals are shifted significantly with respect to those of its uncomplexed constituents (Table 4). In particular, the $\Delta\delta$ values associated with the resonances of the polymethylene chain increase in the order $\alpha < \beta < \gamma$ in a manner that is reminiscent of the [BPP34C10 · **4**]$^{2+}$ complex. The strong shielding effect is presumably a repercussion of the ring current arising from the π face of the BPP34C10 macrocycle's hydroquinone rings that sandwich the hexamethylene chain within the [BPP34C10 · **5**]$^{2+}$ complex. Moreover, the displacement of the hydroquinone resonances toward lower field, is suggestive of the existence of [C–H ··· π] interactions[16] between the hydroquinone unit and the proximal hexamethylene chain. In this instance, the

Table 4. Selected ^{1}H NMR resonances[a] for 1) uncomplexed BPP34C10/**5**·2PF$_6$, and 2) 1:1 mixtures of these two constituents.

	δ_u[d]	δ_c[e, g]	$\Delta\delta$[f]
CH_2–Tmn[b]	4.16	4.23	+0.07
CH_2–α[c]	3.04	2.75	−0.29
CH_2–β[c]	1.78	0.98	−0.80
CH_2–γ[c]	1.52	0.34	−1.18
CH–Hq[b]	6.76	6.96	+0.20

[a] The ^{1}H NMR spectra were recorded on a Bruker AC300 (300.1 MHz) spectrometer in CD_2Cl_2 at 30 °C. [b] Descriptor is defined in Table 1. [c] Descriptor is defined in Table 3. [d] δ values for the resonances of BPP34C10 and **5**·2PF$_6$ in their uncomplexed states (ca. 5×10^{-3} M). [e] δ values for the resonances of BPP34C10 and **5**·2PF$_6$ in an equimolar solution of both components (ca. 5×10^{-3} M). [f] $\Delta\delta$ values were obtained employing the relationship $\Delta\delta=\delta_c-\delta_u$. [g] The assignments for the resonances of both species were confirmed by a (^{1}H–^{1}H) NOESY experiment, recorded in CD_2Cl_2 on a Bruker AMX400 (400.1 MHz) spectrometer at −30 °C.

chemical shift displacements are larger than those associated with the related [BPP34C10·**4**]$^{2+}$ complex, indicating that, as anticipated, the guest unit **5**$^{2+}$ binds more efficiently to the BPP34C10 receptor.

Variable-temperature ^{1}H NMR spectroscopy was then employed to probe further the complexation phenomena associated with the BPP34C10–**5**·2PF$_6$ system in solution. A gradual broadening of the resonances, obtained from an equimolar CD_2Cl_2 solution of both components, was observed upon cooling the sample. The resonances were assigned with the aid of a (^{1}H–^{1}H) NOESY experiment at −33 °C. Interestingly, at this temperature, the signals associated with the crown ether's four constitutionally heterotopic methylene groups separate into two sets of multiplets (Figure 9), indicating that the system operates under the slow kinetic exchange regime under these conditions. An outcome of this slow kinetic exchange—on the ^{1}H NMR timescale (400.1 MHz) at −33 °C—is that the crown ether's two faces express their diastereotopicity in the centrosymmetric [2]pseudorotaxane superarchitecture. Therefore, the shielding influence of each of the dication's 3,5-di-*tert*-butylbenzyl termini is experienced by only one (proximal) proton from each pair of diastereotopic protons on the macrocyclic polyether. Conversely, the other (remote) protons, from each pair of diastereotopic protons on the macrocycle, do not experience the shielding effect of the terminal 3,5-di-*tert*-butylbenzyl groups to such a great extent; their chemical shift values are largely unaffected by complex formation. Another outcome of the slow kinetic exchange is that signals for both uncomplexed species, receptor and guest, can be observed concurrently with those of the 1:1 complex. An examination of the relative intensities of the peaks associated with the uncomplexed crown ether/salt and the 1:1 complex (Figure 9) reveals that a fourfold excess of the complex exists compared with its uncomplexed constituents—in other words, the [BPP34C10·**5**](PF$_6$)$_2$ complex is extremely stable under the conditions of the experiment. Furthermore, the slow exchange observed in this system can be employed to estimate the complex's stoichiometry; a simple comparison between the relative intensities of the appropriate probe protons reveals that the complex's constituents are present in a 1:1 ratio. All of the aforementioned observations are in good accord with the generation of an inclusion complex in which the hexamethylene spacer unit resides within the macrocycle's cavity with a pseudorotaxane co-conformation.[14] The slow kinetic exchange observed for the BPP34C10–**5**·2PF$_6$ system at −33 °C differs markedly from the situation in the related BPP34C10–**4**·2PF$_6$ system, in which, under otherwise indistinguishable conditions, broad signals are detected for the proton resonances of the macrocyclic polyether. Presumably, the less intelligible spectral pattern for the BPP34C10–**4**·2PF$_6$ system suggests that several different co-conformations are accessible to the [BPP34C10·**4**]$^{2+}$ complex that are still interconverting over the energy hypersurface rapidly at this

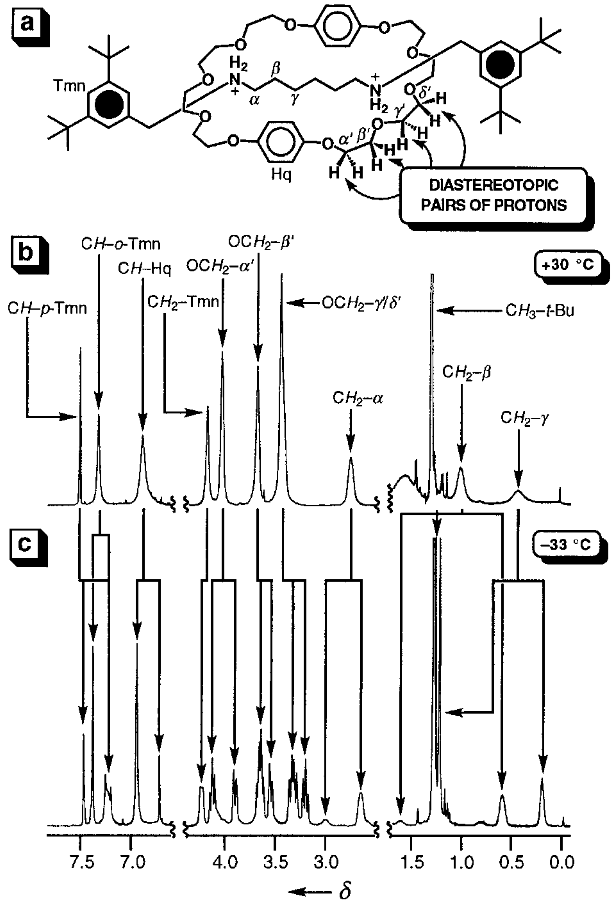


Figure 9. a) Diagram depicting the probable co-conformation of the doubly docked [2]pseudorotaxane [BPP34C10·**5**]$^{2+}$ and highlighting the pairs of diastereotopic protons that are located on the BPP34C10 macroring. Diastereotopicity is conferred upon these protons since the two faces of the crown ether become inequivalent upon complexation. b) Partial ^{1}H NMR spectrum (400.1 MHz, CD_2Cl_2, 30 °C) of an equimolar mixture of BPP34C10 and **5**·2PF$_6$ (both 5×10^{-3} M). At this temperature, time-averaged signals are observed for both compounds, since the pairs of diastereotopic protons on the crown ether, in addition to those of the free and complexed crown ether/salt, are undergoing rapid site exchange on the ^{1}H NMR timescale. c) Partial ^{1}H NMR spectrum (400.1 MHz, CD_2Cl_2, −33 °C) of the aforementioned mixture. At this lower temperature, the site exchanges between diastereotopic protons and bound–unbound species are slow enough that individual species can be observed on the ^{1}H NMR timescale. Consequently, each of the diastereotopic pairs on the macrocycle's polyether loop resonate as two separate sets of signals, while the signals for the protons on the hydroquinone ring of the BPP34C10 macrocycle, together with those of the salt's α, β, and γ protons, are divided into peaks for free and complexed species.

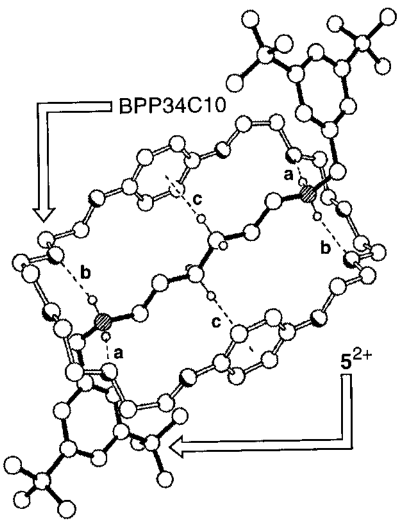


Figure 10. View of the solid-state structure of the centrosymmetric, doubly docked [2]pseudorotaxane superarchitecture of $[BPP34C10\cdot\mathbf{5}]^{2+}$. The intrasupermolecule $[N^+-H\cdots O]$ hydrogen-bonding geometries are ($[N^+\cdots O]$, $[H\cdots O]$ distances (Å), $[N^+-H\cdots O]$ angles (°)) a) 2.95, 2.05, 176; b) 2.90, 2.04, 161. The geometry for the intracomplex $[C-H\cdots\pi]$ interaction is ($[H\cdots\pi]$ distance (Å), $[C-H\cdots\pi]$ angle (°)) c) 3.00, 141.

low temperature. On the other hand, the inclusion geometry for the $[BPP34C10\cdot\mathbf{5}]^{2+}$ complex dominates over all other alternative co-conformations, probably as a result of the better complementarity between the receptor and the guest, simplifying the spectrum.

The stability of the inclusion complex was confirmed in the gas phase from the LSI mass spectrum, which displayed intense peaks at $m/z = 1204$ and 1059 that correspond to the $[BPP34C10\cdot\mathbf{5}](PF_6)_2$ complex with the loss of either one or two counterions, respectively.

The X-ray analysis of the $[BPP34C10\cdot\mathbf{5}]^{2+}$ complex[12] reveals (Figure 10) that the extension of the spacer's length by one methylene unit (i.e., from pentamethylene to hexamethylene) does indeed allow the formation of a [2]pseudorotaxane in which the dication $\mathbf{5}^{2+}$ threads centrosymmetrically through the cavity of the macrocyclic polyether BPP34C10. The crown ether has an open boxlike conformation, with the centers of the hydroquinone rings separated by 7.8 Å. Host–guest stabilization is achieved by $[N^+-H\cdots O]$ hydrogen bonds between each NH_2^+ center and the second and fourth oxygen atoms of their neighboring polyether loops. Additionally, the [2]pseudorotaxane complex is stabilized by weak secondary noncovalent interactions between the γ-CH_2 hydrogen atoms and the π systems of the hydroquinone rings. Although the $[H\cdots\pi]$ distances are fairly long (3.0 Å), the $[H\cdots Ar]$ vectors are oriented approximately orthogonally to the planes of the hydroquinone rings in each instance. The guest's $CH_2NH_2^+(CH_2)_6NH_2^+CH_2$ backbone adopts an all-*anti* conformation; the $[N^+\cdots N^+]$ separation is 8.8 Å. Once again, there is no evidence for any significant interpseudorotaxane associations.

A chromophoric pH-controlled supramolecular switch: In order to see if the molecular switch (Figure 2) would be a practicable one, we examined the competitive complexation phenomena associated with the salts $\mathbf{5}\cdot 2PF_6$ and $\mathbf{6}\cdot 2PF_6$.[9] Both of these species form stable complexes in solution (Figure 11) and in the solid state with the macrocyclic polyether BPP34C10 ; the $[BPP34C10\cdot\mathbf{5}](PF_6)_2$ complex is colorless, while the $[BPP34C10\cdot\mathbf{6}](PF_6)_2$ complex is red by virtue of charge-transfer interactions. Accordingly, these species may be considered as the forerunners of a chromophoric pH-driven molecular switch.[7]

Gratifyingly, deep red CD_2Cl_2 solutions, containing equimolar quantities of BPP34C10 and $\mathbf{6}\cdot 2PF_6$, decolorize instantaneously upon treatment with a molar equivalent of the salt $\mathbf{5}\cdot 2PF_6$, indicating that the crown ether complexes primarily with the bisammonium dication under these conditions. Moreover, the deep red coloration can be reestablished when the NH_2^+ centers are deprotonated quantitatively with iPr$_2$NEt, a non-nucleophilic base that does not destroy compounds containing 4,4′-bipyridinium units.[18] Completion of the supramolecular switching cycle occurs when the mixture is treated with CF_3CO_2H, an acid that reprotonates the NH groups and decolorizes the solution once again. The higher selectivity of BPP34C10 toward the bisammonium dication $\mathbf{5}^{2+}$ was confirmed by ^{1}H NMR spectroscopic experiments. An inspection of the resonances associated with the 4,4′-bipyridinium unit in the ^{1}H NMR spectrum of a 1:1:1 mixture of BPP34C10, $\mathbf{5}\cdot 2PF_6$, and $\mathbf{6}\cdot 2PF_6$, recorded in CD_2Cl_2 at −43 °C, demonstrates that the macrocyclic polyether complexes preferentially with the bisammonium dication (Figure 12).[19] However, when ap-

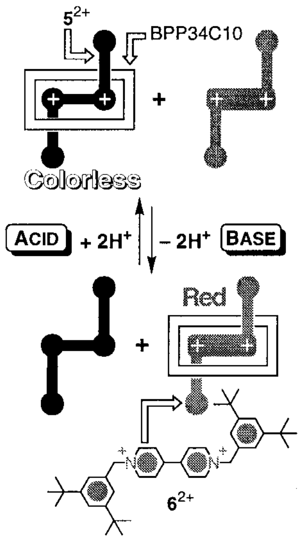


Figure 11. Schematic diagram portraying a chromophoric supramolecular switch that functions by means of pH control.

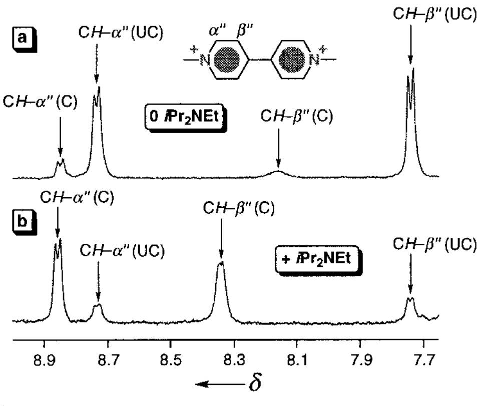
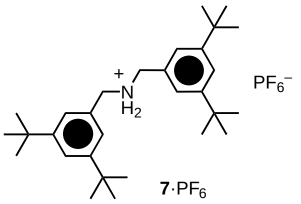


Figure 12. Partial ^{1}H NMR spectra (400.1 MHz, CD_2Cl_2, −43 °C) illustrating the resonances associated with the bipyridinium unit of the dication $\mathbf{6}^{2+}$ in a) a 1:1:1 mixture of BPP34C10, $\mathbf{5}\cdot 2PF_6$ and $\mathbf{6}\cdot 2PF_6$, and b) the same mixture with added iPr$_2$NEt (ca. 2 mol equiv.). Upon addition of the base, the resonances ascribable to the protons of the complexed (C) bipyridinium unit increase in intensity, while those of the uncomplexed (UC) bipyridinium unit decrease in intensity.

proximately one molar equivalent of $i\mathrm{Pr_2NEt}$ was added to this solution, the binding selectivity of the macrocycle toward the guests reverted almost completely to the 4,4′-bipyridinium derivative $\mathbf{6}\cdot 2\,\mathrm{PF_6}$ since the $\mathrm{NH_2^+}$ centers of the dication $\mathbf{5}^{2+}$ had been deprotonated. Employing more polar solvents that have stronger hydrogen-bond accepting ability, such as MeCN and $\mathrm{Me_2CO}$, altered the competitive complexation phenomena identified with this system. In these instances, the color only changed from deep red to orange when one molar equivalent of $\mathbf{5}\cdot 2\,\mathrm{PF_6}$ was added to an equimolar solution of BPP34C10 and $\mathbf{6}\cdot 2\,\mathrm{PF_6}$, suggesting that two equilibrating complexes (namely, $[\mathrm{BPP34C10}\cdot\mathbf{5}]^{2+}$ and $[\mathrm{BPP34C10}\cdot\mathbf{6}]^{2+}$) were present in the solutions. This observation may be presumed to be a consequence of the polar solvents interfering with the hydrogen bonds that stabilize the $[\mathrm{BPP34C10}\cdot\mathbf{5}]^{2+}$ complex,[1e, 5a, 5c–d] in addition to augmenting the $\pi-\pi$ stacking interactions that stabilize the $[\mathrm{BPP34C10}\cdot\mathbf{6}]^{2+}$ complex.[20] Finally, we examined the competitive complexation phenomena associated with BPP34C10 and the monocation $\mathbf{7}^+$ in order to make a comparison between cationic units bearing different numbers of $\mathrm{NH_2^+}$ centers. When an equivalent amount of $\mathbf{7}\cdot\mathrm{PF_6}$ was added to a solution of BPP34C10 and $\mathbf{6}\cdot 2\,\mathrm{PF_6}$ in $\mathrm{CD_2Cl_2}$, the only color change observed was merely from deep red to orange, indicating the formation of a mixture of several different inclusion complexes, and that the self-assembly of the pseudorotaxane $[\mathrm{BPP34C10}\cdot\mathbf{5}]^{2+}$ is a cooperative process.[21]



$\mathbf{7}\cdot\mathrm{PF_6}$

Conclusions

We have extended the paradigm that states that the crown ether BPP34C10 can accommodate two dibenzylammonium centers from distinct cationic units within its macrocyclic interior,[5b–e, 8] so that we can synthesize singly stranded, doubly docked [2]pseudorotaxanes noncovalently. In these two-component superarchitectures, one dicationic thread—bearing a suitable spacer unit between its $\mathrm{NH_2^+}$ centers, in addition to bulky termini—interpenetrates the macrocycle's cavity by virtue of $[\mathrm{N^+{-}H\cdots O}]$ hydrogen bonds with auxiliary stabilization occurring by either $\pi-\pi$ or $[\mathrm{C{-}H}\cdots\pi]$ interactions. "Suitable spacer unit" may be the key phrase for the systems described here, since we have found that the supramolecular syntheses of the [2]pseudorotaxanes are highly dependent on the length of the spacer unit between the $\mathrm{NH_2^+}$ centers. Indeed, [2]pseudorotaxane formation, in this instance, may be described as a linear recognition process[6] that utilizes length complementarity in a ditopic binding mode. Nonetheless, one cannot discount the role of the bulky 3,5-di-*tert*-butylbenzyl termini in these self-assembly processes, for they assist undoubtedly in the creation of the [2]pseudorotaxane supermolecules by 1) preventing the intrusion of two dicationic strands through one BPP34C10 macrocycle and 2) disfavoring the formation of interwoven[10] supramolecular arrays that are held together through the binding of $\mathrm{PF_6^-}$ anions by neighboring pseudorotaxane supermolecules. In summary, by suitable tailoring of the dicationic $\mathrm{NH_2^+}$-bearing guests, we can effect 1) the specific binding geometries, 2) the stoichiometries, and 3) the recognition properties of the ensuing superarchitectures.

The findings reported in this paper conjure up the prospect of engineering the physical and chemical properties of molecular-sized systems in a precise fashion. By way of illustration, one might consider undertaking the construction of rotaxanes and pseudorotaxanes incorporating different recognition sites within their respective molecular and supramolecular environments. These entities could possess device-like properties,[7, 22] as external stimuli could be employed to drive the macrocyclic beadlike component between distinct recognition sites either inter- or intramolecularly. To this end, the $[\mathrm{BPP34C10}\cdot\mathbf{5}](\mathrm{PF_6})_2-[\mathrm{BPP34C10}\cdot\mathbf{6}](\mathrm{PF_6})_2$ system represents a prototype for molecular/supramolecular devices that could be controlled by changes in pH.

Experimental Section

General methods: BPP34C10 was prepared by a literature procedure.[23] Anhydrous THF was obtained by distillation from $\mathrm{Na-Ph_2CO}$. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on either Bruker AC300 (300.1 MHz) or Bruker AMX400 (400.1 MHz) spectrometers, with either the solvent as reference or TMS as the internal standard. ^{13}C NMR spectra were recorded on the Bruker AC300 (75.5 MHz) spectrometer with the PENDANT pulse sequence.[24] Low-resolution liquid secondary ion (LSI) mass spectra were obtained from a VG Zabspec mass spectrometer with a *m*-nitrobenzyl alcohol matrix and operating in the positive-ion mode at a scan speed of 5 s per decade. High-resolution mass measurements, by LSI mass spectrometry, were obtained from a Zabspec instrument operating at a resolution of approximately 10000, while employing narrow-range voltage scanning and a reference of cesium/rubidium iodides mixed in equimolar proportions. Electrospray (ES) mass spectra were measured on a VG Auto SpecQ spectrometer. Microanalyses were performed by the University of North London Microanalytical Service.

General procedure—*α*,*α*′-bis(3,5-di-*tert*-butylbenzylammonium)-*p*-xylene bis(hexafluorophosphate) ($\mathbf{2}\cdot 2\,\mathrm{PF_6}$): A solution of 3,5-di-*tert*-butylbenzaldehyde[25] (4.00 g, 18.5 mmol) and *p*-xylylenediamine (1.20 g, 8.8 mmol) in PhMe (80 mL) was stirred and heated under reflux (azeotropic distillation of $\mathrm{H_2O}$ employing a Dean–Stark apparatus) for 10 h. After the reaction mixture had been allowed to cool down to room temperature, the solvent was evaporated off under reduced pressure to furnish *α*,*α*′-bis(3,5-di-*tert*-butylbenzylidene)-*p*-xylylenediamine as a brown oil [^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 1.34$ (s, 36 H), 4.87 (s, 4 H), 7.31 (s, 4 H), 7.48 (t, $J = 2$ Hz, 2 H), 7.62 (d, $J = 2$ Hz, 4 H), 8.37 (s, 2 H)], which was dissolved in MeOH (50 mL). After being heated to boiling, $\mathrm{NaBH_4}$ (3.80 g, 100.0 mmol) was added portionwise to the solution, which was then heated under reflux for a further 8 h. Upon cooling down to ambient temperature, 12 N HCl was added to the methanolic solution to adjust the pH to less than 2. Following evaporation of the solvents, the residue was suspended in $\mathrm{H_2O}$ (30 mL) and washed with $\mathrm{CH_2Cl_2}$ (4×50 mL). The aqueous layer was rendered basic (pH > 9) by addition of solid KOH, before being extracted with $\mathrm{CH_2Cl_2}$ (3×30 mL). The combined organic extracts were washed with 5% aqueous $\mathrm{NaHCO_3}$ (2×60 mL), $\mathrm{H_2O}$ (50 mL), and dried ($\mathrm{MgSO_4}$). Removal of the solvent in vacuo furnished a solid residue that was dissolved in MeOH (30 mL). HCl(g) was then bubbled through the solution, and the solvents were evaporated off under reduced pressure. Recrystallization of the residue from $\mathrm{EtOH/Et_2O}$ afforded the salt $\mathbf{2}\cdot 2\,\mathrm{Cl}$ as colorless crystals (2.50 g, 46%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 1.35$ (s, 36 H), 3.66 (s, 4 H), 4.29 (s, 4 H), 7.21 (s, 4 H), 7.43 (t, $J = 2$ Hz, 2 H), 7.73 (d, $J = 2$ Hz, 4 H); ^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 31.4, 35.0, 49.9, 52.5, 123.0, 126.2, 129.1, 131.2, 131.7, 151.3$; MS (LSI): *m*/

z: 541 $[M-2\,Cl]^+$; $C_{38}H_{58}Cl_2N_2$ (613.8): calcd C 74.36, H 9.52, N 4.56; found C 74.29, H 9.37, N 4.63. This solid was dissolved in MeOH (20 mL), then a saturated aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The white crystals of $\mathbf{2}\cdot 2\,PF_6$ obtained were collected and air-dried (1.30 g, 39%). ^1H NMR (CD_2Cl_2): $\delta = 1.33$ (s, 36H), 3.66 (s, 4H), 4.07 (s, 4H), 4.26 (s, 4H), 7.30 (s, 4H), 7.43–7.45 (m, 2H), 7.52–7.54 (m, 4H).

2,6-Bis(3,5-di-*tert*-butylbenzylammoniummethyl)naphthalene bis(hexafluorophosphate) ($\mathbf{3}\cdot 2\,PF_6$): 2,6-Naphthalenedicarboxaldehyde[26] (139 mg, 0.76 mmol) was condensed with 3,5-di-*tert*-butylbenzylamine[27] (332 mg, 1.52 mmol) to provide 2,6-bis(3,5-di-*tert*-butylbenzylideneaminomethyl)-naphthalene as a brown solid [^1H NMR ($CDCl_3$): $\delta = 1.32$ (s, 36H), 4.87 (s, 4H), 7.21 (d, $J = 2$ Hz, 4H), 7.35 (t, $J = 2$ Hz, 2H), 7.91 (d, $J = 9$ Hz, 2H), 8.02 (s, 2H), 8.08 (d, $J = 9$ Hz, 2H), 8.56 (s, 2H)], which was reduced with $NaBH_4$ in MeOH to give $\mathbf{3}\cdot 2\,Cl$ (400 mg, 81%), after treatment with HCl(g) and recrystallization from EtOH/H_2O. ^1H NMR (CD_2Cl_2): $\delta = 1.32$ (s, 36H), 3.29 (s, 4H), 4.04 (s, 4H), 7.31 (d, $J = 2$ Hz, 4H), 7.42–7.55 (m, 6H), 7.68 (d, $J = 9$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 31.4$, 35.0, 48.3, 49.9, 123.3, 124.5, 127.9, 128.9, 129.7, 130.0, 132.4, 151.9, 152.0; HRMS (LSI) $C_{42}H_{59}N_2$: $[M-HCl-Cl]^+$ calcd 591.4678, found 591.4668. The salt $\mathbf{3}\cdot 2\,Cl$ was transformed into the title compound by use of the general procedure desribed above (405 mg, 76%). ^1H NMR (CD_2Cl_2): $\delta = 1.33$ (s, 36H) 4.09 (s, 4H), 4.19 (s, 4H), 7.28 (m, 4H), 7.34–7.37 (m, 2H), 7.52 (m, 2H), 7.73–7.76 (m, 4H).

1,5-Bis(3,5-di-*tert*-butylbenzylammonium)pentane bis(hexafluorophosphate) ($\mathbf{4}\cdot 2\,PF_6$): Condensation of 3,5-di-*tert*-butylbenzaldehyde[25] (3.00 g, 13.7 mmol) with 1,5-diaminopentane (0.70 g, 6.8 mmol) furnished 1,5-bis(3,5-di-*tert*-butylbenzylidene)pentanediamine as a yellow oil [^1H NMR ($CDCl_3$): $\delta = 1.34$ (s, 36H), 1.41–1.49 (m, 2H), 1.70–1.78 (m, 4H), 3.62 (t, $J = 7$ Hz, 4H), 7.49 (t, $J = 2$ Hz, 2H), 7.56 (d, $J = 2$ Hz, 4H), 8.27 (s, 2H)], which was reduced with $NaBH_4$ in MeOH/THF (1:5) to provide a solid residue. The residue was transformed into $\mathbf{4}\cdot 2\,Cl$, which was obtained as a white solid (3.46 g, 86%) after treatment with acid and recrystallization from EtOAc/nC_6H_{14}. M.p. 190 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 1.26$–1.38 (br, 38H), 1.85–1.95 (m, 4H), 2.71 (m, 4H), 3.96 (s, 4H), 7.42 (m, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 24.4$, 26.5, 31.5, 35.2, 46.2, 51.7, 123.0, 129.1, 129.9, 152.0; HRMS (LSI) $C_{35}H_{59}N_2$: $[M-HCl-Cl]^+$ calcd 507.4678, found 507.4664. Thereupon, $\mathbf{4}\cdot 2\,Cl$ was transformed to the title compound (2.06 g, 70%) by use of the standard anion exchange procedure. ^1H NMR (CD_2Cl_2): $\delta = 1.32$ (s, 36H) 1.40–1.55 (m, 2H), 1.70–1.85 (m, 4H), 2.90–3.00 (m, 4H), 4.08 (s, 4H), 7.27–7.29 (m, 4H), 7.47–7.48 (br, 2H).

1,6-Bis(3,5-di-*tert*-butylbenzylammonium)hexane bis(hexafluorophosphate) ($\mathbf{5}\cdot 2\,PF_6$): 3,5-Di-*tert*-butylbenzaldehyde[25] (3.75 g, 17.0 mmol) was condensed with 1,6-diaminohexane (1.00 g, 8.0 mmol) to give 1,6-bis(3,5-di-*tert*-butylbenzylidene)hexanediamine as a yellow oil [^1H NMR ($CDCl_3$): $\delta = 1.34$ (s, 36H), 1.41–1.49 (m, 4H), 1.70–1.78 (m, 4H), 3.62 (t, $J = 7$ Hz, 4H), 7.49 (t, $J = 2$ Hz, 2H), 7.56 (d, $J = 2$ Hz, 4H), 8.27 (s, 2H)], which was reduced with $NaBH_4$ in MeOH/THF (1:5). After standard workup, acid treatment, and recrystallization (EtOAc/nC_6H_{14}), $\mathbf{5}\cdot 2\,Cl$ was retrieved as a white amorphous solid (3.50 g, 84%). ^1H NMR ($CDCl_3$): $\delta = 1.26$–1.38 (br, 36H), 1.42–1.47 (br, 4H), 1.76–1.86 (br, 4H), 2.76 (t, $J = 7$ Hz, 4H), 4.10 (s, 4H), 7.40 (m, 2H), 7.44 (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 25.5$, 25.8, 31.5, 35.0, 46.1, 51.7, 123.1, 124.9, 129.4, 151.7; MS (LSI): *m/z*: 522 $[M-2\,Cl]^+$; $C_{36}H_{62}Cl_2N_2$ (593.8): calcd C 72.82, H 10.52, N 4.72; found C 72.87, H 10.54, N 4.63. This material was transformed into the white solid $\mathbf{5}\cdot 2\,PF_6$ (3.54 g, 76%) in the usual manner. ^1H NMR (CD_2Cl_2): $\delta = 1.32$ (s, 36H), 1.46–1.54 (br, 4H), 1.76–1.80 (br, 4H), 3.02–3.06 (m, 4H), 4.16 (s, 4H), 7.28 (d, $J = 2$ Hz, 4H), 7.50 (t, $J = 2$ Hz, 2H).

4,4′-Bis(3,5-di-*tert*-butylbenzyl)bipyridinium bis(hexafluorophosphate) ($\mathbf{6}\cdot 2\,PF_6$): An MeCN (30 mL) solution of 4,4′-bipyridine (1.00 g, 6.4 mmol) was added dropwise with stirring to a hot solution of 3,5-di-*tert*-butylbenzyl bromide[28] (7.26 g, 25.6 mmol) in MeCN (30 mL). The reaction mixture was further stirred and heated under reflux for 36 h. Upon cooling, the resulting yellow precipitate was collected and air-dried. This solid was dissolved in Me_2CO/H_2O (8:2), before being treated with a saturated aqueous solution of NH_4PF_6 until no further precipitate was obtained. This precipitate was collected, washed with H_2O, and air-dried to furnish the title compound as a white solid (4.36 g, 80%). ^1H NMR ($(CD_3)_2CO$): $\delta = 1.31$ (s, 36H), 6.10

Table 5. Crystal data, data collection, and refinement parameters.[a]

	$[\text{BPP34C10}\cdot\mathbf{2}](PF_6)_2$	$[\text{BPP34C10}\cdot\mathbf{3}](PF_6)_2$	$[\text{BPP34C10}\cdot\mathbf{4}\cdot Me_2CO](PF_6)_2$	$[\text{BPP34C10}\cdot\mathbf{4}](PF_6)_2$	$[\text{BPP34C10}\cdot\mathbf{5}](PF_6)_2$
formula	$C_{66}H_{98}N_2O_{10}\cdot 2\,PF_6$	$C_{70}H_{100}N_2O_{10}\cdot 2\,PF_6$	$C_{66}H_{106}N_2O_{11}\cdot 2\,PF_6$	$C_{63}H_{100}N_2O_{10}\cdot 2\,PF_6$	$C_{64}H_{100}N_2O_{10}\cdot 2\,PF_6$
solvent	–	–	–	$0.5CH_2Cl_2$	–
M_r	1369.4	1419.5	1393.5	1377.9	1347.4
color, habit	pale yellow plates	clear needles	clear blocks	clear platy needles	clear triangular plates
crystal size [mm]	0.30 × 0.10 × 0.10	0.67 × 0.17 × 0.10	0.33 × 0.17 × 0.10	0.87 × 0.23 × 0.05	0.30 × 0.27 × 0.10
lattice type	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	Pn	$P2_1/c$	$P\bar{1}$
a [Å]	13.623(4)	11.448(2)	16.645(14)	19.942(1)	11.409(1)
b [Å]	16.753(2)	16.652(1)	10.831(6)	18.996(1)	12.822(1)
c [Å]	16.440(2)	19.682(2)	20.461(10)	20.165(3)	13.375(1)
α [°]	–	–	–	–	79.55(1)
β [°]	103.60(1)	90.94(1)	94.69(5)	103.67(1)	68.28(1)
γ [°]	–	–	–	–	84.88(1)
V [Å]^3	3647(1)	3751.7(8)	3676(4)	7422(1)	1786.9(3)
Z	2[b]	2[b]	2	4	1[b]
D_c [g cm^{-3}]	1.247	1.257	1.259	1.233	1.252
$F(000)$	1452	1504	1484	2924	716
radiation used	$Cu_{K\alpha}$	$Cu_{K\alpha}$	$Cu_{K\alpha}$[c]	$Cu_{K\alpha}$	$Cu_{K\alpha}$
μ [mm^{-1}]	1.268	1.252	1.275	1.570	1.284
θ range [°]	3.3–55.0	3.5–55.0	3.3–62.0	2.3–57.5	3.5–60.0
unique reflections measured	4581	4708	5974	10163	3698
unique reflections observed, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	2557	3385	4731	6644	2790
parameters	464	433	851	938	406
R_1[d]	0.110	0.079	0.067	0.101	0.094
wR_2[e]	0.284	0.219	0.177	0.291	0.262
weighting factors a, b[f]	0.201, 2.355	0.123, 3.904	0.126, 1.809	0.219, 4.955	0.140, 2.967
largest difference peak, hole [e Å^{-3}]	0.55, −0.36	0.49, −0.43	0.45, −0.37	0.97, −0.48	0.72, −0.49

[a] Details in common: graphite monochromated radiation, ω scans, Siemens P4 diffractometer, 293 K, refinement based on F^2. [b] The supermolecule has crystallographic C_i symmetry. [c] Rotating anode source. [d] $R_1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$. [e] $wR_2 = \sqrt{\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}}$. [f] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

(s, 4H), 7.63 (m, 6H), 8.78 (d, $J = 9$ Hz, 4H), 9.54 (d, $J = 9$ Hz, 4H); ^{13}C NMR ($(CD_3)_2CO$): $\delta = 30.1$, 35.6, 66.5, 124.7, 124.9, 128.4, 133.3, 146.5, 151.2, 153.2.

Bis(3,5-di-*tert*-butylbenzyl)ammonium hexafluorophosphate (**7** $\cdot$ PF_6): By means of the standard protocol, 3,5-di-*tert*-butylbenzylamine[27] (0.41 g, 1.8 mmol) was condensed with 3,5-di-*tert*-butylbenzaldehyde[25] (0.40 g, 1.8 mmol) in PhMe (70 mL) to generate 3,5-di-*tert*-butylbenzylidene-3,5-di-*tert*-butylbenzylamine as a yellowish oil [^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (s, 18H), 1.38 (s, 18H), 4.82 (s, 2H), 7.21 (d, $J = 2$ Hz, 2H), 7.33 (t, $J = 2$ Hz, 1H), 7.51 (t, $J = 2$ Hz, 1H), 7.65 (d, $J = 2$ Hz, 2H), 8.43 (s, 1H)], which was reduced with $NaBH_4$. The salt **7** $\cdot$ Cl was isolated as a white solid (0.45 g, 55%) after regular workup, acid treatment, and recrystallization from EtOH/H_2O. ^{1}H NMR ($CDCl_3$): $\delta = 1.29$ (s, 36H), 3.86 (s, 4H), 7.36 (br, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 31.5$, 35.0, 48.8, 123.0, 124.2, 129.8, 151.7; MS (LSI): m/z: 422 $[M - Cl]^+$; $C_{30}H_{48}Cl$ N (458.2): calcd C 78.64, H 10.56, N 3.06; found C 78.75, H 10.45, N 3.17. Counterion exchange, in the usual fashion, provided **7** $\cdot$ PF_6 as a white solid (0.30 g, 66%). ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (s, 36H), 4.12 (s, 4H), 7.18 (s, 4H), 7.47 (s, 2H).

X-ray crystallography: Table 5 provides a summary of the crystal data, data collection, and refinement parameters for the five crystal structures reported in this paper. All of the superstructures were solved by direct methods (SIR92[29] for [BPP34C10 $\cdot$ **4**]$(PF_6)_2$ and SHELXS[30] for the rest) and were refined by full matrix least-squares based on F^2. In the [BPP34C10 $\cdot$ **4** $\cdot$ Me_2CO]$(PF_6)_2$ complex, one of the *tert*-butyl groups of the thread was found to be disordered; this disorder was resolved into two alternate 60 and 40% occupancy orientations, the former of which was refined anisotropically. Similar disorder was found for two of these groups in both the complexes [BPP34C10 $\cdot$ **4**]$(PF_6)_2$ (all four 50% occupancy orientations refined anisotropically) and [BPP34C10 $\cdot$ **2**]$(PF_6)_2$ (all four 50% occupancy orientations refined isotropically). A single PF_6^- anion was found to be disordered in the structures of both [BPP34C10 $\cdot$ **4**]$(PF_6)_2$ and [BPP34C10 $\cdot$ **2**]$(PF_6)_2$; in each case this disorder was resolved into two alternate 50% occupancy orientations (refined anisotropically). Structure [BPP34C10 $\cdot$ **4**]$(PF_6)_2$ was found to contain a 50% occupancy CH_2Cl_2 molecule that was refined anisotropically. All the remaining non-hydrogen atoms in all five structures were of full occupancy and were refined anisotropically. In each structure, the N–H hydrogen atoms were located from ΔF maps and subsequently idealized. The C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2\,U_{eq}(C/N)$ $[U(H) = 1.5\,U_{eq}(C-Me)]$, and allowed to ride on their parent atoms. The polarity of [BPP34C10 $\cdot$ **4** $\cdot$ Me_2CO]$(PF_6)_2$ was determined unambiguously by use of the Flack parameter, which refined to a value of $-0.01(8)$. Refinements were carried out with the SHELXTL PC program system.[30] 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-101113. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] The term *rotaxane* derives (G. Schill, *Catenanes, Rotaxanes, and Knots*, Academic Press, New York, **1971**, p. 3) from the Latin words *rota*, meaning wheel, and *axis*, meaning axle. In these molecular compounds, one or more wheel and axle components are constrained to be bound to one another mechanically, since the axle(s) is/are endowed with bulky stopper groups that prevent the extrusion of the wheel(s). The addition of the appendage *pseudo* indicates (P. R. Ashton, D. Philp, N. Spencer, J. F. Stoddart, *J. Chem. Soc. Chem. Commun.* **1991**, 1677 – 1679) that the wheel(s) is/are free to dissociate from the axle(s), that is, that they are, in actual fact, similar to conventional complexes. Consequently, in chemical terms, the complementary molecular components of *pseudorotaxanes* are held together principally by attractive noncovalent bonds. The number of components of which rotaxanes and pseudorotaxanes are comprised is indicated by the prefix [*n*]. See: a) D. B. Amabilino, P.-L. Anelli, P. R. Ashton, G. R. Brown, E. Córdova, L. A. Godínez, W. Hayes, A. E. Kaifer, D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, M. S. Tolley, D. J. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 11142 – 11170; b) P. R. Ashton, S. J. Langford, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Commun.* **1996**, 1387 – 1388; c) H. Sleiman, P. N. W. Baxter, J.-M. Lehn, K. Airola, K. Rissanen, *Inorg. Chem.* **1997**, *36*, 4734 – 4742; d) A. Mirzoian, A. E. Kaifer, *Chem. Eur. J.* **1997**, *3*, 1052 – 1058. However, it has been shown recently that all pseudorotaxanes are held together, to a certain extent, by mechanical bonding interactions. See: e) P. R. Ashton, I. Baxter, M. C. T. Fyfe, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 2297 – 2307.

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[11] Molecular modeling was employed to estimate the requisite design criteria for guest molecules that could bind efficiently to the macrocyclic polyether BPP34C10. The coordinate data for the crown ether were obtained from the Daresbury Crystallographic Database (D. A.

Fletcher, R. F. McMeeking, D. Parkin, *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746–749), as well as from 3D Search and Research from the Cambridge Structural Database (F. H. Allen, O. Kennard, *Chem. Design Automat. News* **1993**, *8*, 31–37). The prospective guest species were assembled within the program Macromodel 5.0 (F. Mahamadi, N. G. K. Richards, W. C. Guida, R. Liskamp, M. Lipton, D. Caufield, G. Chang, T. Hendrickson, W. C. Still, *J. Comput. Chem.* **1990**, *11*, 440–467) and their suitability for inclusion into the crown ether's cavity assessed employing either the AM1 semiempirical Hamiltonian, as utilized in the program Spartan 4.1.1 (Spartan V 4.1, Wavefunction, 18401 Von Karman Ave., #370 Irvine, CA 92715 (USA)), or the MonteCarlo conformational-searching routines present within Macromodel 5.0. Generally, the correlation between the estimated and gross observed solid-state structures, obtained by X-ray crystallography (vide infra), were good, with the pseudorotaxane co-conformations[5f–g] suggested by the modeling procedures being largely reflected in the co-conformations of the real structures.

[12] Single crystals of the complexes [BPP34C10 · **2**]$(PF_6)_2$, [BPP34C10 · **3**]$(PF_6)_2$, and [BPP34C10 · **5**]$(PF_6)_2$, which were suitable for X-ray crystallographic analysis, were obtained when equimolar CH_2Cl_2 solutions of BPP34C10 and the appropriate salt were layered with nC_6H_{14}.

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