Selective Self-Assembly and Acid–Base Controlled De-/Rethreading of Pseudorotaxanes Constructed Using Multiple Recognition Motifs**

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Abstract: The selective self-assembly of a threadlike tetracation, containing two dialkylammonium (NH_2^+) centers and a 4,4′-bipyridinium ($bpym^{2+}$) unit, with an assortment of macrocyclic polyethers has been investigated. Spectroscopic studies, supported by X-ray crystallographic analyses, have demonstrated the formation of pseudorotaxanes between the thread and the macrocyclic polyethers. In particular, the macrocyclic polyethers dibenzo[24]crown-8 (DB24C8) and bis-*p*-phenylene[34]crown-10 (BPP34C10) associate selectively with the thread's NH_2^+ and $bpym^{2+}$ units, respectively, to generate novel multicomponent pseudorotaxane and pseudopolyrotaxane superarchitectures as a consequence of hydrogen-bonding and charge-transfer interactions. BPP34C10's preference for $bpym^{2+}$ units is shared by several of its dinaphtho-containing crown-10 congeners, which self-assemble with the tetracationic thread to produce [2]pseudorotaxanes in which the $bpym^{2+}$ moiety is encircled by the macrocyclic polyether. The reversible acid–base controlled de-/rethreading of [*n*]pseudorotaxanes based on the multifunctional tetracationic thread has also been studied by ^1H NMR, absorption, and fluorescence spectroscopies. Only one DB24C8 macrocycle is ejected from a [3]pseudorotaxane—created from the tetracationic thread and two DB24C8 molecules—when both of its DB24C8-encircled NH_2^+ centers are deprotonated with base, leading to a [2]pseudorotaxane whose $bpym^{2+}$ unit is associated with the remaining DB24C8 macroring. The [3]pseudorotaxane is reestablished upon reprotonation of the thread with a stoichiometric amount of acid. Treatment of this species with an excess of acid causes protonation of the DB24C8 macrorings, which are completely dethreaded thereafter. Again, the dethreading process can be reversed upon neutralization of the surplus acid with base. Addition of dicyclohexano[24]crown-8 (DCy24C8) to a solution of the [3]pseudorotaxane induces the dethreading of one of the two DB24C8 macrocycles, so that a [4]pseudorotaxane is produced in which the tetracation's NH_2^+ and $bpym^{2+}$ units are encircled by DCy24C8 and DB24C8 macrorings, respectively. Reversible acid–base de-/rethreading processes have also been observed for [2]pseudorotaxanes bearing the dinaphtho-containing crown-10s.

Keywords: molecular recognition · pseudorotaxanes · self-assembly · supramolecular chemistry

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Introduction

Pseudorotaxanes[1] constitute appealing targets for the engineering of molecular assemblies and supramolecular arrays that can exhibit switching properties in response to various stimuli.[2, 3] One particularly fertile route to the supramolecular synthesis[4] of pseudorotaxanes utilizes (Figure 1) π-electron deficient 4,4′-bipyridinium ($bpym^{2+}$) dications (e.g., the 4,4′-dimethylbipyridinium ($\mathbf{1a}^{2+}$) and 4,4′-dibenzylbipyridinium ($\mathbf{1b}^{2+}$) dications) and crown ethers containing π-electron donor units [e.g., bis-*p*-phenylene[34]crown-10 (BPP34C10)] within their macrocyclic frameworks.[5] Employment of such complementary components has led to the self-assembly[6] of numerous rotaxanes and catenanes.[7] More recently, self-assembling systems have been described[1f, 8] that depend upon the mutual recognition between secondary dialkylammonium (NH_2^+) ions [e.g., the dibenzylammonium cation ($\mathbf{2}$–H^+)] and macrocyclic polyethers of dissimilar sizes and constitutions, such as dibenzo[24]crown-8 (DB24C8) and

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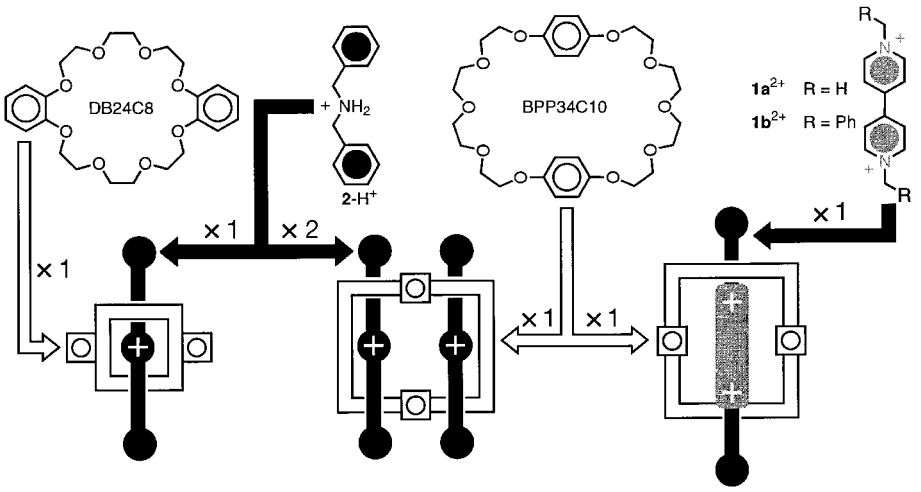

Figure 1. Various noncovalent syntheses of multicomponent pseudorotaxane superstructures. $Bpym^{2+}$-bearing dications self-assemble with BPP34C10 to generate [2]pseudorotaxanes that are stabilized by, inter alia, charge-transfer (CT) interactions. The dibenzylammonium cation (**2**–H^+) self-assembles, separately, with DB24C8 and BPP34C10 to create [2]- and [3]pseudorotaxanes that are stabilized principally through hydrogen-bonding interactions.

BPP34C10. These complexes are stabilized predominantly by electrostatic interactions, including hydrogen bonds between the NH_2^+ cations and one or more of the polyether loops within the crown ether's cavities. One unit of the cation **2**–H^+ interpenetrates the DB24C8 macrocycle to form a [2]pseudorotaxane, while two such units thread through the cavity of BPP34C10 to create a doubly stranded [3]pseudorotaxane.

The rapid increase in the size and intricacy of some of the complex architectures that are being self-assembled currently[9] may be attributed, in part, to the notion that supramolecular syntheses are simplified spectacularly by operating several independent recognition motifs coincidentally.[10] Accordingly, we reasoned that we could augment the superstructural complexity of the pseudorotaxanes, described above, by mixing the recognition motifs observed in the $[BPP34C10 \cdot \mathbf{1a}]^{2+}$, $[BPP34C10 \cdot \mathbf{1b}]^{2+}$, $[DB24C8 \cdot \mathbf{2}–H]^+$, and $[BPP34C10 \cdot (\mathbf{2}–H)_2]^{2+}$ complexes. The question we asked was: would a threadlike tetracation such as $[\mathbf{3}–H_2]^{4+}$ (bearing both $bpym^{2+}$ and NH_2^+ recognition sites, Figure 2) self-assemble discerningly with a mixture of two different crown ethers to provide pseudorotaxanes in which the $bpym^{2+}$ site would associate selectively with one crown ether, while the NH_2^+ site would interact concurrently with the other? Here, we describe[11] the selective self-assembly of the thread $[\mathbf{3}–H_2]^{4+}$ with DB24C8 and BPP34C10, as probed by liquid secondary ion (LSI) mass spectrometry, ^1H NMR spectroscopy, and X-ray crystallography (in the gas phase, in solution, and in the solid state, respectively). We have also investigated

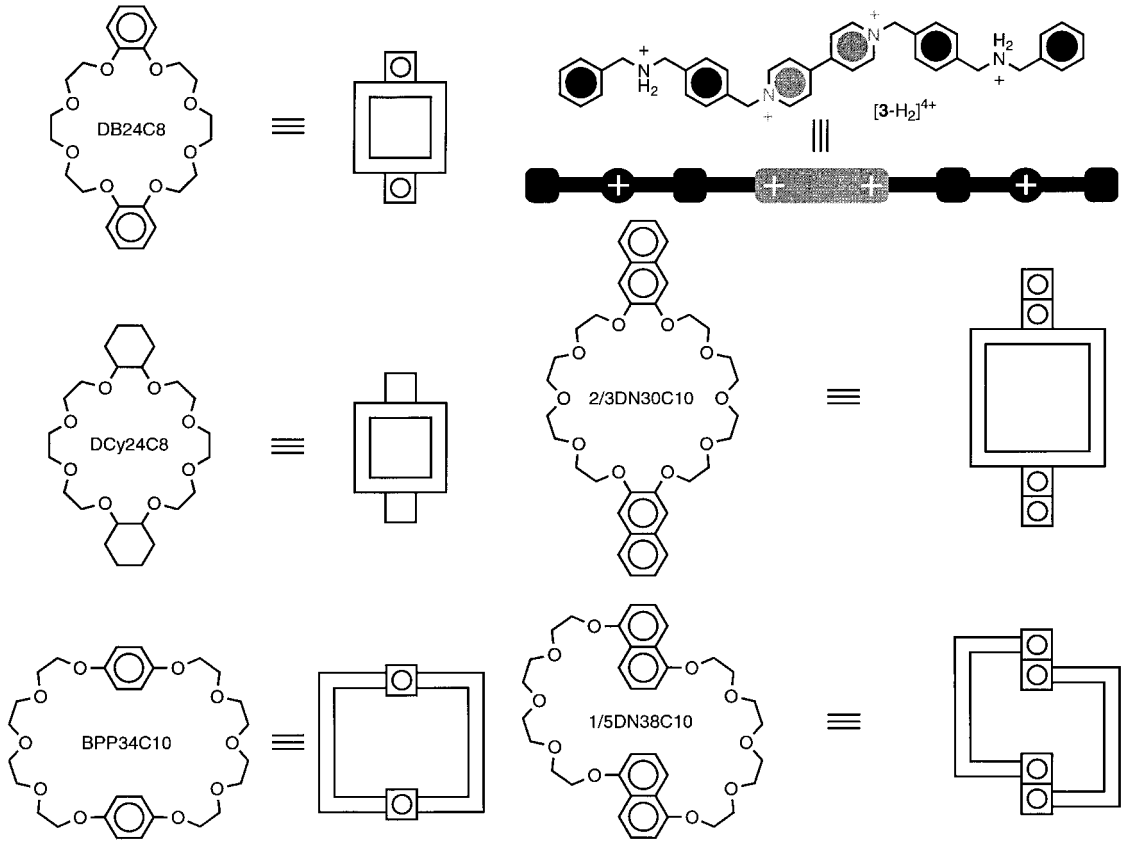

Figure 2. Chemical formulas and schematic representations of the building blocks.

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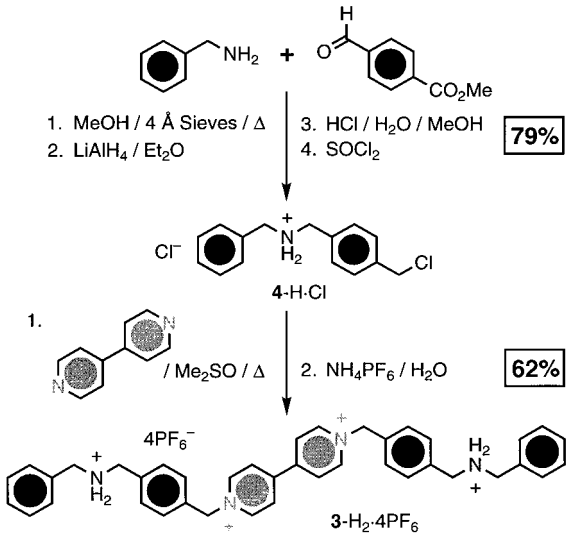
the acid–base controlled de-/rethreading of [*n*]pseudorotaxanes, based upon the multifunctional thread $[\mathbf{3}{-}H_2]^{4+}$ and various crown ethers, by absorption, luminescence, and ^{1}H NMR spectroscopies.

Results and Discussion

Synthesis: The tetracationic salt $\mathbf{3}{-}H_2\cdot 4PF_6$ was prepared (Scheme 1), in good overall yield, from commercially available starting materials, namely, methyl 4-formylbenzoate and



Scheme 1. Synthetic protocol employed to prepare the tetracationic salt $\mathbf{3}{-}H_2\cdot 4PF_6$.

benzylamine, employing a multistep synthetic procedure. Reduction of the aldimine formed from the condensation of these two components, followed by protonation and reaction with an excess of $SOCl_2$, produced $\mathbf{4}{-}H\cdot Cl$. Condensation of this compound with 4,4′-bipyridine, followed by counterion exchange, provided the salt $\mathbf{3}{-}H_2\cdot 4PF_6$, which is endowed with both NH_2^+ and $bpym^{2+}$ recognition sites.

Selective complexation: The selective complexation of the tetracation $[\mathbf{3}{-}H_2]^{4+}$, incorporating two NH_2^+ centers and one $bpym^{2+}$ unit, with the crown ethers DB24C8, BPP34C10, dicyclohexano[24]crown-8 (DCy24C8), 1,5-dinaphtho[38]-crown-10 (1/5DN38C10), and 2,3-dinaphtho[30]crown-10 (2/3DN30C10) was investigated utilizing several techniques. The results obtained are cataloged below.

Complexation with BPP34C10: Deep orange solutions were obtained when equimolar quantities of $\mathbf{3}{-}H_2\cdot 4PF_6$ and BPP34C10 were mixed in $(CD_3)_2CO$ (salt concentration = 3.3×10^{-3} M), thus providing strong evidence for the formation of a complex between the BPP34C10 macrocycle and the tetracation's $bpym^{2+}$ unit that is stabilized, in part, by charge-transfer (CT) interactions. The ^{1}H NMR spectrum of the solution displays only time-averaged resonances for both the host and the guest species, indicating that there is a fast rate of exchange between uncomplexed and complexed states on the NMR timescale (300.1 MHz). The $bpym^{2+}$ unit experiences the largest chemical shift displacement in the spectrum (Table 1), whereas the benzylic protons, adjacent to the NH_2^+ centers, are almost unaffected upon complexation with BPP34C10. However, when the spectrum was recorded with a fourfold excess of BPP34C10, under otherwise identical conditions, the chemical shift changes for the proton resonances associated with both the $bpym^{2+}$ and the benzylic units became larger, perhaps indicating that, under these circumstances, the NH_2^+ centers of the tetracation become involved in complexation to a larger extent. The LSI mass spectrum of crystals of the complex exhibited peaks at $m/z = 1549$, 1403, and 1257, corresponding to a 1:1 complex with the loss of one, two, and three PF_6^- counterions, respectively.

Orange crystals of the complex were acquired from a $MeCN/CH_2Cl_2$ (1:1 v/v) solution of BPP34C10 and $\mathbf{3}{-}H_2\cdot 4PF_6$ (4:1 molar ratio) that had been layered with nC_6H_{14}. The X-ray crystallographic analysis[12] of one of these crystals reveals (Figure 3) the creation of a complex with an empirical

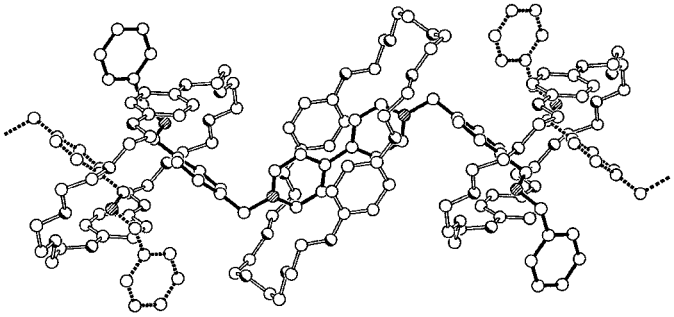


Figure 3. View of the crystal structure of the C_i-symmetric 2:1 complex formed between BPP34C10 and $[\mathbf{3}{-}H_2]^{4+}$. The broken bonds represent segments of lattice-translated tetracationic threads.

Table 1. ^{1}H NMR spectroscopic data [δ and ($\Delta\delta$ values)] for the complexes formed between $\mathbf{3}{-}H_2\cdot 4PF_6$ and the crown ethers BBP34C10 and DB24C8.[a]

	α-*H*[b]	β-*H*[c]	*p*-C_6H_4	CH_2N^+	$CH_2NH_2^+$
$\mathbf{3}{-}H_2\cdot 4PF_6$	9.44	8.77	7.73	6.21	4.70, 4.63
$\mathbf{3}{-}H_2\cdot 4PF_6$ + 1 mol equiv BPP34C10	9.33	8.54	7.79, 7.77	6.19	4.70, 4.61
	(−0.11)	(−0.23)	(0.06, 0.04)	(−0.02)	(0.00, −0.02)
$\mathbf{3}{-}H_2\cdot 4PF_6$ + 4 mol equivs BPP34C10	9.24	8.36	7.83, 7.78	6.17	4.67, 4.58
	(−0.20)	(−0.41)	(0.10, 0.05)	(−0.04)	(−0.03, −0.05)
$\mathbf{3}{-}H_2\cdot 4PF_6$ + 6 mol equivs DB24C8	9.23	8.72	7.43	5.91	4.88, 4.78
	(−0.21)	(−0.05)	(−0.30)	(−0.30)	(0.18, 0.15)
$\mathbf{3}{-}H_2\cdot 4PF_6$ + 4 mol equivs BPP34C10	9.09	8.22	–	6.02	4.92, 4.75
+ 6 mol equivs DB24C8	(−0.35)	(−0.55)	–	(−0.19)	(0.22, 0.12)

[a] Conditions: 300.1 MHz, $(CD_3)_2CO$, 20 °C. [b] $Bpym^{2+}$ protons located on the α-positions with respect to the nitrogen atoms. [c] $Bpym^{2+}$ protons situated in the β-positions with respect to the nitrogen atoms.

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2:1 stoichiometry (i.e., $\{[(BPP34C10)_2 \cdot \mathbf{3}{-}H_2]^{4+}\}_n$) in which the tetracation $[\mathbf{3}{-}H_2]^{4+}$ is threaded through the cavities of three BPP34C10 macrorings. The complex has crystallographic C_i symmetry, with one of the BPP34C10 molecules encircling the tetracation's $bpym^{2+}$ component; two other macrocyclic rings are positioned concurrently around each of the NH_2^+-bearing termini. At the same time, the NH_2^+-bearing termini of other centrosymmetrically related tetracations are threaded through these latter BPP34C10 molecules, in a fashion similar to that observed[8] for the 1:2 complex formed between BPP34C10 and the cation $\mathbf{2}{-}H^+$, to generate a pseudopolyrotaxane[10] that is stabilized by a combination of $[N^+{-}H\cdots O]$ and $[C{-}H\cdots O]$ hydrogen bonds, reinforced by aromatic–aromatic $\pi-\pi$-stacking interactions. The PF_6^- counterions and included solvent molecules are positioned between the polymeric rods. The two crystallographically independent BPP34C10 macrocycles have similar conformations, retaining conventional *gauche* and *anti* geometries about the $CH_2{-}CH_2$ and $CH_2{-}O$ bonds in each of their polyether linkages, respectively. The separation between the parallelly aligned hydroquinone rings in each of the terminal BPP34C10 molecules is 6.66 Å (centroid–centroid separation of 6.91 Å), while the associated separation between the diametrically opposite, centrally located polyether oxygen atoms is 13.5 Å. The equivalent values for the central BPP34C10 macrocycle are 6.78 (with an associated centroid–centroid separation of 6.81 Å) and 14.1 Å, respectively. The π-electron-deficient C_i-symmetric $bpym^{2+}$ unit is sandwiched evenly between the two π-electron-rich hydroquinone rings of the central BPP34C10 macrocycle ($\pi-\pi$-stacking separation of 3.39 Å) with each $[N^+\cdots N^+]$ axis inclined by about 30° to the macrocycle's $O{-}C_6H_4{-}O$ axes. Secondary stabilization is achieved by $[C{-}H\cdots O]$ hydrogen bonds between one hydrogen atom of each CH_2N^+ unit and the central oxygen atoms of the polyether linkages ($[C\cdots O]$, $[H\cdots O]$ distances 3.26, 2.30 Å; $[C{-}H\cdots O]$ angle 173°), in a manner reminiscent of the $[BPP34C10 \cdot \mathbf{1a}]^{2+}$ complex.[5a] Binding to the terminal BPP34C10 macrocycles is achieved through $[N^+{-}H\cdots O]$ hydrogen bonds between the NH_2^+ centers and the second and fourth oxygen atoms of each polyether linkage, a mode of binding similar to that observed[8] for the 1:2 complex between BPP34C10 and the cation $\mathbf{2}{-}H^+$ (the $[N^+\cdots O]$, $[H\cdots O]$ distances are 2.94, 2.89 and 1.99, 2.01 Å, respectively, with the $[N^+{-}H\cdots O]$ angles being 166 and 151°). The separation of the pair of co-threaded NH_2^+ centers is 8.6 Å, with the centroid–centroid separation of the proximal *p*-xylyl rings being 6.02 Å. The conformation of the tetracation's dibenzylammonium component differs from that observed[8] in the $[BPP34C10 \cdot (\mathbf{2}{-}H)_2]^{2+}$ complex, in that the geometry about the $N^+{-}$*p*-xylyl bond is *anti*, while that about the $N^+{-}$benzyl bond is approximately *gauche* (torsional twist of 70°). The plane of the terminal phenyl ring is approximately orthogonal to the plane of the $CH_2{-}NH_2^+{-}CH_2$ linkage (twist 84°), whereas the *p*-xylyl ring is rotated by only 33° to this linkage. The angular relationship between the *p*-xylyl ring and the planar $bpym^{2+}$ unit is comprised of two torsional twists of 73° and 61° about the $CH_2{-}C_6H_4$ and $CH_2{-}bpym^{2+}$ bonds, respectively. The consequence of these torsional twists within the tetracation and the resultant overall zigzag geometry for the thread is a steep inclination between the axes of adjacent BPP34C10 molecules. Viewed along the long axis of the pseudopolyrotaxane, the hydroquinone ring centroid–centroid vectors within each of the adjacent BPP34C10 molecules are inclined by 83° to one other. Inspection of the packing of the pseudopolyrotaxane does not reveal any strong interpseudopolyrotaxane $\pi-\pi$, $[C{-}H\cdots\pi]$, or $[C{-}H\cdots O]$ interactions. The only proximal relationship of note is an approach of the tetracation's terminal benzyl rings of the adjacent chains, suggesting the possibility for cross-linking[10a, 13] and alternative chain-propagation directions. However, although the interplanar separation between the terminal phenyl groups is favorable, at 3.1 Å, the centroid–centroid separation, at 5.3 Å, is too large to represent any significant $\pi-\pi$ interactions.

Complexation with DB24C8: A pale yellow solution was obtained when a $(CD_3)_2CO$ solution of $\mathbf{3}{-}H_2 \cdot 4PF_6$ was treated with two molar equivalents of DB24C8. The ^1H NMR spectrum of the solution displayed signals for 1) free DB24C8, 2) uncomplexed $[\mathbf{3}{-}H_2]^{4+}$, and 3) the corresponding 1:1 and 2:1 complexes. This predictable feature of the spectrum arises[8] by virtue of the slow complexation–decomplexation rates on the ^1H NMR timescale (300.1/400.1 MHz) at room temperature; these slow rates originate as a result of the relatively large size of the thread's benzyl termini compared with the cavity of the DB24C8 macrocycle. Upon addition of a sixfold excess of DB24C8 to the solution, the only signals that could be observed (Figure 4a) in the ^1H NMR spectrum were attributable to 1) the excess of the free DB24C8 macrocycle and 2) a 2:1 complex $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2]^{4+}$. The complex's 2:1 stoichiometry was established, under the aforementioned conditions of slow kinetic exchange, by comparison of the relative intensities of the appropriate resonances associated with the complexed species. The large shifts observed (Table 1) for the protons associated with the tetracation's dibenzylammonium subunits indicate that the crown ether is probably complexing preferentially with the NH_2^+ centers. LSI mass spectrometric analysis further confirmed the presence of the $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2]^{4+}$ complex; peaks corresponding to the $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2][PF_6]_4$ complex, with the respective losses of one and two PF_6^- counterions, were observed at $m/z = 1910$ and 1765 in the LSI mass spectrum of a mixture of both components.

The selective association between the NH_2^+ center and DB24C8 was also studied by monitoring the changes in the absorption and luminescence properties of the crown ether upon formation of the supramolecular species. It is well known that formation of adducts can cause changes in the absorption and emission spectra.[5] The observation of electron donor–acceptor interactions between the components of a pseudorotaxane implies the presence of a low-energy excited state that 1) gives rise to a CT band in the absorption spectrum between the π-electron-rich aromatic units of the crown ether and the π-electron-deficient $bpym^{2+}$ unit of the thread, and 2) causes the nonradiative deactivation of upper-lying, potentially fluorescent excited states localized in the superstructure's macrocyclic or thread-type components. For the $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2]^{4+}$ pseudorotaxane, interaction be-

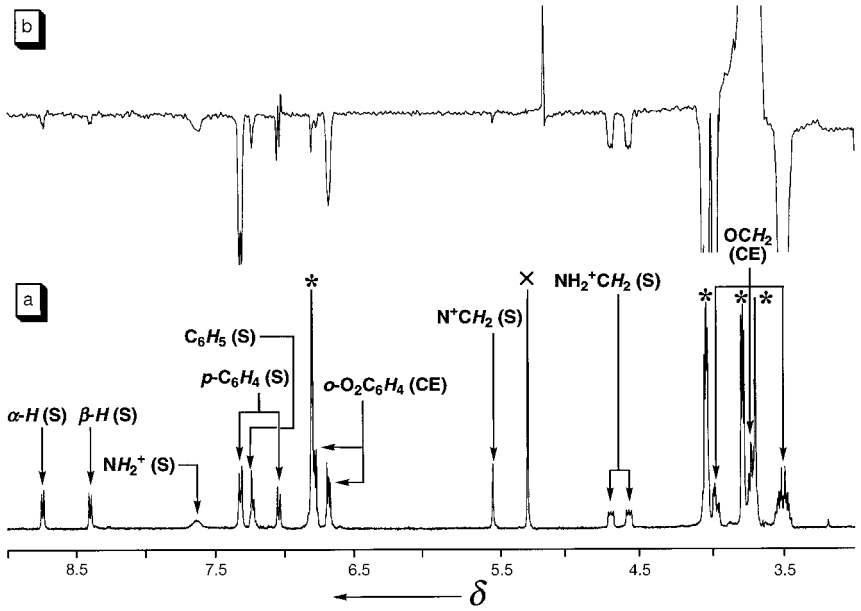


Figure 4. a) The ^{1}H NMR spectrum (400.1 MHz, CD_3CN/CD_2Cl_2 (1:4 v/v), 30 °C) of a solution of DB24C8 (sixfold excess) and the salt **3**–$H_2 \cdot 4PF_6$. Peaks associated with the complexed crown ether and salt are designated by (CE) and (S), respectively. Signals affiliated with the solvent and the excess of the crown ether are denoted separately by a cross and asterisks, respectively. b) Selected row of the (^{1}H – ^{1}H) NOESY experiment's [same conditions as in a)] 2D matrix, which intersects the diagonal through the region associated with the resonances of the crown ether's polyether loops.

tween the crown ether DB24C8 and the thread's $bpym^{2+}$ unit is expected to give rise to a CT band, in addition to complete quenching of the strong fluorescence band ($\lambda_{max} = 308$ nm) that is characteristic[14] of the free DB24C8 crown ether. Consequently, the association of DB24C8 with $[\mathbf{3}–H_2]^{4+}$ was also investigated by monitoring the changes in the absorption and emission spectra. Titration of a 3×10^{-5} M solution of **3**–$H_2 \cdot 4PF_6$ with DB24C8 (in a 1:4 v/v $MeCN/CH_2Cl_2$ solution) induced strong changes in the intensity of the crown ether's fluorescence spectrum, indicative[5a] of association between the components. A quantative analysis shows that when the concentration of DB24C8 is at least six times that of $[\mathbf{3}–H_2]^{4+}$, two crown ether molecules per thread have lost their fluorescent signals, indicating the formation of the [3]pseudorotaxane $[(DB24C8)_2 \cdot \mathbf{3}–H_2]^{4+}$. We have also found that addition of a sixfold excess of DB24C8 to 3×10^{-5} M solutions containing the salts of either of the cations $\mathbf{1b}^{2+}$ or $\mathbf{2}–H^+$ did not cause any fluorescence quenching. This outcome is hardly surprising, since NH_2^+-bearing species afford[8] adducts with DB24C8, but cannot quench its fluorescence (because such adducts are not based on CT interactions), whereas the $bpym^{2+}$ units, which would give CT-type adducts,[5] do not associate appreciably with DB24C8 under such dilute conditions.[15] These results show clearly that the fluorescence quenching, observed upon formation of the pseudorotaxane $[(DB24C8)_2 \cdot \mathbf{3}–H_2]^{4+}$, results from the cooperative effect of having NH_2^+ and $bpym^{2+}$ units linked together within the same thread. That is, when the crown ether complexes with the NH_2^+ centers (which cannot, by themselves, quench the crown ether's fluorescence), it gets close enough to the $bpym^{2+}$ unit to cause a catechol – $bpym^{2+}$ CT interaction. This rationalization is supported by the presence of an absorption tail in the 360 – 500 nm region of the spectrum that can be assigned to a CT band whose maximum is covered by much more intense bands that are present at higher energy.

A (^{1}H – ^{1}H) NOESY experiment on a 4:1 mixture of DB24C8 and **3**–$H_2 \cdot 4PF_6$ was recorded in a CD_3CN/CD_2Cl_2 (1:4 v/v) solution at 30 °C. The 2D matrix exhibits (Figure 4b) intense cross-coupled peaks between the methylene protons located on DB24C8's polyether loops and 1) the $CH_2NH_2^+$ protons, as well as 2) the protons of the *p*-xylyl spacer. This result is in good agreement with the postulate that the $[(DB24C8)_2 \cdot \mathbf{3}–H_2]^{4+}$ complex exists with a pseudorotaxane co-conformation in which the crown ether rings interact preferentially with the NH_2^+ centers. Moreover, this observation suggests that the catechol units of the DB24C8 macrocycle are presumably folded toward the thread's *p*-xylyl spacer unit, as opposed to its benzyl termini (Figure 5). This model also accounts well for the quenching, detected in the presence of the tetracationic salt **3**–$H_2 \cdot 4PF_6$, of the luminescence associated with the crown ether's aromatic units.

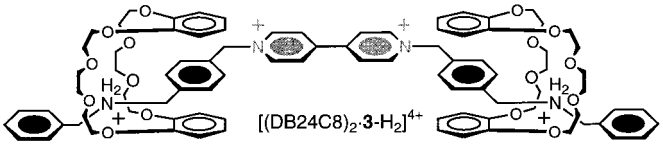


Figure 5. One of the co-conformations of the $[(DB24C8)_2 \cdot \mathbf{3}–H_2]^{4+}$ complex in which the crown ether's catechol units interact with the *p*-xylyl spacers.

Concurrent complexation with both DB24C8 and BPP34C10: The high selectivity of macrocycle DB24C8 toward NH_2^+ centers, and that of BPP34C10 in relation to the $bpym^{2+}$ dication, prompted us to probe the complexation phenomena associated with the salt **3**–$H_2 \cdot 4PF_6$ and a mixture of these crown ethers. The ^{1}H NMR spectrum (300.1 MHz, $(CD_3)_2CO$, 20 °C) of **3**–$H_2 \cdot 4PF_6$ in the presence of both BPP34C10 and DB24C8 (1 and 2 molar equivalents, respectively) displayed a complicated set of resonances that can be associated with many different complexes exchanging slowly with one another on the ^{1}H NMR timescale. However, upon addition of a fourfold excess of BPP34C10, along with a sixfold excess of DB24C8, the only signals that could be identified were associated (Table 1) with a 2:1:1 complex and the uncomplexed macrocyclic polyethers. Strong support for the formation of a 2:1:1 complex was also obtained by LSI mass spectrometric analysis. The mass spectrum showed intense peaks at $m/z = 2592$, 2447, and 2301, corresponding to the mass of the $[(DB24C8)_2 \cdot BPP34C10 \cdot \mathbf{3}–H_2][PF_6]_4$ complex with the loss of none, one, or two PF_6^- counterions, respectively.

  0947-6539/98/0411-2336 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 11

Orange single crystals, suitable for X-ray crystallographic analysis, were obtained from a 1:4:6 solution of **3**–$H_2 \cdot 4PF_6$, BPP34C10, and DB24C8 in Me_2CO that had been layered with nC_6H_{14}. The X-ray analysis[12] reveals the formation of a 2:1:1 complex $[(DB24C8)_2 \cdot BPP34C10 \cdot \mathbf{3}\text{–}H_2]^{4+}$ (Figure 6), in which the tetracationic unit **3**–H_2^{4+} is threaded through the cavity of the three crown ether macrocycles to generate a [4]pseudorotaxane. The tetracation's π-electron-deficient $bpym^{2+}$ hub is sandwiched between the BPP34C10 macrocycle's π-electron-donor hydroquinone units, while its two terminal NH_2^+ centers are encircled by the smaller DB24C8 crown ethers. The overall co-conformation approximates very closely to a C_i-symmetric arrangement that is broken only by the adoption of an *anti* geometry for one of the CH_2–O-C_6H_4O–CH_2 fragments of the BPP34C10 macrocycle (the other one has a *syn* geometry for these bonds). Stabilization of the four-component superstructure is achieved by a combination of 1) π–π stacking and [C–H···O] hydrogen bonds (between the CH_2N^+ unit and BPP34C10), and 2) [N^+–H···O] and [C–H···O] hydrogen bonds between hydrogen atoms of both the NH_2^+ centers, and their adjacent *p*-xylyl–CH_2 groups, and the oxygen atoms of the DB24C8 macrocycle. As a consequence of the pseudorotaxane's lack of symmetry, these terminal subcomplexes, identified as sites **A** and **B** in Figure 6, are not identical. The π–π stacking separations between the $bpym^{2+}$ unit and the approximately parallel (6° tilt) hydroquinone rings of the BPP34C10 macrocycle are 3.48 and 3.54 Å, respectively (the associated hydroquinone–hydroquinone centroid–centroid separation is 7.04 Å), the [N^+···N^+] axis of the $bpym^{2+}$ unit being tilted by about 24° to the mean plane of the four hydroquinone oxygen atoms. The secondary [C–H···O] hydrogen bonds occur between one of each of the CH_2N^+ hydrogen atoms and the central polyether oxygen atoms of BPP34C10 ([C···O] and [H···O] distances are 3.19, 3.28 and 2.27, 2.33 Å, with associated [C–H···O] angles of 161 and 173°, respectively). The [C–H···O] and [N^+–H···O] hydrogen-bonding pattern to the terminal DB24C8 macrocycles is complex, though essentially the same for both macrocycles. Both of the NH_2^+ hydrogen atoms are involved in bifurcated hydrogen bonds (Figure 7), one to both of the oxygen atoms of one of the catechol units, the other to the adjacent second and third oxygen atoms of the polyether linkages. One of the CH_2 hydrogen atoms of the *p*-xylyl unit is hydrogen bonded to one of the oxygen atoms of the other catechol unit. Comparing the conformation of the cationic thread [**3**–H_2^{4+}] in $[(DB24C8)_2 \cdot BPP34C10 \cdot \mathbf{3}\text{–}H_2]^{4+}$ with that in the (empirical) 2:1 complex $\{[(BPP34C10)_2 \cdot \mathbf{3}\text{–}H_2]^{4+}\}_n$, both Ph–$CH_2$–$NH_2^+$–$CH_2$–$C_6H_4$ backbones have essentially planar all-*anti* geometries, with their associated terminal phenyl and internal *p*-xylyl rings inclined by 46 and 66° in one instance (unit **A**), and by 57 and 66° in the other (unit **B**). The angular relationship between the *p*-xylyl rings and the central planar $bpym^{2+}$ unit is, in each case, comprised of two torsional twists, one about the CH_2–C_6H_4 bonds, the other about the CH_2–$bpym^{2+}$ bonds. In unit **A**, the CH_2–C_6H_4 torsion angle is about 25° for the *p*-xylyl ring, while that for the CH_2–$bpym^{2+}$ unit is about 63°. For unit **B**, the respective torsional twists are about 22 and 65°. The tetracation's *p*-xylyl units are not positioned centrally with respect to their associated DB24C8 macrocycles. For both units **A** and **B**, the *p*-xylyl ring is inclined toward one of DB24C8's catechol rings by about 20°; the respective mean interplanar separations are 4.25 (in **A**) and 4.31 Å (in **B**), distances that are much too large to represent any significant π–π stabilization. Although the conformations of the two DB24C8 macrocycles are very similar, there are small differences in the cleft angles between the catechol rings (70° in **A** and 73° in **B**). The associated catechol–catechol centroid–centroid separations are 9.23 Å in **A** and 9.39 Å in **B**. Both terminal phenyl rings in units **A** and **B** are arranged in parallel overlapping π–π-stacking relationships with their centrosymmetrically related counterparts. For **A**, the mean interplanar separation is 3.77 Å with a centroid–centroid separation of 4.48 Å, while for **B** the corresponding values are 3.66 and 3.88 Å, respectively. The combination of all of these π–π-intercomplex interactions, coupled with all the hydrogen-bonding and intracomplex π–π-stacking interactions, results in the formation of a loosely bound pseudopolyrotaxane[10] superstructure that is not involved in any further significant interpseudopolyrotaxane interactions.

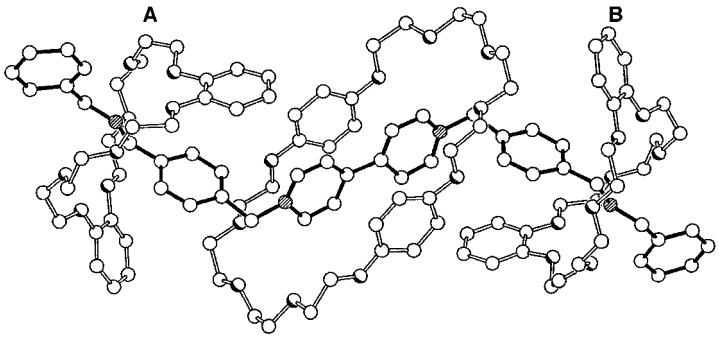


Figure 6. The X-ray crystal structure of the [4]pseudorotaxane that is self-assembled selectively from one unit of the tetracation $[\mathbf{3}\text{–}H_2]^{4+}$, two DB24C8 macrocycles, and one molecule of BPP34C10.

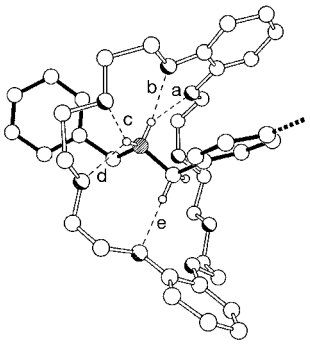


Figure 7. Ball-and-stick representation of the terminal unit **A** (vide Figure 6) of the [4]pseudorotaxane $[(DB24C8)_2 \cdot BPP34C10 \cdot \mathbf{3}\text{–}H_2]^{4+}$ showing the noncovalent bonding interactions between its dibenzylammonium terminus and its encircling DB24C8 macrocycle. The geometries for the hydrogen bonds are {[X···O], [H···O] distances (Å), [X–H···O] angles (°)} a) 2.99, 2.26, 133; b) 3.02, 2.15, 149; c) 3.01, 2.14, 151; d) 3.01, 2.29, 131; e) 3.32, 2.40, 160. These values are slightly different for the terminal unit **B** (vide Figure 6): a) 3.08, 2.21, 151; b) 3.02, 2.26, 136; c) 3.01, 2.29, 131; d) 2.99, 2.12, 150; e) 3.29, 2.36, 162.

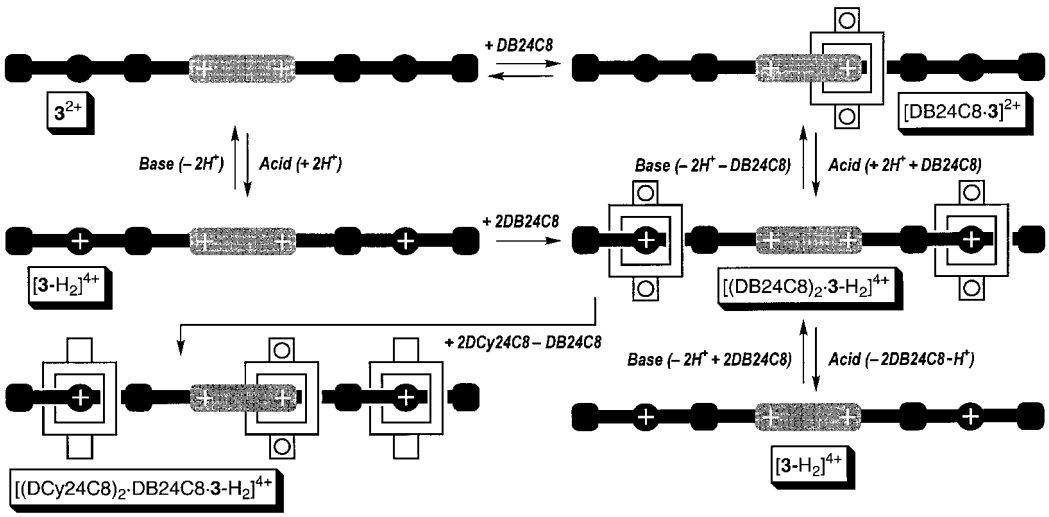
Complexation with 1,5-dinaphtho[38]crown-10 (1/5DN38C10) and 2,3-dinaphtho[30]crown-10 (2/3DN30C10): The interaction of $[\mathbf{3}\text{–}H_2]^{4+}$ with the crown ethers 1/5DN38C10 and 2/3DN30C10 was followed by the appearance of new CT

bands, centered on 520 and 430 nm, respectively, in the visible absorption spectra. Titration of $[\mathbf{3}{-}H_2]^{4+}$ with 1/5DN38C10 produces an increase in the absorbance in the region of the CT band and a quenching of the intensity of the crown ether's structured fluorescence band ($\lambda_{max} = 347$ nm). Finally, a plateau is reached when the crown ether is present in a tenfold excess with respect to the salt $\mathbf{3}{-}H_2 \cdot 4PF_6$. Under the plateau conditions, one crown ether molecule per tetracation $[\mathbf{3}{-}H_2]^{4+}$ has lost its fluorescence signal. The results indicate that, within the complex, only one 1/5DN38C10 molecule is interacting with the $bpym^{2+}$ unit. Identical results have been obtained in complexation studies with the macrocyclic polyether 2/3DN30C10. Experiments, carried out under the same conditions, with the dication $\mathbf{1b}^{2+}$, instead of $[\mathbf{3}{-}H_2]^{4+}$, showed the emergence of the same CT bands ($\lambda_{max} = 520$ nm, $\varepsilon = 700\,M^{-1}cm^{-1}$ for 1/5DN38C10 and $\lambda_{max} = 430$ nm, $\varepsilon = 600\,M^{-1}cm^{-1}$ for 2/3DN30C10). The same CT band and fluorescence quenching of the aromatic units of 1/5DN38C10 were observed previously in catenanes[5c] and rotaxanes[5d,e] based on 1,5-dimethoxynaphthalene and $bpym^{2+}$ units.

Acid–base switching experiments: Since we had established that crown ethers self-assemble site-selectively with the tetracation $[\mathbf{3}{-}H_2]^{4+}$, we next embarked on a study of the pseudorotaxanes' mechanical-switching properties. The building blocks for such pseudorotaxane switches have characteristics that allow the facile conversion from one state to another by means of external stimuli; the crown ethers' affinities for the NH_2^+ centers are suppressed by deprotonation, while their affinities for the $bpym^{2+}$ unit can be canceled by reduction. We now describe the acid–base manipulated switching of the pseudorotaxanes formed from $[\mathbf{3}{-}H_2]^{4+}$ and the crown ethers DB24C8 and 2/3DN30C10.

Mechanochemical-switching properties of the [3]pseudorotaxane $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2][PF_6]_4$ (Scheme 2): Addition of 6 molar equivalents of DB24C8 to a $MeCN/CH_2Cl_2$ (1:4 v/v) solution of $\mathbf{3}{-}H_2 \cdot 4PF_6$ leads (vide supra) to the formation of the [3]pseudorotaxane $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2][PF_6]_4$. In this solution, the free crown ether molecules exhibit fluorescence ($\lambda_{max} = 308$ nm), while the fluorescence of those threaded to the tetracation $[\mathbf{3}{-}H_2]^{4+}$ is quenched. Addition of $n Bu_3N$ causes the crown ether's fluorescence intensity to increase, indicating that deprotonation of the NH_2^+ centers is followed by a dethreading reaction. An elaboration of the fluorescence intensity signals as a function of the concentration of added base shows that only one crown ether molecule per thread has lost its fluorescence after addition of one molar equivalent of the amine. No further change in the fluorescence intensity is observed after addition of a second equivalent of base. This demonstrates that only one of the two crown ether molecules encircling the NH_2^+ centers is ejected from the threadlike component after deprotonation. The other DB24C8 macroring remains threaded, presumably by means of CT interactions with the $bpym^{2+}$ unit, to afford the [2]pseudorotaxane $[DB24C8 \cdot \mathbf{3}]^{2+}$. This interpretation is consistent with the fact that addition of 6 molar equivalents of DB24C8 to a $MeCN/CH_2Cl_2$ (1:4 v/v) solution of deprotonated $[\mathbf{3}{-}H_2]^{4+}$ (i.e., $\mathbf{3}^{2+}$) leads to the disappearance of one-sixth of the crown ether's fluorescence intensity, as expected for the formation of a [2]pseudorotaxane. The changes brought about by the addition of base to a solution of the [3]pseudorotaxane $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2]^{4+}$ can be reversed quantitatively by adding two molar equivalents of triflic acid (TfOH). In other words, the switching between the [3]pseudorotaxane $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2]^{4+}$ and the [2]pseudorotaxane $[DB24C8 \cdot \mathbf{3}]^{2+}$ is fully acid–base reversible. In principle, the de-/rethreading processes involve changes in the CT absorption bands. However, such changes are very small and, because of the intense tail of the $bpym^{2+}$ band, cannot be identified easily.

The switching process has likewise been confirmed by ^1H NMR spectroscopic experiments. Addition of 2 molar equivalents of $i Pr_2NEt$ to a solution of DB24C8 and $\mathbf{3}{-}H_2 \cdot 4PF_6$ in CD_3CN/CD_2Cl_2 (1:4 v/v) effected almost complete deprotonation of the two NH_2^+ centers within the thread $[\mathbf{3}{-}H_2]^{4+}$, as no resonances associated with $CH_2NH_2^+$ protons could be observed. The partial ^1H NMR spectrum displays two sets of resonances for the α- and β-$bpym^{2+}$ protons that, based upon



Scheme 2. Schematic representation illustrating the reversible, pH-controlled, mechanical-switching properties of the [3]pseudorotaxane $[(DB24C8)_2 \cdot \mathbf{3}{-}H_2]^{4+}$, in addition to the selective recognition events involving the DB24C8 and DCy24C8 macrocycles.

0947-6539/98/0411-2338 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 11

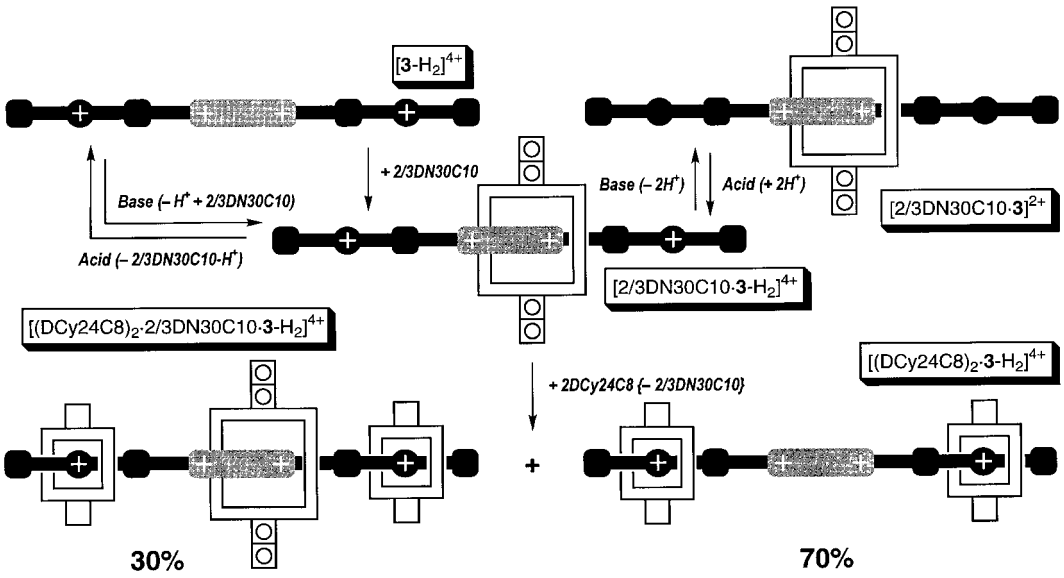
the results obtained from the luminescence studies, can be assigned to 1) the deprotonated thread $\mathbf{3}^{2+}$ and 2) the 1:1 complex $[DB24C8\cdot\mathbf{3}]^{2+}$. In addition, the same ^1H NMR spectrum could be obtained when four molar equivalents of DB24C8 were added to a $(CD_3)_2CO$ solution of $\mathbf{3}{-}H_2\cdot 4PF_6$ and two molar equivalents of iPr$_2$NEt. Interestingly, the ^1H NMR spectra (300.1 MHz, $(CD_3)_2CO$, 20 °C) of 1:1:1 solutions of DB24C8 with both of the salts $\mathbf{1b}\cdot 2PF_6$ and $\mathbf{2}{-}H\cdot PF_6$ implied that, upon deprotonation, the DB24C8 macrocycle was ejected only from the cation $\mathbf{2}{-}H^+$. Other interesting properties associated with the [3]pseudorotaxane $[(DB24C8)_2\cdot\mathbf{3}{-}H_2]^{4+}$ have also been uncovered. Addition of an excess of TfOH (at least one molar equivalent per crown ether) to a solution of this pseudorotaxane induces an increase in the fluorescence intensity as a result of the protonation-driven dethreading of the two crown ether components. This process is, once again, completely reversible, as shown by the changes in the fluorescence spectra observed upon neutralization of the TfOH with nBu$_3$N.

We have also discovered that addition of an excess (20 molar equivalents with respect to DB24C8) of the aliphatic crown ether DCy24C8 to a solution of the [3]pseudorotaxane $[(DB24C8)_2\cdot\mathbf{3}{-}H_2]^{4+}$ produces an increase in the solution's fluorescence intensity. Elaboration of the results obtained reveals that one of the pseudorotaxane's two DB24C8 units undergoes dethreading upon addition of the surplus of the aliphatic crown ether. This observation is consistent with the formation of the [4]pseudorotaxane $[(DCy24C8)_2\cdot DB24C8\cdot\mathbf{3}{-}H_2]^{4+}$, and with the fact that one of the two DB24C8 molecules, when forced to abandon an NH_2^+ center, can find a suitable binding site in the $bpym^{2+}$ unit.

*Mechanochemical-switching properties of the [2]pseudorotaxane [2/3DN30C10·**3**–H$_2$][PF$_6$]$_4$ (Scheme 3)*: As we have seen above, addition of at least 10 molar equivalents of 2/3DN30C10 to a MeCN/CH_2Cl_2 (1:4 v/v) solution of $\mathbf{3}{-}H_2^{4+}$ (as its PF_6^- salt) leads to the formation of the [2]pseudorotaxane $[2/3DN30C10\cdot\mathbf{3}{-}H_2]^{4+}$. In this solution, the uncomplexed crown ether molecules exhibit fluorescence ($\lambda_{max} = 343$ nm), whereas the fluorescence of those threaded onto $[\mathbf{3}{-}H_2]^{4+}$ is quenched. Formation of the pseudorotaxane can be followed clearly by the appearance of a CT absorption band ($\lambda_{max} =$ 430 nm) that is identical to that obtained upon complexation of $\mathbf{1b}^{2+}$ with 2/3DN30C10. In this case, addition of a base (nBu$_3$N) that deprotonates the NH_2^+ centers does not cause any change in the fluorescence intensity or the CT absorption, that is, the macroring is not ejected from the [2]pseudorotaxane $[2/3DN30C10\cdot\mathbf{3}]^{2+}$ under these conditions. This observation confirms that 2/3DN30C10 interacts with the $bpym^{2+}$ unit in both of the [2]pseudorotaxanes $[2/3DN30C10\cdot\mathbf{3}{-}H_2]^{4+}$ and $[2/3DN30C10\cdot\mathbf{3}]^{2+}$. Addition of an excess (at least twice the crown ether concentration) of TfOH to the [2]pseudorotaxane $[2/3DN30C10\cdot\mathbf{3}{-}H_2]^{4+}$ causes the disappearance of the CT band, demonstrating that the crown ether undergoes dethreading when it is protonated. This process can be completely reversed once again by the addition of base. Finally, we have found that addition of an excess (at least 10 molar equivalents with respect to 2/3DN30C10) of DCy24C8 to a solution of the [2]pseudorotaxane $[2/3DN30C10\cdot\mathbf{3}{-}H_2]^{4+}$ produces a 70% decrease in the intensity of the CT absorption. This observation can be explained by the formation of the [4]pseudorotaxane $[(DCy24C8)_2\cdot 2/3DN30C10\cdot\mathbf{3}{-}H_2]^{4+}$ in 30% yield and the [3]pseudorotaxane $[(DCy24C8)_2\cdot\mathbf{3}{-}H_2]^{4+}$ in 70% yield.

Conclusions

It has been demonstrated that the binding sites of macrocyclic polyethers, bearing different sizes and constitutions, pair off selectively with the multiple recognition sites of the tetracationic thread $[\mathbf{3}{-}H_2]^{4+}$ to generate multicomponent pseudo-



Scheme 3. Schematic diagram portraying the acid–base reversible, mechanochemical-switching properties associated with the [2]pseudorotaxane $[2/3DN30C10\cdot\mathbf{3}{-}H_2]^{4+}$, together with the selective binding of the macrocycles DCy24C8 and 2/3DN30C10 to the NH_2^+ and $bpym^{2+}$ moieties, respectively, of the tetracation $[\mathbf{3}{-}H_2]^{4+}$.

rotaxanes that have varying stoichiometries. In other words, we have shown that the simultaneous operation[10] of several independent recognition algorithms can be employed profitably for the noncovalent synthesis[4] of elaborate superarchitectures. This protocol has been utilized to construct supramolecular switches based on de-/rethreading processes. Such processes, induced by acid–base stimuli, can be monitored easily by spectroscopic techniques. However, the research presented here is just a start, for the application of selective self-assembly processes to the production of working device-like[3, 16] nanostructures will become the precept that synthetic supramolecular chemists will rely upon, so that they can manufacture systems that resemble the complex machines of the natural world in the future.

Experimental Section

Materials and methods: The crown ethers DB24C8 and DCy24C8 are commercially available, while the crown ethers BPP34C10,[5a] 2/3DN30C10,[17] and 1/5DN38C10[5c] were prepared through the use of previously published protocols. Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AC300 (300.1 MHz) spectrometer with either the solvent as reference or TMS as the internal standard. ^{13}C NMR Spectra were recorded on the same spectrometer (75.5 MHz) using the PENDANT pulse sequence.[18] Fast atom bombardment (FAB) and liquid secondary ion (LSI) mass spectra were obtained from Kratos MS80RF and VG Zabspec mass spectrometers, with krypton and cesium ion sources, respectively, and *m*-nitrobenzyl alcohol matrices. Electron impact (EI) mass spectra were obtained from a VG Prospec mass spectrometer. Microanalyses were performed by the University of North London Microanalytical Services.

4-Carbomethoxybenzylidene-benzylamine (**5**): A solution of methyl 4-formylbenzoate (5.68 g, 34.6 mmol) and benzylamine (3.76 g, 35.1 mmol) in MeOH (100 mL) was heated under reflux for 4 h in the presence of 4 Å molecular sieves. The solvent was evaporated off under reduced pressure and the remainder treated with CH_2Cl_2 (100 mL). The suspension was filtered through a Celite pad, which was then washed with more CH_2Cl_2 (100 mL). The combined filtrates were concentrated in vacuo to furnish the title compound (8.46 g, 96%) as a white solid. M.p. 95–96 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 3.95$ (s, 3H), 4.87 (s, 2H), 7.24–7.45 (m, 5H), 7.85 (d, $J = 8$ Hz, 2H), 8.09 (d, $J = 8$ Hz, 2H), 8.45 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): $\delta = 52.0$, 65.0, 127.0, 127.9, 128.4, 128.0, 129.7, 131.8, 138.8, 139.9, 160.7, 166.4; MS (EI): *m/z* (%): 253 (59) $[M]^+$, 222 (12) $[M - OMe]^+$, 194 (12) $[M - CO_2Me]^+$, 91 (100) $[C_7H_7]^+$; IR (Nujol): $\tilde{\nu} =$ 1716, 1644, 1277 cm^{-1}; $C_{16}H_{15}NO_2$ (253.3): calcd C 75.87, H 5.97, N 5.53; found C 75.95, H 5.83, N 5.46.

Benzyl-4-hydroxymethylbenzylammonium chloride (**6**–H · Cl): A solution of **5** (6.67 g, 26.3 mmol) in Et_2O (200 mL) was added dropwise to a suspension of $LiAlH_4$ (2.90 g, 76.4 mmol) in Et_2O (60 mL) over 40 min at 0 °C. The reaction mixture was stirred at room temperature for 12 h, before being cooled down to 0 °C. H_2O (300 mL) was added carefully, then the mixture was extracted with $CHCl_3$ (300 mL). The organic layer was filtered through a Celite pad, and the filtrate washed with brine (250 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to provide benzyl-4-hydroxymethylbenzylamine as a brown oil (5.62 g, 93%). ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 1.82$ (s, 1H), 3.78 (s, 4H), 4.65 (s, 2H), 7.20–7.40 (m, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): $\delta = 52.5$, 52.7, 64.2, 126.9, 128.0, 128.1, 128.3, 129.2, 138.7, 139.6, 140.1; MS (EI): *m/z* (%): 227 (51) $[M]^+$, 226 (49) $[M - H]^+$, 196 (28) $[M - OMe]^+$, 136 (70) $[M - C_7H_7]^+$, 121 (60) $[M - PhCH_2NH]^+$, 106 (73) $[M - HOCH_2C_6H_4CH_2]^+$, 91(100) $[C_7H_7]^+$; IR (neat): $\tilde{\nu} = 3301$, 3085, 3061, 3026, 2918, 2847, 1709, 1495, 1453, 1419, 1362, 1221, 1017, 910, 733, 699 cm^{-1}; $C_{15}H_{17}NO$ (229.3): calcd C 68.30, H 6.88, N 5.31; found C 68.54, H 6.66, N 5.18**.** A solution of this amino alcohol (5.44 g, 23.7 mmol) in MeOH (70 mL) was treated dropwise with HCl (12 N, 5.0 mL) over a period of 3 min. The mixture was stirred at room temperature for 2 h, before being treated with Et_2O (50 mL). The resulting white precipitate was filtered off and air-dried to give white crystals of **6**–H · Cl (5.82 g, 93%). M.p. 204–205 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 4.09$ (s, 4H), 4.50 (d, $J = 5$ Hz, 2H), 5.29 (t, $J = 5$ Hz, 1H), 7.37–7.46 (m, 3H), 7.34 (d, $J = 8$ Hz, 2H), 7.50 (d, $J = 8$ Hz, 2H), 7.57–7.60 (m, 2H), 9.80 (br s, 2H); ^{13}C NMR (75.5 MHz, $(CD_3)_2SO$, 20 °C): $\delta = 49.4$, 49.5, 62.4, 126.4, 128.5, 128.8, 129.0, 130.0, 130.2, 131.9, 143.3; MS (FAB): *m/z* (%): 228 (100) $[M - Cl]^+$; $C_{15}H_{18}ClNO$ (263.8): calcd C 63.84, H 6.07, N 4.96; found C 63.85, H 6.19, N 4.93.

Benzyl-4-chloromethylbenzylammonium chloride (**4**–H · Cl): Over 5 min, the hydrochloride salt **6**–H · Cl (4.36 g, 16.5 mmol) was added to $SOCl_2$ (50 mL) in small portions. The mixture was stirred at 20 °C for 22 h, then the solvent was evaporated off in vacuo to furnish a white solid that was dissolved in MeOH (80 mL). Et_2O (180 mL) was added to the solution so that a white precipitate formed, which was filtered off and dried to furnish the title compound (4.46 g, 96%). M.p. 228–229 °C (with decomp); ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 4.12$ (s, 4H), 4.77 (s, 2H), 7.35–7.61 (m, 9H), 9.82 (br s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): $\delta = 45.7$, 49.2, 49.6, 128.5, 128.8, 128.9, 130.2, 130.5, 131.9, 132.0, 138.2; MS (FAB): *m/z* (%): 246 (100) $[M - Cl]^+$; $C_{15}H_{17}Cl_2N$ (282.2): calcd C 75.87, H 5.97, N 5.53; found C 75.95, H 5.83, N 5.46.

4,4′-Di(benzylammonium-*p*-xylylene)bipyridinium tetrakis(hexafluorophosphate) (**3**–$H_2 \cdot 4PF_6$): A solution of 4,4′-bipyridine (72 mg, 0.46 mmol) in Me_2SO (5 mL) was added dropwise to a stirred solution of the salt **4**–H · Cl (520 mg, 1.84 mmol) in Me_2SO (5 mL), and the whole was heated under reflux for 2 d. After cooling to ambient temperature, the white precipitate generated was collected and washed with DMF and Et_2O, before being dissolved in H_2O. A saturated aqueous solution of NH_4PF_6 was added to the solution until no further precipitation of the title compound occurred, which was recovered as a white solid (330 mg, 62%) after filtration and drying. M.p. 240 °C (with decomp); ^{1}H NMR (300.1 MHz, $(CD_3)_2CO$, 20 °C): 4.63 (s, 4H), 4.70 (s, 4H), 6.21 (s, 4H), 7.40–7.50 (m, 6H), 7.50–7.60 (m, 4H), 7.73 (s, 8H), 8.77 (d, $J = 8$ Hz, 4H), 9.44 (d, $J = 8$ Hz, 4H); MS (LSI): *m/z* (%): 1013 (100) $[M - PF_6]^+$.

Absorption and luminescence measurements: The experiments were carried out in air-equilibrated $MeCN/CH_2Cl_2$ (1:4 v/v, Merck Uvasol) solutions at room temperature. Electronic absorption spectra were recorded with a Perkin–Elmer λ6 spectrophotometer. Emission spectra were obtained with a Perkin–Elmer LS50 spectrofluorimeter. For the absorption spectra, the concentration of $[\mathbf{3}{-}H_2]^{4+}$ was in the order of 10^{-4} M, while in the luminescence experiments, the concentration of this tetracation was in the range $3-5 \times 10^{-5}$ M. In the luminescence experiments, the measured intensity values were corrected in order to account for 1) the inner filter effect at the excitation wavelength, 2) the nonlinear response of the instrument to the absorbance of the solution, and 3) re-absorption of the emitted light. These corrections were made according to the literature procedure.[19]

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