

# X-ray Crystallographic Studies on the Noncovalent Syntheses of Supramolecules<sup>a</sup>

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## Abstract

An approach to the supramolecular syntheses of discrete multicomponent aggregates of noncovalently bound molecules, i.e., supermolecules, is described. This approach involved the careful analysis of X-ray crystal structures so as to permit a gradual increase in superstructural complexity. Many elaborate supermolecules were synthesized noncovalently from dialkylammonium-containing cations and crown ethers, following the initial observation that the dibenzylammonium ion threads through dibenzo[24]crown-8 to generate a singly stranded, singly encircled [2]pseudorotaxane, principally as a result of  $[N^+—H\cdots O]$  and  $[C—H\cdots O]$  hydrogen bond formation. The scope of the fundamental recognition motif obtained from this initial observation was then broadened, through the use of thread-like ions with multiple dialkylammonium centers and/or larger crown ethers, so that multiply stranded and/or multiply encircled pseudorotaxanes could be prepared. Cations bearing both dialkylammonium and crown ether recognition sites were also used for the noncovalent synthesis of a discrete daisy chain supermacrocycle and the basic recognition motif was combined with other motifs for the production of a wide range of novel superarchitectures. As a greater understanding of the noncovalent interactions governing the self-assembly of the complex superarchitectures was acquired, new protocols for the noncovalent syntheses of doubly docked pseudorotaxanes and interwoven supramolecular bundles, including a supramolecular analogue of the photosynthetic special pair, were developed. The discovery that anions can play a prominent role in the solid-state self-assembly of some of the supermolecules was a valuable spinoff of the research.

## Keywords

Noncovalent interactions • Pseudorotaxanes • Self-assembly • Solid-state structures • Supramolecular chemistry

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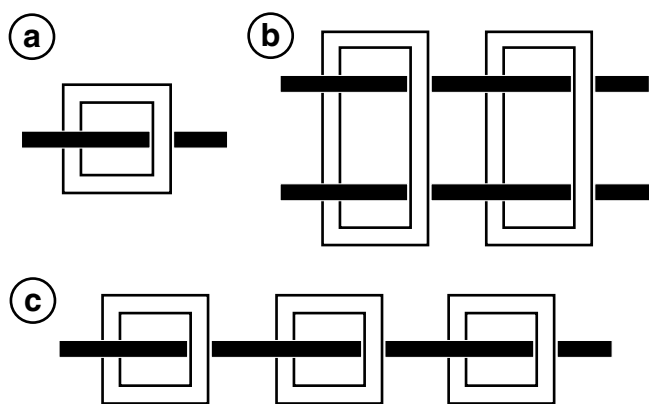
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## Introduction

In the past few years, the noncovalent bond [1] has become an increasingly important constituent of the synthetic chemist's repertoire, partly because the chemistry of the covalent bond has been almost stretched to its limits [2]. As a result, the field of supramolecular synthesis [3], i.e., the preparation of supramolecular [1] entities using noncovalent bonds, has become a flourishing area of contemporary chemical research to the extent that

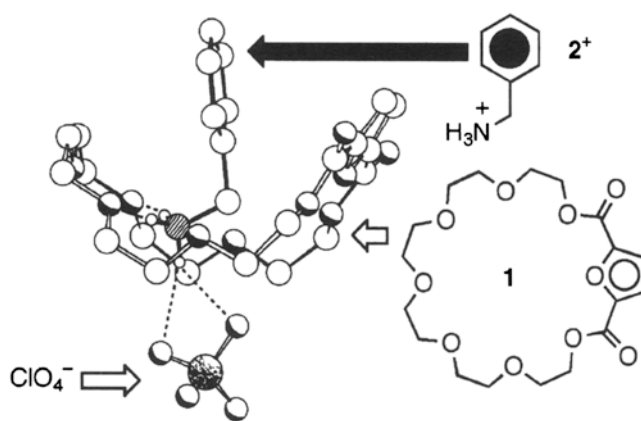


**Fig. 1** Diagrams depicting the superstructures of several multicomponent pseudorotaxanes. Pseudorotaxanes are inclusion complexes that have been defined [11] as the noninterlocked counterparts of rotaxanes [12]. They are formed when one or more thread-like molecules/ions interpenetrate the cavities of one or more macrocyclic species. As distinct from their mechanically interlocked congeners, i.e., the rotaxanes, these supramolecular complexes are free to dissociate into their separate components as they do not possess bulky stopper groups. Their analogy in the macroscopic world would consist of one or more beads being threaded onto one or more strings (that have no knots at their ends). Pseudorotaxanes are comprised of  $n$  components, as indicated by the prefix  $[n]$ . Thus, the diagrams show (a) [2]-, (b) [4]-, and (c) [4]pseudorotaxanes.

synthetic chemists are now able to utilize noncovalent bonding interactions for the self-assembly [4] of a diverse series of intermolecularly bound entities, ranging from the discrete, oligomeric supermolecules [5] to the infinite, polymeric supramolecular arrays [6]. X-ray crystallography has played [7] a pivotal role in this aspect of synthetic supramolecular chemistry [3]. By carefully analyzing the noncovalent interactions that hold certain superstructures together in the solid state, the synthetic supramolecular chemist has been able to prepare ever more complex and intricate supramolecular architectures noncovalently, with a view to the ultimate creation of devices [8] and materials [9], the likes of which have been observed previously only in the natural world. In this review, we discuss how X-ray crystallography has aided our noncovalent syntheses of discrete supramolecular entities, i.e., supermolecules, using recognition motifs based upon the interaction between crown ethers and secondary dialkylammonium ions [10]. Initially, these recognition motifs were employed solely to synthesize simple pseudorotaxanes (Fig. 1) noncovalently. Subsequently, we have been able to increase superstructural complexity gradually, through the application of X-ray crystallography as a tool that augments our basic understanding of the recognition motifs.

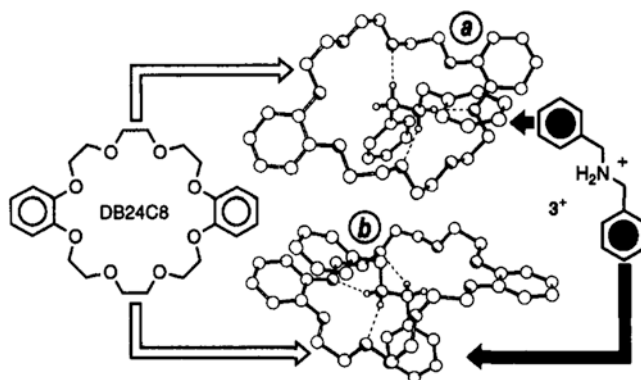
### Discovery of a New Recognition Motif

The motivation for our initial investigations [13] on the noncovalent synthesis of pseudorotaxanes from crown ethers and dialkylammonium ions was obtained from the crystal

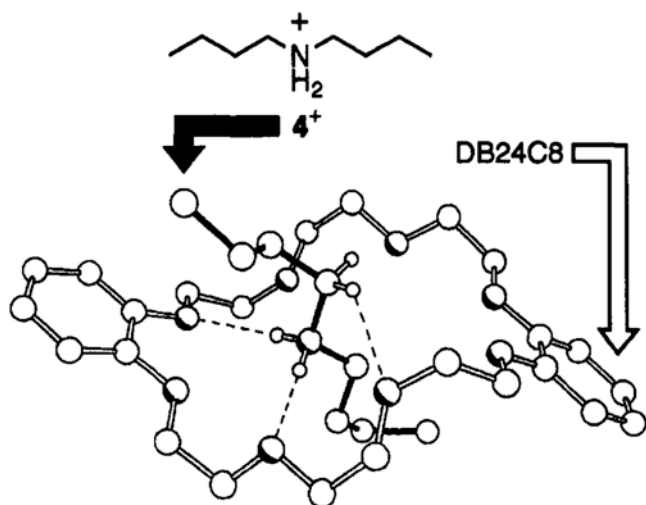


**Fig. 2** The crystal structure of the ion-pair pseudorotaxane [1·2]  $[\text{ClO}_4^-]$  generated as a result of the bifurcated  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  hydrogen bonds between one of the  $\text{NH}_3^+$  hydrogen atoms and two of the oxygen atoms of the  $\text{ClO}_4^-$  counterion.

structure [14] of the 1:1 complex formed (Fig. 2) between the [24]crown-8 derivative **1** and benzylammonium perchlorate ( $2 \cdot \text{ClO}_4^-$ ). In this complex, only two of the  $\text{NH}_3^+$  hydrogen atoms are involved in hydrogen bonds with the oxygen atoms of the crown ether, the other hydrogen atom interacting with the  $\text{ClO}_4^-$  counterion, via hydrogen bonding *through* the macrocycle's cavity, to generate, what has been termed [13c–d], an ionpair pseudorotaxane. This crystal structure led us to conclude that we could effect the noncovalent syntheses of crown ether–dialkylammonium ion-based pseudorotaxanes by replacing this superstructure's  $\text{—H} \cdots \text{ClO}_4^-$  unit with an alkyl substituent. Indeed, co-crystallization [13a, c–d] of the crown ether dibenzo[24]crown-8 (DB24C8) with dibenzylammonium hexafluorophosphate ( $3 \cdot \text{PF}_6^-$ ) furnishes (Fig. 3) two crystallographically independent [2] pseudorotaxanes  $[\text{DB24C8} \cdot 3][\text{PF}_6^-]$ , where, in both superstructures, the cation is threaded through the macrocycle



**Fig. 3** The two crystallographically independent [2]pseudorotaxanes (a and b) that self-assemble from DB24C8 and  $3^+$ . In addition to the hydrogen bonds that stabilize both complexes, pseudorotaxane (b) is stabilized by a  $\pi$ - $\pi$  stacking interaction between both components.

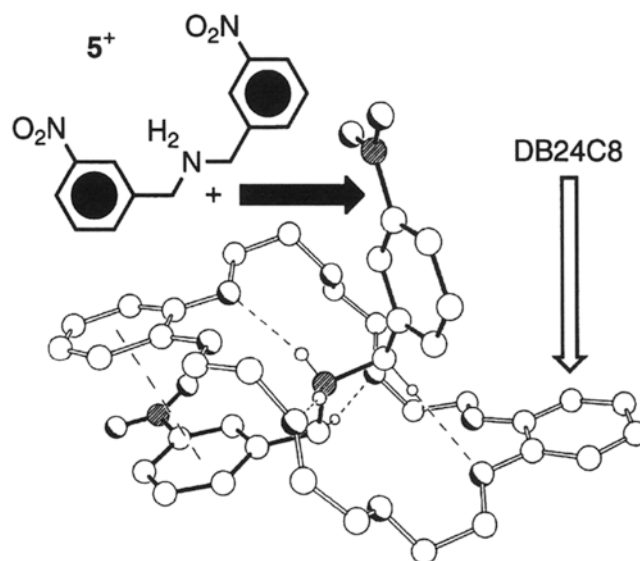


**Fig. 4** The crystal structure of [2]pseudorotaxane [DB24C8·4]<sup>+</sup>, which is stabilized by means of [N<sup>+</sup>—H···O] and [C—H···O] hydrogen bonds.

primarily by means of [N<sup>+</sup>—H···O] and [C—H···O] hydrogen bonds from the hydrogen atoms of the cation's NH<sub>2</sub><sup>+</sup> and CH<sub>2</sub> units, respectively, to the polyether oxygen atoms of DB24C8. Thereafter, several similar [2]pseudorotaxanes were synthesized noncovalently from DB24C8 and other dialkylammonium ions, including the di-*n*-butylammonium ion (4<sup>+</sup>) ([13a, c–d], Fig. 4), two dicycloalkylammonium ions [15], and a wide range of substituted dibenzylammonium ions ([16], Fig. 5). Moreover, all of these pseudorotaxanes form in solution, as evidenced by <sup>1</sup>H NMR spectroscopic studies. FAB/LSI mass spectrometric analyses have also permitted pseudorotaxane characterization in the gas phase. The observation of pseudorotaxane formation in solution has led to several novel syntheses [17] of rotaxanes and molecular switches.

### Extending the Recognition Motif

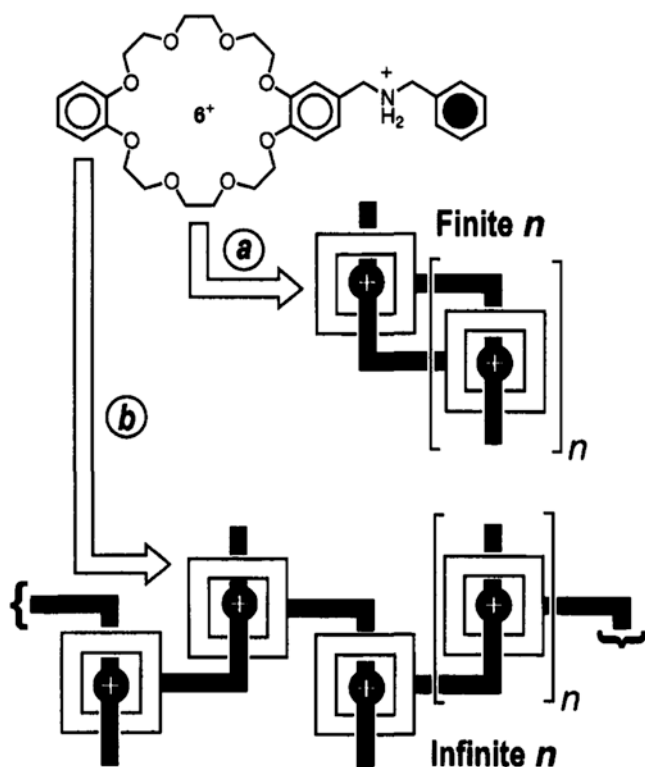
Recently, we have situated both the DB24C8 and secondary dialkylammonium recognition sites on the same covalent skeleton in order to effect the noncovalent synthesis of daisy chain superarchitectures [18]. The cation **6**<sup>+</sup> (Fig. 6) was designed in such a way that its complementary recognition sites would interact with each other in an intermolecular [19], rather than an intramolecular [20], sense, i.e., instead of biting its own tail, the self-complementary monomer **6**<sup>+</sup> would be predisposed to self-assemble into a supramolecular daisy chain. However, one question still remained: Would **6**<sup>+</sup> oligomerize noncovalently to generate discrete daisy chain supermacrocycles, or would it polymerize, via noncovalent bonds, to produce a macromolecular daisy



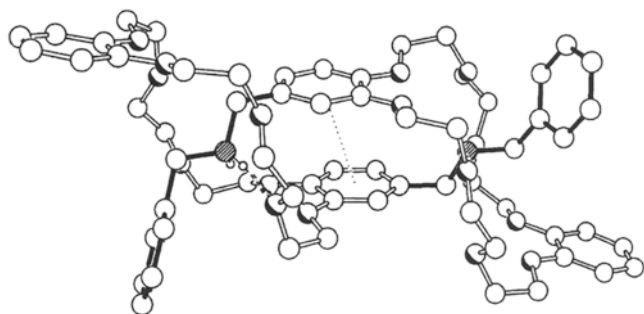
**Fig. 5** The crystal structure of the [2]pseudorotaxane formed from DB24C8 and the bis(3-nitrobenzyl)ammonium ion (5<sup>+</sup>). This superstructure is stabilized by two [N<sup>+</sup>—H···O] and two [C—H···O] hydrogen bonds, together with a  $\pi$ - $\pi$  stacking interaction between one of the  $\pi$ -electron-rich catechol rings and one of the  $\pi$ -electron-deficient nitrobenzyl groups.

chain [21]? The answer came from X-ray crystallography, which demonstrated, along with LSI mass spectrometry, that **6**<sup>+</sup> dimerizes noncovalently to create a two-component supramolecular macrocycle that is equivalent to the smallest possible cyclic daisy chain. The X-ray crystallographic analysis of **6**·O<sub>2</sub>CCF<sub>3</sub> reveals (Fig. 7) the formation of this C<sub>2</sub>-symmetric daisy chain, in which each component's dialkylammonium-bearing sidearms are threaded concurrently through the complementary DB24C8 recognition sites of their counterparts. The [(**6**)<sub>2</sub>]<sup>2+</sup> supermolecules are stabilized, once again, by [N<sup>+</sup>—H···O] hydrogen bonds, as well as by  $\pi$ - $\pi$  stacking interactions between the DB24C8 catechol rings that support the dialkylammonium-containing sidearms.

Could the primitive recognition motif exhibited by the [DB24C8·**3**]<sup>+</sup> complex be developed further so that multiply encircled pseudorotaxanes, consisting of one oligo(dialkylammonium) chain threaded through several DB24C8 macrorings, could be synthesized noncovalently? These multicomponent complexes would be the precursors of polyrotaxanes [22], each comprised of numerous crown ethers threaded onto a poly(dialkylammonium) strand. The answer to the question posed at the beginning of this paragraph is yes [13b–d], as [3]pseudorotaxanes, composed of a bis(dialkylammonium) strand threaded through two crown ether macrorings, were generated when DB24C8, or its asymmetric congener asym-DB24C8, was co-crystallized

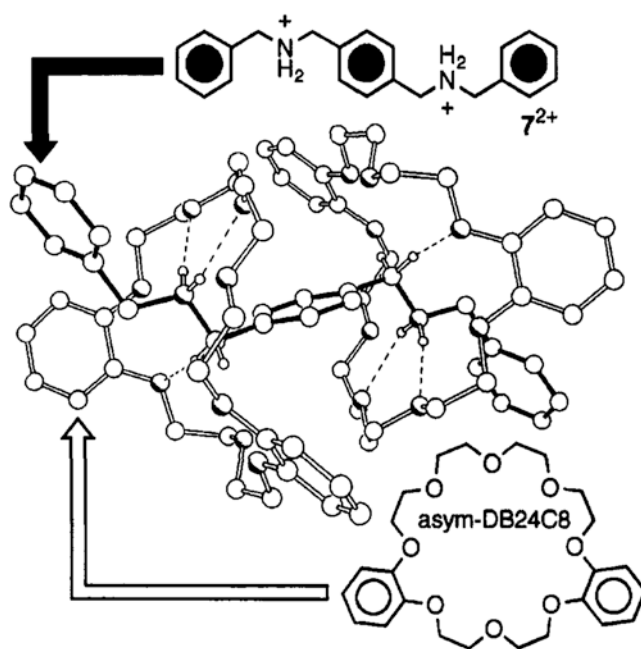


**Fig. 6** Two options are open to the self-complementary cation  $6^+$  upon self-assembly. (a) A finite number of cations can aggregate, in a cyclic fashion, to generate oligomeric daisy-chain-like supermacrocycles, or (b) an infinite number of  $6^+$  monomers can polymerize noncovalently to create a macromolecular daisy chain.



**Fig. 7** View of the two-component supermolecule  $[(6)_2]^{2+}$  in the solid state. Interestingly, only the  $C_2$ -symmetric supermolecule shown and its enantiomer were discovered [18] in the crystal structure, the diastereoisomeric  $C_1$ -symmetric (or *meso*) complex not being observed. In other words, the noncovalent dimerization of the cation  $6^+$  proceeds diastereoselectively, at least in the solid state, to give a racemic mixture of supramolecular stereoisomers with  $C_2$  symmetry.

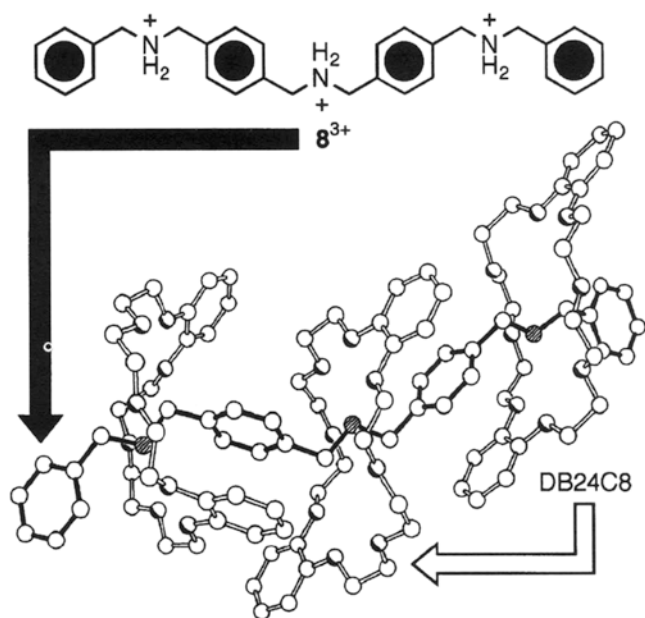
The  $[(6)_2]^{2+}$  superstructure has been classed as a  $[c_2]$ daisy chain, where the  $c$  and 2 designate, respectively, that the daisy chain is cyclic and that it is comprised of two components. Using this nomenclature, the macromolecular daisy chain, illustrated in Fig. 6b, is an  $[a\infty]$ daisy chain, because it is acyclic and is composed of an infinite number of components.



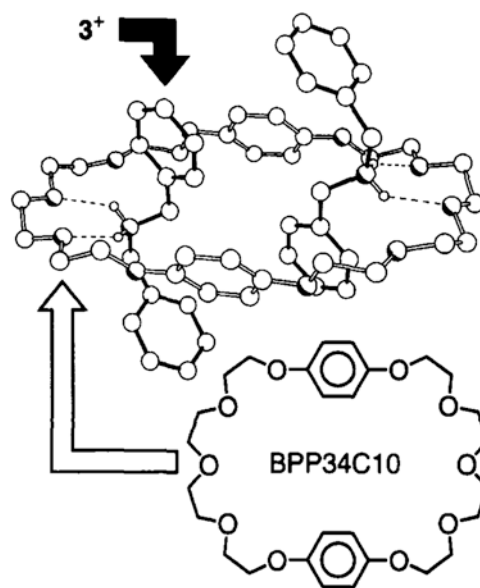
**Fig. 8** View of the crystal structure of the [3]pseudorotaxane  $[(\text{asym-DB24C8})_2 \cdot 7]^{2+}$ .

with the salt  $7 \cdot 2\text{PF}_6$ . Figure 8 shows how one  $7^{2+}$  dication pierces the cavities of two asym-DB24C8 macrocycles to generate a [3]pseudorotaxane that is stabilized, like the  $[\text{DB24C8} \cdot 3]^+$  complex, by both  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  and  $[\text{C} \cdots \text{H} \cdots \text{O}]$  hydrogen bonds. By the same token, the [4] pseudorotaxane  $[(\text{DB24C8})_3 \cdot 8]^{3+}$  was observed (Fig. 9), in the solid state, when DB24C8 was co-crystallized [23] with the trication  $8 \cdot 3\text{PF}_6$ . Stabilization of this triply encircled pseudorotaxane supermolecule is achieved by a combination of  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  and  $[\text{C} \cdots \text{H} \cdots \text{O}]$  hydrogen bonds, supplemented by  $\pi$ - $\pi$  stacking between the trication's *p*-xylylene rings and one of the catechol rings from each of the DB24C8 macrocycles.

Having established that the recognition motif displayed by the  $[\text{DB24C8} \cdot 3]^+$  complex can be extended in one direction, viz., by increasing the number of dialkylammonium centers within the pseudorotaxanes' threadlike components, there was another issue that needed to be addressed, i.e., could we expand the recognition motif in the other direction? Put another way, would several dialkylammonium strands thread their way through the cavity of larger crown ethers to generate multiply stranded pseudorotaxanes? The answer to this question was provided initially [13b–d] by bis-*p*-xylylene[34]crown-10 (BPP34C10), a crown ether that had been utilized by us previously [12a] for the synthesis of a wide range of catenanes, rotaxanes, and pseudorotaxanes. Gratifyingly, crystals of the complex produced from



**Fig. 9** View of the solid-state structure of the [4]pseudorotaxane generated when the trication  $8^{3+}$  interpenetrates the cavities of three DB24C8 macrocyclic receptors.



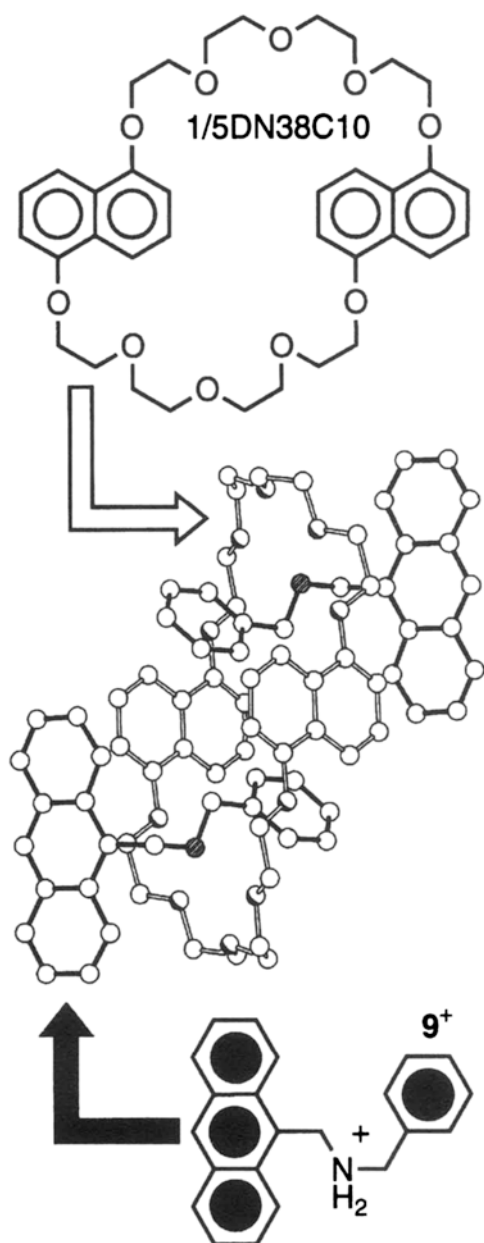
**Fig. 10** The solid-state structure of the complex  $[BPP34C10 \cdot (3)_2]^{2+}$  in which two  $3^+$  cations are threaded through the BPP34C10 macrocyclic receptor by virtue of  $[N^+ \cdots O]$  hydrogen bonds.

BPP34C10 and  $3 \cdot PF_6$  did, indeed, show (Fig. 10) the formation of a doubly stranded [3]pseudorotaxane  $[BPP34C10 \cdot (3)_2]^{2+}$  consisting of pairs of  $3^+$  cations threaded symmetrically through the BPP34C10 macrocyclic receptor. The complex is stabilized primarily by means of  $[N^+ \cdots O]$  hydrogen bonds from the  $NH_2^+$  hydrogen atoms to pairs of oxygen atoms located in both of the crown ether's disassociated polyether loops, with secondary stabilization occurring via edge-to-face interactions between one of each cation's phenyl rings and the hydroquinone rings of the crown ether. Notably, however, in contrast with the aforementioned  $[DB24C8 \cdot 3]^+$  complex, here no  $[C \cdots O]$  hydrogen bonds are present to aid in holding the  $[BPP34C10 \cdot (3)_2]^+$  superstructure together.

A short while ago, the paradigm, stating that two dialkylammonium strands doubly thread through the cavity of a crown ether bearing two isolated polyether arcs, was developed further [24] in our laboratories. The crown ether 1,5-dinaphtho[38]crown-10 (1/5DN38C10) is similar to BPP34C10 in that it is endowed with two separated polyether loops, but differs in that these polyether loops are separated by 1,5-dioxynaphthalene residues, as opposed to hydroquinone rings. It cocrystallizes with the cation  $9^+$  to generate (Fig. 11) the centrosymmetric doubly stranded [3] pseudorotaxane  $[1/5DN38C10 \cdot (9)_2]^{2+}$  that is stabilized, like the related complex  $[BPP34C10 \cdot (3)_2]^{2+}$ , by virtue of  $[N^+ \cdots O]$  hydrogen bonds and aromatic edge-to-face

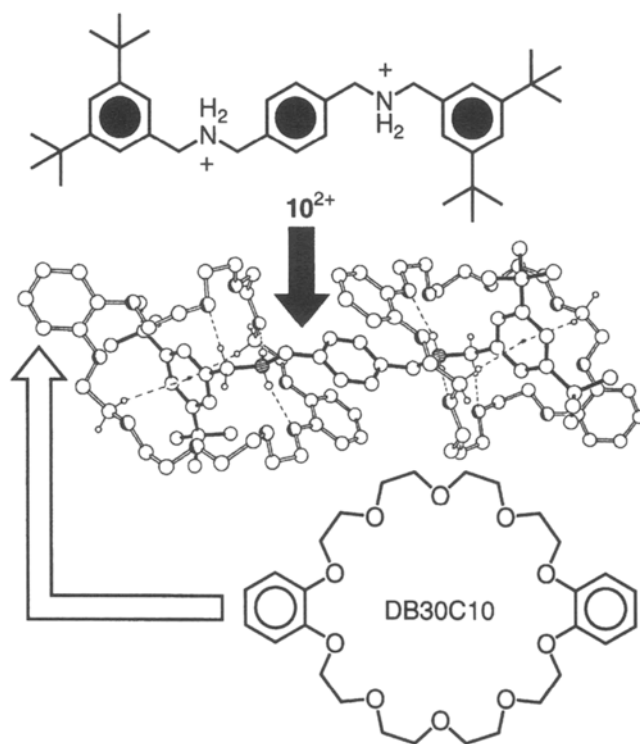
interactions. Nonetheless, not all crown ethers with two disassociated  $OCH_2(CH_2OCH_2)_3CH_2O$  polyether arcs form doubly stranded [3]pseudorotaxanes with dialkylammonium ions. If these arcs are appended to *o*-phenylene units, as in dibenzo[30]crown-10 (DB30C10), the crown ether's cavity becomes so small that it can accommodate only one dialkylammonium ion, resulting in the formation of singly stranded pseudorotaxanes. This fact is illustrated by the crystal structure [25] of complex  $[(DB30C10)_2 \cdot 10]^{2+}$ —prepared from DB30C10 and  $10 \cdot 2PF_6$  via the slippage [26] approach—in which (Fig. 12) each of the dication's two dialkylammonium centers is encircled by only one DB30C10 macrocyclic receptor. The  $C_2$ -symmetric [3]pseudorotaxane  $[(DB30C10)_2 \cdot 10]^{2+}$  is stabilized by  $[N^+ \cdots O]$  and  $[C \cdots O]$  hydrogen bonds, supplemented by both face-to-face and edge-to-face  $\pi$ - $\pi$  interactions.

What happens when a mixture of DB24C8 and BPP34C10 self-assembles with a thread bearing both dialkylammonium and 4,4'-bipyridinium recognition sites? This question is particularly interesting since BPP34C10 can bind either two dialkylammonium centers or one 4,4'-bipyridinium unit [12a, [27] within its cavity. In a bid to answer this question, we have found [28] that a mixture of DB24C8 and BPP34C10 self-assembles self-selectively with the tetracationic thread  $11^{4+}$  to produce (Fig. 13) the [4]pseudorotaxane supermolecule  $[(DB24C8)_2 \cdot BPP34C10 \cdot 11]^{4+}$ . In this discrete superstructure, the DB24C8 macrocyclic receptors encircle the dialkylammonium



**Fig. 11** The 1:2 doubly stranded pseudorotaxane complex formed by 1/5DN38C10 and 9<sup>+</sup> in the solid state. The intrapseudorotaxane [N<sup>+</sup>...N<sup>+</sup>] separation is 9.1 Å in the [1/5DN38C10·(9)<sub>2</sub>]<sup>2+</sup> complex, an increase of 0.7 Å compared to the corresponding distance in [3] pseudorotaxane [BPP34C10·(3)<sub>2</sub>]<sup>2+</sup>. This elongation of the distance between the two NH<sub>2</sub><sup>+</sup> centers is presumably a consequence of the larger size of the 1/5DN38C10 host with respect to its congener BPP34C10.

centers by virtue of the usual [N<sup>+</sup>—H...O] and [C—H...O] hydrogen bonds, while the 4,4'-bipyridinium unit complexes with BPP34C10 through  $\pi$ - $\pi$  stacking and [C—H...O] hydrogen bonding interactions, in a manner reminiscent of the 1:1 complex formed [27] between

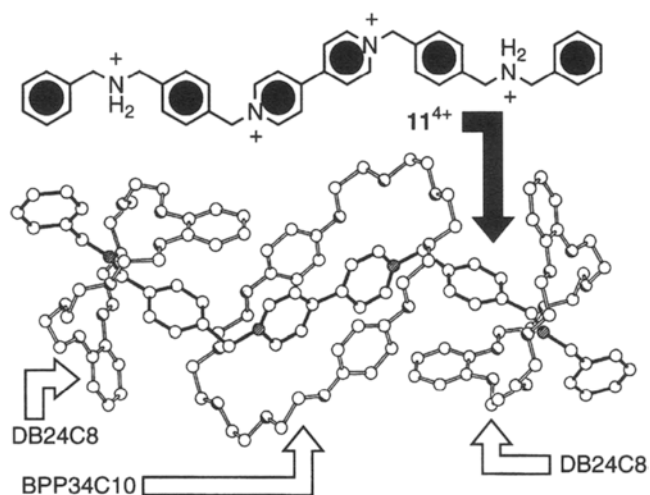


**Fig. 12** Doubly stranded pseudorotaxanes are not produced when the size of the spacer unit between two OCH<sub>2</sub>(CH<sub>2</sub>OCH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>O polyether arcs is reduced from *p*-phenylene (as in BPP34C10) to *o*-phenylene (as in DB30C10). This fact is highlighted by the crystal structure of the pseudorotaxane [(DB30C10)<sub>2</sub>·10]<sup>2+</sup>.

BPP34C10 and the paraquat (1,1'-dimethyl-4,4'-bipyridinium) dication. The preparation of the complex [(DB24C8)<sub>2</sub>·BPP34C10·11]<sup>4+</sup> demonstrates adroitly how an intricate superarchitecture can be generated through the operation of two different recognition motifs simultaneously and selectively. It is believed [29] that such concurrent usage of numerous recognition motifs, in a self-selective manner, will become a routine tactic of synthetic supramolecular chemists in future noncovalent syntheses, for the reason that superstructural complexity becomes amplified as the number of intermolecular bonding tools used increases.

### Never Forget the Counterions!

During our studies, we discovered an interesting feature associated with some of the complexes formed between crown ethers and dialkylammonium-containing cations, that is, they interact with their associated anions. Since anion binding and recognition play a pivotal role in several essential chemical and biological processes, it is hardly surprising that the design of anion-binding receptors is



**Fig. 13** Operating several distinct recognition motifs judiciously, at the same time, allows the preparation of elaborate superstructures, as demonstrated by the crystal structure of the [4]pseudorotaxane generated when DB24C8 and BPP34C10 interact, in an independent and self-selective manner, with the respective dialkylammonium and 4,4'-bipyridinium portions of the tetracationic thread  $11^{4+}$ .

currently [30] arousing considerable attention within the supramolecular community. We were enticed into this field by several serendipitous discoveries relating to anion-assisted self-assembly [31]. All of our work pertains to  $\text{PF}_6^-$  anions, species that usually adopt random orientations in crystal lattices because of their “spherical” nature. Indeed, these anions are disordered in the crystal structures illustrated in Figs. 3, 4, and 5 and 8, 9, 10, 11, 12, and 13, structures in which there is no interaction with the cationic species. This disorder is relinquished, however, when the  $\text{PF}_6^-$  anions interact with cationic superarchitectures in the solid state.

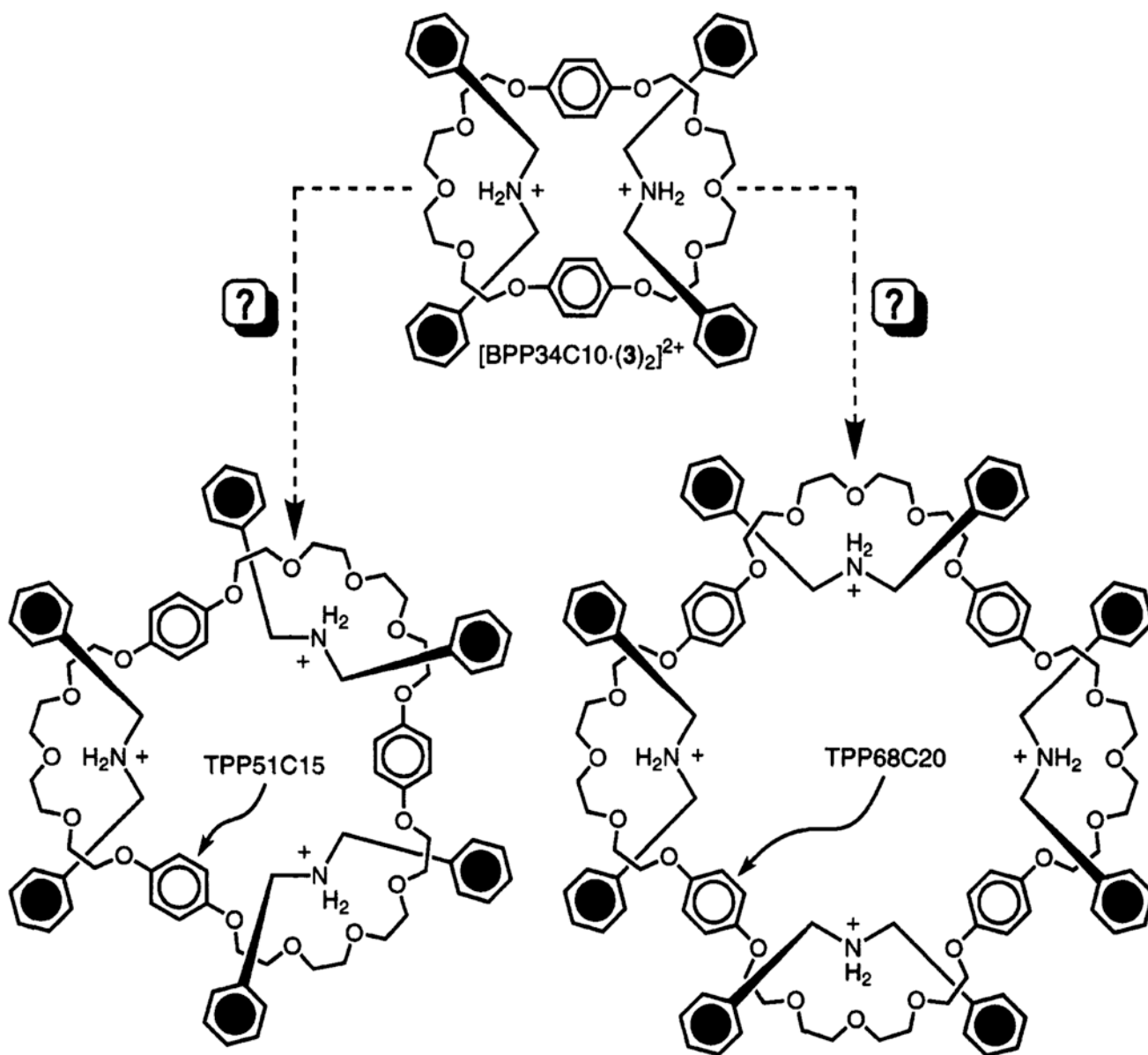
It all started during our investigations [23, 32] on the supramolecular synthesis of multiply stranded pseudorotaxanes (Fig. 14) from higher homologues of BPP34C10, viz., tris-*p*-phenylene[51]crown-15 (TPP51-C15) and tetrakis-*p*-phenylene[68]crown-20 (TPP68-C20), and the cation  $3^+$ . We believed that TPP51C15 and TPP68C20 were natural extensions of BPP34C10, whose distinct arrays of three and four hydroquinone-spaced polyether loops should be able to bind to three and four  $3^+$  cations, respectively. Indeed, the X-ray analysis of crystals generated when TPP51C15 was co-crystallized with  $3 \cdot \text{PF}_6^-$  reveals (Fig. 15) the formation of a 1:3 complex, i.e., the triply stranded [4]pseudorotaxane  $[\text{TPP51C15} \cdot (3)_3]^{3+}$ , wherein three  $3^+$  ions are bound independently to each of the crown ether's separate polyether loops by means of  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  and  $[\text{C} \cdots \text{H} \cdots \text{O}]$  hydrogen bonds. A closer investigation of this superarchitecture reveals

that one of its affiliated  $\text{PF}_6^-$  counterions is bound within a cleft, created by the pseudorotaxane's saddle-like co-conformation, by the intermediacy of a series of  $[\text{C} \cdots \text{H} \cdots \text{F}]$  hydrogen bonds to the hydrogen atoms of the crown ether's hydroquinone rings and the cation's benzylic  $\text{CH}_2$  groups.

The above-mentioned observation led us to believe that we could encapsulate a  $\text{PF}_6^-$  ion completely within the [5] pseudorotaxane superstructure  $[\text{TPP68C20} \cdot (3)_4]^{4+}$ . We reasoned that the increased empty space in the pseudorotaxane's core, brought about by the increased dimensions of the crown ether TPP68C20, should allow the complete envelopment of a  $\text{PF}_6^-$  ion by means of hydrogen bonding and anion-dipole interactions. As expected, the X-ray analysis of crystals obtained from a 1:4 solution of TPP68C20 and  $3 \cdot \text{PF}_6^-$  reveals (Fig. 16a) the formation of two, practically identical, crystallographically independent, quadruply stranded [5]pseudorotaxanes  $[\text{TPP68C20} \cdot (3)_4]^{4+}$  that are stabilized, yet again, by  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  and  $[\text{C} \cdots \text{H} \cdots \text{O}]$  hydrogen bonds. Even more interestingly, however, there are single ordered  $\text{PF}_6^-$  ions in the cores of both [5]pseudorotaxanes. In each superstructure, the anion is encapsulated completely by the four hydroquinone rings and four  $\text{CH}_2\text{NH}_2^+\text{CH}_2$  regions of the pseudorotaxanes, stabilization arising from a series of  $[\text{C} \cdots \text{H} \cdots \text{F}]$  hydrogen bonds. Anion envelopment may be viewed as resulting from supramolecular preorganization of the anion recognition sites, i.e., where the macrocycle preorganizes [33] the  $\text{CH}_2\text{NH}_2^+\text{CH}_2$  units (anion recognition sites) for  $\text{PF}_6^-$  binding. The fact that the macrocycle also interacts with the anion means that the [5]pseudorotaxane  $[\text{TPP68C20} \cdot (3)_4]^{4+}$  provides (Fig. 16b) elegant concentric spheres of cationic and neutral ligands for complete anion encapsulation.

Anions were also found to play a role in the selfassembly of BPP34C10 with the dication  $7^{2+}$ . Originally, we envisaged (Fig. 17) two possible supramolecular outcomes when these two components aggregate with each other, viz., the doubly docked [2]pseudorotaxane  $[\text{BPP34C10} \cdot 7]^{2+}$  or the doubly stranded, doubly encircled [4]pseudorotaxane  $[(\text{BPP34C10})_2 \cdot (7)_2]^{4+}$ . In actual fact, we found [13b–d] that the latter four-component supermolecule was generated, through the intermediacy of  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  and  $[\text{C} \cdots \text{H} \cdots \text{O}]$  hydrogen bonds, when BPP34C10 and  $7 \cdot 2\text{PF}_6^-$  were crystallized together. However, a closer analysis [34] of the crystal structure reveals (Fig. 18) that  $\text{PF}_6^-$  counterions are located in the cavities formed between  $2_1$ -screw-related [4]pseudorotaxanes, creating an interwoven one-dimensional supramolecular array through  $[\text{C} \cdots \text{H} \cdots \text{O}]$  hydrogen bonding.

Is it the  $\text{PF}_6^-$  ions that direct the solid-state self-assembly of the discrete supermolecule  $[(\text{BPP34C10})_2 \cdot (7)_2]^{4+}$ ? We are not entirely sure, to be honest, but this question played a part

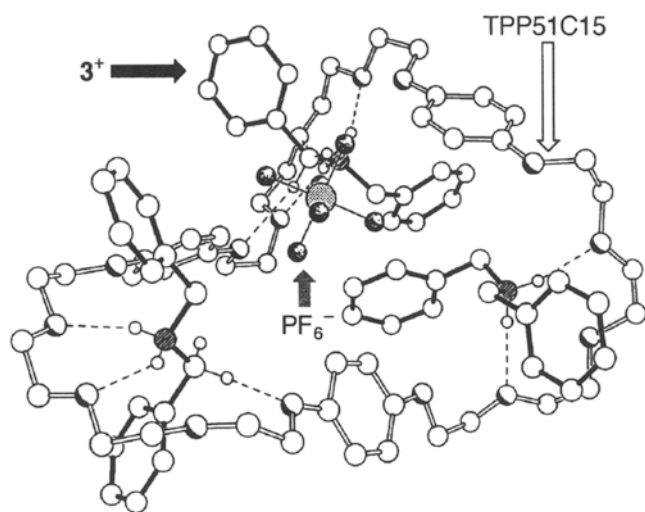


**Fig. 14** Complexation of BPP34C10 with  $3^+$  yields a doubly stranded [3]pseudorotaxane. The question we asked subsequently was: Do larger crown ethers, such as TPP51C15 and TPP68C20, allow the synchronous threading of three and four  $3^+$  ions through their respective cavities? The answer is yes.

in our thinking when we embarked on a program designed to synthesize doubly docked [2]pseudorotaxanes noncovalently. In this program [34], we utilized bis(dialkylammonium) dicationic species bearing two 3,5-di-*tert*-butylbenzyl termini. These bulky groups were introduced to prevent two separate dicationic species from fitting inside one BPP34C10 macrocyclic cavity and to prohibit the occurrence of solid-state, anion-assisted self-assembly. Indeed, the doubly docked [2]pseudorotaxanes  $[\text{BPP34C10} \cdot \mathbf{10}]^{2+}$  and  $[\text{BPP34C10} \cdot \mathbf{12}]^{2+}$  were observed

(Fig. 19), respectively, in the solid state, when BPP34C10 was crystallized with either of the aryl-spaced bis(dialkylammonium) salts  $\mathbf{10} \cdot 2\text{PF}_6^-$  or  $\mathbf{12} \cdot 2\text{PF}_6^-$ . In both of these  $C_1$ -symmetric supermolecules, stabilization is achieved through the agency of the usual hydrogen bonding interactions, together with  $\pi$ - $\pi$  stacking interactions. Notably, in both examples, no  $\text{PF}_6^-$  ions associate with the pseudorotaxane supermolecules. Nevertheless, the hydrogen bonding interactions are not optimal in either of the superstructures



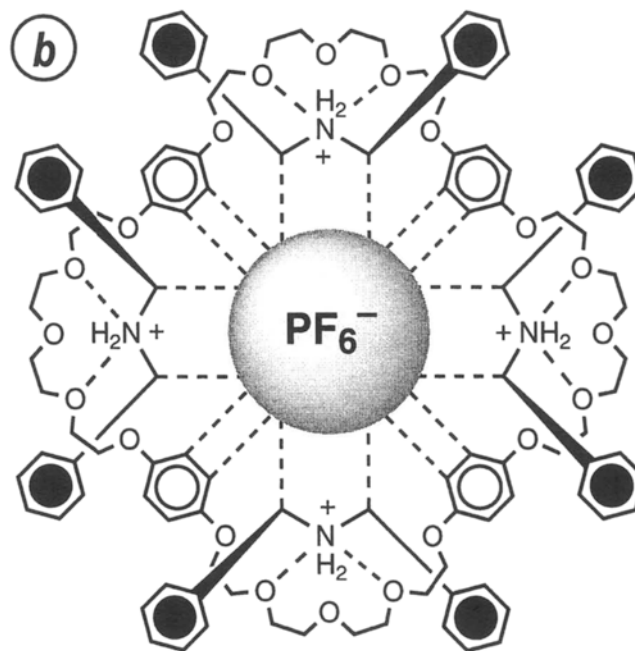
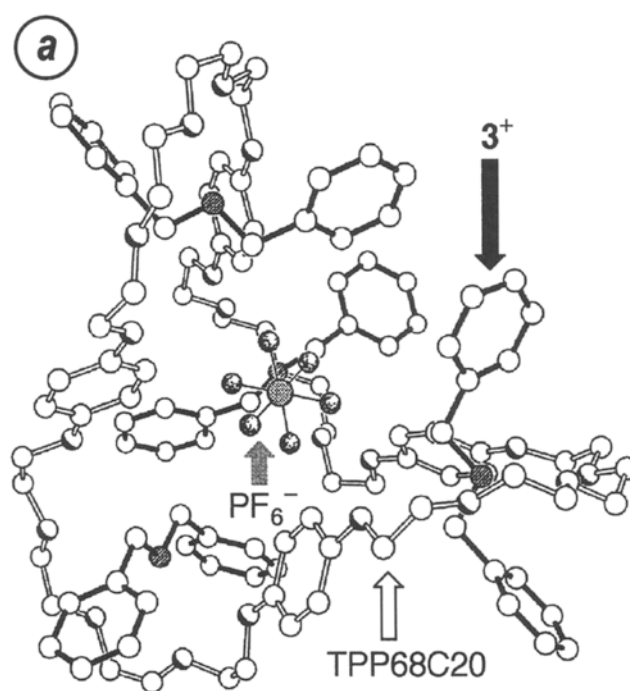


**Fig. 15** The solid-state structure of [4]pseudorotaxane [TPP51C15 · (3)<sub>3</sub>]<sup>3+</sup> shows that it partially envelops a PF<sub>6</sub><sup>-</sup> counterion through [C—H...F] hydrogen bonding.

[BPP34C10 · 10]<sup>2+</sup> and [BPP34C10 · 12]<sup>2+</sup>: The former is stabilized partly by hydrogen bonds involving the less basic hydroquinone oxygen atoms, while the latter achieves stabilization through the use of the weaker [C—H...O] hydrogen bonds.

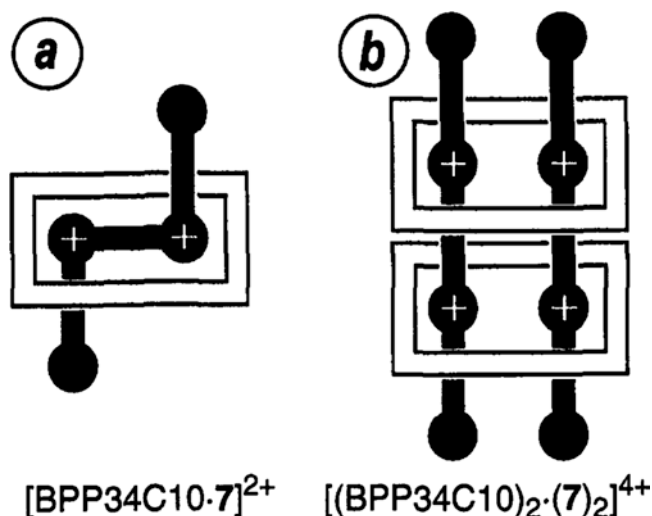
In order to maximize the stabilization imparted to these structures by hydrogen bonding interactions, we then examined the possibility of spacing the dialkylammonium centers with more flexible alkyl units. The X-ray analysis of the 1:1 complex formed between BPP34C10 and the pentyl-spaced dication **13**<sup>2+</sup> reveals (Fig. 20) the failure to form a pseudorotaxane at all. In this instance, a hot dog-like supermolecule [BPP34C10 · 13]<sup>2+</sup>, possessing a face-to-face [35] co-conformation, is produced as a result of [N<sup>+</sup>—H...O] and [C—H...π] hydrogen bonds. This species is formed presumably because of the smaller spacer unit between the NH<sub>2</sub><sup>+</sup> centers, which means that both the BPP34C10 macrocycle and dication **13**<sup>2+</sup> have to adopt unusually distorted geometries in order that the supermolecule can achieve stabilization via two pairs of [N<sup>+</sup>—H...O] hydrogen bonds. Also of note in this case is the fact that the folding of the dication creates, in conjunction with pairs of hydroquinone hydrogen atoms, a hydrophobic cavity, within which one of the PF<sub>6</sub><sup>-</sup> counterions is bound through a combination of electrostatic interactions and [C—H...F] hydrogen bonds.

Next, we decided to increase the length of the spacer unit: Studies were instigated on the complexation phenomena associated with BPP34C10 and the hexamethylene-spaced dication **14**<sup>2+</sup>. These investigations revealed that the two components self-assemble in the solid state to form (Fig. 21)

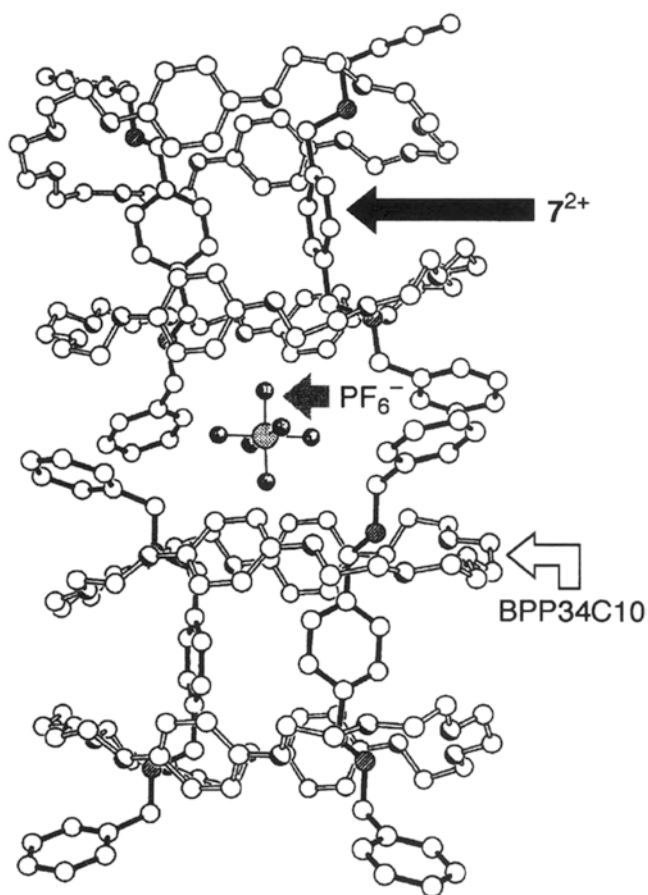


**Fig. 16** The two crystallographically independent [5]pseudorotaxanes [TPP68C20 · (3)<sub>4</sub>]<sup>4+</sup> totally encapsulate a PF<sub>6</sub><sup>-</sup> ion within their cores. (a) Ball-and-stick view of one of the crystallographically independent [TPP68C20 · (3)<sub>4</sub>]<sup>4+</sup> · PF<sub>6</sub><sup>-</sup> complexes. (b) Schematic representation of the anion encapsulation by the pseudorotaxane.

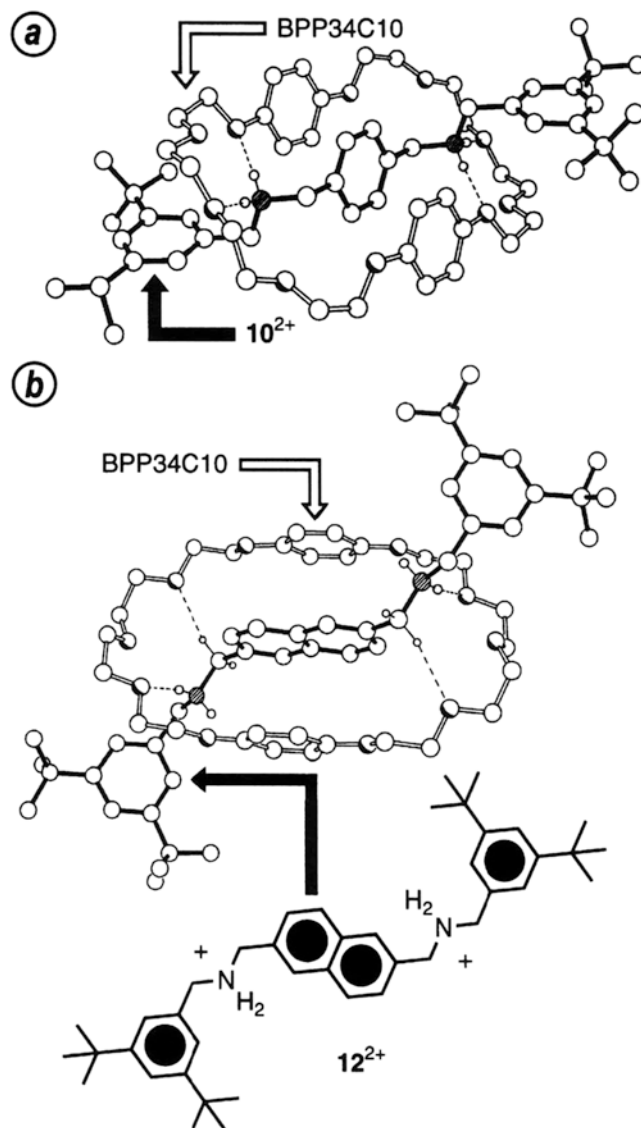
a doubly docked [2]pseudorotaxane with the desired hydrogen bonding pattern. The centrosymmetric [2]pseudorotaxane [BPP34C10 · 14]<sup>2+</sup> is generated when each NH<sub>2</sub><sup>+</sup> center hydrogen bonds to the second and fourth oxygen



**Fig. 17** Diagrams illustrating two of the ways in which BPP34C10 can self-assemble with the dication  $7^{2+}$ . (a) A doubly docked [2] pseudorotaxane. (b) A doubly stranded, doubly encircled [4] pseudorotaxane.



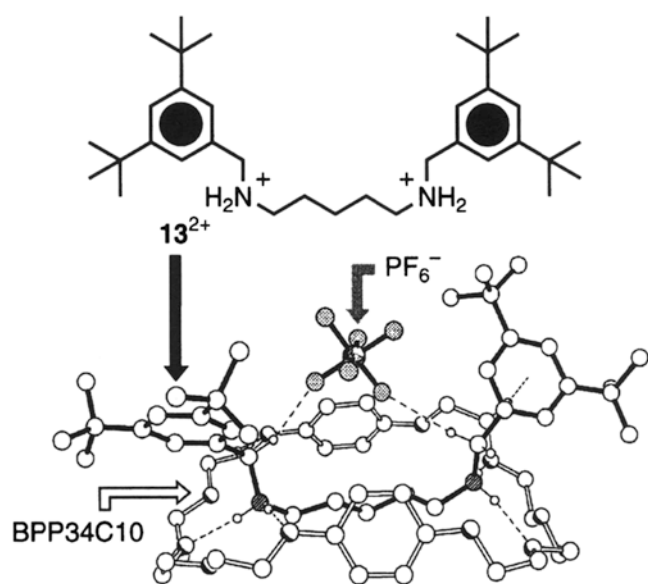
**Fig. 18** View of the solid-state structure acquired from co-crystals of BPP34C10 and  $7^{2+}$ . A one-dimensional supramolecular array is created because distinct  $[(BPP34C10)_2 \cdot (7)_2]^{4+}$  supermolecules interconnect through the intermediacy of hydrogen-bonded  $PF_6^-$  ions.



**Fig. 19** The crystal structures of two doubly docked [2]pseudorotaxanes that are stabilized by both hydrogen bonding and  $\pi$ - $\pi$  stacking interactions. (a)  $[BPP34C10 \cdot 10]^{2+}$  (b)  $[BPP34C10 \cdot 12]^{2+}$ .

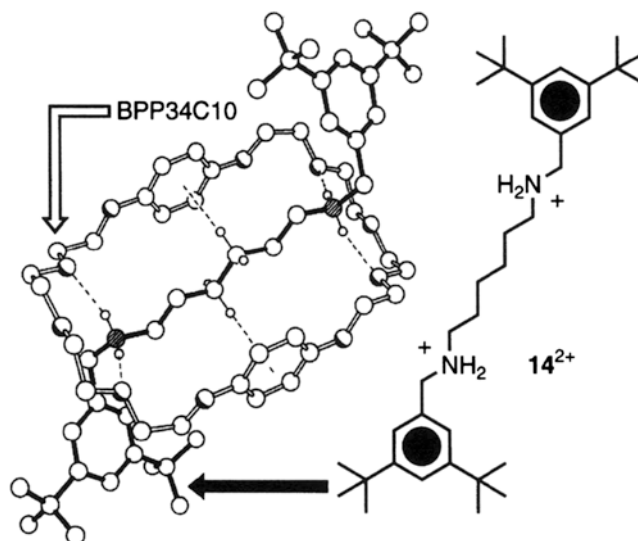
atoms of each polyether loop. Supplementary stabilization is conferred upon this two-component supermolecule via  $[C-H \cdots \pi]$  interactions between the dication's central  $CH_2$  groups and the hydroquinone rings of the crown ether. Yet again,  $PF_6^-$  ions were not perceived to influence this self-assembly process.

We have also become acquainted with other examples of anion-assisted self-assembly [31, 32] in our studies [36] on crystal engineering [7b] through the noncovalent association of carboxyl-substituted crown ether–dialkylammonium ion-based pseudorotaxanes. In particular, we have discovered that  $PF_6^-$  ions can have (Fig. 22) a strong effect on the crystal



**Fig. 20** BPP34C10 and  $13^{2+}$  assume distorted conformations in the solid-state structure of the hot dog-like 1:1 complex  $[\text{BPP34C10} \cdot 13]^{2+}$ . These distortions produce a hydrophobic pocket that binds a  $\text{PF}_6^-$  counterion.

structures of the doubly stranded [3]pseudorotaxanes generated from BPP34C10 and secondary dialkylammonium salts possessing one aromatic ring substituted with carboxyl groups. In these structures, BPP34C10 acts as a girdle that holds two dialkylammonium ions together in space, while the directions in which the ensuing [3]pseudorotaxanes' carboxyl-bearing aromatic rings point depend on the  $\text{PF}_6^-$  counterions. We found that the carboxyl-substituted aromatic rings are oriented in the same direction if the  $\text{PF}_6^-$  anions associate with the [3]pseudorotaxanes, but that they are guided in opposing directions if no anion-[3]pseudorotaxane interaction is present. For instance, the X-ray analyses of the [3]pseudorotaxanes  $[\text{BPP34C10} \cdot (15)_2]^{2+}$  and  $[\text{BPP34C10} \cdot (16)_2]^{2+}$  reveal (Fig. 23) that both cations are threaded co-directionally through the macrocycle's center as a consequence of the  $\text{PF}_6^-$  ions that are located, by virtue of  $[\text{C}-\text{H} \cdots \text{F}]$  hydrogen bonds, in the clefts formed between the cations' unsubstituted phenyl rings. This important secondary interaction leads to the noncovalent dimerization of pairs of  $C_1$ -symmetrically related [3]pseudorotaxanes to generate doubly encircled eight-component supermolecules that are linked through the strong  $[\text{O}-\text{H} \cdots \text{O}]$  hydrogen bonds of the carboxyl dimer [37]. In both complexes  $[\text{BPP34C10} \cdot (15)_2]^{2+}$  and  $[\text{BPP34C10} \cdot (16)_2]^{2+}$ , the BPP34C10 macrorings and  $\text{PF}_6^-$  counterions combine to effect supramolecular preorganization of the carboxyl groups for dimerization.

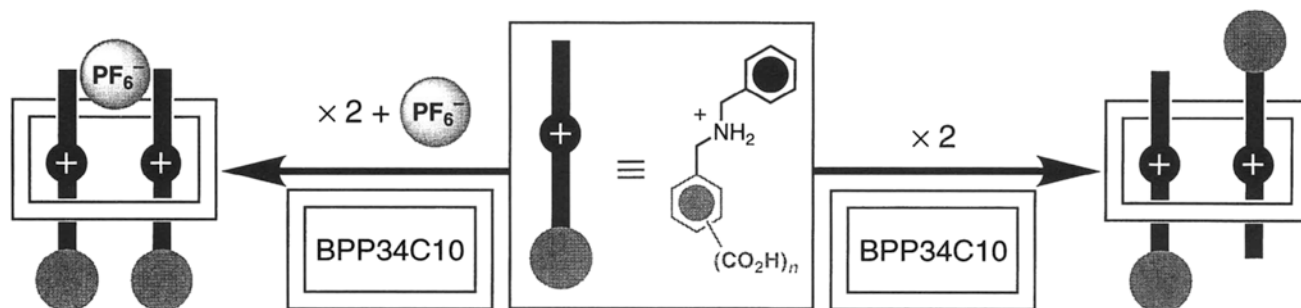


**Fig. 21** The crystal structure of the complex  $[\text{BPP34C10} \cdot 14]^{2+}$ —a “flawless” doubly docked [2]pseudorotaxane.

On the other hand,  $\text{PF}_6^-$  ions were observed not to associate with the [3] pseudorotaxane  $[\text{BPP34C10} \cdot (17)_2]^{2+}$ . Here, two cations  $17^+$  thread centrosymmetrically through the BPP34C10 macrocycle with respect to each other, i.e., in an antiparallel orientation, so that their isophthalate units are oriented in opposing directions. By employing carboxyl dimers, these isophthalate units then form the tapes that are present [38] in the crystal structure of isophthalic acid itself to generate (Fig. 24) an interwoven supramolecular cross-linked polymer, in which polymeric isophthalic acid tapes are interlinked through the [3]pseudorotaxane unit. In this instance, the disordered  $\text{PF}_6^-$  counterions are located in the interstices between the pseudopolyrotaxane sheets.

### Interwoven Supramolecular Bundles

The noncovalent syntheses of the pseudorotaxane supermolecules  $[\text{BPP34C10} \cdot (3)_2]^{2+}$  and  $[(\text{BPP34C10})_2 \cdot (7)_2]^{4+}$  form the foundations of a new paradigm for supramolecular synthesis. This paradigm states that  $n$  molecules of BPP34C10, which possess a total of  $2n$  dialkylammonium binding sites, are capable of tying two oligo(dialkylammonium) cations, each bearing  $n$  dialkylammonium centers, together to generate discrete multicomponent superarchitectures. We conjectured that, by applying this principle to systems involving branched oligo(dialkylammonium) ions endowed with  $n$  cationic “spokes,” we could self-assemble multicomponent

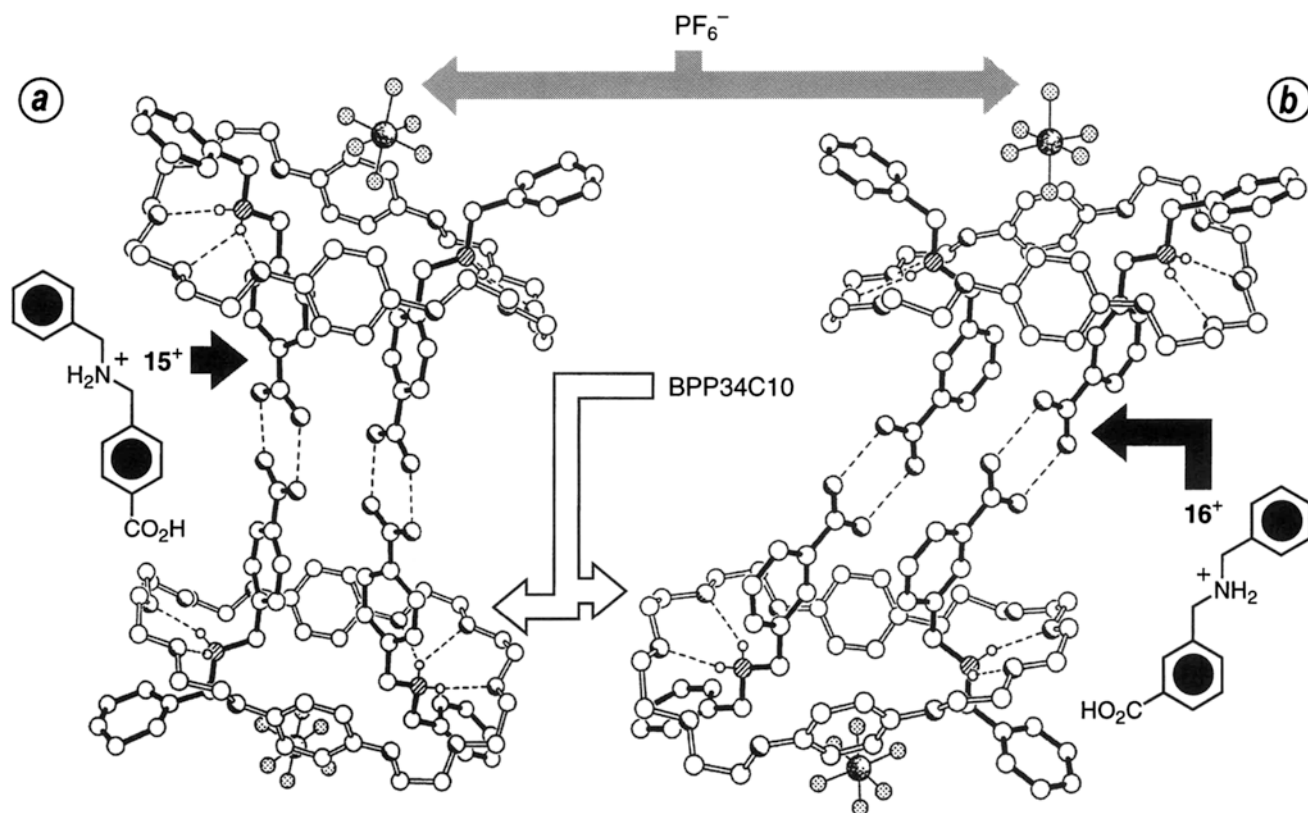


**Fig. 22** The BPP34C10 macrocycle supports two dialkylammonium ions within its interior to generate [3]pseudorotaxanes.  $\text{PF}_6^-$  ions can interact with these pseudorotaxanes to orient recognition sites (in the examples discussed here, these are carboxyl groups) in space for further noncovalent association.

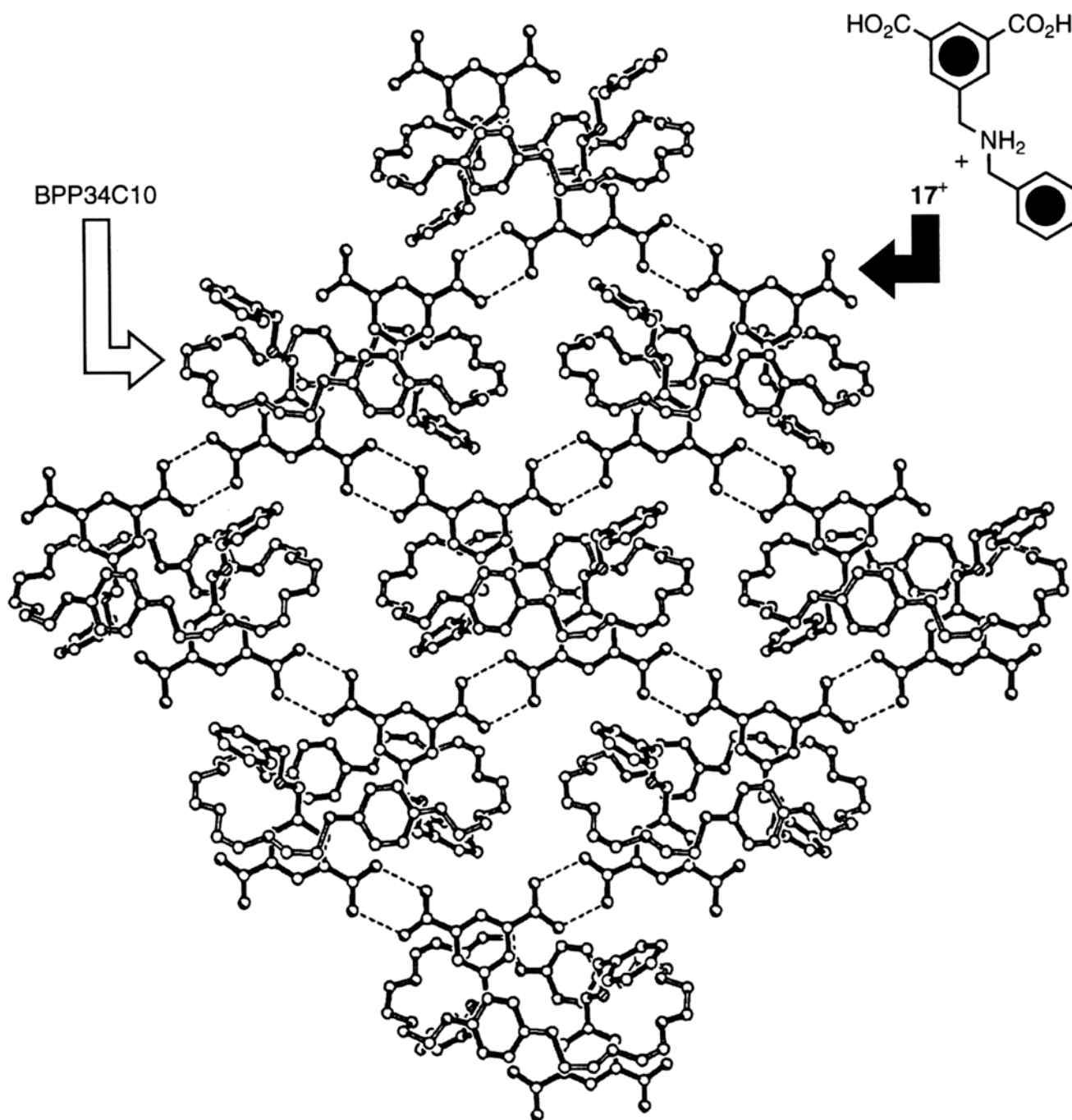
interwoven supramolecular bundle-like architectures, i.e., clusters [32, 39]. In these supermolecules, each of the  $n$  spokes from one oligo(dialkylammonium) ion would be inserted through half of the cavities of  $n$  separate BPP34C10 molecules, such that the  $n$  vacant receptor sites remaining in the crown ethers' cavities would be free to accept another  $n$

spokes from a second cation. In other words,  $n$  BPP34C10 macrocycles would clamp two branched oligo (dialkylammonium) ions together, employing, for the most part,  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  hydrogen bonds.

Our initial studies concentrated [40] on the trifurcated trisammonium trication  $\mathbf{18}^{3+}$ , whose covalent skeleton consists



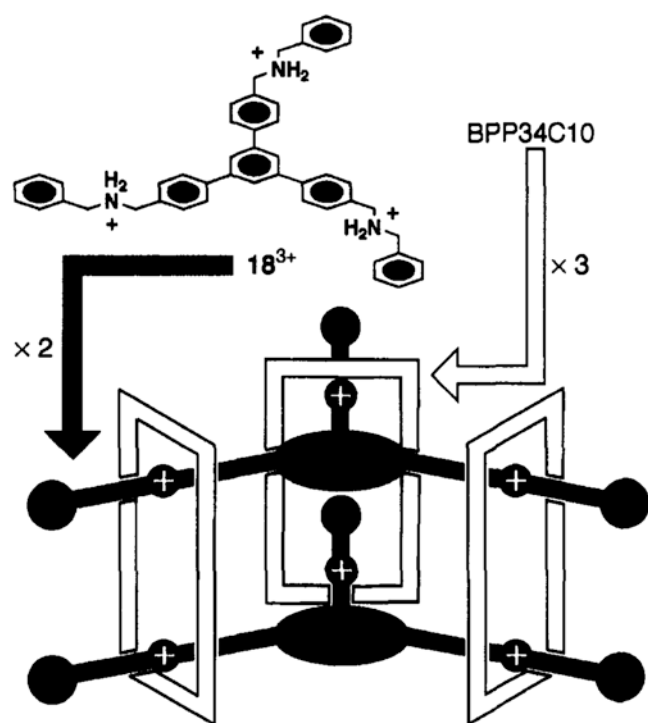
**Fig. 23** The crystal structures of two [6]pseudorotaxanes whose self-assembly is assisted by  $\text{PF}_6^-$  ions. (a)  $\left\{ [\text{BPP34C10} \cdot (\mathbf{15})_2]^{2+} \right\}_2 \cdot 2\text{PF}_6^-$ . (b)  $\left\{ [\text{BPP34C10} \cdot (\mathbf{16})_2]^{2+} \right\}_2 \cdot 2\text{PF}_6^-$ .



**Fig. 24** Portrayal of the interwoven pseudopolyrotaxane sheets  $\{[\text{BPP34C10} \cdot (\mathbf{17})_2]^{2+}\}_n$  that form in crystals of BPP34C10 and  $\mathbf{17} \cdot \text{PF}_6$ . This example emphasizes the fact that operating several different recognition motifs—in this case, the carboxyl dimer and double threading motifs—both simultaneously and selectively allows the noncovalent synthesis of diverse and complicated superarchitectures.

of three secondary dialkylammonium branches emanating out from a central polyaromatic core. We hypothesized that two units of this trication would self-assemble with three BPP34C10 molecules to form (Fig. 25) a five-component interwoven superbundle. Gratifyingly, the X-ray analysis of single crystals, obtained from a 3:2 solution of

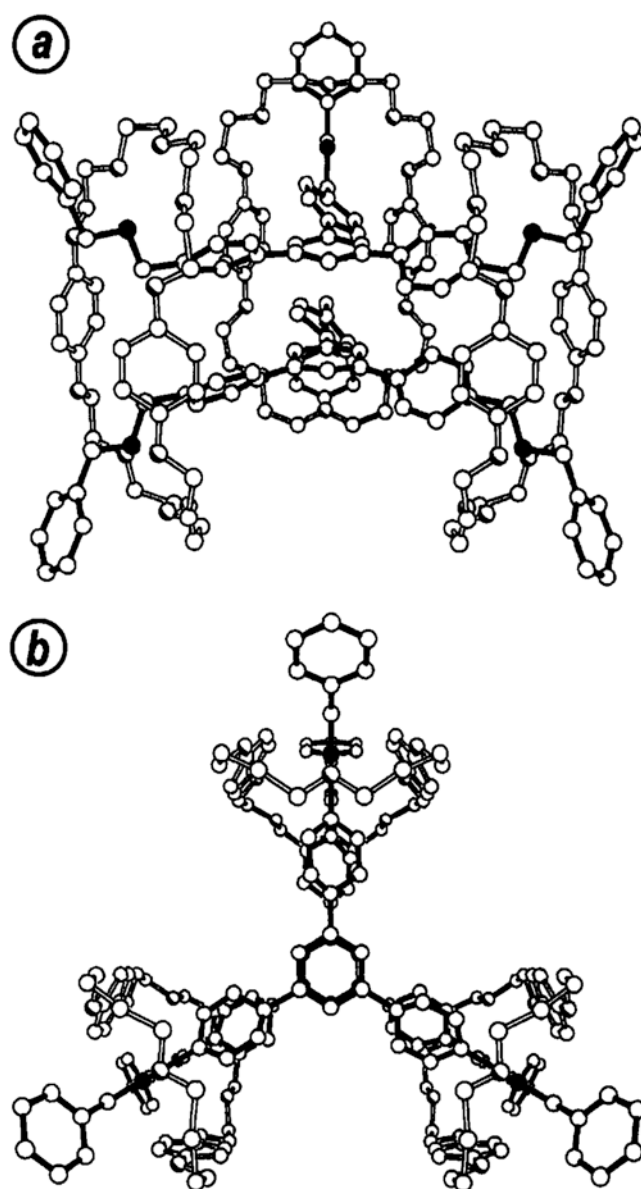
BPP34C10 and  $\mathbf{18} \cdot 3\text{PF}_6$ , revealed (Fig. 26) the creation of a highly symmetrical bundle supermolecule, wherein three BPP34C10 macrocycles tie two  $\mathbf{18}^{3+}$  trications together primarily by means of  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  hydrogen bonds. The supermolecule has  $D_3$  symmetry, with the principal axis passing (Fig. 26b) through the centers of the two



**Fig. 25** Schematic diagram illustrating the anticipated [3+2] self-assembly of the interwoven superbundle  $[(\text{BPP34C10})_3 \cdot (\mathbf{18})_2]^{6+}$ , wherein two trications  $\mathbf{18}^{3+}$  are fastened together by three BPP34C10 macrocycles.

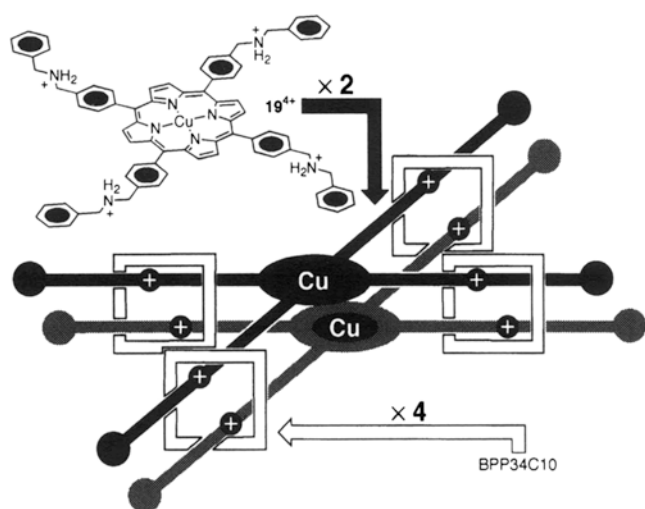
1,3,5-triarylbenzene rings, which experience a mean interplanar separation of ca. 4.0 Å.

Next, we decided [41] to synthesize noncovalently a supramolecular analogue of the photosynthetic special pair [42, 43] using the protocol that we had developed beforehand. We anticipated that two units of the tetrafurcated tetrakisammonium tetracation  $\mathbf{19}^{4+}$ , possessing four dialkylammonium spokes fanning out from a central porphyrin core, could be tied together by four BPP34C10 molecules to produce (Fig. 27) a six-component interwoven aggregate bearing two cofacially disposed porphyrinoid nuclei, much like the special pair found in the photosynthetic reaction center [42]. The X-ray analysis of the 4: 2 complex formed from BPP34C10 and  $\mathbf{19} \cdot 4\text{PF}_6$  revealed (Fig. 28) a six-component supermolecule that had self-assembled in accordance with our design criteria. Pairs of  $\text{C}_i$ -related  $\mathbf{19}^{4+}$  tetracations have their dibenzylammonium sidearms threaded concurrently through the cavities of four cyclically disposed BPP34C10 macrocycles in characteristic fashion. In addition to conventional  $\pi$ - $\pi$  stacking between the porphyrin nuclei (mean interplanar separation = 3.65 Å), the  $[(\text{BPP34C10})_4 \cdot (\mathbf{19})_2]^{8+}$  supermolecule is stabilized via  $[\text{N}^+ \cdots \text{H} \cdots \text{O}]$  and  $[\text{C} \cdots \text{H} \cdots \text{O}]$  hydrogen bonding between the tetracation's  $\text{NH}_2^+$  and  $\text{CH}_2$  groups, respectively, and the oxygen atoms of BPP34C10's polyether linkages. The pairs of stacked porphyrin hubs adopt (Fig. 28b),



**Fig. 26** Views of the crystal structure of the five-component interwoven superbundle  $[(\text{BPP34C10})_3 \cdot (\mathbf{18})_2]^{6+}$ . (a) Elevation. (b) Plan view.

like the special pair of the photosynthetic reaction center, a sheared relationship [44], the copper atoms being offset laterally by ca. 3.05 Å with a nonbonded  $[\text{Cu} \cdots \text{Cu}]$  separation of 4.76 Å. Interestingly, EPR spectroscopy reveals that there are no intermolecular interactions between distinct  $\mathbf{19}^{4+}$  porphyrin nuclei in BPP34C10-free solutions, probably as a consequence of charge repulsion. However, these same nuclei do aggregate, under otherwise indistinguishable conditions, in the presence of two molar equivalents of crown ether, indicating that the  $[(\text{BPP34C10})_4 \cdot (\mathbf{19})_2]^{8+}$  superbundle is formed in solution as well as in the solid state.

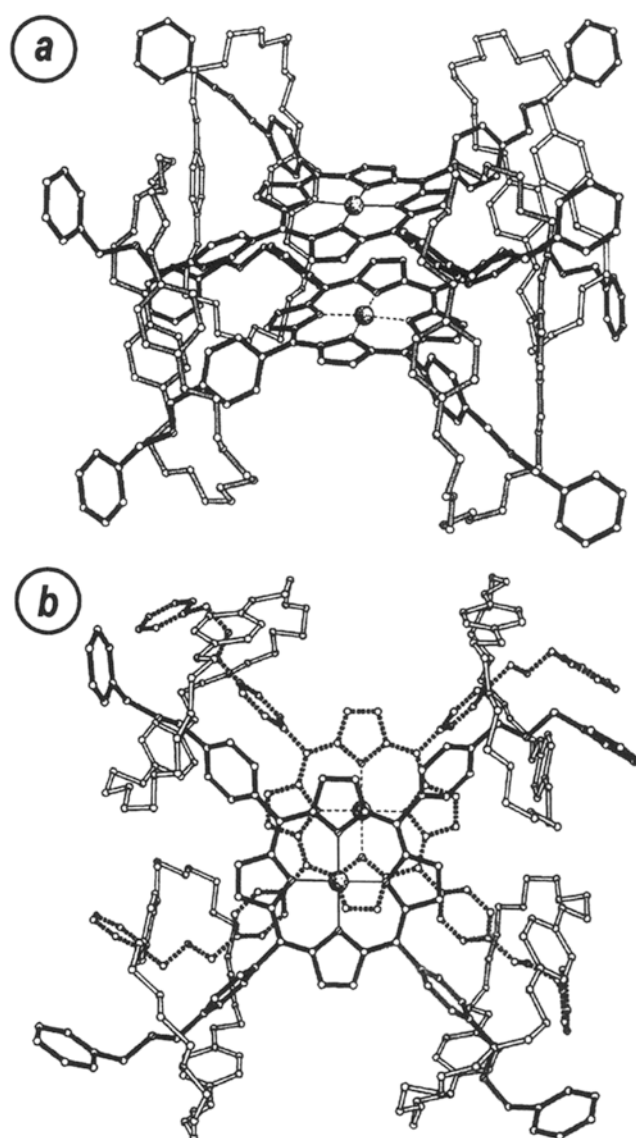


**Fig. 27** The noncovalent synthesis of a supramolecular analogue of the special pair of the photosynthetic reaction center. Four BPP34C10 molecules tie two tetracations  $19^{4+}$  together to create a supermolecule bearing a pair of cofacially disposed porphyrinoid nuclei.

## Summary and Outlook to the Future

We have demonstrated how a set of elaborate recognition motifs for the noncovalent synthesis of discrete supermolecules can be developed systematically from an elementary recognition motif, which, in this case, involves the threading of a dialkylammonium strand through a crown ether to generate a pseudorotaxane. The recognition motifs were progressively made more complex by exploiting the intimate relationship between synthetic supramolecular chemistry and X-ray crystallography. Thus, complicated supermolecules, such as daisy chains, interwoven superbundles, and multiply stranded pseudorotaxane anion binders, were synthesized noncovalently following the X-ray crystallographic analysis of the “original” pseudorotaxane  $[(DB24C8) \cdot 3]^+$ .

In the future, we intend to continue to develop and refine the recognition motifs based upon crown ethers and dialkylammonium ions so that we can prepare even more intricate molecular (using supramolecular assistance to synthesis) and supramolecular (utilizing supramolecular synthesis) entities that could be incorporated into “intelligent” materials with predetermined functions. By way of illustration, we envisage manipulating the girdle-like properties of the ditopic crown ether BPP34C10 to tie two oligoammonium cavitands [45] together to create supramolecular capsules [4c] that could perhaps be utilized for, *inter alia*, recognition, transport, and catalysis at the nanoscale level. Additionally, we intend to marry the chemistry that we have profiled in this review with polymer and dendrimer chemistry so as to provide an entry into a whole new range of



**Fig. 28** Views of the crystal structure of the six-component interwoven superbundle  $[(BPP34C10)_4 \cdot (19)_2]^{8+}$  (a) Elevation. (b) Plan view showing the slipped cofacial [44] orientation of the superbundle's porphyrinoid nuclei.

supramolecular materials for the next millennium. For instance, who is to say that fully mechanically interlocked macromolecular daisy chains [21] or dendrimers [46] endowed with rotaxane-based molecular switches attached to their surfaces will not have remarkable, promethean properties? Likewise, the solid-state noncovalent synthesis of the supermolecule  $[(DB24C8)_3 \cdot 8]^{3+}$  has indicated that the preparation of polyrotaxanes is within our grasp. However, a great deal of fundamental research lies ahead of us, both in the solid state and in solution, before these and other goals can be fulfilled.

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