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Interwoven supramolecular arrays via the noncovalent polymerization of pseudorotaxanes

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Contents

Abstract

This review describes how the noncovalent polymerization of pseudorotaxanes—inclusion complexes in which thread-like molecules or ions interpenetrate macrorings' central cavities without the formation of a mechanical bond—leads to the production of interwoven supramolecular arrays in the solid state. The noncovalent synthesis of these polymeric supramolecular architectures requires the independent and simultaneous operation of at least two different orthogonal recognition algorithms, viz. a threading algorithm, for the formation of the pseudorotaxane, and a noncovalent polymerization algorithm, that permits interpseudorotaxane association in the crystal. The information required for the operation of these orthogonal recognition algorithms is preprogrammed into the covalent frameworks of the interwoven supramolecular arrays' precursors. Several different types of intermolecular interactions have been employed by crystal engineers for the noncovalent synthesis of interwoven supramolecular arrays in the solid state, in particular, metal–ligand, π–π stacking and hydrogen bonding interactions. © 1999 Elsevier Science S.A. All rights reserved.

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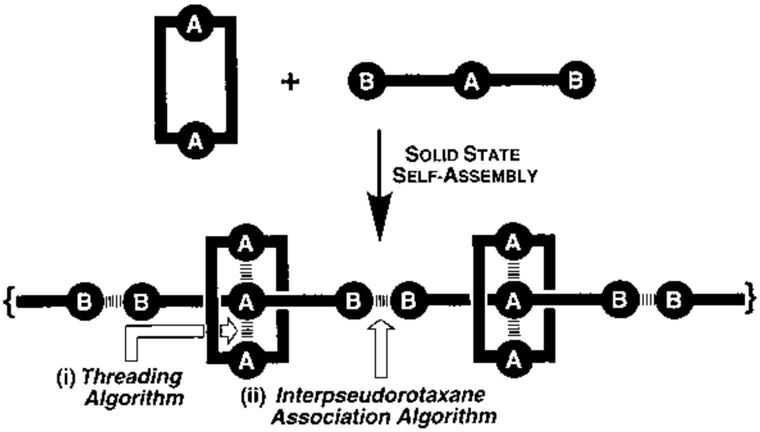
1. Preamble

In recent years, scientists engaged in research in the field of supramolecular chemistry [1]—the chemistry of the noncovalent, intermolecular bond—have profited greatly from the simultaneous deployment of several orthogonal recognition motifs/algorithms[1,2] for the construction of elaborate multicomponent superarchitectures [3]. Employing such orthogonal recognition algorithms concurrently diversifies, in a dramatic manner, the range of self-assembled [4] superstructures—many of which would have been inconceivable not all that long ago—that are



Scheme 1. Representative schematic diagram showing how two recognition algorithms—namely, (i) a *threading* algorithm and (ii) an *interpseudorotaxane association* algorithm—can be combined for the noncovalent synthesis of an interwoven supramolecular array in the solid state via self-assembly. (i) Recognition events between the **A** sites on the macrocyclic bead and the linear filament produce a pseudorotaxane that (ii) polymerizes noncovalently using intersupramolecular recognition events between the **B** sites.

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[1] The expression 'algorithm' has been used by Lehn (Ref. [1], pp. 143–144) to characterize programmed supramolecular systems whose response relies upon molecular information handling procedures. *Molecular programming* involves situating the information for a particular superstructure's construction in the covalent skeletons of its precursors. This information constitutes the molecular *program* which operates through noncovalent recognition *algorithms*.

[2] We have borrowed the term 'orthogonal' from classical synthetic chemistry, where it is used [2] to describe sets of protecting groups that can be deprotected independently of one another using different types of reagents. By the same token, orthogonal recognition motifs/algorithms are intermolecular interactions that operate independently of one another so that no intermotif/interalgorithm crossover or interference occurs.

Table 1
The combinations of recognition algorithms that have been utilized for the solid state noncovalent syntheses of interwoven supramolecular arrays

Ref.	Recognition algorithm[a]	
	Threading	Interpseudorotaxane association
[10]	π–π Stacking	π–π Stacking
[13]	π–π Stacking	Hydrogen bonding
[18]	π–π Stacking/hydrogen bonding	π–π Stacking/hydrogen bonding
[19]	Hydrogen bonding	π–π Stacking
[20]	Hydrogen bonding	Metal–ligand
[22]	Hydrogen bonding	Hydrogen bonding

[a] Only the primary noncovalent interactions used in the recognition algorithms have been indicated in this Table.

accessible to the contemporary synthetic supramolecular chemist [5]. Indeed, the simultaneous application of several recognition algorithms to supramolecular syntheses may be likened to a traditional synthetic chemist employing several different covalent bond-manipulating reactions, in a synthetic sequence, for the total synthesis of a complex natural product. Thus, the level of superstructural complexity that may be created by a synthetic supramolecular chemist becomes amplified as the number of noncovalent bonding tools that (s)he uses is increased. This Review surveys the solid state noncovalent syntheses of a particular class of complex superstructures—namely, interwoven supramolecular arrays[3] that are created via the noncovalent polymerization[4] [6] of pseudorotaxane[5] [7] supermolecules[6]. The

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[3] Note that supramolecular arrays are [5] macrosupramolecular species that are produced via the noncovalent polymerization of an infinite number of molecular components, as opposed to *supermolecules*, which are [5] discrete oligomolecular entities that are generated via the noncovalent association of a finite number of molecular components.

[4] The intermolecular association of a large number of molecular monomers to form supramolecular arrays (polymers) is at the heart of noncovalent polymerization processes [6].

[5] *Pseudorotaxanes* are inclusion complexes that are formed when one or more thread-like species, i.e. filaments, interpenetrate the cavities of one or more macrorings, i.e. beads. Since they are free to dissociate into their separate constituents, these *supramolecular* complexes are distinct from their mechanically-interlocked *molecular* counterparts, the rotaxanes. For examples, see Ref. [7]. Rotaxanes are [26] members of a class of compounds that are held together using “mechanical bonds”. Such bonds occur when two or more discrete chemical entities are constrained to be bound to one another without the aid of any valence forces.

[6] Interwoven supramolecular arrays may be considered to be superarchitectures that are obtained from the weaving together of supramolecular components, employing noncovalent bonds, in a manner reminiscent of mechanically-interlocked species [26]. The interweaving of the supramolecular components may occur by one of two mechanisms: specifically, via either (i) the noncovalent aggregation of a large number of pseudorotaxanes or (ii) the mutual concatenation of supramolecular networks. The interwoven supramolecular arrays obtained by the latter mechanism are usually [8]a–c composed of *rigid* molecular building blocks and will not be discussed in this review. It should also be noted, however, that researchers have recently discovered [8]d–f similar interpenetrated supramolecular arrays that arise from *flexible* molecular building blocks.

syntheses of this particular class of supramolecular array rely (Scheme 1) upon the coordinated manipulation of at least two orthogonal recognition algorithms for their construction, specifically, (i) a *threading* algorithm, for the creation of the pseudorotaxane supermolecules that then polymerize noncovalently via (ii) an *interpseudorotaxane association* algorithm. In other words, the threading of a linear filament through the cavity of a bead-like macrocycle produces a pseudorotaxane that has divergently-oriented recognition sites for further intersupermolecule association. The full range of noncovalent interactions that may be employed orthogonally for the solid state noncovalent synthesis [9] of these interwoven supramolecular arrays is only just starting to be exploited (Table 1) by the synthetic supramolecular chemist. The information necessary for the concurrent and independent operation of these noncovalent bonding algorithms must be preprogrammed (see footnote 1) into the skeletons of the interwoven supramolecular arrays' *molecular* building blocks using traditional organic synthesis.

2. Supramolecular polymerization of pseudorotaxanes in the solid state

Our first forays into the field dealing with the crystal engineering of interwoven supramolecular arrays were concerned with the noncovalent polymerization of the pseudorotaxane inclusion complexes formed between the π-electron deficient tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) ($\mathbf{1}^{4+}$) and π-electron rich filaments, such as the polyether **2**. In the $[\mathbf{1}\cdot\mathbf{2}]^{4+}$ pseudorotaxane [10]a, the polyether filament interpenetrates the cavity of the $\mathbf{1}^{4+}$ tetracation primarily as a result of face-to-face π–π stacking interactions [11], with additional secondary stabilization occurring via weak [C–H$\cdots\pi$] interactions [12]. Noticeably, only the central hydroquinone unit of **2** is encircled by the tetracationic cyclophane $\mathbf{1}^{4+}$, thus permitting both of the terminal 3,5-dimethoxyphenoxy units of this filament to enter into aryl–aryl stacking interactions with the encircling cyclophane's 4,4′-bipyridinium units when the polyether chains curl back on themselves. However, this type of interaction means that the 3,5-dimethoxyphenoxy units of the $[\mathbf{1}\cdot\mathbf{2}]^{4+}$ complex have free faces that can interact with other π-systems. In fact, these units associate with the *exo* faces of adjacent $[\mathbf{1}\cdot\mathbf{2}]^{4+}$ pseudorotaxanes to form (Fig. 1) a π–π-linked interwoven supramolecular array in the solid state, as evidenced by X-ray crystallography. Likewise, the 1,5-dioxynaphthalene-containing filament **3** self-assembles [7]a, [10]b with $\mathbf{1}^{4+}$ to form the pseudorotaxane $[\mathbf{1}\cdot\mathbf{3}]^{4+}$, which possesses a comparable π–π stabilized superstructure to that of $[\mathbf{1}\cdot\mathbf{2}]^{4+}$. However, in this instance, the peripheral 1,5-dioxynaphthalene units of the $[\mathbf{1}\cdot\mathbf{3}]^{4+}$ complexes associate (Fig. 2) with the *p*-xylyl spacer units of neighboring pseudorotaxanes—via π–π stacking interactions—thus creating a two-dimensional, interwoven grid-like supramolecular array in the crystalline phase.

The interlinking of the pseudorotaxanes formed between the macrocyclic tetracation $\mathbf{1}^{4+}$ and π-electron rich polyethers is not only limited to aryl–aryl stacking interactions. Recently, during our Birmingham era, we discovered [13]a how to link pseudorotaxanes—stabilized by, inter alia, π–π stacking—employing the directional features of the hydrogen bond [14]. By way of illustration, the tetracation $\mathbf{1}^{4+}$ is interpenetrated by π-electron excessive polyether **4** to form the pseudorotaxane $[\mathbf{1}\cdot\mathbf{4}]^{4+}$ which is stabilized (vide supra) principally by aryl–aryl stacking interactions, with additional secondary stabilization coming from [C–H···π] interactions and [C–H···O] hydrogen bonds [15]. However, the $[\mathbf{1}\cdot\mathbf{4}]^{4+}$ pseudorotaxane has pendent carboxyl groups that are available for further divergent recognition events employing the strong hydrogen bonds associated [16] with the carboxyl dimer, i.e. using a second, orthogonal recognition algorithm. Consequently, units of the $[\mathbf{1}\cdot\mathbf{4}]^{4+}$ pseudorotaxane act as self-associating exoreceptors that, in the solid state, form (Fig. 3) an interwoven supramolecular array that has been termed [13]a 'a hydrogen bonded pseudopolyrotaxane' [17]. In addition, the hydrogen bonded pseudopolyrotaxane chains interact with one another—via aryl–aryl stacking of the tetracation's p-xylyl spacer units—to form a two-dimensional interwoven supramolecular array in the solid state. The noncovalent linking of $[\mathbf{1}\cdot\text{polyether}]^{4+}$ pseudorotaxanes is not only limited to strong

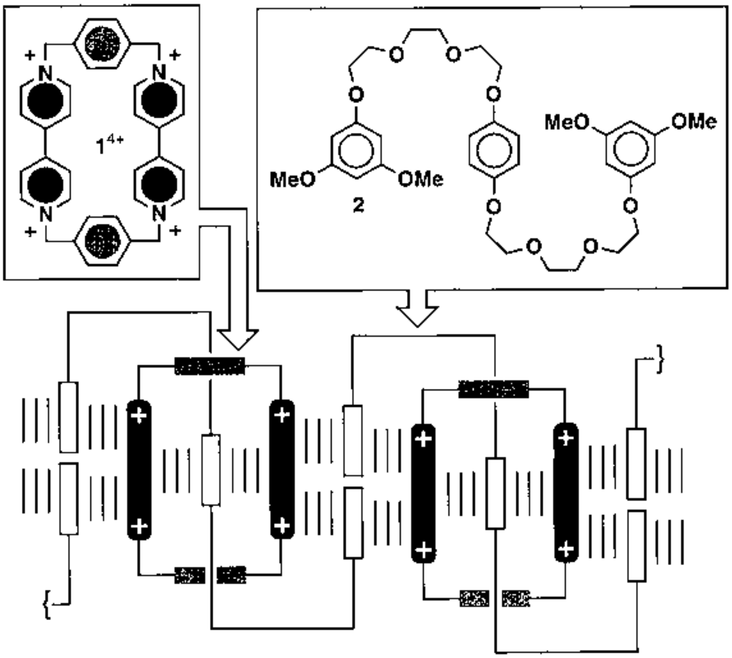

Fig. 1. Cartoon representation of the crystal structure of the interwoven supramolecular polymer $\{[\mathbf{1}\cdot\mathbf{2}]^{4+}\}_n$.

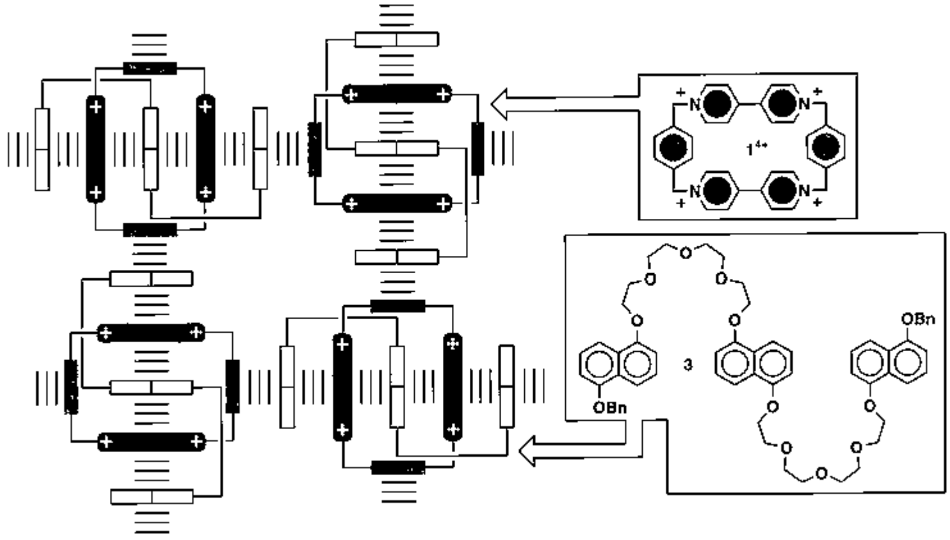

Fig. 2. Cartoon depicting the interwoven grid-like supramolecular array generated via the solid state noncovalent polymerization of the pseudorotaxane $[\mathbf{1}\cdot\mathbf{3}]^{4+}$.

hydrogen bonds, like those observed in the example discussed already, for we have also described [7]a the solid state noncovalent polymerization of pseudorotaxanes—stabilized principally by π–π stacking interactions—using cooperative [C–H···O] hydrogen bonds and [C–H···π] interactions. Additionally, it has been demonstrated that similar principles can be employed to produce linear pseudopolyrotaxanes when π-electron rich *macrocyclic polyethers* cocrystallize with π-electron poor *filaments* bearing functional groups that are inclined to form hydrogen bonds, i.e. where the roles of the pseudorotaxanes' π-excessive/deficient subunits have been reversed. For instance, the bipyridinium dication $\mathbf{5}^{2+}$ threads [13]b through the cavity of the macrocyclic polyether bis-*p*-phenylene[34]crown-10 (BPP34C10) to form the pseudorotaxane $[\text{BPP34C10}\cdot\mathbf{5}]^{2+}$ which is stabilized by the usual π–π stacking interactions, in addition to [C–H···O] hydrogen bonds. This pseudorotaxane's pendent hydroxyl groups act as hydrogen bond donors and are bound to an Me_2CO connector molecule to form (Fig. 4) an interwoven pseudopolyrotaxane superarchitecture in the solid state. Moreover, in this instance, the pseudopolyrotaxane chains are associated with one another using aryl–aryl edge-to-face interactions to form an interwoven supramolecular array of even higher order. Another example involves the trication $\mathbf{6}^{3+}$, which bears complementary protonated 4,4′-bipyridinium (hydrogen bond donor) and 4,4′-pyridylpyridinium (hydrogen bond acceptor) subunits linked through a 2,8-dibenzofuranbis(methylene) spacer, and has been discovered [13]c in our research laboratories recently. This trication can thread its way through the cavity of the macrocyclic polyether BPP34C10 to form a pseudorotaxane [BPP34C10 · **6**]$^{3+}$ that is stabilized by π–π stacking interactions. This pseudorotaxane then polymerizes noncovalently—via head-to-tail [N$^+$–H···N] hydrogen bonding of its complementary 4,4′-bipyridinium and 4,4′-pyridylpyridinium moieties—to form (Fig. 5) a pseudopolyrotaxane that maintains a novel sinusoidal arrangement and which extends the π-donor–π-acceptor stacking motif throughout the crystal.

Recently, members of our Birmingham laboratories have developed [18] a system wherein *both* π–π stacking and hydrogen bonding interactions are utilized for *both* threading and interpseudorotaxane motifs in order to effect the noncovalent syntheses of interwoven pseudopolyrotaxane supramolecular arrays in the crystalline state (Fig. 6). The tetracationic filament **7**$^{4+}$ is endowed with both 4,4′-bipyridinium and secondary dibenzylammonium recognition sites that can interact with macrocyclic polyethers as a result of π–π stacking and hydrogen bonding

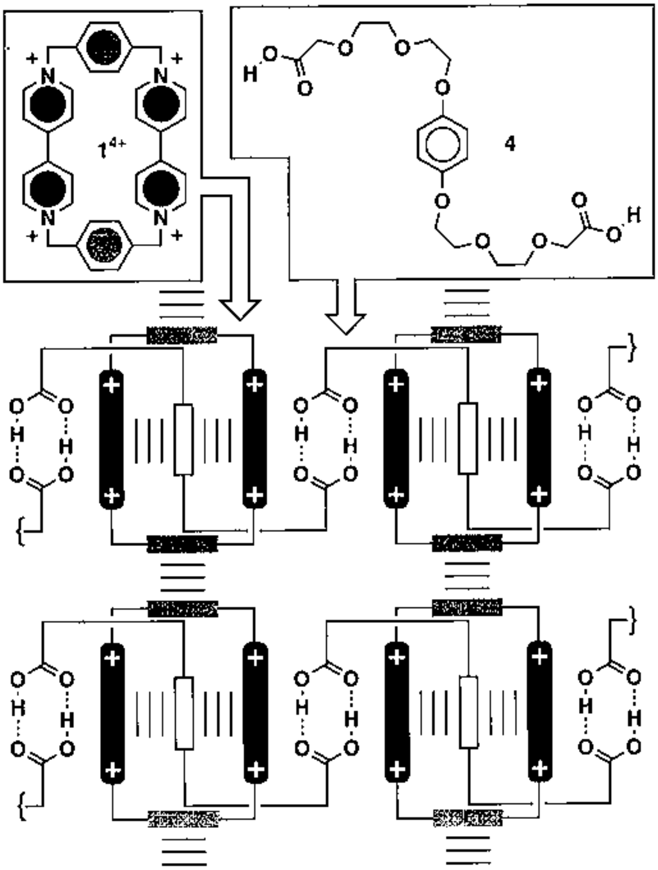

Fig. 3. Cartoon portrayal of the solid state structure of the interwoven supramolecular array {[**1** · **4**]$^{4+}$}$_n$, which is stabilized primarily by a combination of π–π stacking and [O–H···O] hydrogen bonding interactions.

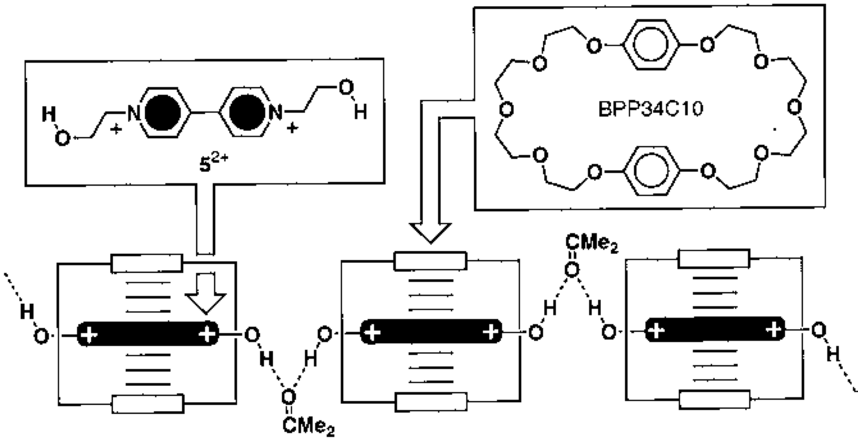

Fig. 4. Cartoon illustrating the interwoven supramolecular array that is formed when the pseudorotaxane [BPP34C10 · **5**]$^{2+}$ associates with Me$_2$CO in the solid state via hydrogen bonds. Interchain associations are not shown in the cartoon for the sake of clarity.

interactions, respectively, to form pseudorotaxanes. When **7**$^{4+}$ was cocrystallized with BPP34C10, the X-ray analysis revealed the formation of a complex in which one **7**$^{4+}$ filament is threaded through the cavities of three macrocycles to generate a pseudorotaxane. In this pseudorotaxane, the π-electron deficient 4,4′-bipyridinium subunit of the tetracation **7**$^{4+}$ is sandwiched by one π-excessive BPP34C10 molecule, while each of the two ammonium centers interact, via hydrogen bonds, with only one of the polyether arcs of another two BPP34C10 molecules so that half of these macrorings' cavities are left vacant. This vacant receptor site in the BPP34C10 macrocycle is occupied by a C_i-related dibenzylammonium center from another **7**$^{4+}$ filament, leading to the generation of an interwoven pseudopolyrotaxane supramolecular array. In addition, the tetracation **7**$^{4+}$ was demonstrated to undergo self-assembly in an entirely self-selective manner when combined with a mixture of the macrocyclic polyethers dibenzo[24]crown-8 (DB24C8) and BPP34C10. DB24C8 associates only very weakly with 4,4′-bipyridinium subunits, while it interacts strongly with dibenzylammonium centers using a combination of [N$^+$–H···O] and [C–H···O] hydrogen bonds. On the other hand, BPP34C10 has a greater propensity to enter into stabilizing noncovalent bonding interactions with 4,4′-bipyridinium subunits compared to dibenzylammonium centers. Consequently, a 2:1:1 pseudorotaxane complex [(DB24C8)$_2$ · (BPP34C10) · **7**]$^{4+}$—in which the **7**$^{4+}$ tetracation's 4,4′-bipyridinium subunit is sandwiched by a BPP34C10 molecule, while its two dibenzylammonium centers are encircled by DB24C8 molecules—was the only product observed upon cocrystallization of a mixture of the three components, thus demonstrating the independent operation of two different recognition algorithms simultaneously. Moreover, the terminal benzyl groups of this four-component supermolecule are involved in interpseudorotaxane π–π stacking interactions with their centrosymmetrically-related counterparts to generate a π–π-linked pseudopolyrotaxane superstructure. In similar fashion, it has been found [19] that the hydrogen bond-stabilized pseudorotaxane formed between DB24C8 and the related dibenzylammonium cation (**8**$^+$) self-associates, using aryl–aryl stacking interactions, to generate (Fig. 7) a pseudopolyrotaxane in the solid state.

The growth of the domain dealing with the crystal engineering of interwoven supramolecular arrays has been stimulated recently by the highly innovative work of Kim and his associates, who have employed [20] the extraordinary capabilities of the metal–ligand coordinate covalent bond [21] for their supramolecular syntheses. By linking hydrogen bonded pseudorotaxane monomer units via coordinate covalent bonds with transition metal cations, they have synthesized noncovalently a unique range of bead-encircled coordination polymers in the solid state. The diammmonium filament **9**$^{2+}$ interpenetrates the cavity of polycyclic torus-shaped macrocycle cucurbituril **10** to generate a pseudorotaxane that is stabilized by strong [N$^+$–H···O] hydrogen bonds between the filament's ammonium centers and the oxygen atoms of the macrocycle's two

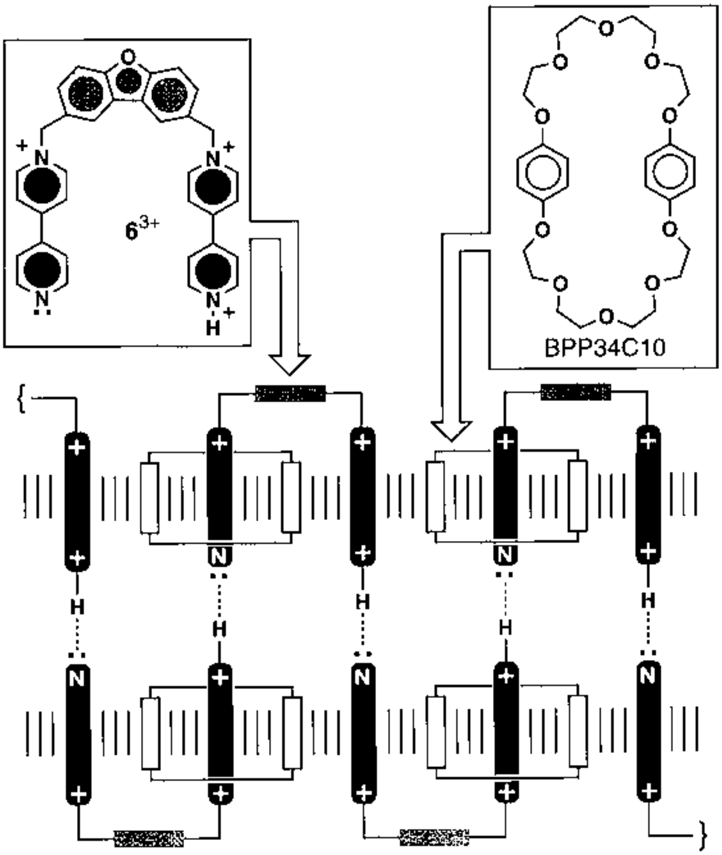

Fig. 5. Cartoon representation of the X-ray crystal structure of the sinusoidal pseudopolyrotaxane {[BPP34C10 · **6**]$^{3+}$}$_n$.

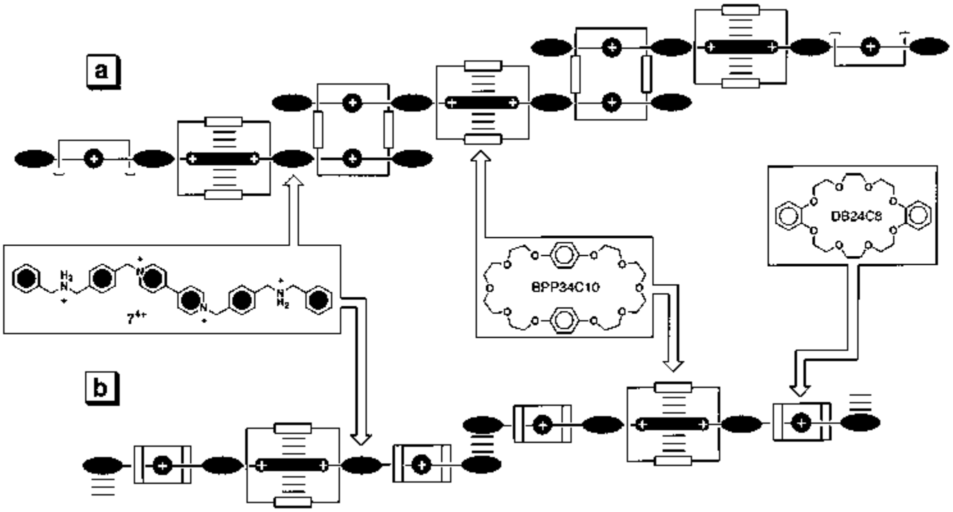

Fig. 6. Cartoon representations of the pseudopolyrotaxane superstructures generated when the tetra cation $\mathbf{7}^{4+}$ crystallizes with crown ethers. (a) Pseudopolyrotaxane created when $\mathbf{7}^{4+}$ crystallizes solely with BPP34C10. (b) Pseudopolyrotaxane generated via the supramolecular polymerization of the pseudorotaxane $[(\text{DB24C8})_2 \cdot (\text{BPP34C10}) \cdot \mathbf{7}]^{4+}$.

carbonyl-fringed portals. By virtue of its two 4-pyridyl-bearing termini, this pseudorotaxane acts as a metallo-exoreceptor. Accordingly, Cu(II)- or Ag(I)-bridged one-dimensional interwoven supramolecular arrays were generated (Fig. 8) in the solid state when the $[\mathbf{10} \cdot \mathbf{9}]^{2+}$ pseudorotaxane was crystallized in the presence of either $Cu(NO_3)_2$ or AgOTs, respectively. However, the self-assembly process with Ag(I) cations has been found [20]b to be anion-dependent [7]e: when the $[\mathbf{10} \cdot \mathbf{9}]^{2+}$ pseudorotaxane was crystallized in the presence of $AgNO_3$, a completely different type of interwoven supramolecular polymer was formed. In this case, a *two*-dimensional coordination polymer—based upon hydrogen bond-stabilized pseudorotax-

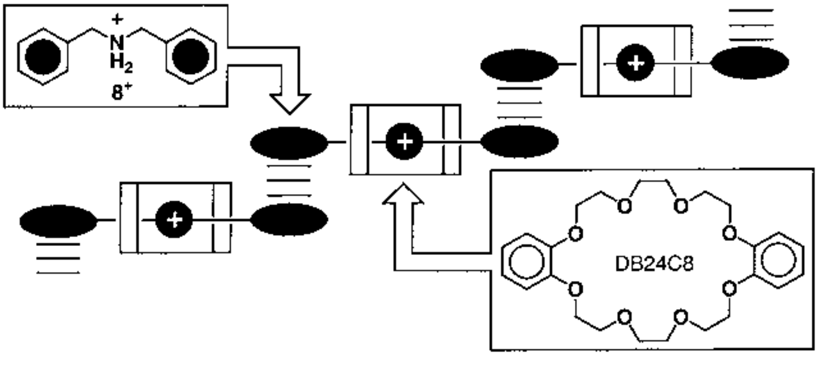

Fig. 7. Cartoon portraying the X-ray crystal structure of the pseudopolyrotaxane $\{[\text{DB24C8} \cdot \mathbf{8}]^{+}\}_n$.

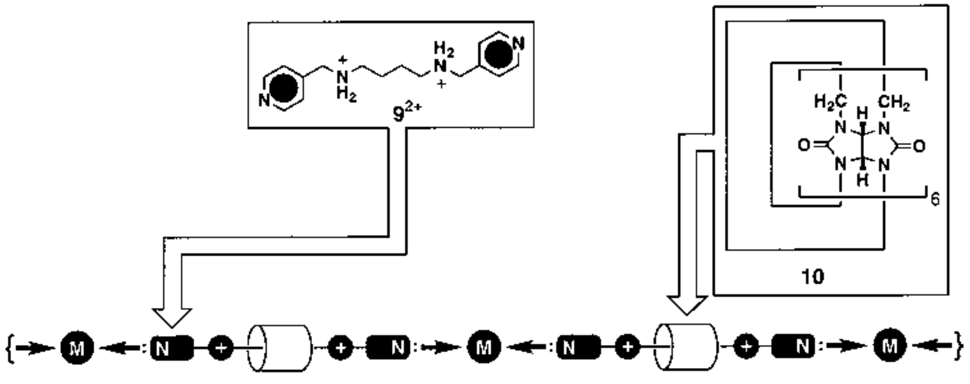

Fig. 8. Cartoon illustrating the interwoven supramolecular array generated when the pseudorotaxane $[\mathbf{10}\cdot\mathbf{9}]^{2+}$ interacts with transition metal salts {M = Cu(II) or Ag(I)}—by virtue of coordinate covalent bonds—in the solid state.

ane monomer units linked via Ag(I)–N bonds—self-assembled (Fig. 9) in the solid state. Moreover, networks of these two-dimensional interwoven arrays interlock completely with one another—hence, the overall superstructure symbolizes [20]b the first example of a polycatenated polyrotaxane net. The anion dependence [7]e exhibited by Kim's examples highlight some of the problems associated with the solid state supramolecular syntheses of interwoven supramolecular arrays and, indeed, crystal engineering in general. In many instances, changing the counterions (or solvents) associated with a particular system alters the nature of the superarchitecture realized. In general, the cationic species originating in our laboratories are accompanied by PF_6^- anions which do not interact strongly with the organic portions of our systems. Nevertheless, it is quite likely that we would obtain different superarchitectures if different anions were used.

Kim and his research group [22]a have also linked cucurbituril–diammonium-based pseudorotaxanes using hydrogen bonding interactions in the solid state, thus demonstrating that two distinct algorithms of the same class—in this instance, hydrogen bonding algorithms—can be employed for the solid state supramolecular synthesis of interwoven superstructures. The X-ray crystallographic analysis of the doubly-zwitterionic pseudorotaxane [**10** · **11**]—created when the pseudorotaxane [**10** · spermine–H_4][Cl]$_4$ is treated with $NaHCO_3$—reveals (Fig. 10) the formation of a pseudopolyrotaxane that is linked via head-to-tail hydrogen bonding of its carbamate functionalities. In our Birmingham era [22]b–c, we have also combined two distinct hydrogen bonding algorithms—viz. (i) the threading of secondary dibenzylammonium cations through the cavities of crown ethers [19], and (ii) the supramolecular dimerization of carboxyl groups [16]—for the solid state noncovalent synthesis of a wide range of interwoven superarchitectures. By way of illustration, the cation $\mathbf{12}^+$ cocrystallized [22]c with DB24C8 to form (Fig. 11) a pseudopolyrotaxane, possessing crown ether units at every ammonium center along its main-chain, which is held together using the carboxyl dimer. This paradigm could be extended further: when the isophthalic acid-substituted dialkylammonium cation **13**$^+$ was cocrystallized [22]c with DB24C8, a side-chain, hydrogen bonded pseudopolyrotaxane—consisting of a carboyxl dimer-stabilized isophthalic acid main-chain with macrocyclic polyether units threaded onto the dialkylammonium side-chains—was formed (Fig. 12), as opposed to the main-chain, hydrogen bonded pseudopolyrotaxane revealed in the crystal structure of the [DB24C8·**12**]$^+$ system. Moreover, when **13**$^+$ self-assembled with BPP34C10—a ditopic receptor for dibenzylammonium cations—in the solid state, the formation of another novel class of interwoven supramolecular array was encountered (Fig. 13). In this instance, the dibenzylammonium filaments thread centrosymmetrically with respect to one another—i.e. in an antiparallel orientation—through the cavity of the BPP34C10 macrocycle to form a double-stranded pseudorotaxane. Supramolecular polymerization of these pseudorotaxanes—employing the carboxyl dimer—furnishes [22]b–c an interwoven

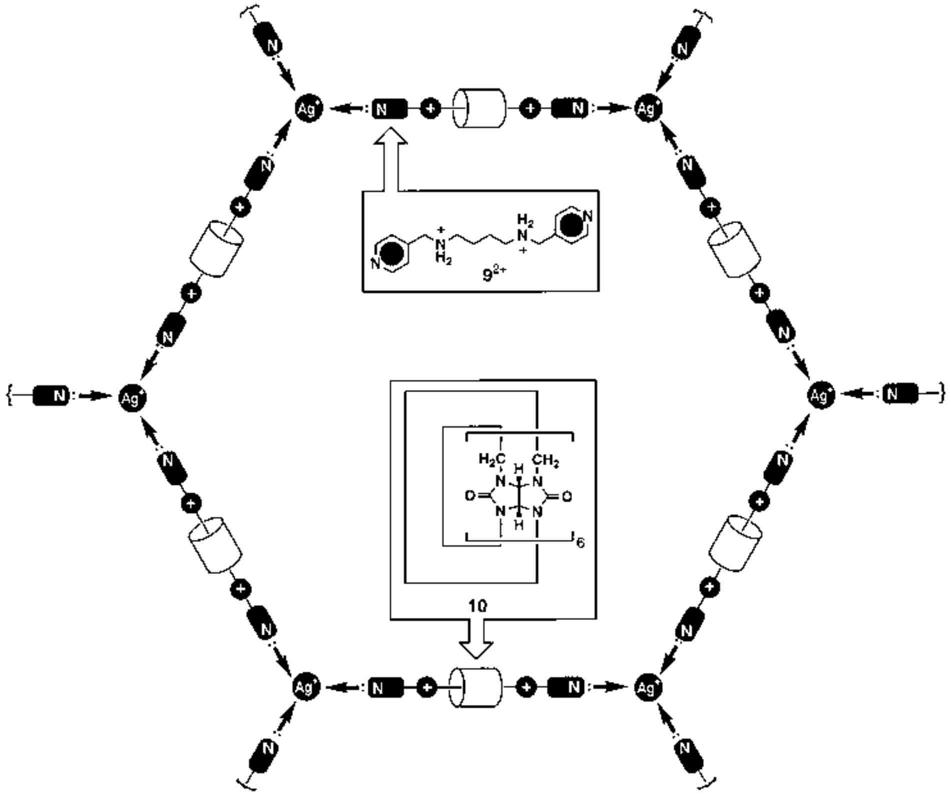

Fig. 9. Cartoon representation of the X-ray crystal structure of the interwoven supramolecular network that is produced when hydrogen bond-stabilized pseudorotaxane monomer units [**10** · **9**]$^{2+}$ react with AgNO$_3$. Interlocking of these {[**10** · **9** · Ag]$^{3+}$}$_n$ networks is not displayed in the cartoon for the sake of clarity.

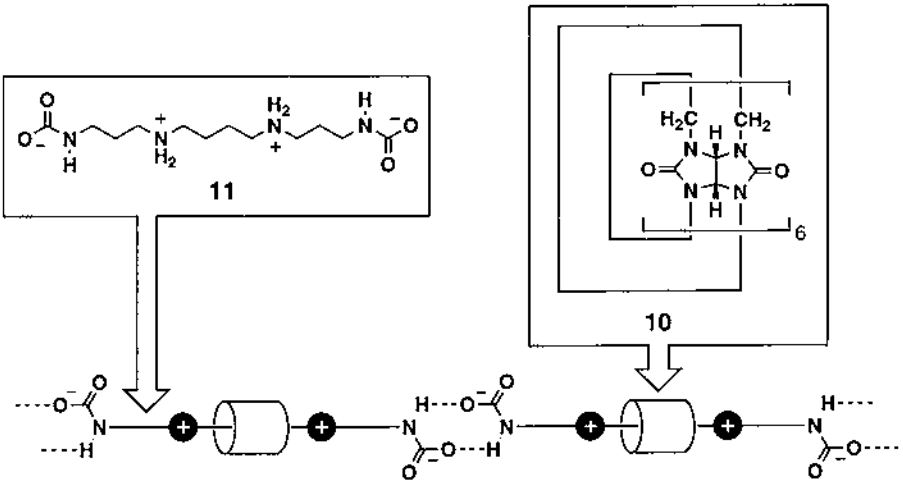

Fig. 10. Cartoon representation illustrating the X-ray crystal structure of the pseudopolyrotaxane [**10** · **11**]$_n$ that is formed by combining two distinct hydrogen bonding algorithms.

supramolecular cross-linked polymer in which the macrocyclic polyether induces cross-linking of polymeric isophthalic acid tapes by guiding the isophthalic acid moieties of two **13**$^+$cations in opposing directions. Nevertheless, we have not observed the independent and synchronous operation of the crown ether–dialkylammonium cation and carboxyl dimer recognition algorithms in all the cases that we have studied to date. When the benzoic acid-substituted cation **14**$^+$ was crystallized [22]c in the presence of DB24C8, an interwoven supramolecular architecture—resembling a macromolecular daisy chain [23]—was formed (Fig. 14), in which the [DB24C8 · **14**]$^+$pseudorotaxane's carboxyl hydrogen is bound—via

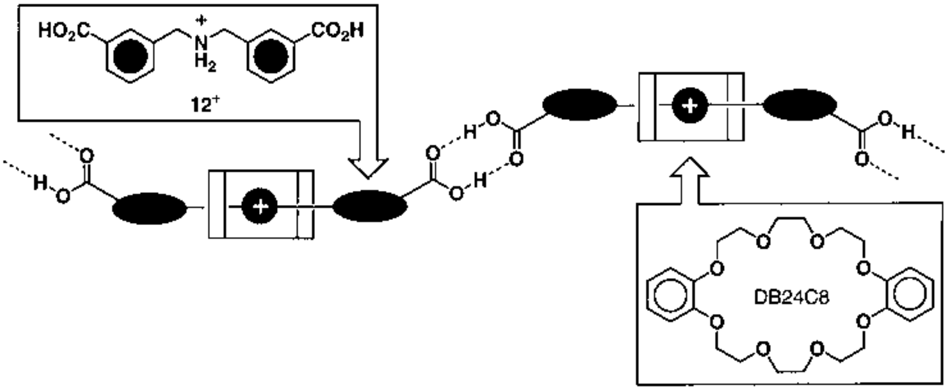

Fig. 11. Cartoon portrayal of the solid state structure of the main-chain, hydrogen bonded pseudopolyrotaxane {[DB24C8 · **12**]$^+$}$_n$, which is generated by virtue of mixing the DB24C8–dialkylammonium cation threading motif with the carboxyl dimer interpseudorotaxane association motif.

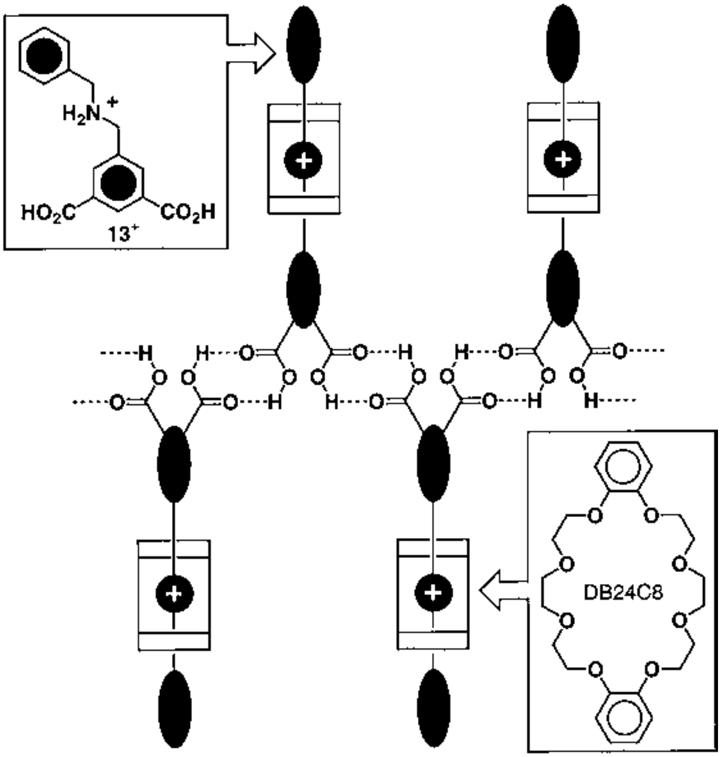

Fig. 12. Cartoon depiction of the X-ray crystal structure of the side-chain, hydrogen bonded pseudopolyrotaxane $\{[\text{DB24C8}\cdot\mathbf{13}]^+\}_n$ that is produced as a result of combining the DB24C8–dialkylammonium cation threading motif with the carboxyl dimer interpseudorotaxane association motif.

bifurcated hydrogen bonds—to the oxygen atoms of a catechol unit on a neighboring pseudorotaxane. We believe that this polymeric interwoven superarchitecture is generated as a result of the secondary stabilizing π–π stacking interactions—revealed in the X-ray crystallographic analysis—that influence the self-assembly process. Since, in this instance, the π-electron deficient benzoic acid ring of the cation $\mathbf{14}^+$ is sandwiched by the π-electron rich catechol units of the DB24C8 macroring, the head-on dimerization of the $[\text{DB24C8}\cdot\mathbf{14}]^+$ pseudorotaxane is disfavored because the catechol moieties from adjacent pseudorotaxanes would be in very close proximity to one another, leading to detrimental nonbonding interactions.

3. Epilogue

We have authenticated the potential of a paradigm—stating that applying two dissimilar recognition motifs simultaneously and independently of one another, i.e. without any crossover or interference, drastically enhances the capabilities of the synthetic supramolecular chemist [5]—within the context of the logical solid state noncovalent synthesis of interwoven supramolecular arrays. We hope that this paradigm will assist synthetic supramolecular chemists, by allowing them to be able to position specific units at certain places in crystal lattices with a view to creating a functioning supramolecular workshop for the next century. By way of illustration, we envisage utilizing the principles described here for organizing supramolecular bundles/containers [24] or devices [25], in the solid state, to form part of our workshop. Furthermore, it must be noted that the paradigm delineated in this Review is not limited only to the noncovalent syntheses of interwoven superarchitectures, for it can also [3] be utilized for the construction of other complex supramolecular species. Nature has developed, perfected and used it for the assembly of complex, functioning biosystems over millions of years. It is evident that the synthetic supramolecular chemist has a lot of catching-up to do, before (s)he can synthesize functioning nanoscopic device-like systems noncovalently, the likes of which have been observed solely in the natural world hitherto.

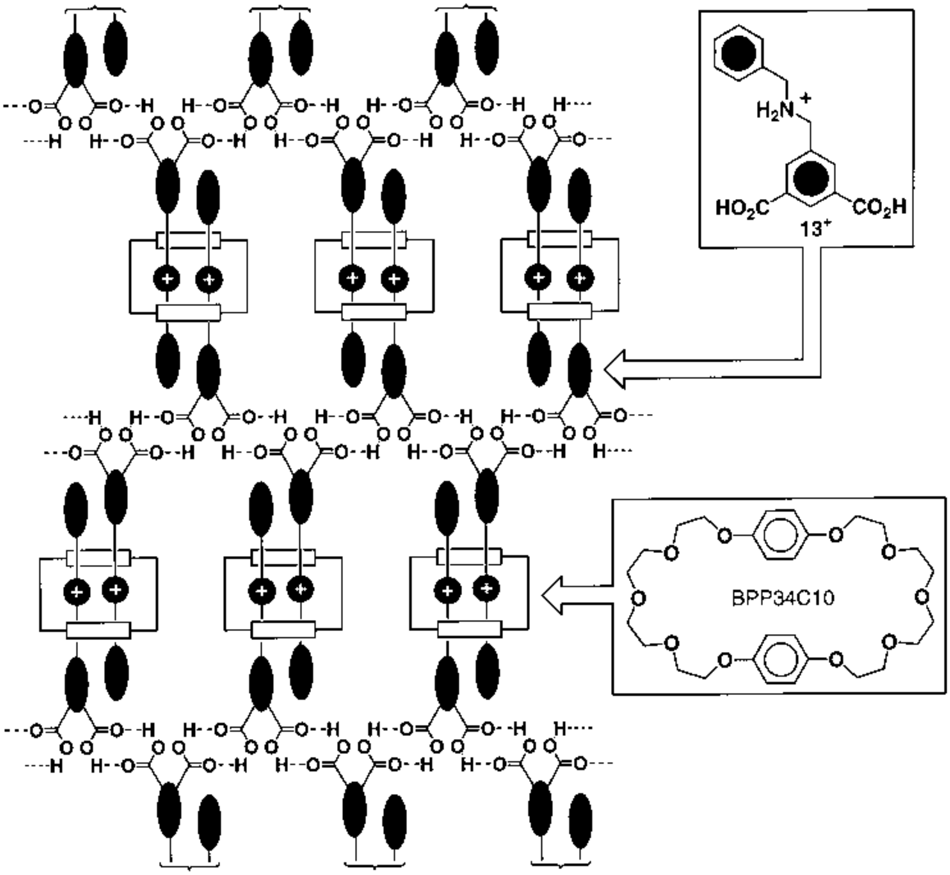

Fig. 13. Cartoon representation of the interwoven supramolecular cross-linked polymer $\{[\mathrm{BPP34C10} \cdot (\mathbf{13})_2]^+\}_n$.

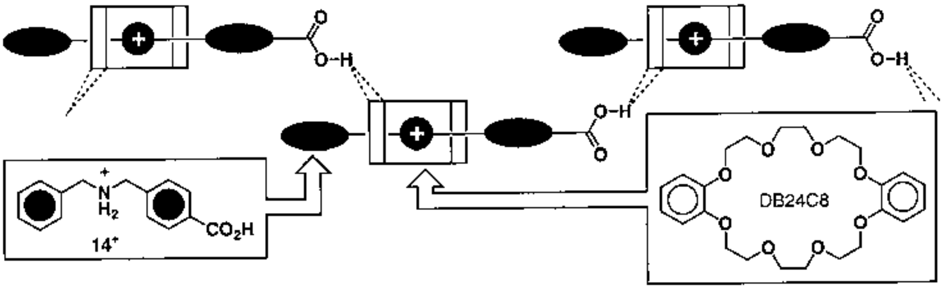

Fig. 14. Cartoon representation of the daisy chain-like interwoven supramolecular array $\{[\mathrm{DB24C8}\cdot\mathbf{14}]^+\}_n$.

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