From Solid-State Structures and Superstructures to Self-Assembly Processes

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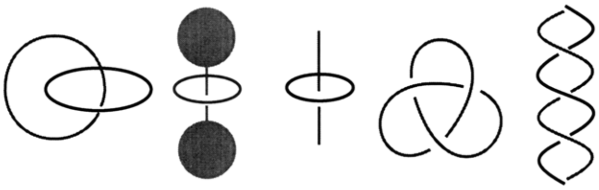
An empirically-driven approach to the design and synthesis of highly ordered molecular assemblies and supramolecular arrays is described. In general, the approach is dependent upon a very close interplay between X-ray crystallography and synthetic chemistry. In particular, the approach is dependent upon π–π stacking interactions between π-donors, such as hydroquinone rings and 1,5-dioxynaphthalene residues, incorporated into both acyclic (e.g., 1,4-dimethoxybenzene) and macrocyclic (e.g., bisparaphenylene-34-crown-10 and 1,5-dinaphtho-38-crown-10) polyethers, and the π-accepting bipyridinium ring system, present either singly, as in the simple paraquat dication, or, as a pair in tetracationic cyclophanes, such as cyclobis(paraquat-*p*-phenylene), cyclobis(paraquat-*m*-phenylene), and cyclobis(paraquat-4,4′-biphenylene). The molecular recognition associated with the π–π stacking interactions is augmented in the structures and superstructures by hydrogen bonding and other electrostatic interactions. The systems employed for the development of the concept of self-assembly in chemical synthesis have been mechanically-interlocked structures (e.g., catenanes) and mechanically-intertwined superstructures (e.g., pseudorotaxanes). The manner in which such intellectually-appealing molecules and supermolecules can contribute to an understanding of noncovalent bonding at both the structural and superstructural levels, during and after self-assembly processes, is described by reference to numerous solid-state structures and superstructures.

Introduction

Margaret Etter's research was concerned[1–4] in large measure with the challenge to characterize and to predict hydrogen-bonding patterns in supramolecular systems. She strove to understand the fundamental factors which enable the crystallization of hydrogen-bonded supramolecular arrays that are a consequence of molecular recognition in action. She showed that numerous complementary components can be brought together through intermolecular hydrogen bonding[5] to create solid-state superstructures, capable of exhibiting properties which the individual building blocks in isolation were unable to demonstrate. She also recognized[6,7] the significance of her research in the design of systems that can self-organize and self-assemble via hydrogen bonding.

In general, the design of a set of matching molecules that will self-assemble[8] efficiently and selectively to form ordered supramolecular arrays in the solution and solid states[9] requires a precise understanding of all the noncovalent bonding forces that can exist between the components of a particular supramolecular array. Molecular biology has shown[10] that a full appreciation of the recognition properties of protein subunits can be employed successfully to predict the shapes of much larger superstructures. In a highly creative way, chemists can exploit the information[11] contained in supramolecular complexes of relatively small chemical species for the design of mutually compatible structural features within molecular components that, upon combination, will self-assemble into well-defined nanometer scale superstructures.[12]



A [2]Catenane A [2]Rotaxane A Pseudo-[2]Rotaxane A Trefoil Knot A Double Helix

Figure 1. Interlocked and intertwined chemical structures whose synthesis is being addressed through self-assembly processes.

Our research is targeted toward the self-assembly[13] of mechanically-interlocked and/or mechanically-intertwined structures and superstructures (Figure 1), such as the so-called catenanes,[14] rotaxanes,[14,15] pseudorotaxanes,[16]

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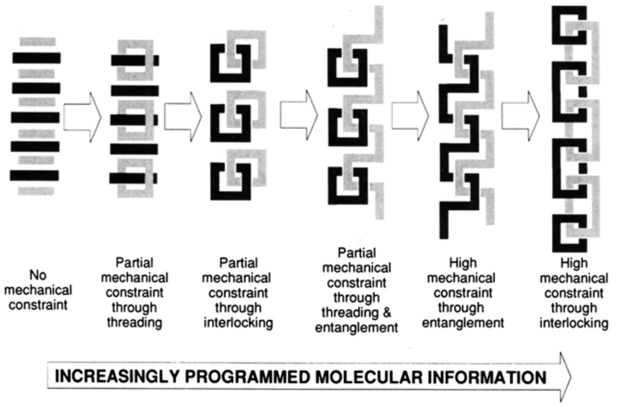

Figure 2. Conceptual journey from a simple donor–acceptor stack through to a double helix and a polycatenane. The spontaneous self-assembly of these structures requires an increasing amount of chemical information in their components on progressing from the DA stack on the left to the polycatenane on the right.

knots,[14,17] and double helices.[18] The development of the particular conceptual approach that led us logically toward these challenging structures and superstructures[19] is summarized in Figure 2. First, consider a simple alternating stack of π-electron-rich and π-electron-deficient aromatic rings in a crystal. It is not imaginable that such a stacked array of π-electron-donors and π-electron acceptors could prevail in solution without some form of additional stabilization. The increased amount of "molecular information" that is necessary[20] to facilitate association of π-electron-rich and π-electron-deficient aromatic rings in solution can be achieved by incorporating a covalently fixed spacer between either the two π-electron-donor (referred to as the donor D from here onward) or the two π-electron-acceptor (referred to as the acceptor A from here onward) unit, thus forming a macrocycle. With this considerable mechanical constraint of the two linked units and provided there is some degree of preorganization[21] in the macrocycle, a complementary guest can be incorporated, forming a 1:1 complex that has a much better chance of being stable in solution. In practical terms, of course, the penalty to be paid for this enhanced molecular recognition is in the synthesis of the macrocycle. In principle, a 2:1 complex is capable of sustaining an alternating donor-acceptor (DA) stack. An additional mechanical constraint can be envisaged by connecting the remaining acyclic components, so as to form a second macrocycle threaded through the first, resulting in two interlocked rings, that is, a [2]catenane, which can also sustain a DA stack. (The number in square brackets refers to the number of macrocyclic components in the mechanically-interlocked system.) A disconnection and reconnection of the spacers between either the donors or the acceptors conjures up the prospect of polymeric threads with macrocycles threaded along their length, forming a pseudopolyrotaxane or a "molecular abacus" incorporating a DA stack. With a further hypothetical disconnection and reconnection, a polymeric double helix still based on a DA stack can also be envisaged. Finally, to achieve one of our ultimate targets—a polycatenane comprised of a linear array of interlocked macrocycles, one containing only donors and the other only acceptors—we must break the continuous DA sequence and replace it by a DDAA one. This might not be such a problem as it first appears.

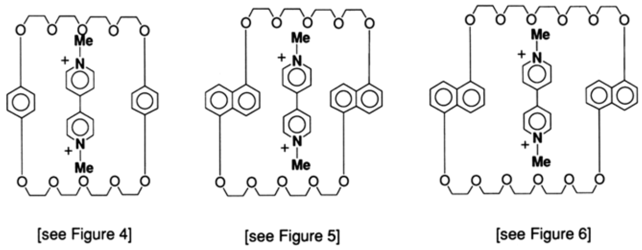

Figure 3. Complexes of paraquat with crown ethers incorporating two aromatic units for which solid state structures are illustrated.

Throughout the conceptual progression, we have altered the relative locations of the connectors between the donor and acceptor building blocks and, in so doing, have increased the amount of chemical information that each component must contain in order that superstructures will form. This increased information may be regarded as related to the number of noncovalent bonding interactions between the two components of the supermolecule. It may be achieved either by increasing the size of the components and/or incorporating extra molecular recognition features into the components of the structure. This concept is demonstrated in the natural world by the DNA double helix, in which the base pairs are the molecular information-containing units through their abilities to π–π stack as well as to hydrogen bond.

To design the synthetic components of these complex interlocked and intertwined species from the "bottom-up",[22] a foundation of structural knowledge is essential. In many ways, the starting point in our current research program was a series of solid-state structural studies[23] of the complexes formed between macrocyclic polyethers containing π-electron-rich units and π-electron-deficient dications, such as paraquat.

Receptors for π-Electron-Deficient Guests

Our design concept for a receptor for a planar π-electron-deficient dication was to position two π-electron-rich aromatic units within a macrocyclic polyether, separated in such a way that they could sandwich the guest species. One of the best receptors (Figure 3) that has so far been designed for paraquat (Chart 1) is[24] the crown ether bisparaphenylene-34-crown-10 (BPP34C10).[25] This mac-

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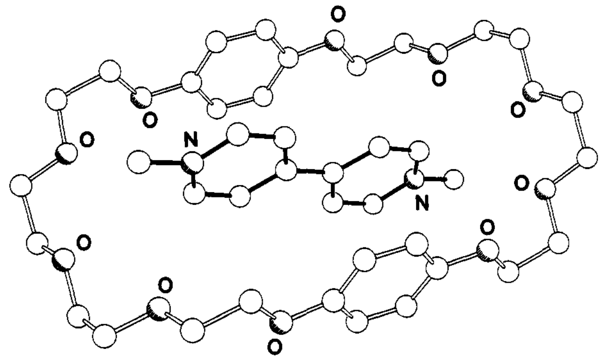
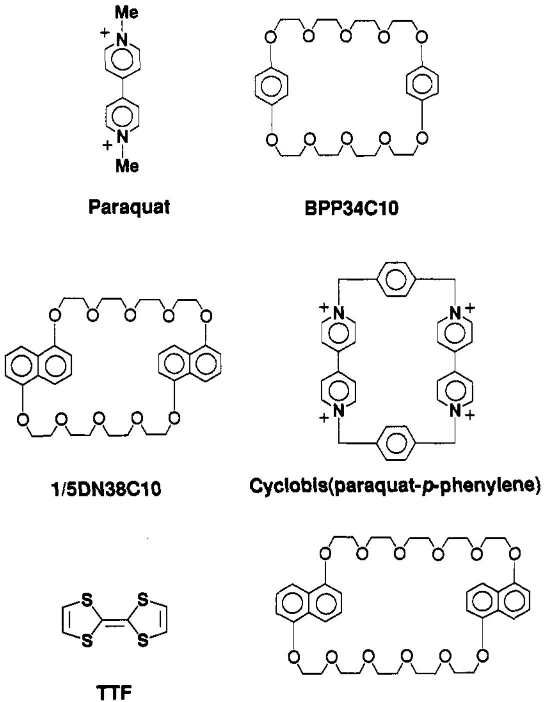


Figure 4. Solid-state structure of the [paraquat·BPP34C10] complex.

Chart 1



Paraquat **BPP34C10**

1/5DN38C10 **Cyclobis(paraquat-*p*-phenylene)**

TTF **1/5DN44C12**

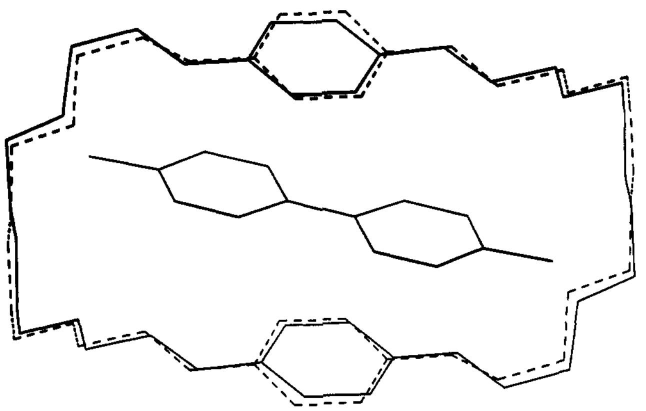


Figure 5. Best least-squares fit of the conformation of free macrocyclic polyether BPP34C10 (dashed line) with that of BPP34C10 as the host in the [paraquat·BPP34C10] complex (solid line).

rocyclic polyether forms a 1:1 complex with the dication in acetone solution, exhibiting a binding constant[24] of 730 dm^3 mol^{-1}. The solid-state structure (Figure 4) of the [paraquat·BPP34C10][PF$_6$]$_2$ complex reveals that the π-electron-deficient dication is indeed sandwiched between the two π-electron-rich hydroquinone residues in BPP-34C10. The central axis of the guest is inclined by 28° relative to the O···O axes of the hydroquinone residues of the macrocyclic polyether and the separation between each of the π-electron-rich rings and π-electron-deficient units is 3.7 Å, in keeping with significant π–π stacking. The aryl oxygen atoms of both hydroquinone residues are positioned axially either side of the electropositive carbon atoms α to nitrogens in the paraquat dication, giving rise to stabilizing electrostatic interactions. In addition, there is hydrogen bonding between one of the protons attached to each methyl group of the paraquat dication and one of the oxygen atoms in each tetraethylene glycol spacer units in BPP34C10 ([C···O] = 3.33 Å, [O···H] = 2.51 Å), and between one of the α-CH protons of each pyridinium ring of the guest and two other oxygen atoms in the host ([C···O] = 3.28 Å). The conformation of the crown ether in the 1:1 complex is remarkably similar (Figure 5) to that observed in the crystals of the free receptor,[26] suggesting that BPP34C10 is preorganized for ready complexation of the dication. Thus, the noncovalent bonding interactions in the [paraquat·BPP34C10][PF$_6$]$_2$ complex reflect a balance of **(i)** π–π stacking interactions[27–29] between the aromatic rings in the host and guest, **(ii)** electrostatic interactions involving the oxygen atoms attached to the aromatic rings of the host, and **(iii)** [C–H···O] and van der Waals interactions in which some of the polyether chain oxygen atoms participate.

A range of crystalline complexes were subsequently synthesized[30] in which the guest dications were derived from bipyridine, symmetrically substituted on each nitrogen atom with either a proton or a homologous series of ethylene glycol units. All of the alkylated bipyridinium dicationic guests penetrate through the center of the BPP34C10 macrocycle in both solution and solid states, demonstrating the pseudo[2]rotaxane-like nature of the structures.[16] In each of these superstructures, all the principle host–guest interactions observed in the [paraquat·BPP34C10][PF$_6$]$_2$ complex are retained.

In common with the crown ether (BPP34C10) incorporating hydroquinone residues, 1,5-dinaphtho-38-crown-10 (1/5DN38C10) also forms a 1:1 crystalline complex[31] with paraquat bishexafluorophosphate. The π-electron-deficient bipyridinium unit is once again located between the two π-electron-rich 1,5-dioxynaphthalene residues of the host. There are hydrogen bonds between the "second" oxygen atom in each tetraethylene glycol chain and a methyl hydrogen atom of the guest ([H···O] = 2.35 Å) and between the "fourth" oxygen atom in the same tetraethylene glycol chain and a proton attached to one of the

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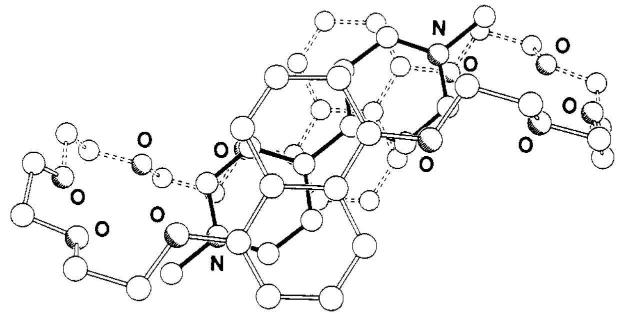


Figure 6. Solid-state structure of the [paraquat·1/5DN38C10] complex viewed from the normal to the mean plane of the paraquat dication.

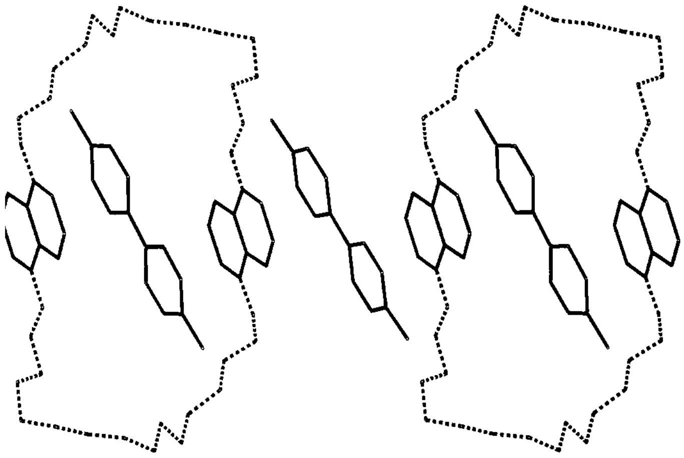
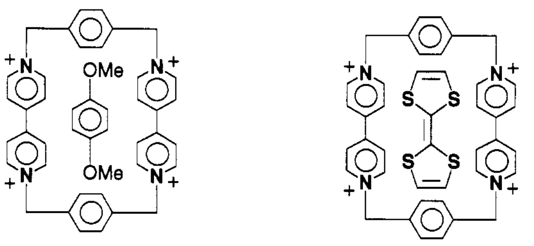


Figure 7. Part of the continuous DADA stack in the 2:1 crystalline complex represented by [(paraquat)$_2$·1/5DN44C12].



[see Figure 10] [see Figure 11]

Figure 8. Complexes of the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate with π-electron-rich guests for which solid-state structures are illustrated.

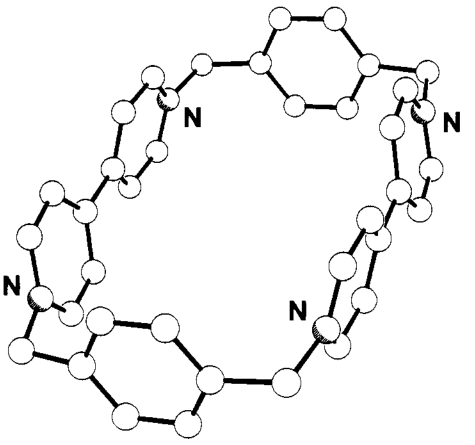


Figure 9. Solid-state structure of the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate.

α-carbon atoms of the paraquat dication ([H···O] = 2.70 Å). However, in this superstructure, the hydrogen bonding appears to be less important than either the π–π stacking interactions or the electrostatic interactions between the naphthoxy oxygen atoms and α- and β-carbon atoms adjacent to the quaternary nitrogen atoms (Figure 6).

If the constitution of the dinaphtho crown ether is enlarged symmetrically by incorporating synthetically two extra bismethyleneoxy units, to form 1,5-dinaphtho-44-crown-12 (1/5DN44C12), then the resulting complex formed with the paraquat dication has a host:guest stoichiometry of 1:2 in the solid state.[32] The X-ray crystallographic analysis of the complex reveals that, in addition to the expected encapsulation of a paraquat dication within the 1/5DN44C12 macrocycle, a second paraquat dication is sandwiched between adjacent 1:1 [paraquat·1/5DN44C12][PF$_6$]$_2$ complexes, to form a continuous DA stack that extends along one of the crystallographic directions (Figure 7). In contrast with the [paraquat·1/5DN38C10][PF$_6$]$_2$ complex, the interplanar separation between the two naphtho units in each [paraquat·1/5DN44C12][PF$_6$]$_2$ complex is reduced significantly from 7.1 to 6.8 Å, with a consequent reduction in the donor–acceptor interplanar separation. The same interplanar separation is also present between the naphtho units of adjacent complexes and the intercalated Paraquat dications. This solid-state structure proved to be very important. It provided the inspiration for the design of a receptor for π-electron-rich guests. The distance between the methyl groups (Figure 7) of the included and sandwiched paraquat dications is ideally suited for their connection by a *p*-phenylene unit.

Receptors for π-Electron-Rich Guests

The tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene),[33] proved to be an ideally-preorganized host (Figure 8) for π-electron-rich aromatic guests. The solid state structure (Figure 9) of this host reveals its box-like shape, in which the four sides are comprised of two *p*-xylyl spacers and two bipyridinium units. When an acetonitrile solution of cyclobis(paraquat-*p*-phenylene) is mixed with 1,4-dimethoxybenzene, a red color develops instantly, implying that the guest has entered the cavity of the host. The solid state structure of the resulting red crystalline complex[34] confirms that the planar π-electron-rich guest[35] is nestling centrosymmetrically in the middle of the tetracationic cyclophane, with the terminal methoxyl groups of the guest protruding above and below the upper and lower rims, respectively, of the host (Figure 10). The gross structure of the host is essentially unchanged upon complexation. However, there is a distinct reduction in the twist angle between the pyridinium rings of each bipyridinium unit from 13° to 4°, i.e., the tetracationic

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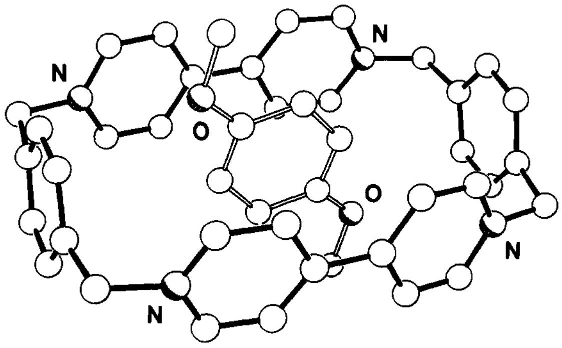

Figure 10. Structure of the 1:1 crystalline complex formed between the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate and 1,4-dimethoxybenzene.

cyclophane flexes itself to accommodate the π-electron-rich guest. In addition to the face-to-face π–π stacking and electrostatic interactions observed in the crown ether complexes with paraquat, there are aromatic-aromatic edge-to-face "T-type" interactions[36] between the *p*-phenylene spacers of the host and the orthogonally-aligned 1,4-dimethoxybenzene guest molecules (centroid–centroid distance is ca. 5 Å).

An illustration of the versatility of cyclobis(paraquat-*p*-phenylene) as a host for π-electron-rich guests is further demonstrated by the 1:1 complex which it forms[37] with tetrathiafulvalene (TTF). The incorporation of TTF units into rotaxanes[38] is an attractive proposition since its π-electron-rich rings exhibit reliable and reversible electrochemical behavior at an easily-accessible oxidation potential (ca. 0.4 V). Interlocked structures containing TTF units could be amenable to electrochemical control and thereby display device-like properties, e.g., switching within a molecule. When TTF and cyclobis(paraquat-*p*-phenylene) are mixed together in acetonitrile, charge transfer occurs and results in an intensely green-colored solution, into which isopropyl ether can be diffused, effecting crystallization of a centrosymmetric 1:1 complex. The solid-state crystal structure (Figure 11) shows that the π-electron-rich guest is threaded through the center of the tetracationic cyclophane, with the long axis of the TTF molecule tilted by 66° relative to the $N^+\cdots N^+$ vector of the two bipyridinium residues, reminiscent of a pseudorotaxane-like structure. Moreover, the tetracationic cyclophanes are arranged in stacks with the TTF molecules aligned end-to-end through their centers almost perfectly along one crystallographic direction, without any encroachment of either the hexafluorophosphate counterions or solvent of crystallization. The distance between the olefinic carbon atoms of adjacent TTF molecules is 4.87 Å. It is possible to visualize the joining up of the TTF molecules to form a polymeric chain over which numerous cyclophane molecules could be threaded, producing a kind of polyrotaxane[39] or "molecular abacus". A demonstration[40] of the plausibility of this approach to increased supramolecular design has been described in the stacked structure observed for the crystalline 2:1 complex formed between cyclobis(paraquat-*p*-phenylene) and 1,3-bis(5-hydroxy-1-naphthyloxy)propane, in which the host is inserted through the center of the stack of tetracationic cyclophanes in a disordered array, simulating a threaded polymer chain.

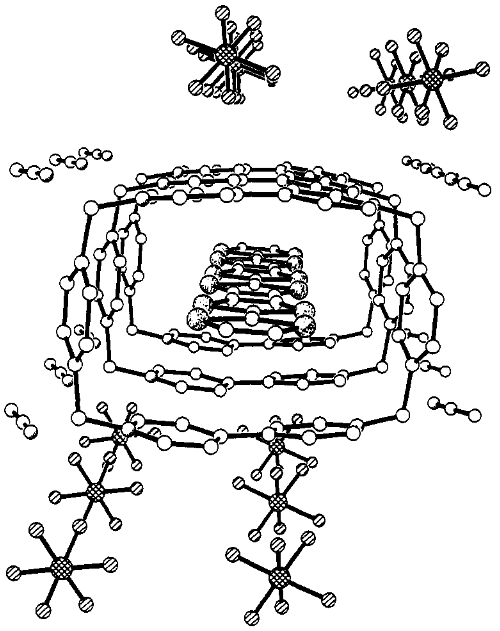

Figure 11. Part of the channel-like structure of the solvated (MeCN) crystalline 1:1 complex formed between cyclobis(paraquat-*p*-phenylene) tetrakis hexafluorophosphate and TTF.

Pseudorotaxanes in the Solid State

Greater order can be imposed upon the complexes formed with cyclobis(paraquat-*p*-phenylene) (Figure 12) simply by increasing the number of molecular recognition sites in the guest molecule.[16] When a thread, comprised of hydroquinone rings substituted with two tetraethylene glycol chains terminated with 4-benzyloxyphenoxy groups, is added to a solution of the tetracationic cyclophane in acetonitrile, a deep red color forms. Upon vapor diffusion of isopropyl ether into the colored solution, deep red crystals are formed of a 1:1 complex. X-ray crystallography reveals (Figure 13) that the polyether thread is inserted through the cavity of the cyclophane in a rotaxane-like manner,[41] such that the central hydroquinone ring is sandwiched between the bipyridinium units of the host. The face-to-face and edge-to-face π–π interactions, observed in all the previous cyclophane complexes, are also evident in this complex. The $O\cdots O$ axis of the included hydroquinone ring makes an angle of 48° with the $N^+\cdots N^+$ vector of the two bipyridinium residues of the host. Each polyether chain of the guest is curled back on itself, allowing the two "outside" hydroquinone residues to form "alongside" stacking interactions with the exterior surface of the π-electron-deficient cyclophane. Two of the oxygen atoms in each of the polyether chains form [$O\cdots H$–C] hydrogen bonds with protons attached to the tetracationic cyclophane—the second oxygen atom from the center of the thread interacts with one of the α-protons on the cyclophane ([$H\cdots O$] distance = 2.66 Å), and the fourth oxygen atom hydrogen bonds with one of the methylene protons in the host ([$H\cdots O$] distance = 2.53 Å).

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[36] Burley, S. K.; Petsko, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 7995.

[37] Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1584.

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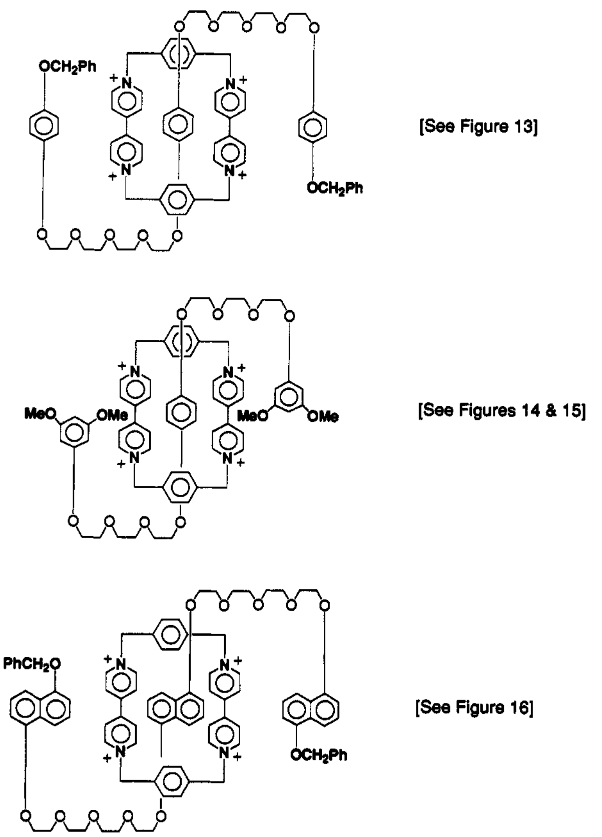

Figure 12. Pseudorotaxanes for which solid-state structures are available.

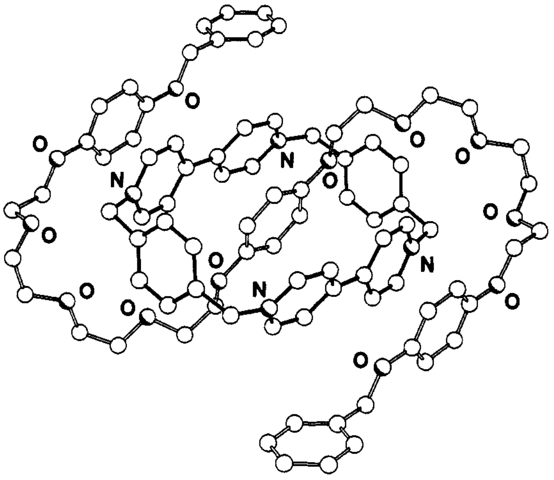

Figure 13. Solid-state structure of the pseudorotaxane, formed by the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate and a thread containing three π-electron-rich hydroquinone residues linked by two tetraethylene glycol chains and terminated by two benzyl ether functions.

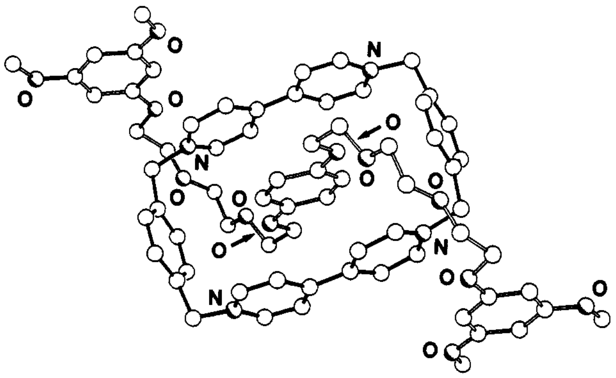

Figure 14. Solid-state structure of the pseudorotaxane, formed between the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate and a thread containing a hydroquinone residue linked by two triethylene glycol chains to terminal 3,5-dimethoxyphenol ether functions.

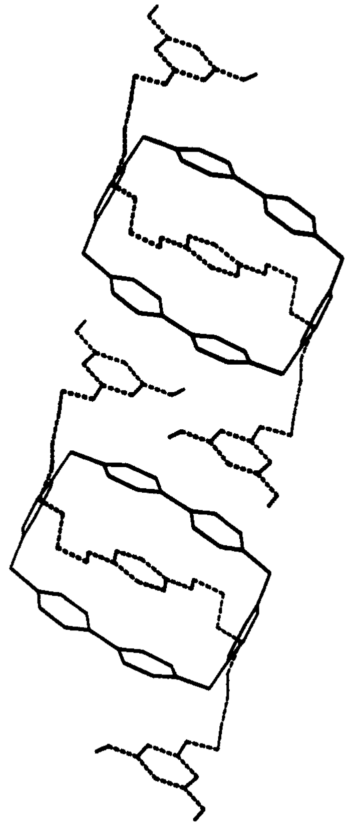

Figure 15. Part of the continuous DADADA stack formed in the crystal by the pseudorotaxane depicted in Figure 14.

A shortening of the two polyether chains from tetraethylene glycol units to triethylene glycol units between the three hydroquinone residues resulted in a guest molecule which formed a 1:1 complex with the tetracationic cyclophane but was poorly crystalline.[16] Replacement of the terminal 4-benzyloxyphenoxy groups with 3,5-dimethoxyphenoxy groups results in a material which forms a crystalline 1:1 complex with the tetracationic cyclophane (Figure 14). Here, in contrast to the solid-state structure (Figure 13) of the previous pseudorotaxane, a continuous donor–acceptor stack forms in the crystal (Figure 15). The terminal π-accepting groups of the thread component are "shared" in a π–π stacking motif between the tetracationic cyclophane through which the thread passes and the outside face of a bipyridinium unit in neighboring pseudo[2]rotaxane complexes.

Replacing the hydroquinone rings as the π-electron-rich components with 1,5-dioxynaphthalene residues in the thread incorporating two tetraethylene glycol chains results in a crystalline 1:1 complex with the same gross pseudo[2]rotaxane superstructure.[42] However, the situation at the supramolecular level throughout the crystal is very different (Figure 16). The pseudo[2]rotaxane units arrange themselves into infinite two-dimensional sheets. This extended gridlike pattern is sustained by additional

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(42) Ashton, P. R.; Philp, D.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 181.

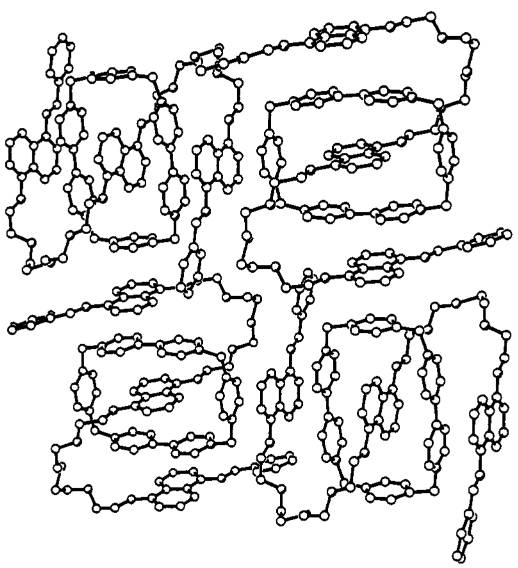

Figure 16. Part of the infinite two-dimensional array in the crystal structure of a pseudorotaxane, formed between the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakis-hexafluorophosphate and a thread containing three π-electron-rich 1,5-dioxynaphthalene units linked by two tetraethylene glycol chains and terminated by two benzyl ether functions.

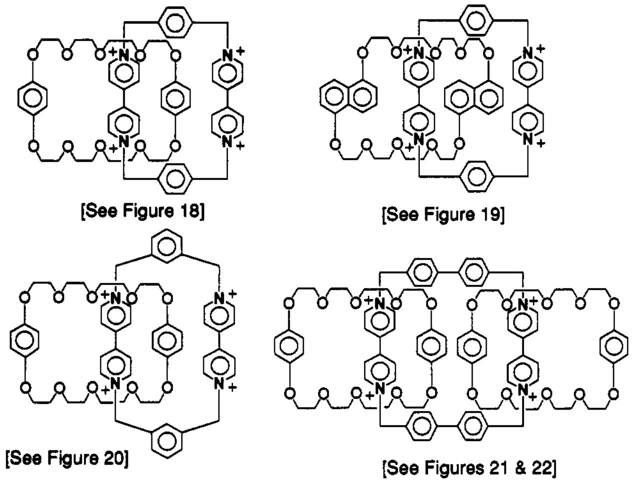

Figure 17. Catenanes for which solid-state structures are illustrated.

π–π stacking of the "alongside" dioxynaphthalene units with the *p*-xylyl spacer of the tetracationic cyclophane in an adjacent pseudo[2]rotaxane complex.

Catenanes in the Solid State

The design of the components of the [2]catenane (Figure 17), comprised of the macrocyclic polyether BPP34C10 containing π-electron-rich rings and cyclobis(paraquat-*p*-phenylene) containing π-electron-deficient units, was originally inspired by consideration of supramolecular complexes such as the continuous donor–acceptor stack formed[32] by the [paraquat$_2$·1/5DN44C12][PF$_6$]$_4$ complex (Figure 7). Further vindication of our conceptual approach (Figure 2) was provided[23] by the complexes of π-electron-deficient threads in π-electron-rich crown ethers[25,31] (Figure 3) and the complementary "reverse-logic" pseudorotaxanes[16] with π-electron-rich molecules threaded through the tetracationic cyclophane (Figure 12).

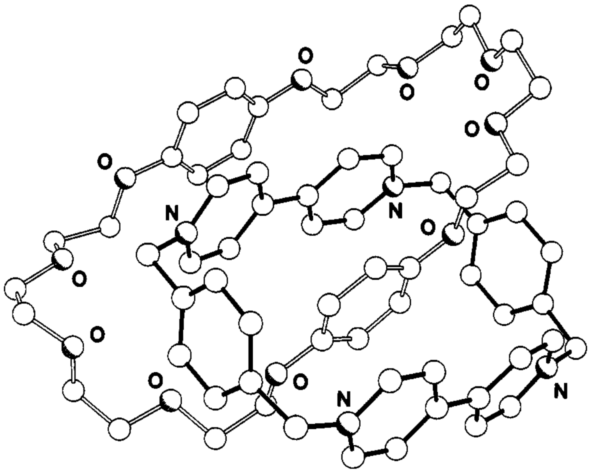

Figure 18. Solid-state structure of the [2]catenane incorporating the macrocyclic polyether BPP34C10 and the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate.

When the acyclic compound consisting of two 4,4′-bipyridyl units linked by a *p*-xylyl unit is reacted with α,α′-dibromo-*p*-xylene in the presence of the macrocyclic polyether, BPP34C10, in acetonitrile an intensely red-colored solution results. The major product of this reaction is the [2]catenane (Chart 1),[43,44] comprising one BPP34C10 macrocycle and one cyclobis(paraquat-*p*-phenylene)cyclophane. The noncovalent bonding interactions that assist in the self-assembly of the [2]catenane are evident in its solid-state structure (Figure 18). One of the hydroquinone residues resides within the cavity of the tetracationic cyclophane in the same orientation as that adopted by the complexed 1,4-dioxybenzene rings in the π-electron-deficient host (Figure 10). The same face-to-face and edge-to-face aromatic interactions are also present in the [2]catenane. The interplanar separations between the π-electron-rich and π-electron-deficient aromatic rings are, in all cases, approximately 3.5 Å within the interlocked rings. In addition, there are two hydrogen bonds between the diametrically opposite central oxygen atoms in the tetraethylene glycol spacer of the crown ether and two of the α-proton atoms on the included bipyridinium unit, the [H···O] distances being 2.60 and 2.64 Å, respectively.

An analogous [2]catenane,[45] comprising the crown ether 1/5DN38C10 and cycobis(paraquat-*p*-phenylene), displays a very similar gross structure for the isolated molecule. Noteworthy are very strong edge-to-face interactions involving H-4 and H-8 attached to the included naphtho rings. These hydrogen atoms are both directed orthogonally toward the centers of the *p*-phenylene spacers of the tetracationic cyclophane.

The [2]catenanes, containing BPP34C10 and 1/5DN38C10, both self-organize forming continuous donor–acceptor stacks in the solid state (Figure 19). In the case of the dinaphtho derivative, the mean interplanar separation between the "alongside" bipyridinium unit of one catenane molecule and the "alongside" naphtho residue

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(43) Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396.

(44) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193.

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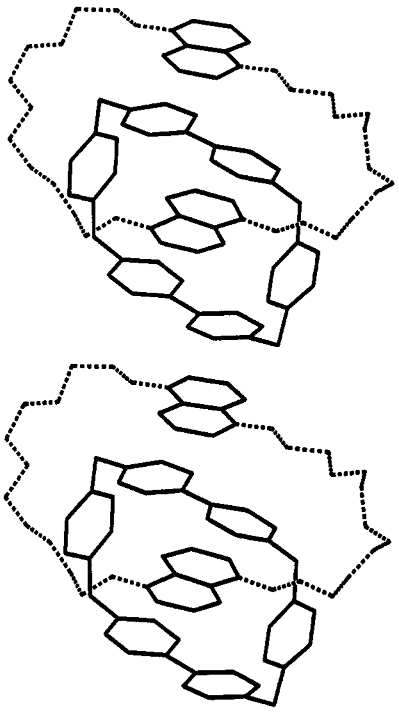


Figure 19. Part of the continuous DADA stack associated with the [2]catenane incorporating the macrocyclic polyether 1/5D-N38C10 and the tetracationic cyclophane component of cyclobis(paraquat-*p*-phenylene) tetrakishexafluorophosphate in the crystal.

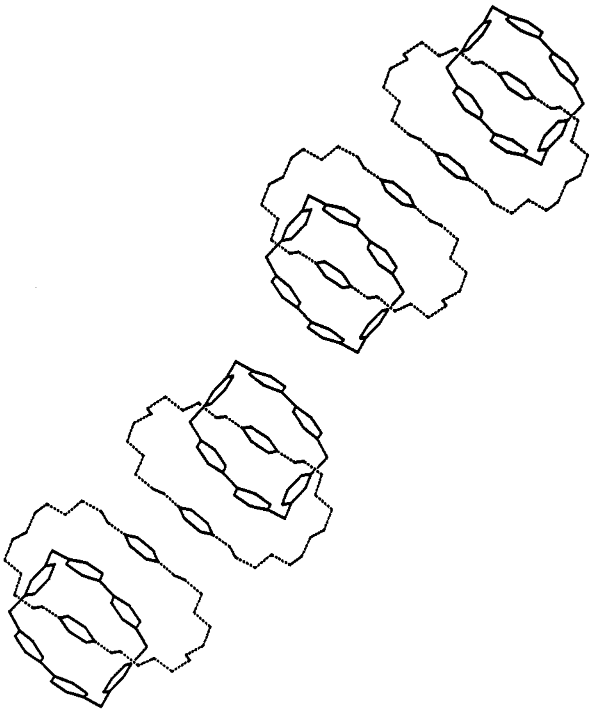
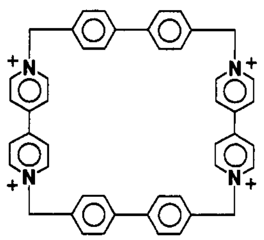


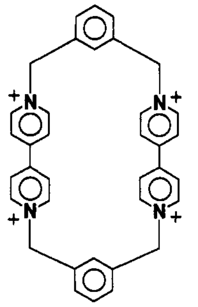
Figure 20. Stacked ADADDADA sequence within the ordered [2]catenane incorporating the macrocyclic polyether BPP34C10 and the tetracationic cyclophane component of cyclobis(paraquat-*m*-phenylene) tetrakishexafluorophosphate in the crystal.

of the next one is only 3.3 Å. The stacks of the [2]catenanes are chiral, i.e., one stack contains exclusively one enantiomer of the structure, while an adjacent stack is comprised of the other enantiomer.

Chart 2



Cyclobis(paraquat-4,4'-biphenylene)



Cyclobis(paraquat-*m*-phenylene)

Constitutional change can also play a significant part[46] in influencing the relative solid-state orientations of catenated molecules of this type. Replacement of one of the *p*-xylyl spacers in the tetracationic cyclophane with a *m*-xylyl spacer in the catenane involving the BPP34C10 macrocycle results in a stacking of the catenane molecules in the crystal very similar to that observed for the bis-*p*-xylyl analogue. As before, chiral donor–acceptor stacks are formed. However, replacement of the second *p*-xylyl spacer with a *m*-xylyl spacer results in a compound in which the molecules stack differently in the solid state (Figure 20). In this particular [2]catenane, where both spacers in the tetracationic cyclophane are *m*-xylyl units (Chart 2), the bipyridinium dicationic units are noticeably more bent when compared with those in the corresponding bis-*p*-xylyl derivative. Perhaps, as a consequence of this bowing, the "alongside" bipyridinium units are not encouraged to stack with "alongside" hydroquinone residues of another [2]catenane molecule. Instead, two of the π-electron-rich rings stack adjacent to one another in the crystal, the separation between their mean planes being 3.62 Å (centroid–centroid distance 3.99 Å).

The same interplanar distance between hydroquinone residues is also observed (Figure 21) in the crystal structure of a [3]catenane[47] incorporating two BPP34C10 macrocycles and the cyclobis(paraquat-4,4'-biphenylene) cyclophane, which was self-assembled (Chart 2) employing a strategy similar to that described for the [2]catenane. This donor–donor interaction is present in addition to the "normal" π–π stacking, electrostatic and hydrogen-bonding interactions already noted in the [2]catenanes. Each [3]catenane molecule is stacked next to an adjacent interlocked structure (Figure 22) in such a way that the "alongside" hydroquinone residues of the adjacent catenane molecules are placed next to one another. There is, thus, a DADDAD–DADDAD array extending throughout the crystal.

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(46) Amabilino, D. B.; Ashton, P. R.; Tolley, M. S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1297.

(47) Ashton, P. R.; Brown, C. L.; Chrystal, E. J. T.; Goodnow, T. T.; Kaifer, A. E.; Parry, K. P.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1039.

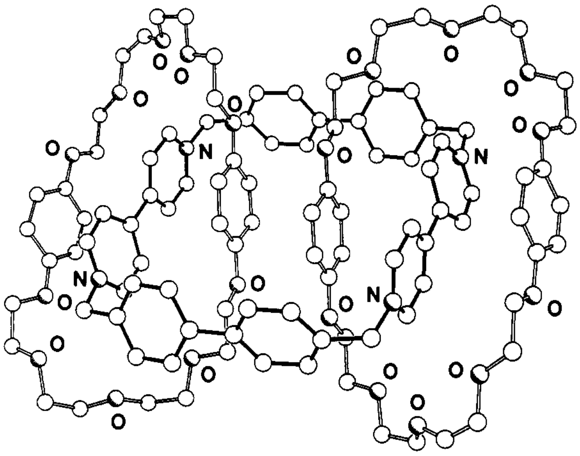

Figure 21. Solid-state structure of the [3]catenane incorporating two BPP34C10 macrocycles linked by the tetracationic cyclophane component of cyclobis(paraquat-4,4′-biphenylene) tetrakishexafluorophosphate.

The importance of the [3]catenane structure and superstructure involving the additional donor–donor interactions throughout the crystal is that it shows how we might begin to overcome the apparent difficulty of self-assembling polycatenanes in which a DDAADDAA sequence is necessary for successful interlocking of macrocyclic rings containing exclusively either donor or acceptor units. The first steps toward this goal have been made[48,49] with the successful self-assembly in two steps of both [4]catenanes and [5]catenanes.

Summary

Molecular recognition phenomena can be employed to develop the concepts of self-organization and self-assembly for the construction of large, functioning multicomponent chemical systems.[20] This short review outlines the major discoveries and key events which have led us logically to the self-assembly of rotaxanes, pseudorotaxanes, and catenanes containing complementary components. The information that we and others, including the late Margaret Etter,[1-7] have gained from solution-state investigations on self-assembled systems and from the careful analysis of the noncovalent bonding interactions present in the solid-state structures and superstructures of their molecules and molecular arrays, respectively, is now guiding us[50] toward the design of the next generation of more "intelligent" components for the construction of new materials by self-assembly on a nanometer scale at both the molecular and supramolecular levels.

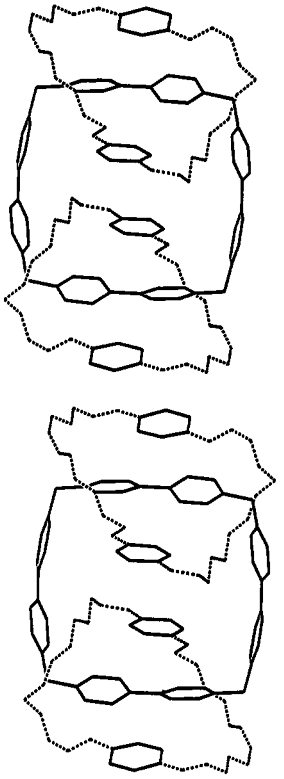

Figure 22. Stacked DADDAD–DADDAD superstructure of the [3]catenane illustrated in Figure 21 in the crystal.

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[48] Amabilino, D. B.; Ashton, P. R.; Reder, A. S.; Spencer, N.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 433.

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[50] Amabilino, D. B.; Stoddart, J. F. *New Sci.* **1994**, *19 Feb, No. 1913*, 25.