DALTON
PERSPECTIVE

A molecular meccano kit†

Stuart J. Cantrill, Anthony R. Pease and J. Fraser Stoddart*

*Department of Chemistry and Biochemistry, University of California, Los Angeles,
405 Hilgard Avenue, Los Angeles, CA 90095-1569, USA. E-mail: stoddart@chem.ucla.edu*

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A range of secondary dialkylammonium ($R_2NH_2^+$) ions has been shown to thread through the cavities of appropriately-sized crown ether compounds to afford interwoven complexes. X-Ray crystallographic investigations to probe the solid-state properties of these supermolecules have revealed that many subtle factors—*e.g.*, solvent of crystallisation, crown ether conformation and anion interactions—can influence the nature of the overall three-dimensional superstructures. Nonetheless, a family of building blocks—namely $R_2NH_2^+$ ions and crown ethers—can be generated, which constitute a molecular meccano kit. By mixing and matching these modules in different ways, intricate interwoven supramolecular architectures can be constructed. From relatively simple beginnings—where *one* $R_2NH_2^+$ ion is threaded through *one* monotopic crown ether (dibenzo[24]crown-8)—the designed evolution of the building blocks in the molecular meccano kit has led to more elaborate *multiply encircled* and/or *multiply threaded* superstructures. The effects of crown ether constitution, macroring size, and both crown ether as well as $R_2NH_2^+$ ion substitution, upon the solid-state behaviour of these interwoven complexes have also been examined. A statistical analysis of the hydrogen bonding interactions observed in these systems has been carried out. It reveals that a reasonable correlation exists between N^+–H · · · O bond angle and H · · · O bond length. The correlation between C–H · · · O bond angle and H · · · O distance is poor, suggesting that C–H · · · O hydrogen bonding interactions are of secondary importance in determining the co-conformations adopted by these supermolecules.

Introduction

One of the goals of contemporary chemistry is the construction of larger and larger ‘structures’. In the realm of covalent chemistry, these ‘structures’ are the numerous synthetic targets—many of them complex natural products—now being pursued in laboratories around the world.[1] With a remarkable degree of precision, chemists routinely string together collections of atoms in a targeted fashion by utilising elegant methodologies[2] which have evolved, for the most part, over the last 50 years.

From auspicious beginnings, strychnine[3] (1954) and prostaglandin $F_{2\alpha}$[4] (1969)—to name but two examples—modern organic synthesis has flourished, rising to, and indeed overcoming, such formidable challenges as palytoxin[5] (1994), taxol[6]

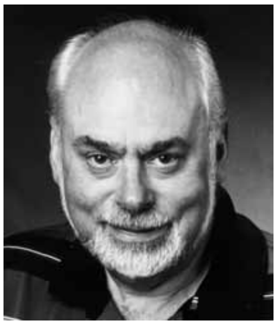
Stuart Cantrill was born in Lichfield, England in 1974. He received both his B.Sc. (1996) and M.Phil. (1997) degrees from the University of Birmingham, where he subsequently began his Ph.D. studies in the laboratories of Professor Fraser Stoddart. In the summer of 1997 he helped relocate the Stoddart Group to UCLA, where he is now in his final year of graduate studies. When he’s not in the laboratory investigating novel, self-assembling, supramolecular daisy-chain-like structures, he finds himself being beaten at badminton or on the losing side at football.

Anthony Pease was born in Essex, England in 1975. After gaining a B.Sc. (Hons) from the University of Salford in 1996, performing a final year project under the tutelage of Damien Arrigan, he started a Ph.D. in the laboratories of Fraser Stoddart in Birmingham. He moved with the Stoddart group to UCLA in 1997, and is currently in the final year of his studies. In the ever decreasing amount of time he spends away from the lab, he plays prop for Santa Monica Rugby Club, and occasionally performs stand-up comedy.

Fraser Stoddart was born in Edinburgh, Scotland in 1942. He received all of his degrees (B.Sc., 1964; Ph.D., 1966; D.Sc., 1980) from the University of Edinburgh. Following postdoctoral work at Queen’s University in Canada he joined the Academic Staff at the University of Sheffield in 1970. Following a seven year spell as Professor of Organic Chemistry at the University of Birmingham, he moved, in 1997, to the Saul Winstein Chair of Organic Chemistry at UCLA. His research goals include the application of self-assembly processes to unnatural systems, with the aim of creating functional superstructures by the mixing and matching of simple building blocks that constitute a molecular meccano kit. Such a kit can then be used in the construction of molecular machines.

Stuart Cantrill

Anthony Pease



Fraser Stoddart

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Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b003769i/

This review is dedicated to Professor David J. Williams on the occasion of his 60th birthday.

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(1994), and brevetoxin B[7] (1995). However, these triumphs have come at a considerable price. Even when they are performed in a convergent manner, these daunting syntheses are not only time-consuming, but are also costly and inefficient in terms of materials consumed, time elapsed, and personnel employed. The limits of traditional covalent bond-forming chemistry must also be questioned—just how far can *molecular* synthesis[8] be taken? Although there is no definitive answer to this question, as we demand larger and larger 'structures', the practicalities of utilising the *covalent* bond—to act as the 'glue' which holds the pieces together—are debatable. This realisation prompts us to seek alternative strategies for the construction of extended 'structures' and leads us to consider the chemistry of the *noncovalent* bond, and consequently, interactions between molecules, *i.e.*, supramolecular chemistry[9] and hence *supramolecular* synthesis.[10]

A thorough knowledge and understanding of molecular recognition processes—particularly those based upon hydrogen bonding,[11] metal–ligand coordination,[12] π–π interactions (face-to-face[13] and edge-to-face[14]), hydrophobic,[15] ion pairing[16] and van der Waals[17] interactions—permits us to design small, relatively simple, building blocks—a molecular meccano kit—that are capable of assembling into larger superstructures. In effect, as a consequence of the synthetic chemist's own judicious design, the components do all of the hard work by themselves, self-assembling[18] into extended arrays by virtue of complementary recognition features.

Application of the chemistry of the noncovalent bond to the challenge of fabricating larger and larger 'structures', has proved to be very effective, resulting in the creation of many elaborate, and indeed intricate, supramolecular architectures,[10–19] as well as assisting in the realisation of molecular topologies[20,21] held together by mechanical bonds. When translated into the solid state, this rational design approach is the driving force behind the field of *crystal engineering*[22]—a discipline that tempts us with the prospect of, one day, being able to predict crystal structures simply by extrapolation from the individual building blocks. However, will this day ever arrive? Whether it does or not, as time passes, our understanding of the solid state can only increase, and further exploration in this arena is the only sensible way forward. Our own investigations in this field are exemplified by focusing on an extremely reliable supramolecular synthon, developed[23] over the past five years in our laboratories. Although, for many years, it was known[24] that crown ethers were effective hosts for primary alkylammonium ion (RNH_3^+) guests, in recent times, secondary dialkylammonium ions ($R_2NH_2^+$) have also attracted considerable interest.[25,26] The discovery that appropriately-sized crown ethers can bind $R_2NH_2^+$ ions in a *threaded*,[27] rather than a *face-to-face*[28] manner, revealed a new paradigm for the construction of extended interwoven supramolecular arrays. This Perspective will describe our journey through this particular noncovalent landscape, highlighting how we built upon each success, applying the insight we gained at each stage to the incremental development of this story so far.

In the beginning

The concept of threading a molecule, containing an NH_2^+ centre, through the cavity of the crown ether, dibenzo[24]-crown-8 (DB24C8), was first recorded in the literature by Busch[29] in 1995, in a communication describing a rotaxane assembled using this type of recognition motif. Independently of the Kansas group, and as an extension to our work[21] on intertwined and interlocked systems, we were also pursuing investigations on the potential for $R_2NH_2^+$ ions to thread (Fig. 1) through the cavity of DB24C8 in order to generate [2]pseudorotaxanes.

We demonstrated that, in solution, the hexafluorophosphate (PF_6^-) salts of $R_2NH_2^+$ ions—such as the dibenzylammonium ion (DBA^+)—can indeed pierce the macroring of DB24C8, leading to the formation of these threaded complexes. Furthermore, the strength of the interaction was shown to depend markedly upon the nature of the solvent in which the two components were mixed. Polar solvents, *e.g.*, DMSO and DMF, were able to compete effectively with the crown ether in terms of their hydrogen bonding ability, and no complexation—*i.e.*, threading—could be observed by ^1H NMR spectroscopy. However, in poorer donor solvents—*e.g.*, Me_2CO, MeCN, and $CHCl_3$—the magnitude of the stability constant, associated with threading of the $R_2NH_2^+$ ion through DB24C8, was shown to increase (up to values in the region of 3×10^4 M^{-1}) as the solvent polarity—as determined by the Gutmann[31] donor number—decreased. This trend suggested to us that the primary driving force responsible for the threading interaction is the potential for strong hydrogen bonds to be formed between the acidic NH_2^+ protons and the ring of oxygen atoms located in the DB24C8 framework.

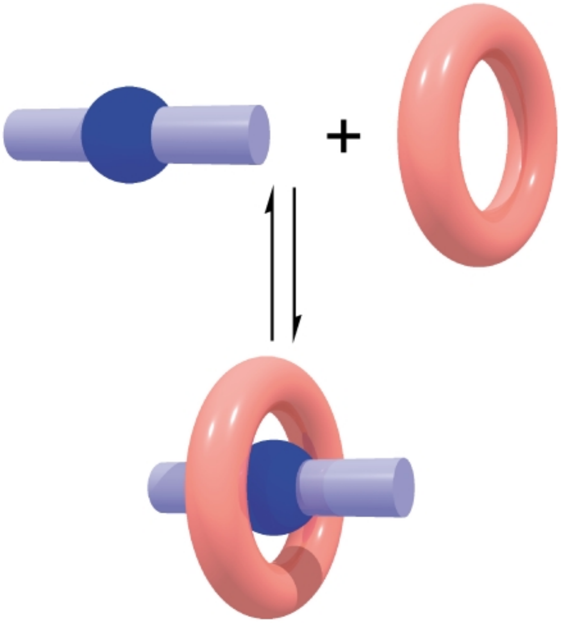


Fig. 1 A schematic representation depicting the formation of a threaded 1 : 1 complex (a [2]pseudorotaxane) between two complementary species wherein the cavity of a suitably-sized macrocycle is pierced by a linear thread.

X-Ray crystallographic analysis of single crystals obtained from a solution containing equimolar quantities of DB24C8 and $DBA{\cdot}PF_6$ revealed (Fig. 2) the formation—in the solid state—of the expected 1 : 1 complex, possessing a pseudorotaxane geometry. Two crystallographically independent 1 : 1 complexes were present in the asymmetric unit—only one of which is shown in Fig. 2—and, in each case, close contacts were observed between *both* of the NH_2^+ protons of the DBA^+ ion and oxygen atoms located in the polyether's macroring, indicating the formation of $N^+–H\cdots O$ hydrogen bonds. Additionally, in each independent complex, one of the CH_2 protons of the DBA^+ ion also approaches—within hydrogen bonding distance—one of the oxygen atoms of the DB24C8 macrocycle, further suggesting the formation of $C–H\cdots O$ hydrogen bonds. Therefore, the prevalence of hydrogen bonding interactions in the solid state seems to be consistent with the solution-phase observations. In terms of an extended 'structure', the X-ray crystallographic analysis also revealed that individual [2]-pseudorotaxane supermolecules form a column-like superstructure (Fig. 3) in which the DB24C8 macrocycles form channels through which a continuous π–π stacked chain of DBA^+ ions are threaded.

So, as 1995 drew to a close, although our molecular meccano kit was still quite small, we were armed with a fundamental

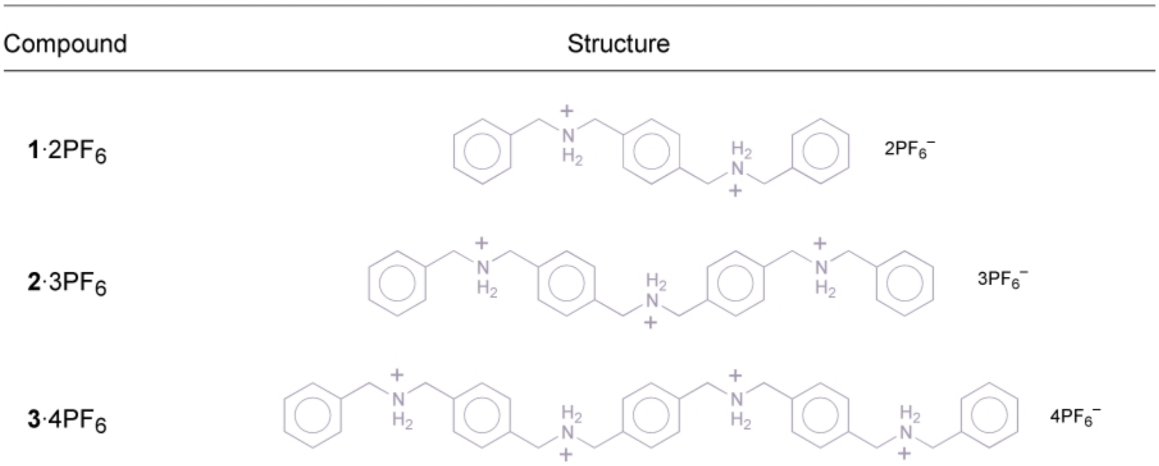


Chart 1 Threads have been synthesised containing two ($\mathbf{1}^{2+}$), three ($\mathbf{2}^{3+}$), and four ($\mathbf{3}^{4+}$) secondary ammonium ion centres.

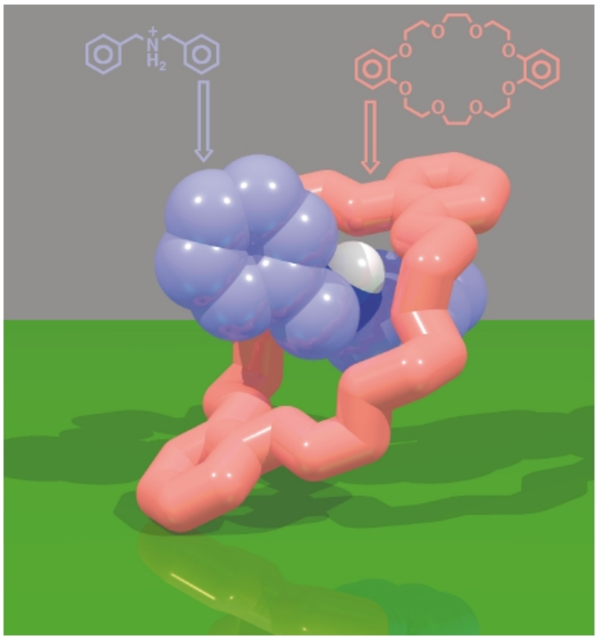


Fig. 2 One of the two distinct superstructures adopted in the solid state by the [2]pseudorotaxane [DB24C8·DBA]$^+$.

understanding of how and why certain building blocks associated with each other in the fashion we observed. Logically, the next challenge was to increase the size of the tool kit—in a designed, incremental fashion—by synthesising other small building blocks that would ultimately allow us to expand the repertory of self-assembled superstructures.

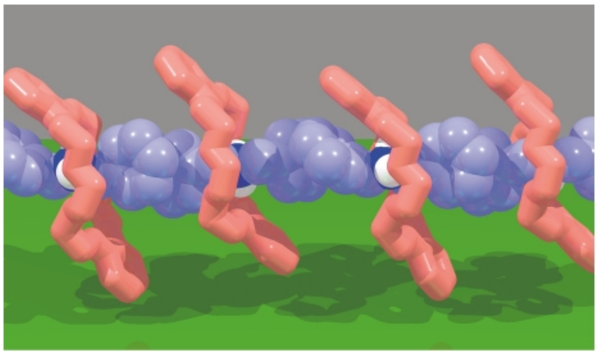


Fig. 3 π–π Stacking of the benzyl rings of the [2]pseudorotaxane [DB24C8·DBA]$^+$ produces an infinite linear pseudopolyrotaxane.

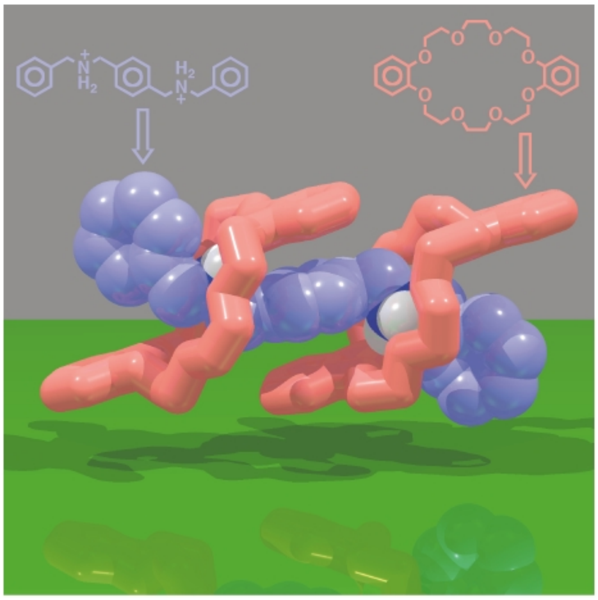


Fig. 4 The solid-state superstructure of a [3]pseudorotaxane $[(\mathrm{DB24C8})_2\cdot\mathbf{1}]^{2+}$ formed between a thread-like molecule—containing *two* ammonium centres ($\mathbf{1}\cdot2\mathrm{PF}_6$)—and *two* DB24C8 macrocycles.

Multiply encircled complexes

Our initial investigations had revealed that *one* DB24C8 macrocycle would encircle *one* DBA$^+$ ion. Therefore, it seemed that an obvious extension of this concept would be to make linear thread-like molecules containing more than one NH_2^+ site and explore the possibility of threading the appropriate number of DB24C8 rings onto such a species, *i.e.*, could we thread *n* DB24C8 rings onto a thread with *n* NH_2^+ sites, affording an [*n* + 1]pseudorotaxane? To this end, thread-like molecules containing two ($\mathbf{1}\cdot2\mathrm{PF}_6$), three ($\mathbf{2}\cdot3\mathrm{PF}_6$), and four ($\mathbf{3}\cdot4\mathrm{PF}_6$) NH_2^+ sites, respectively (Chart 1), were synthesised. The *molecular* synthesis complete, *supramolecular* synthesis afforded[32,33] the desired complexes in which a full complement of crown ethers were found to encircle each of the extended DBA$^+$ homologues **1**–**3**·$n\mathrm{PF}_6$. Gratifyingly, the [3]pseudorotaxane $[(\mathrm{DB24C8})_2\cdot\mathbf{1}][2\mathrm{PF}_6]$ and [4]pseudorotaxane $[(\mathrm{DB24C8})_3\cdot\mathbf{2}][3\mathrm{PF}_6]$ were isolated as crystalline materials, which were subjected to X-ray analysis, confirming the integrity (Figs. 4 and 5, respectively) of the NH_2^+/crown ether recognition in each case. In direct analogy with the interactions noted in the crystal structure of the parent [2]pseudorotaxane [DB24C8·DBA][PF$_6$], the [3]pseudorotaxane $[(\mathrm{DB24C8})_2\cdot\mathbf{1}][2\mathrm{PF}_6]$ (Fig. 4) also appears to be stabilised *via* a combination of $\mathrm{N}^+\!-\!\mathrm{H}\cdots\mathrm{O}$ and $\mathrm{C}\!-\!\mathrm{H}\cdots\mathrm{O}$ hydrogen bonding interactions. In addition, one catechol ring from each of the centrosymmetrically-related DB24C8 macrocycles participates in a π–π stacking interaction with the central

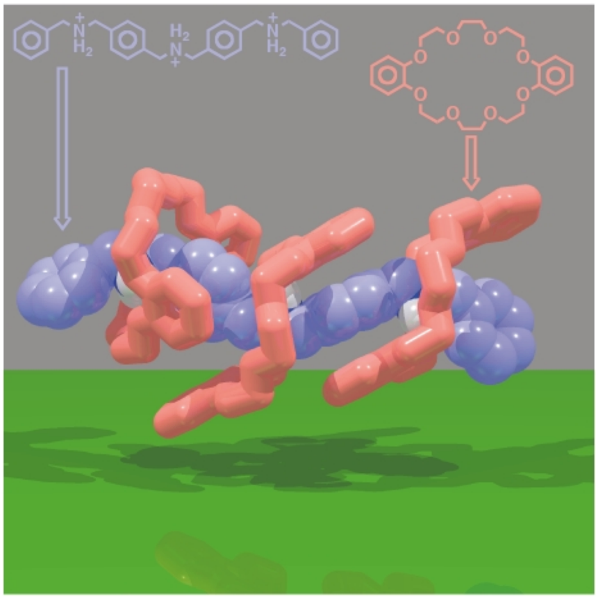


Fig. 5 The solid-state superstructure of a [4]pseudorotaxane $[(DB24C8)_3\cdot\mathbf{2}]^{3+}$ formed between a thread-like molecule—containing *three* ammonium centres ($\mathbf{2}\cdot3PF_6$)—and *three* DB24C8 macrocycles.

aromatic ring of $\mathbf{1}^{2+}$. The X-ray crystal structure of the [4]pseudorotaxane $[(DB24C8)_3\cdot\mathbf{2}][3PF_6]$ (Fig. 5) confirms, once again, that each NH_2^+ site on the thread ($\mathbf{2}^{3+}$) is encircled by a DB24C8 macrocycle as a consequence of the usual combination of $N^+–H\cdots O$ and $C–H\cdots O$ hydrogen bonding interactions. As before, additional stabilisation is provided by supplemental π–π stacking interactions within this four component supermolecule. Interestingly, in contrast with the [3]pseudorotaxane $[(DB24C8)_2\cdot\mathbf{1}][2PF_6]$ in which there are no significant inter-supermolecule interactions, the [4]pseudorotaxane $[(DB24C8)_3\cdot\mathbf{2}][3PF_6]$ forms π–π-linked dimers in the solid state giving rise, in principle, to a [7]pseudorotaxane.

Unfortunately, despite repeated efforts, obtaining a crystalline sample of the [5]pseudorotaxane eluded us. However, solution and gas-phase investigations[33] of this system—employing ^1H NMR spectroscopy and FAB mass spectrometry, respectively—suggested strongly the formation of the five-component complex in which four DB24C8 rings are threaded onto the tetracation $\mathbf{3}^{4+}$, encircling all of the NH_2^+ sites to afford a [5]pseudorotaxane. At this point, we can conclude tentatively that, given a linear thread-like molecule containing n NH_2^+ sites, in all likelihood, under favourable conditions, n DB24C8 macrocycles will shuffle onto such a 'template', locating themselves such that each NH_2^+ centre is encircled by one macrocycle.

Hence, predicting the nature of discrete superstructures, in this case, now appeared plausible. However, one aspect of the solid-state behaviour of these complexes is still apparently random—as it stands, there appears to be no rhyme or reason as to how individual complexes pack with respect to one another. If we consider the extended solid-state superstructures of the [2]-, [3]-, and [4]-pseudorotaxanes (*vide supra*), we note that each of them behaves differently. The [2]pseudorotaxane forms infinite one-dimensional π–π-linked chains, the [3]pseudorotaxane appears to have no desire to interact outside of the discrete 2 : 1 supermolecule units, and the [4]pseudorotaxane forms π–π-linked dimers! Therefore, the next challenge was to try and address this issue, by controlling, in some fashion, interactions between discrete supermolecules.

Controlling the extended superstructure

Perhaps one of the most studied, and well known[34] interactions in the field of crystal engineering is the carboxylic acid dimer supramolecular synthon. What makes this interaction so versatile, and hence so appealing, is the fact that its directionality can be controlled and/or influenced by subtle changes in the design of the species to which it is appended. This property can be exemplified by considering (Fig. 6) three simple examples, namely (a) terephthalic acid,[35] (b) isophthalic acid,[36] and (c) 5-decyloxyisophthalic acid.[37] When the two carboxylic acids are disposed *para* to one another on a benzene ring, as in terephthalic acid, the solid-state superstructure is that of a linear tape. By simply changing the substitution pattern to *meta*, as in isophthalic acid, the solid-state superstructure becomes reminiscent of a crinkled tape. Finally, introducing sterically-demanding groups onto the isophthalic acid ring, as in the case of 5-decyloxyisophthalic acid, disfavours the formation of any kind of tape, and discrete supramolecular macrocycles are produced. With these observations in mind, we set out[38] to marry together the $R_2NH_2^+$/DB24C8 recognition motif with that of the carboxyl dimer supramolecular synthon. An obvious condition is that a high degree of 'orthogonality' exists between the supramolecular synthons, *i.e.*, we want the carboxylic acid groups to form only dimers and we require that each NH_2^+ site be encircled by a DB24C8 macrocycle. Confident in the belief that these two supramolecular synthons would indeed operate independently of one another—*i.e.*, crown ethers would thread onto their NH_2^+ sites oblivious to the formation of carboxyl dimers and *vice versa*—we proceeded with our investigations.

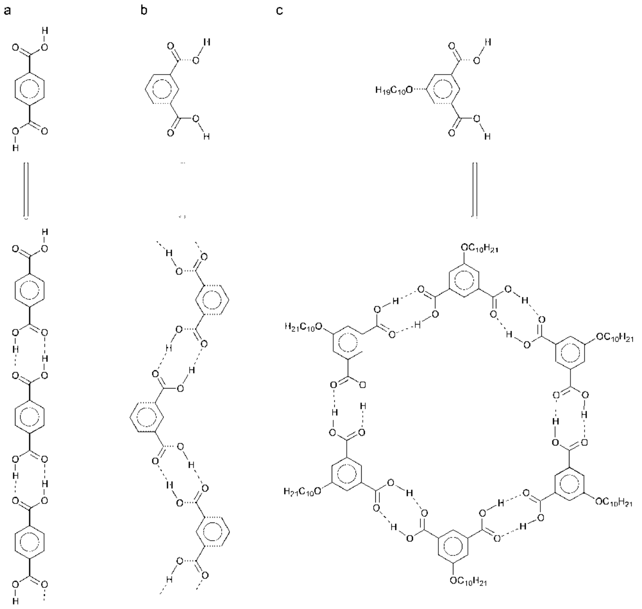


Fig. 6 The influence of both directionality and steric crowding upon solid-state superstructures assembled *via* the carboxylic acid dimer are highlighted. The *para* disposition of carboxylic acid groups in terephthalic acid (a) results in the formation of infinite linear tapes, whereas the *meta* disposition—as in isophthalic acid (b)—produces a crinkled tape. The sterically congested 5-decyloxyisophthalic acid (c) is precluded from forming an extended tape superstructure, assembling instead into discrete hexameric supramacrocycles.

Our investigation began with the *covalent* syntheses of a range of carboxyl-substituted $DBA\cdot PF_6$ derivatives ($\mathbf{4}$–$\mathbf{7}\cdot PF_6$) (Chart 2) in which we varied both (i) the number of CO_2H groups and (ii) their relative dispositions around the DBA^+ skeleton. Each of these carboxyl-substituted thread compounds was mixed, in solution, with an equimolar quantity of DB24C8, thereby initiating the *supramolecular* syntheses. From each of these solutions, good quality single crystals were obtained which were then subjected to X-ray analysis. In each case, the integrity of the $R_2NH_2^+$/DB24C8 recognition was maintained. Our initial hypothesis—essentially that the carboxylic acid groups would not interfere with the threading process and *vice versa*—was correct. Hence, without exception,

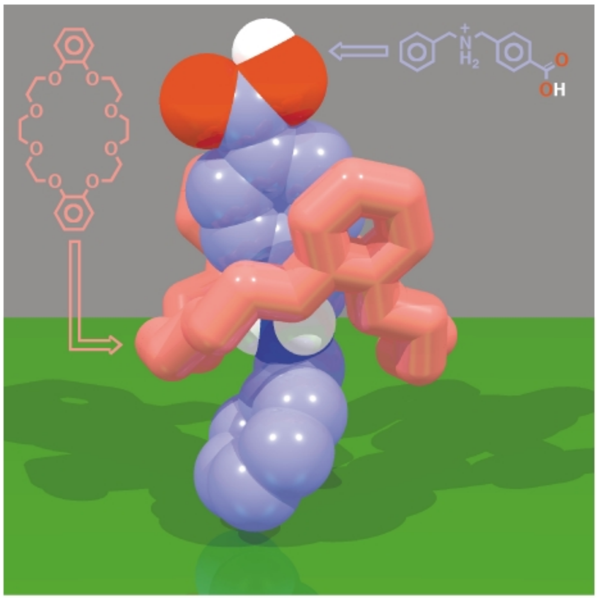


Fig. 7 The solid-state superstructure of the [2]pseudorotaxane [DB24C8·**4**]$^+$ formed between the *para*-carboxylic acid-substituted DBA$^+$ cation **4**$^+$ and DB24C8.

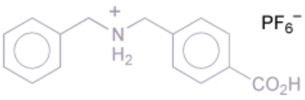
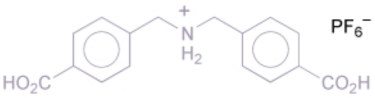
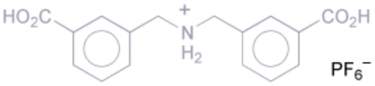
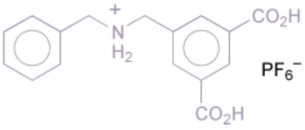
Compound	Structure
4·PF$_6$	
5·PF$_6$	
6·PF$_6$	
7·PF$_6$	

Chart 2 Structures of four carboxylic acid-containing DBA$^+$ derivatives, **4**–**7**·PF$_6$.

a [2]pseudorotaxane was formed in the solid state, accompanied by the now familiar combination of N$^+$–H · · · O and C–H · · · O hydrogen bonds, with, in some cases, supplemental π–π stacking interactions. However, more important was the question—what role do the carboxyl groups play, if any, in orchestrating the overall arrangement of individual 1 : 1 complexes? Let us consider each superstructure in turn, focusing in particular upon the inter-[2]pseudorotaxane interactions arising from the presence of the carboxylic acid groups.

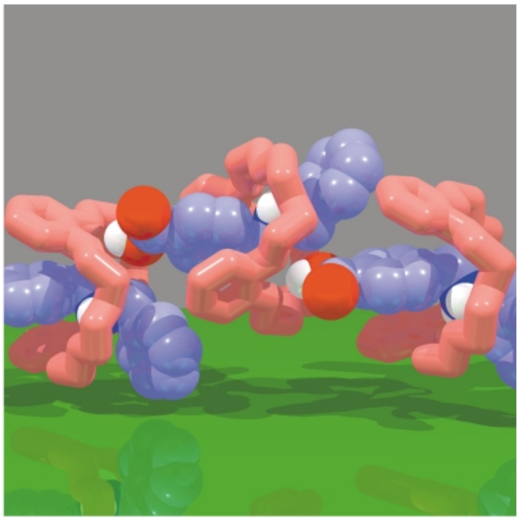


Fig. 8 An infinite linear daisy-chain-like array of [DB24C8·**4**]$^+$ is formed as a result of hydrogen bonding between the carboxylic acid of one thread and the crown ether component of a neighbouring [2]pseudorotaxane.

The X-ray crystallographic analysis of the 1 : 1 complex formed between DB24C8 and **4**·PF$_6$ confirmed (Fig. 7) that the **4**$^+$ cation is, as expected, threaded through the cavity of the DB24C8 macrocycle, affording the [2]pseudorotaxane [DB24C8·**4**][PF$_6$]. Further investigations revealed (Fig. 8) that the individual 1 : 1 complexes are linked in a head-to-tail fashion, resulting in a supramolecular architecture that is somewhat reminiscent of a linear daisy chain[39,40] array. This extended superstructure arises as a consequence of the formation of bifurcated hydrogen bonds between the hydrogen atom of the carboxylic acid group present in **4**$^+$, and both of the oxygen atoms of one of the catechol rings in the DB24C8 component of a neighbouring [2]pseudorotaxane. Therefore, the formation of carboxyl dimers is, in this particular example, not a favourable process. The observations made on this superstructure highlight a very important point, reminding us that we still have a very long way to go in understanding the factors that affect solid-state organisation. As we had predicted, the NH$_2^+$ centre finds itself encircled by a DB24C8 macrocycle. However, we may have reasonably expected that subsequent head-to-head dimerisation of these carboxyl-substituted [2]pseudorotaxanes—*via* the carboxyl dimer—would afford discrete four component supermolecules, possessing a [3]-pseudorotaxane-like structure. However, it is now apparent that the propensity for carboxyl dimer formation is influenced dramatically by the environment surrounding the carboxylic acid groups. In this superstructure, a head-to-head dimerisation would result in the close contact of the DB24C8 rings in adjacent 1 : 1 complexes. This steric clash counters any enthalpic gain from carboxyl dimer formation, forcing the system to adopt an alternative low energy arrangement—namely a head-to-tail linked array. Such subtle effects are difficult to foresee. Our next example serves to reinforce this point.

A logical extension of this project involved attaching one CO$_2$H group to *each* of the phenyl rings of the DBA$^+$ ion, resulting in **5**·PF$_6$. A reasonable expectation—one that arises from such a disposition of carboxyl groups about the DBA$^+$ framework—is the formation of a carboxyl dimer-linked tape of **5**$^+$ cations, in which each NH$_2^+$ centre is encircled by a DB24C8 macrocycle. Subsequent X-ray crystallographic analysis of the 1 : 1 complex formed between DB24C8 and **5**·PF$_6$ confirmed (Fig. 9) that the **5**$^+$ cation is indeed threaded through the cavity of the DB24C8 macrocycle, affording the [2]pseudorotaxane [DB24C8·**5**][PF$_6$]. However, instead of the extended superstructure proposed above, the [2]pseudorotaxanes are observed (Fig. 10) to dimerise *via* π–π stacking interactions. Further propagation of this dimeric superstructure *via* carboxyl dimer formation—between the 'free' carboxyl groups at the termini—is precluded by virtue of the formation of O–H · · · O hydrogen bonds between the carboxylic acid proton and the carbonyl oxygen atom of included acetone molecules. Once again, the system conspires to produce a superstructure in which the anticipated carboxyl dimer supramolecular synthon is absent! Once more, the interaction, that is perhaps—on paper at least—the most obvious, is superseded by other significant noncovalent forces. At the risk of anthropomorphising these

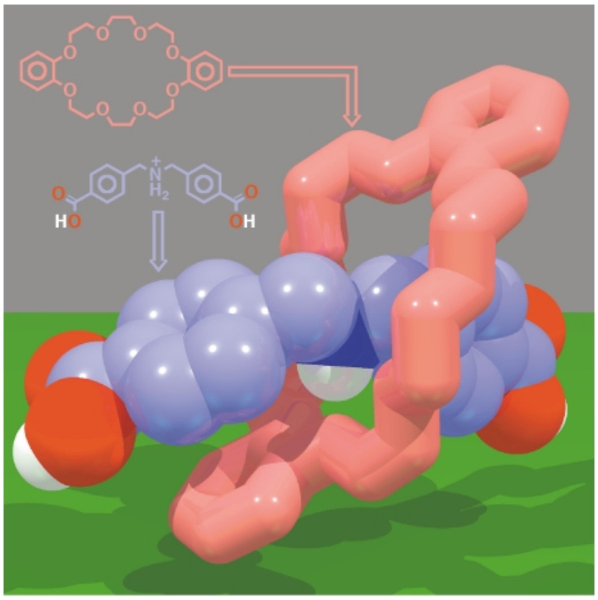


Fig. 9 The solid-state superstructure of the [2]pseudorotaxane [DB24C8·**5**]$^+$ formed between the bis(*para*-carboxylic acid)-substituted DBA$^+$ cation **5**$^+$ and DB24C8.

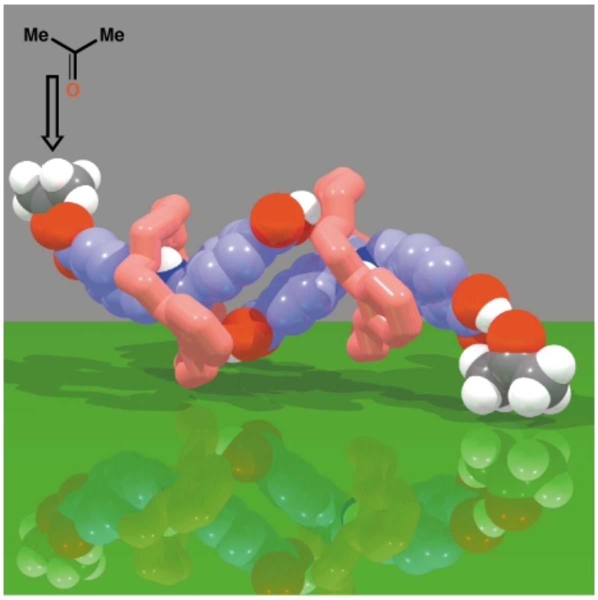


Fig. 10 Despite the formation of a carboxylic acid dimer between individual [2]pseudorotaxanes, the possibility of an infinite hydrogen bonded polymer is negated by the formation of hydrogen bonds from the terminal carboxylic acid protons to included acetone molecules in the solid-state superstructure of [DB24C8·**5**]$^+$.

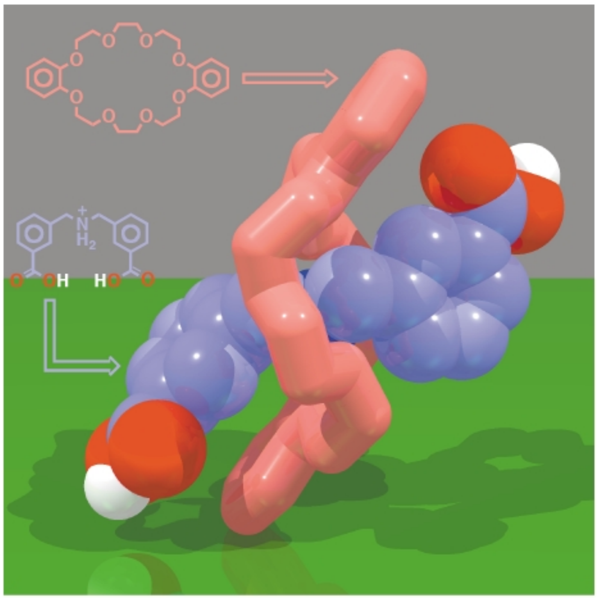


Fig. 11 The solid-state superstructure of the [2]pseudorotaxane [DB24C8·**6**]$^+$ formed between the bis(*meta*-carboxylic acid)-substituted DBA$^+$ cation **6**$^+$ and DB24C8.

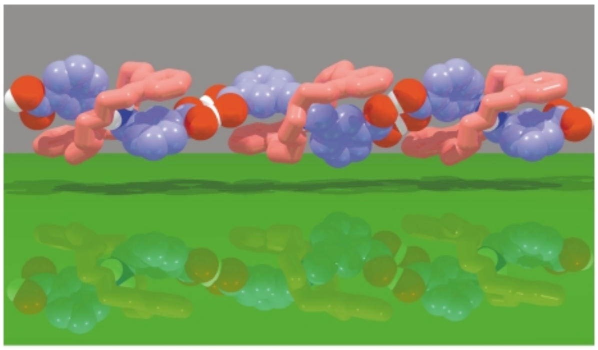


Fig. 12 The X-ray crystallographic analysis of [DB24C8·**6**][PF$_6$] reveals the formation—in the solid state—of a carboxyl-dimer-linked main chain pseudopolyrotaxane.

molecules, we can imagine that, given a choice, the building blocks will always choose to assemble into a minimum energy structure. Although we are able to tempt the building blocks into using one type of intermolecular interaction in preference to another—simply by incorporating the appropriate recognition motifs—only the building blocks themselves will know what the best *overall* combination of these stabilising forces is. Unfortunately, one of the fundamental problems associated with crystal engineering is that each type of noncovalent interaction is essentially considered in isolation. Undaunted, nonetheless, we were interested in studying more analogues of this system in order to gain a greater understanding of the factors at work.

In our next investigation, we focused upon the *meta*, *meta* analogue of **5**·PF$_6$, namely **6**·PF$_6$. Since directionality is an important consideration when studying the carboxyl dimer, we decided to examine the effect of this change in substitution pattern. The X-ray crystallographic analysis of the 1:1 complex formed between DB24C8 and **6**·PF$_6$ revealed (Fig. 11) that the **6**$^+$ cation is again, as expected, threaded through the cavity of the DB24C8 macrocycle, affording the [2]pseudorotaxane [DB24C8·**6**][PF$_6$]. To our delight, for the first time in this series, we observed the formation of carboxylic acid dimers. The [2]pseudorotaxanes are linked together by virtue of carboxyl dimer formation, affording (Fig. 12) an infinite one-dimensional main-chain pseudopolyrotaxane.[41] In this case, it appears that the conditions for the formation of carboxyl dimers are favourable. Specifically, the conformation of the DB24C8 macrocycle allows the linking of 1:1 complexes, in this fashion, without inducing any steric congestion of their catechol units, and, although acetone solvent molecules are present in the crystal lattice, they play no role in determining the extended superstructure. Therefore, it is possible to merge successfully different modes of molecular recognition in order to generate large, architecturally complex superstructures. Unfortunately, we have little control over the *self*-assembly[18] process, since our influence ends with the design and synthesis of the monomers. The best laid plans often do not work out. We can do little more than to suggest a way in which the building blocks—the meccano—should organise themselves, and then see what happens. There are usually many subtle factors at work that are difficult, if not impossible, to compensate for within a system. This sentiment is best expressed with two examples—namely (i) why, in some cases, does the crown ether adopt a conformation that makes carboxyl dimer form-

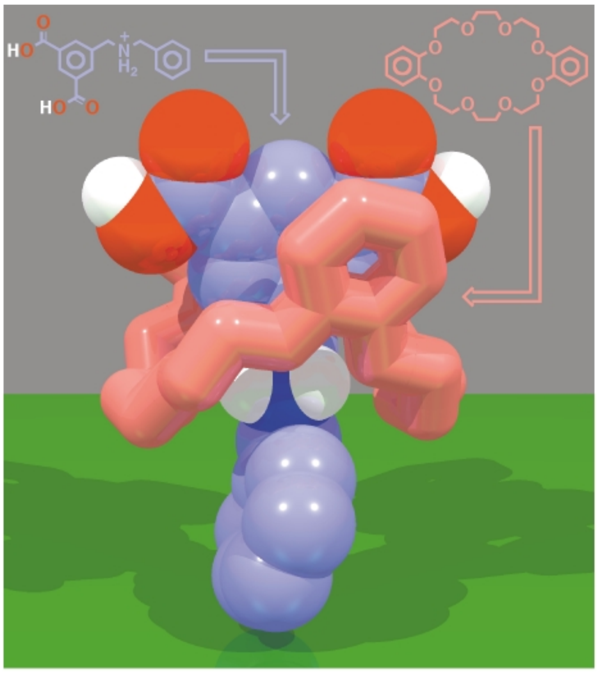


Fig. 13 The solid-state superstructure of the [2]pseudorotaxane $[DB24C8{\cdot}\mathbf{7}]^+$ formed between the isophthalic acid-substituted DBA^+ cation $\mathbf{7}^+$ and DB24C8.

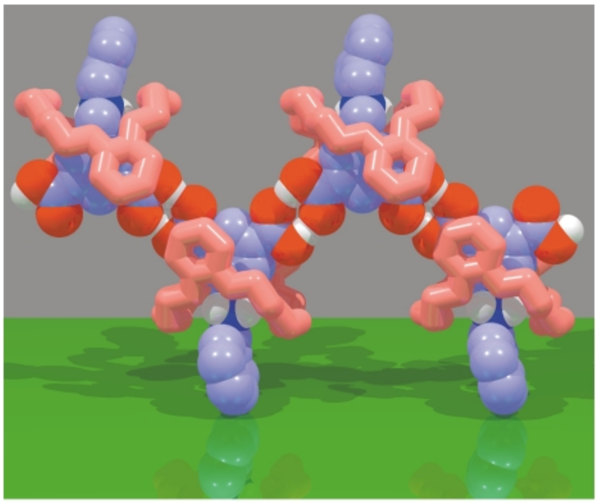


Fig. 14 The side-chain pseudopolyrotaxane formed as a result of carboxylic acid dimerisation in the extended superstructure of $[DB24C8{\cdot}\mathbf{7}]^+$.

ation unfavourable, *i.e.*, what does the system have to gain, and (ii) how do we know when solvent of crystallisation will play a key role in determining the extended superstructure? These comments aside, the cause is not lost. If we are prepared to accept that the discipline of crystal engineering is—at this time at least—not an exact science, it is easy to see how it offers us a set of guidelines with respect to solid-state design. With this caveat in mind, we continued our exploration in this field, by asking ourselves the question—what would be the effect of placing the two CO_2H groups on the same phenyl ring of the DBA^+ cation, as in $\mathbf{7}{\cdot}PF_6$?

Subsequently, the X-ray crystallographic analysis of the 1 : 1 complex formed between DB24C8 and $\mathbf{7}{\cdot}PF_6$ revealed (Fig. 13) that the $\mathbf{7}^+$ cation is, as expected, threaded through the cavity of the DB24C8 macrocycle, affording the [2]pseudorotaxane $[DB24C8{\cdot}\mathbf{7}][PF_6]$. Furthermore, the packing of the 1 : 1 complexes reveals the formation (Fig. 14) of a side-chain[41] pseudopolyrotaxane in which the adjacent [2]pseudorotaxane units are linked by virtue of carboxyl dimer formation, much as they are in $[DB24C8{\cdot}\mathbf{6}][PF_6]$. In summary, we have demonstrated the feasibility of combining different molecular recognition motifs, *i.e.*, supramolecular synthons, for the construction of highly-ordered interwoven networks in the solid state. The $R_2NH_2^+$/crown ether recognition appears, so far, to be general, and persists despite the changes made elsewhere in the building blocks. In contrast, the carboxylic acid dimer is *not* always formed. Initially, perhaps, this result is a little surprising. However, once we cast aside our naïve expectations, it is easy to appreciate that many subtle factors can contribute to the formation of the observed crystalline superstructure.

Changing the rings and ringing the changes

The recognition expressed between DB24C8 and $R_2NH_2^+$ ions has been exploited in the construction of many supramolecular and molecular systems—not just those highlighted so far. Not only have we generated many interwoven complexes as a result of *supramolecular synthesis*,[10] but we have also employed the concept of *supramolecular assistance*[10] *to covalent synthesis* in the creation of interlocked molecules.[20,21] Consequently, there are many examples of $R_2NH_2^+$/DB24C8-based rotaxanes[26,42] including, most recently, two examples[43] of molecular shuttles. So far, we have just considered one particular crown ether—namely DB24C8. However, if we wish to create a molecular meccano set capable of generating a diverse range of ‘structures’, this singular selection of macrocyclic component is somewhat limiting. Consequently, the following sections will describe the consequences—to $R_2NH_2^+$ ion/crown ether recognition—of (i) changing the groups appended to the basic [24]crown-8 framework and (ii) expanding the size of the macrocyclic ring.

Tetrabenzo[24]crown-8 (TB24C8)

As part of our ongoing investigations, we were interested in what the consequences[44] (Chart 3) would be of either adding, or removing, aromatic units from the [24]crown-8 skeleton present in DB24C8. Removal of one aromatic ring affords benzo[24]crown-8 (B24C8) while removal of both results in the wholly aliphatic compound [24]crown-8 (24C8). On the other hand, the addition of two aromatic rings results[45] in tetrabenzo[24]crown-8 (TB24C8), a crown ether in which all eight oxygen atoms are of the less basic phenolic type. The two former compounds—namely B24C8 and 24C8—were observed to thread onto NH_2^+ ion-containing molecules affording pseudorotaxanes in direct analogy with the behaviour observed for DB24C8. Although, in these cases, no solid-state structures could be obtained, there was overwhelming solution and gas-phase evidence supporting the threading process. However, in contrast with these two well-behaved [24]crown-8-derived macrocycles, TB24C8 seemed to have no desire to include within its macrocyclic cavity an $R_2NH_2^+$ ion, at least as evidenced by both solution-state studies (^1H NMR spectroscopy) and gas-phase investigations (FABMS). Initially, this conclusion was reinforced by solid-state studies[46] of crystals grown from solutions containing equimolar quantities of TB24C8 and $DBA{\cdot}PF_6$.

X-Ray analysis of crystals obtained from an $MeCN/Et_2O$ solution revealed[47] the formation of a TB24C8 bis(MeCN) clathrate (Fig. 15), whereas crystals grown from a $CHCl_3/Et_2O$ were shown[48] to consist of ‘free’ TB24C8 molecules (Fig. 16). In each case, despite markedly different crown ether conformations, extended superstructures are formed in which adjacent TB24C8 molecules are linked *via* networks of $C–H \cdots \pi$ interactions.[14] However, perhaps the most important aspect of these two structures is the absence of $DBA{\cdot}PF_6$—*i.e.*, in each case, the crown ether prefers to crystallise alone or with solvent. Therefore, all of our efforts seemed to indicate that the $TB24C8/DBA^+$ interaction is very weak. Consequently, results[49] of the X-ray structural analysis of a third set of

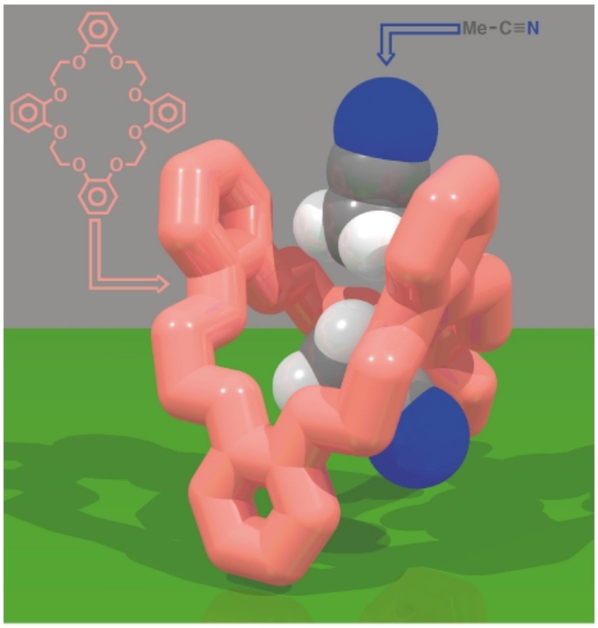


Fig. 15 When grown from a MeCN/Et_2O solution, crystals of TB24C8 can be seen to contain enclathrated acetonitrile molecules.

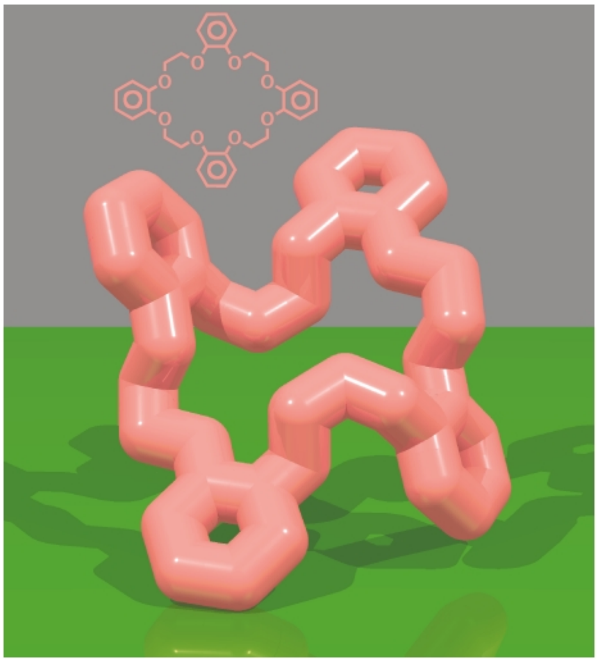


Fig. 16 In the absence of MeCN, the crown ether TB24C8 crystallises without ordered solvent molecules.

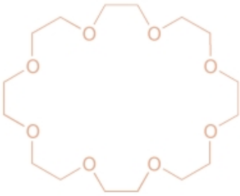
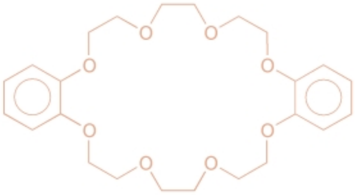
Compound	Structure
24C8	
B24C8	
DB24C8	
TB24C8	

Chart 3 Additional benzo groups can be grafted onto a [24]crown-8 framework, producing benzo-, dibenzo-, and tetrabenzo-[24]crown-8—B24C8, DB24C8, and TB24C8, respectively.

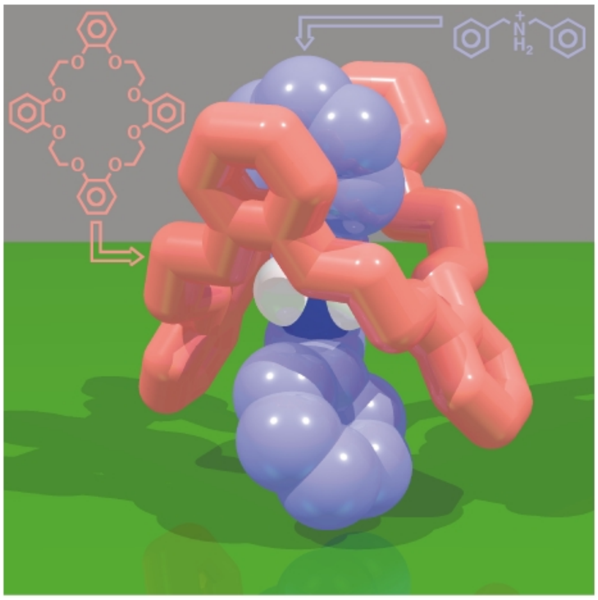


Fig. 17 One of the four crystallographically independent superstructures with a [2]pseudorotaxane geometry observed in the X-ray analysis of [TB24C8·DBA][PF_6].

crystalline material—this time grown from a 1 : 1 mixture of the components in $CHCl_3$/MeCN/n-C_6H_{14} solution—were greeted with a certain degree of surprise. This structure (Fig. 17) not only has a 1 : 1 stoichiometry of TB24C8 and DBA·PF_6, but the DBA^+ cation is indeed threaded through the macrocyclic cavity of the crown ether, affording a [2]pseudorotaxane [TB24C8·DBA][PF_6], that is held together by N^+–H · · · O and C–H · · · O hydrogen bonds, with a supplemental π–π stacking interaction also contributing. In effect, the same interactions that govern the threading of a DBA^+ cation through a DB24C8 macroring are at work here. However, the most striking feature associated with the crystal superstructure (Fig. 18) of [TB24C8·DBA][PF_6] concerns the PF_6^- anions. The 1 : 1 complexes (there are four independent [2]pseudorotaxanes in the asymmetric unit) are organised around a matrix of highly-ordered PF_6^- anions, which appear to stabilise the crystal lattice *via* a myriad of C–H · · · F hydrogen bonding interactions.[50] Presumably, the unusual lack of disorder in these anions reflects their role in directing the kinetic assembly of this particular superstructure in the solid state. Therefore, although the threading of a DBA^+ cation through the cavity of a TB24C8 macrocycle is, in solution, not a thermodynamically favoured process, the act of crystallisation—an inherently kinetic event—favours, in the

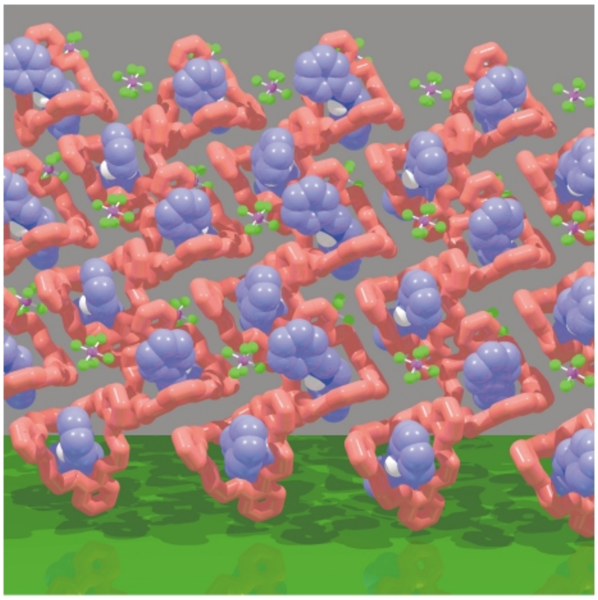


Fig. 18 The extensively C–H · · · F hydrogen bond-stabilised extended superstructure of the complex [TB24C8·DBA][PF_6].

presence of PF_6^- anions, the formation of [2]pseudorotaxanes. This example is the first of many we shall encounter in this Perspective which highlight the pivotal role that PF_6^- anions can play in the solid-state synthesis of interwoven supramolecular arrays.

Benzo(*meta*-phenylene)[25]crown-8 (BMP25C8)

Although the $R_2NH_2^+$ ion/DB24C8 recognition motif has turned out to be particularly effective for the construction of interwoven arrays and interlocked molecules, it is not without its problems. Functionalisation of the aromatic rings of DB24C8 renders the faces of such a substituted macrocycle enantiotopic. Consequently, the threading of an unsymmetrical NH_2^+-containing ion through the cavity of such a crown ether leads to the formation of diastereoisomeric complexes. Therefore, if we desire a system that is rich in interlocked/interwoven motifs, it is possible that a mixture of stereoisomeric complexes may be formed. However, replacing one of the catechol rings of DB24C8 with a resorcinol ring alleviates this problem since substitution at the 5-position of the resorcinol ring does not desymmetrise the molecule. Obviously, however, this strategy[51] is only worthwhile if such a modification does not reduce the macrocycle's propensity for binding $R_2NH_2^+$ ions.

Our investigations[51] into the solid-state superstructure of a 1:1 complex formed between BMP25C8 and DBA·PF_6 revealed (Fig. 19) the formation of a [2]pseudorotaxane [BMP25C8·DBA][PF_6]. The DBA^+ cation is threaded through the cavity of the BMP25C8 macroring, and the complex is stabilised as a result of N^+–H · · · O hydrogen bonding—there are no short C–H · · · O contacts present in this superstructure. In addition, there is a supplemental π–π stacking interaction observed between the thread and crown ether components. Individual [2]pseudorotaxanes are organised into sheets (Fig. 20) as a consequence of inter-complex π–π and C–H · · · π interactions. We have thus demonstrated that this relatively small change in crown ether constitution does not preclude the formation of threaded complexes. Consequently, we note that the molecular meccano kit is slowly expanding. In an effort to characterise, as fully as possible, all of the building blocks in the meccano set, the X-ray crystal structure of 'free' BMP25C8 was also determined (Fig. 21), revealing the formation (Fig. 22) of a constricted nanotube in which the molecules stack one on top of the other. The primary interactions governing this assembly are C–H · · · π hydrogen bonds—originating from the phenoxymethylene hydrogen atoms of both the resorcinol and catechol rings—which are supplemented, to a lesser degree, by partial overlap of both the catechol and resorcinol rings of adjacent molecules within the stack.

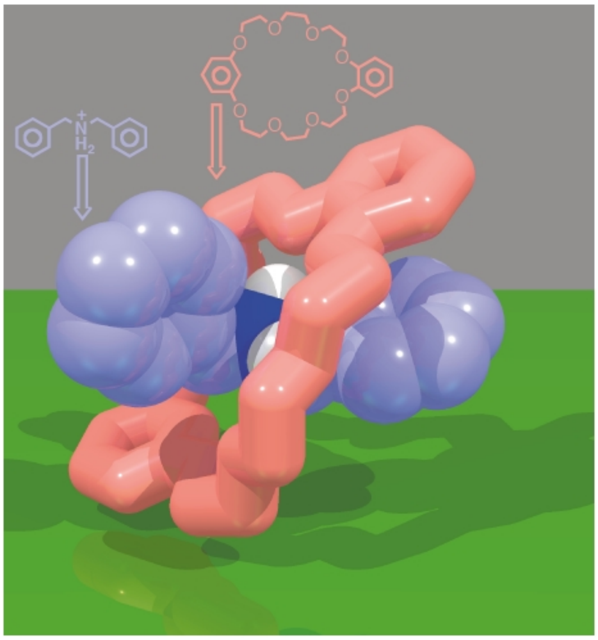


Fig. 19 The solid-state superstructure of the [2]pseudorotaxane [BMP25C8·DBA]$^+$ formed between the DBA^+ cation and BMP25C8.

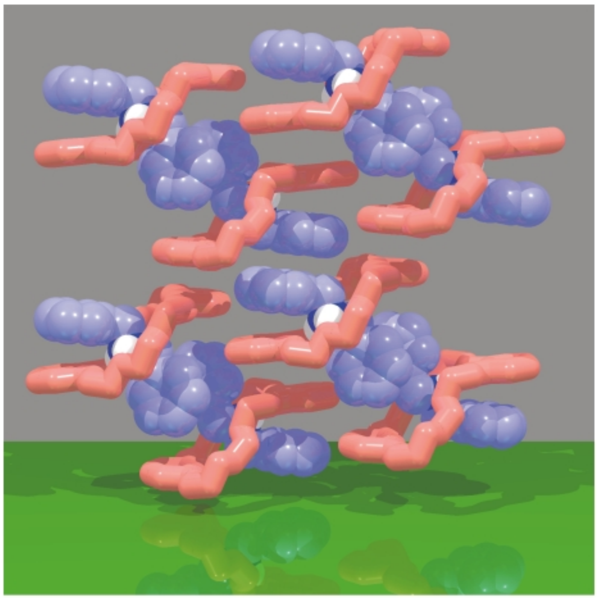


Fig. 20 Discrete [BMP25C8·DBA]$^+$ supermolecules are linked in the solid state to form extended sheets.

Tribenzo[27]crown-9 (TB27C9)

When one starts to think of creating higher-order supramolecular architectures, it becomes apparent that the potential for modification of both the thread and crown ether components is desirable. We have already discussed the placement of additional recognition sites at the termini of the $R_2NH_2^+$ ions. Recall the use of CO_2H groups, which resulted in the formation of interesting extended superstructures. Ultimately, the functionalisation of the crown ether components is a realistic goal. However, placing substituents on the aromatic rings of the DB24C8 macrocycle only presents us with the opportunity of disposing functional groups 180° apart.

With the goal of expanding the molecular meccano kit even further, we decided to investigate[52] a crown ether with three-fold symmetry, namely tribenzo[27]crown-9 (TB27C9), which—

Fig. 21 The solid-state structure of BMP25C8.

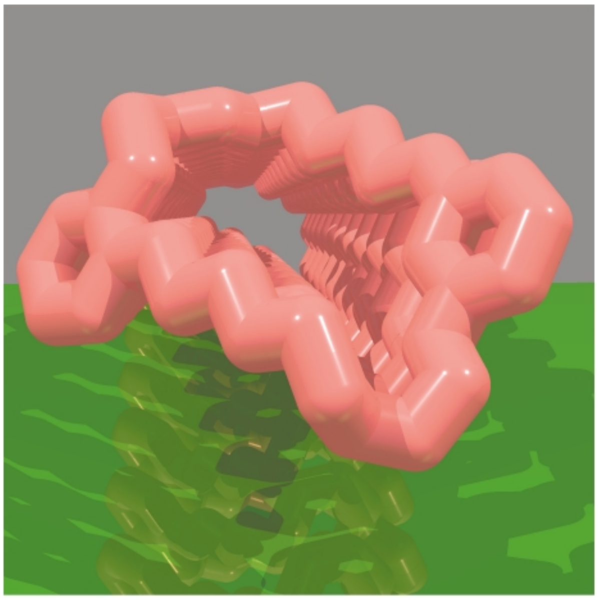


Fig. 22 Constricted nanotubes—stabilised by intermolecular C–H···O hydrogen bonds—are formed by the stacking of BMP25C8 molecules in the solid state.

in the fullness of time—should allow us to present additional recognition sites at 120° angles. The X-ray crystallographic analysis of the solid-state superstructure of a 1:1 complex formed between TB27C9 and (p-$CO_2Me)_2$-DBA·PF_6 revealed (Fig. 23) the formation of a [2]pseudorotaxane [TB27C9·(p-$CO_2Me)_2$-DBA][PF_6]. The $R_2NH_2^+$ ion is threaded through the cavity of the TB27C9 macroring and the complex is stabilised by N^+–H···O hydrogen bonding. Although there are no short C–H···O contacts observed in this superstructure, a supplemental π–π stacking interaction is observed between the thread and crown ether components. Additionally, probing of the inter-[2]pseudorotaxane interactions (Fig. 24) revealed the formation of C–H···π-linked sheets. Therefore, we can now entertain the possibility of creating interwoven $R_2NH_2^+$ ion-based superstructures, utilising a variety of crown ethers, not only those with [24]crown-8 constitutions, but also those involving [25]crown-8 and [27]crown-9 macrorings. Thus, as the molecular meccano kit grows, we can envisage the mixing and matching of crown ethers with $R_2NH_2^+$ ions in an effort to influence the assembly of the final superstructure. Each building block—with its own distinctive particular attributes—can be chosen with the intention of directing higher order superstructure in a deliberate manner.

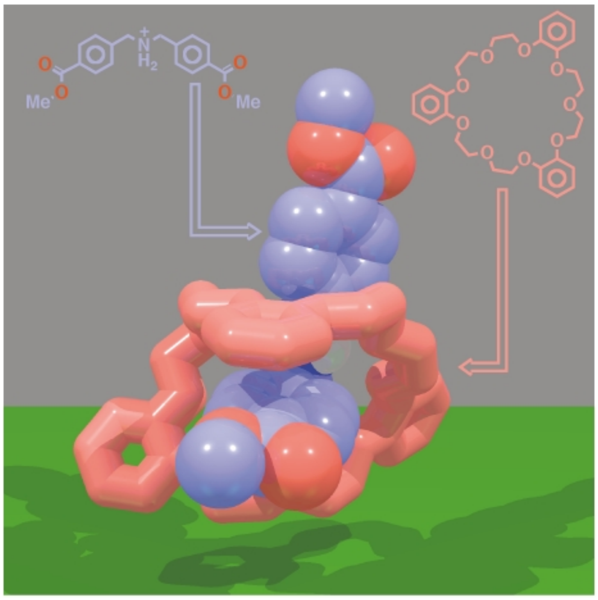


Fig. 23 The solid-state superstructure of the [2]pseudorotaxane [TB27C9·(p-$CO_2Me)_2$-DBA]$^+$ formed between the p-CO_2Me-disubstituted DBA^+ cation and TB27C9.

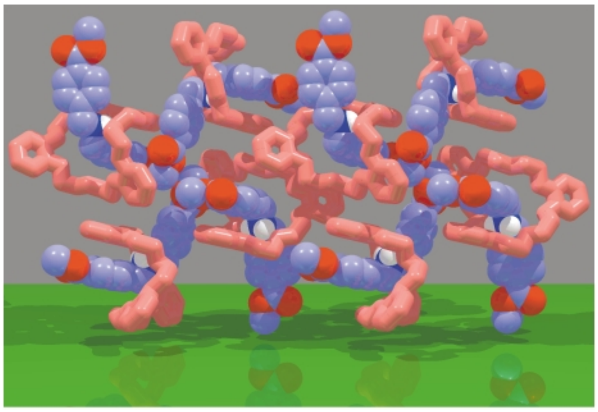


Fig. 24 The extended superstructure of [TB27C9·(p-$CO_2Me)_2$-DBA][PF_6] consists of extended sheets that are stabilised by inter-[2]pseudorotaxane C–H···π hydrogen bonds.

Bis(*para*-phenylene)[34]crown-10 (BPP34C10)

Upon further expansion of the cavity size of a crown ether to 34 atoms, as in bis(*para*-phenylene)[34]crown-10 (BPP34C10), we observe[30,32] the threading of two DBA^+ cations through the macrocyclic polyether. In this particular ditopic crown ether, the two polyether loops are separated to such an extent that each arc can satisfy the hydrogen bonding requirements of a DBA^+ cation. The X-ray crystallographic analysis of the solid-state superstructure of a 1:2 complex formed between BPP34C10 and DBA·PF_6 reveals (Fig. 25) the formation of a *double-stranded* [3]pseudorotaxane [BPP34C10·$(DBA)_2$][2PF_6]. Two DBA^+ ions are threaded simultaneously through the cavity of the BPP34C10 macroring and the complex is stabilised principally by N^+–H···O hydrogen bonding. Although there are no short C–H···O contacts observed in this superstructure, additional stabilisation arises from the formation of edge-to-face aromatic interactions (C–H···π bonds) between one phenyl ring in each DBA^+ cation and the hydroquinone rings of the macrocycle. This result was an exciting one, because we realised we were faced with the prospect of being able to perform the first true mix-and-match experiment.

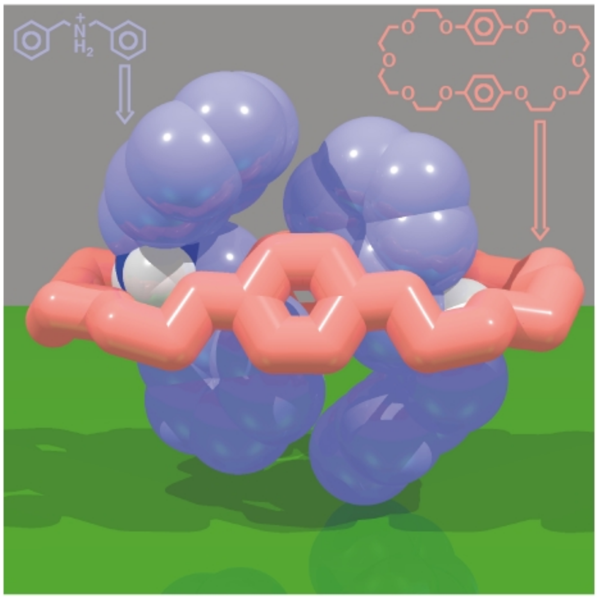


Fig. 25 The solid-state superstructure of a *double-stranded* [3]pseudorotaxane [BPP34C10·(DBA)$_2$]$^{2+}$ formed between BPP34C10 and DBA·PF$_6$.

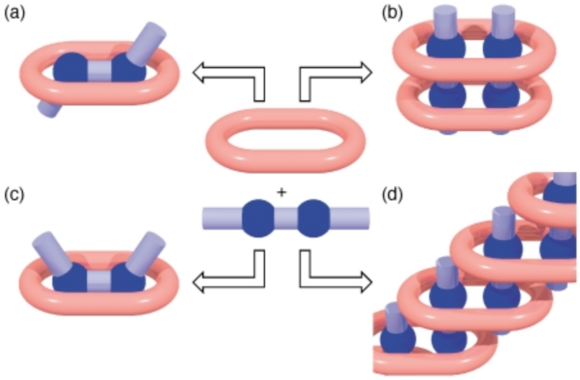


Fig. 26 Conceivably, there are four possible distinct superstructures that may form upon co-crystallisation of BPP34C10 and **1**·2PF$_6$: (a) a *single-threaded, double-docked* [2]pseudorotaxane, (b) a *double-threaded, double-encircled* [4]pseudorotaxane, (c) a face-to-face complex, and (d) a polymer.

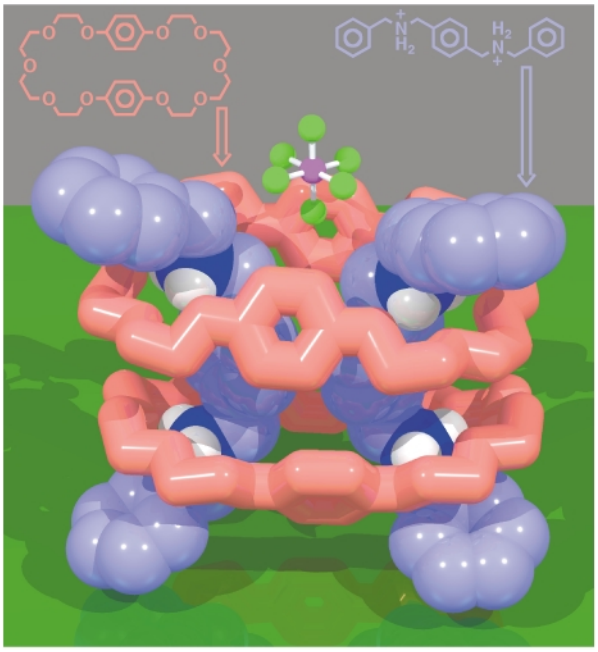


Fig. 27 The solid-state superstructure of the *double-threaded, double-encircled* [4]pseudorotaxane [(BPP34C10)$_2$·(**1**)$_2$]$^{4+}$ formed between BPP34C10 and **1**$^{2+}$.

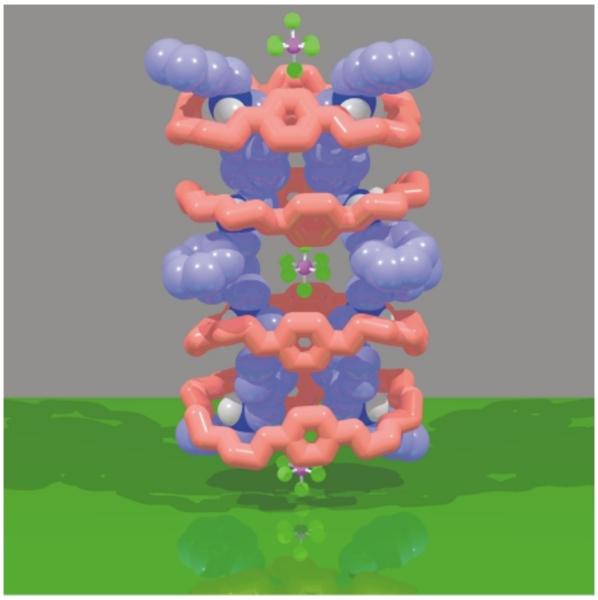


Fig. 28 Individual [2 + 2] superbundles form columns in the solid state. The interstitial PF$_6$$^-$ anions may play some role in the assembly of this infinite one-dimensional array.

In the knowledge that a BPP34C10 macrocycle can accommodate simultaneously two R$_2$NH$_2$$^+$ ions, we posed the following question—what type of superstructure could we form by mixing BPP34C10 with a thread-like molecule containing two NH$_2$$^+$ centres, namely **1**·2PF$_6$? In theory, there are four possible superstructures (Fig. 26) that one could reasonably expect to be formed as a result of satisfying the principle of maximal site occupancy.[53] In practice, the X-ray structural analysis[30] of crystals obtained from an Me$_2$CO/*n*-C$_5$H$_{12}$ solution, containing a 1:1 mixture of BPP34C10 and **1**·2PF$_6$, revealed (Fig. 27) the formation of the *double-encircled*, *double-stranded* four component superstructure [(BPP34C10)$_2$·(**1**)$_2$][4PF$_6$]. Each 2:2 complex is stabilised as a result of the formation of fourteen hydrogen bonding interactions—ten N$^+$–H···O and four C–H···O close contacts are observed. A closer examination of the solid-state superstructure revealed the presence of highly ordered PF$_6$$^-$ anions situated at the termini of this supramolecular bundle. These PF$_6$$^-$ anions enter into C–H···F hydrogen bonding interactions[50] with the two adjacent 2:2 complexes and may be responsible for the formation (Fig. 28) of the one-dimensional array that propagates throughout the crystal lattice. So yet again, we see a clear indication that the counterions associated with the R$_2$NH$_2$$^+$ cations can influence, in some manner, the solid-state assembly of their interwoven superstructures with crown ethers. In essence, this section demonstrates our ability to tie together two NH$_2$$^+$ centres by encircling them with BPP34C10. Next, we set about exploiting this new-found paradigm for the construction of other, more elaborate, interwoven supramolecular bundles.

Supramolecular bundles

The logical, incremental approach adopted in this study had so far served us well. From crown ethers that only accommodate *one* NH$_2$$^+$ centre, we have moved onto those that will welcome *two* at once. Furthermore, the knowledge that *one* BPP34C10 macrocycle will tie together two *mono*cations led us to the discovery that *two* BPP34C10 molecules will tie together two *di*cations. From these observations we can deduce a simple algorithm that correlates with the solid-state self-assembly, that is—*n* BPP34C10 macrocycles will—by virtue of their ditopic nature—tie together two cationic species that each contain *n*

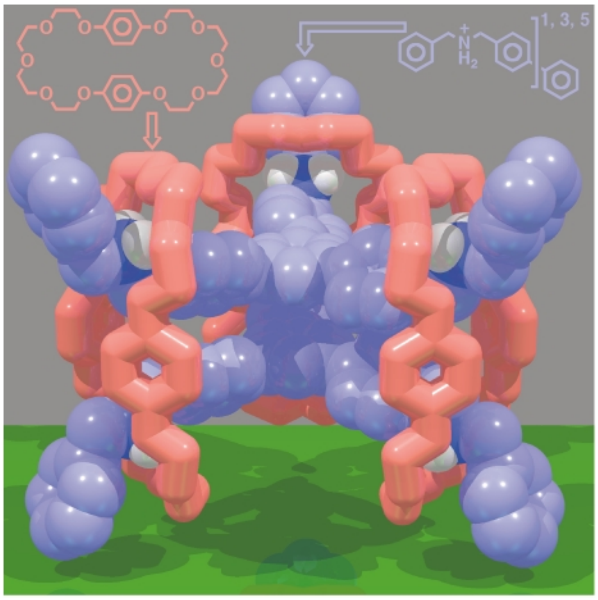


Fig. 29 The solid-state superstructure of the five-component superbundle $[(\text{BPP34C10})_3\cdot(\mathbf{8})_2]^{6+}$ formed between the trifurcated tris(ammonium) cation $\mathbf{8}^{3+}$ and the ditopic crown ether BPP34C10.

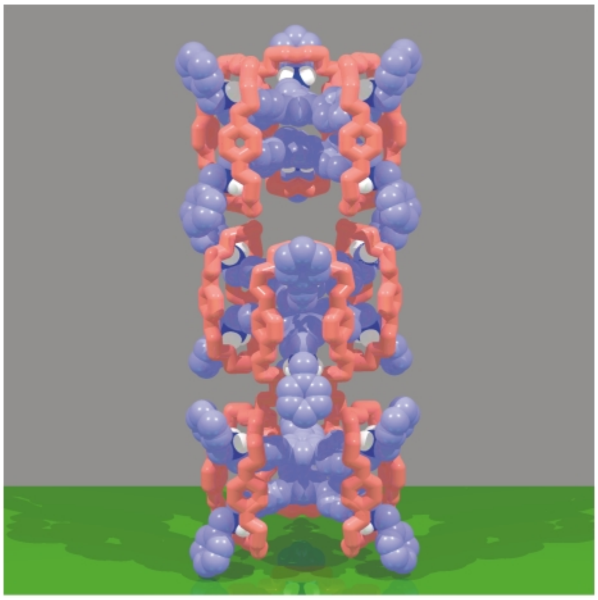


Fig. 30 Interleaved one-dimensional arrays of the five-component superbundle $[(\text{BPP34C10})_3\cdot(\mathbf{8})_2]^{6+}$ are formed in the solid state.

NH_2^+ centres. For example, when BPP34C10 was mixed with the trifurcated tris(ammonium) salt $\mathbf{8}\cdot 3PF_6$, crystals were obtained[54] which were shown (Fig. 29)—by X-ray crystallographic analysis—to consist of the five-component superbundle in which *three* BPP34C10 macrocycles tie together *two* trifurcated tris(cations). This superstructure is stabilised by the now customary N^+–H···O hydrogen bonding interactions; no close C–H···O contacts are observed. The mean interplanar separation of the two 1,3,5-triarylbenzene rings is approximately 4 Å and does not, therefore, represent a significant π–π interaction. Adjacent superbundles are rotated by 60° with respect to each other, and form (Fig. 30) an interleaved one-dimensional array. The self-assembly of this [3 + 2] superbundle is remarkable in that this architecture is just one of many superstructures that could possibly be formed. However, this discrete—or closed—assembly not only satisfies the maximal site occupancy principle,[53] but it is also favoured on entropic grounds. The formation of a porous, three-dimensional, supramolecular array—in which each BPP34C10 ring links an $\mathbf{8}^{3+}$ cation to three different $\mathbf{8}^{3+}$ cations—is also conceivable. However, such a process would be commensurate with a considerable loss of entropy, much more so than upon assembly of discrete [3 + 2] superbundles.

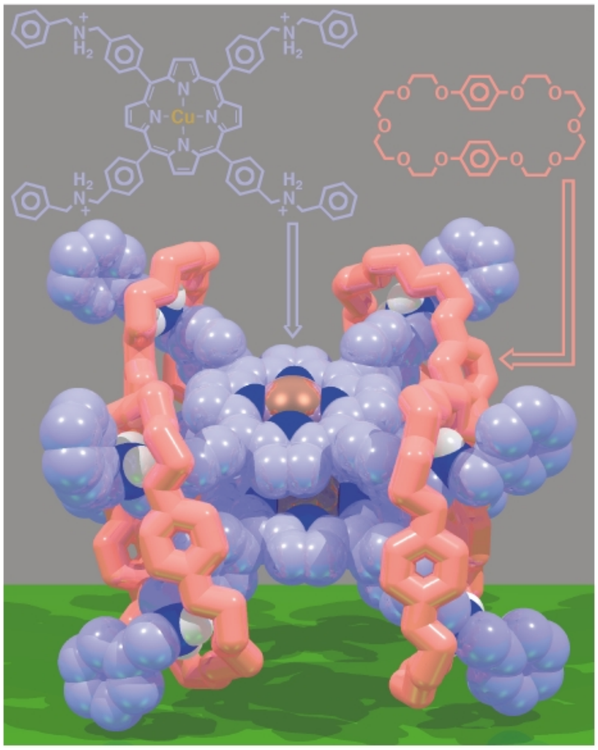


Fig. 31 Co-crystallisation of BPP34C10 and $\mathbf{9}\cdot 4PF_6$ affords a six-component superbundle that is a supramolecular analogue of the photosynthetic special pair.

Using the now-established protocol, we next synthesised[55] noncovalently a supramolecular analogue[56] of the photosynthetic special pair.[57] Conceptually, this task simply involved the extrapolation of the self-assembly algorithm from [2 + 2] and [3 + 2] superbundles to a [4 + 2] superbundle. We anticipated that, by appending four DBA^+ ion-containing side chains onto a porphyrin core, we would observe a superstructure in which two of these tetrafurcated tetrakis(cations) would be tied together by four BPP34C10 macrocycles. This interwoven six-component architecture would require the co-facial stacking of the two porphyrin nuclei much like that observed in the case of the special pair located in the photosynthetic reaction centre. Indeed, the X-ray crystallographic analysis of the 4:2 complex—formed between BPP34C10 and $\mathbf{9}\cdot 4PF_6$—revealed (Fig. 31) the formation of the desired [4 + 2] superbundle, validating our design strategy. The bundle is once again stabilised by the usual N^+–H···O and C–H···O hydrogen bonding interactions, in addition to a π–π stacking interaction between the porphyrin nuclei (mean interplanar separation = 3.65 Å). The relative dispositions of the porphyrin nuclei—similar to those observed in the photosynthetic reaction centre—involve a sheared relationship in which the copper atoms are offset laterally by 3.05 Å and the Cu···Cu separation is 4.76 Å. The assembly of the six-component superbundle also occurs in solution as detected by EPR spectroscopy. In the absence of BPP34C10, EPR spectroscopy reveals that there are no interactions between the porphyrin nuclei. However, upon the addition of two equivalents of BPP34C10 to this solution, electronic coupling of copper centres is observed in the EPR spectrum, indicating the formation of BPP34C10-induced aggregates—presumably the [4 + 2] superbundle.

Mixing and matching

We have proven consistently that two $R_2NH_2^+$ ions will thread simultaneously through the cavity of a BPP34C10 macrocycle.

Fig. 32 In a manner analogous to DBA·PF_6, **4**·PF_6 forms a *double-threaded* [3]pseudorotaxane when co-crystallised with BPP34C10.

We have also shown how the carboxyl dimer—in some cases—can be used to induce long range order in the overall crystalline superstructures. To demonstrate the modular nature of the building blocks in the molecular meccano kit, we decided to investigate[38] the interaction of the carboxylic acid substituted DBA^+ cations—only previously mixed with the monotopic receptor DB24C8—with the ditopic receptor, namely BPP34C10. The X-ray crystallographic analysis of the 1:2 complex, formed between BPP34C10 and **4**·PF_6 revealed (Fig. 32) that, perhaps not surprisingly, *two* of the $\mathbf{4}^+$ cations find themselves encircled by a BPP34C10 macrocycle. The threading occurs in a co-directional manner, resulting in both carboxyl groups pointing in the same direction. This double-stranded [3]pseudorotaxane is stabilised by the formation of $N^+–H\cdots O$ hydrogen bonds—there are no close $C–H\cdots O$ contacts. Interestingly, the PF_6^- anion, once again, appears to play an important role in determining the superstructure. Located in between the cleft—formed by the two unsubstituted phenyl rings of the $R_2NH_2^+$ cations—is one of the fluorine atoms of the anion, from which there appears to be a close contact with a hydrogen atom from one of the threaded cations. Another close contact was observed between one of the other fluorine atoms of the anion and a proton from the hydroquinone ring of BPP34C10. These close contacts may represent $C–H\cdots F$ hydrogen bonding[50] interactions, which, in turn, may dictate the co-directional manner in which the threads align themselves through the centre of the crown ether. Consequently, the formation of an extended, carboxyl dimer-linked, superstructure is precluded as the preferred mode of inter-superstructure interaction is the dimerisation (Fig. 33) of these [3]pseudorotaxanes. This six-component superstructure is highly reminiscent of the double-encircled double-threaded superstructure formed[32] between BPP34C10 and **1**·$2PF_6$. In essence, the carboxyl dimer supramolecular synthon is acting as a surrogate for a *p*-disubstituted phenyl ring.

The X-ray crystallographic analysis of the 1:2 complex formed between BPP34C10 and **10**·PF_6 (the *meta* analogue of **4**·PF_6) revealed (Fig. 34) the formation of a superstructure that is very similar to that observed for $[\text{BPP34C10}\cdot(\mathbf{4})_2]^{2+}$. Once again, the threading of the two cations is co-directional, and appears to result as a consequence of interactions with a similarly located PF_6^- anion. Complex stabilisation is achieved in the same manner as before—namely by $N^+–H\cdots O$ hydrogen bonding, with no close $C–H\cdots O$ contacts observed. Once again, the individual [3]pseudorotaxanes dimerise non-covalently (Fig. 35) by virtue of carboxyl dimer formation. The recurrence of a selective positioning of one of the PF_6^- anions reinforces our belief that the anion plays a role in determining the co-directional manner in which the cations align themselves. In turn, this arrangement results in the carboxyl dimer-linked six-component supermolecules observed in these two examples, demonstrating just how the counterion can affect the overall solid-state superstructure.

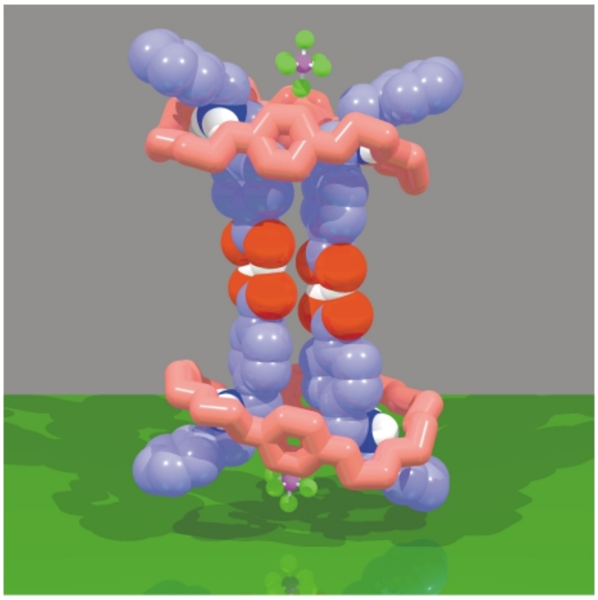


Fig. 33 Individual $[\text{BPP34C10}\cdot(\mathbf{4})_2][2PF_6]$ [3]pseudorotaxanes dimerise in the solid state *via* the formation of carboxylic acid dimers.

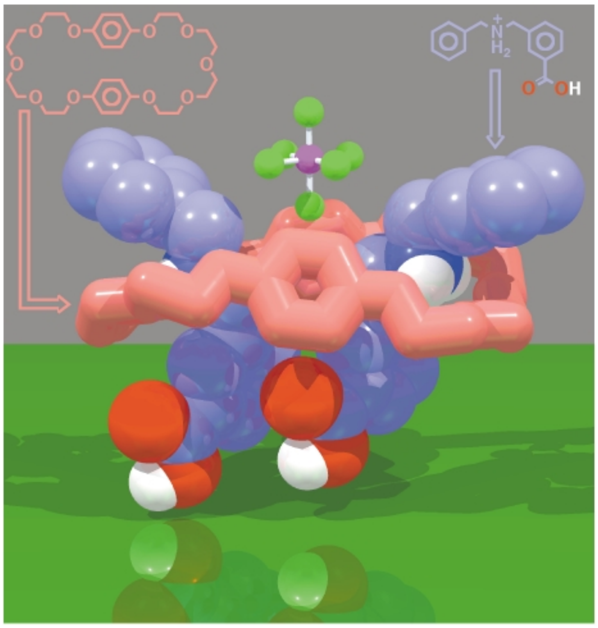


Fig. 34 Similarly to **4**·PF_6, its *meta*-substituted cousin **10**·PF_6 forms a 1:2 complex when co-crystallised with BPP34C10.

In contrast, the X-ray crystallographic analysis of the 1:2 complex formed between BPP34C10 and the isophthalic acid-substituted cation $\mathbf{7}^+$ revealed (Fig. 36) the formation of a double-stranded [3]pseudorotaxane in which the two $\mathbf{7}^+$ cations are threaded *centrosymmetrically* through the crown ether. As we have now come to expect, this three component supermolecule is stabilised as a result of $N^+–H\cdots O$ hydrogen bonding interactions. Apparently, in this case, the PF_6^- anions do not participate actively in the solid-state assembly process, allowing for this head-to-tail threading of the $R_2NH_2^+$ ions. Now that the two carboxyl groups present in each [3]pseudorotaxane are aligned in opposite directions, on opposing sides of the macro-

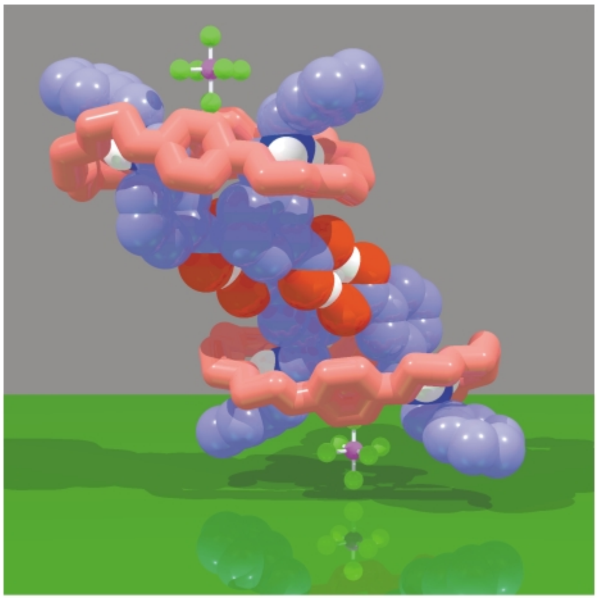


Fig. 35 Discrete [BPP34C10·(**10**)$_2$][2PF$_6$] supermolecules dimerise—in the solid-state—as a result of carboxyl dimer formation.

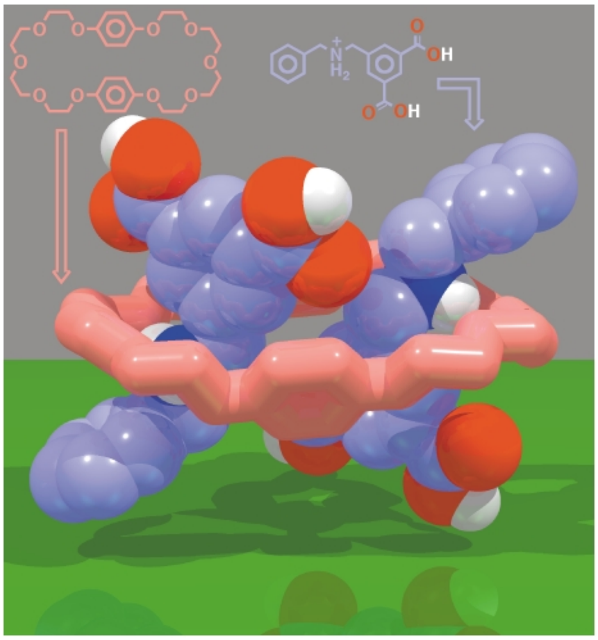


Fig. 36 Two **7**$^+$ cations thread through the cavity of BPP34C10 in a centrosymmetric fashion, resulting in the formation of a [3]pseudorotaxane [BPP34C10·(**7**)$_2$]$^{2+}$ in the solid state.

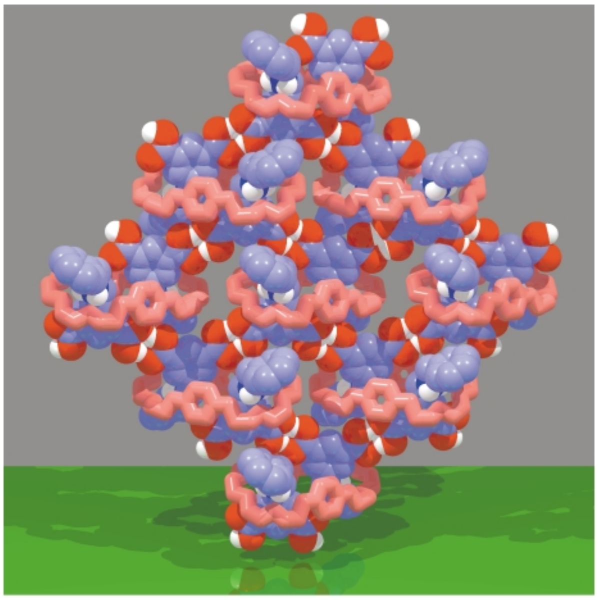


Fig. 37 Analysis of the extended solid-state superstructure adopted by [BPP34C10·(**7**)$_2$]$^{2+}$ reveals the existence of an interwoven cross-linked supramolecular polymer.

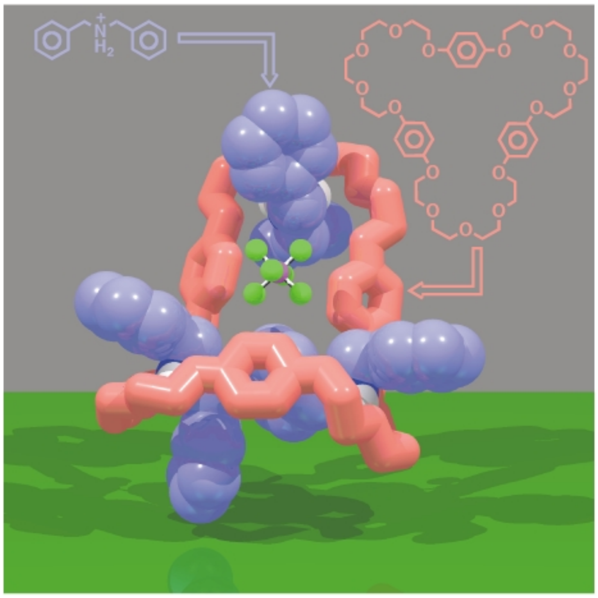


Fig. 38 The extended crown ether TPP51C15 co-crystallises with *three* equivalents of DBA·PF$_6$ to give a *triple-threaded* [4]pseudorotaxane [TPP51C15·(DBA)$_3$]$^{3+}$. Note how a PF$_6$$^-$ anion occupies a cleft in the superstructure.

cycle, discrete dimerisation is precluded. Instead, multiple carboxyl dimer formation results in the formation (Fig. 37) of an interwoven supramolecular cross-linked polymer. We have thus demonstrated that it is possible to mix and match building blocks: the molecular meccano kit is truly modular in design, allowing us to combine orthogonal supramolecular synthons for the fabrication of interwoven superstructures, the architectures of which, to some extent, we can control, by judicious choice of both crown ether and R$_2$NH$_2$$^+$ ion.

How big can we go?

Once we noted that BPP34C10 can, with its two polyether loops, reliably complex with two equivalents of DBA·PF$_6$ or structural analogues thereof, our curiosity was aroused. We decided to examine whether larger macrocyclic polyethers—comprised of more than two polyether loops—could accommodate[33,58] even more R$_2$NH$_2$$^+$ ions within their macrocyclic cavities. Preliminary extraction experiments suggested that the crown ethers tris(*para*-phenylene)[51]crown-15 (TPP51C15) and tetrakis(*para*-phenylene)[68]crown-20 (TPP68C20) were capable of solubilising, in CD$_2$Cl$_2$, three and four equivalents of DBA·PF$_6$, respectively. Subsequent X-ray crystallographic analysis of the 1:3 complex formed between TPP51C15 and DBA·PF$_6$ revealed (Fig. 38) the formation of a *triple-stranded* [4]pseudorotaxane, in which each DBA$^+$ cation nestles into one of the three polyether loops present in the crown ether's framework. Stabilisation of this four-component supermolecule arises as a consequence of both N$^+$–H···O and C–H···O hydrogen bonding interactions. Upon closer investigation, it was discovered that, yet again, the PF$_6$$^-$ anion plays a prominent role in the solid-state superstructure. One of the three PF$_6$$^-$ anions is located almost centrally within a cleft present in the [TPP51C15·(DBA)$_3$]$^{3+}$ supermolecule. This anion can be considered to be 'complexed' by the [4]pseudorotaxane *via* a series of C–H···F hydrogen bonding interactions to hydrogen atoms

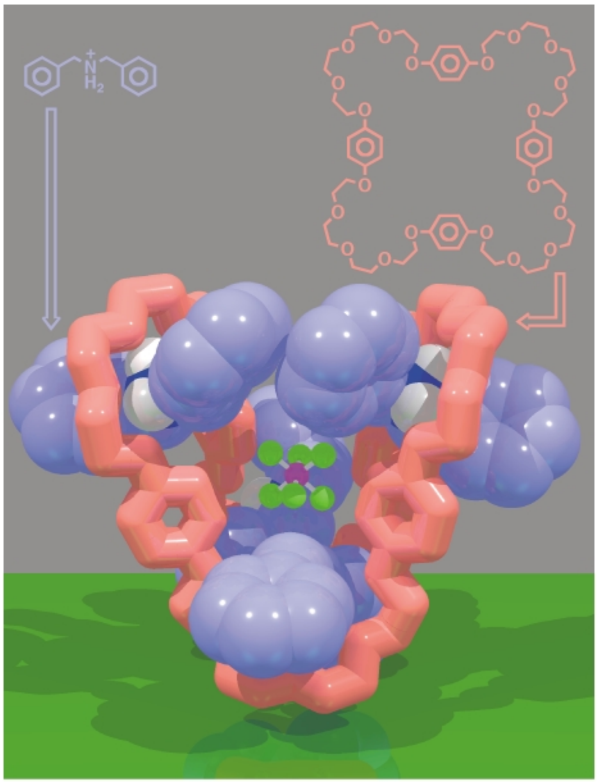


Fig. 39 The extended crown ether TPP68C20 co-crystallises with *four* equivalents of DBA·PF_6 to give a *quadruple-threaded* [5]pseudorotaxane $[TPP68C20·(DBA)_4]^{4+}$. One PF_6^- anion is encapsulated completely within the superstructure.

of (i) the hydroquinone rings of the crown ether, and (ii) the benzylic methylene groups of the threaded DBA^+ cations.

By analogy with this triple-threaded superstructure, the X-ray crystallographic analysis of the 1:4 complex formed between TPP68C20 and DBA·PF_6 revealed (Fig. 39) the formation of a *quadruple-stranded* [5]pseudorotaxane. Once again, each DBA^+ cation resides in one of the four isolated polyether loops present in the crown ether's framework, and likewise, stabilisation of this five component supermolecule arises as a consequence of the familiar combination of both $N^+–H\cdots O$ and $C–H\cdots O$ hydrogen bonding interactions. A striking feature of this superstructure is once again associated with the positioning of one of the PF_6^- anions. In contrast with the [4]pseudorotaxane $[TPP51C15·(DBA)_3]^{3+}$, the supermolecule generated using the larger TPP68C20 macrocycle has enough room in its interior to encapsulate[59] completely one of the PF_6^- anions. The complexation of this highly-ordered PF_6^- anion is presumably stabilised by an array of $C–H\cdots F$ hydrogen bonding[50] interactions, as well as by a coulombic term arising from siting an anion within the influence of four, tetrahedrally-disposed, NH_2^+ centres. Although the PF_6^- anions may not be influencing directly the formation of these four- and five-component supermolecules, respectively, the active role they play in contributing to the overall superstructure may be important nonetheless.

Daisy chains and superbundle polymers

Now, let us consider some of the lessons we have learned from bringing the more simple building blocks together and apply what we have learned to the construction of yet more intricate systems. The formation of supramolecular polymers[60] can be achieved wherein the polymerisation of monomers occurs *via* a threading interaction—a subtly different propagation step compared to that of carboxyl dimer formation. One such monomer designed with this behaviour in mind is the crown ether/$R_2NH_2^+$ ion hybrid[40] shown in Fig. 40. This self-complementary monomer was fashioned in such a way that intramolecular[61] self-complexation is geometrically impossible. The system is compelled, therefore, to interact intermolecularly, in a manner which may result (Fig. 41) in the formation of (i) discrete supramolecular macrocycles (cyclic daisy chains), or (ii) linear one-dimensional rods—namely acyclic daisy chains. The X-ray crystallographic analysis of this compound revealed (Fig. 42) the formation, in the solid state, of discrete head-to-tail[62] dimers, which represent the smallest possible cyclic daisy chain. The two-component superstructure is stabilised, as usual, by $N^+–H\cdots O$ hydrogen bonding interactions, while no short $C–H\cdots O$ contacts are observed. In addition, the head-to-tail threading also mediates the close contact (mean separation = 3.36 Å) of the monomers' central aromatic rings, representing a significant stabilising π–π stacking interaction. Subsequently, these cyclic dimers pack to form a sheet-like superstructure, which is held together by virtue of both $C–H\cdots\pi$ and π–π interactions.

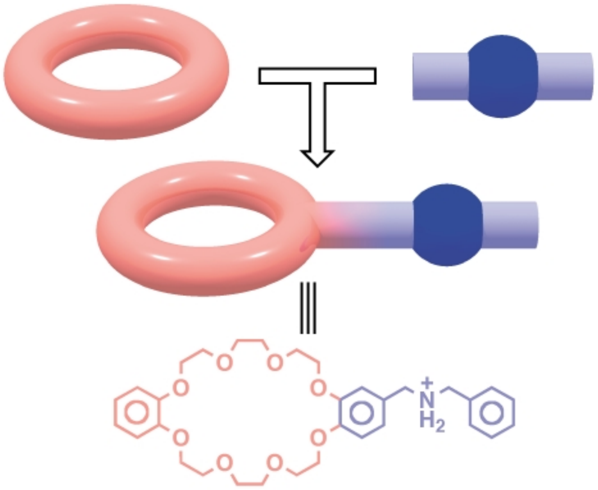


Fig. 40 A hybrid molecule in which a crown ether is coupled to a secondary ammonium ion.

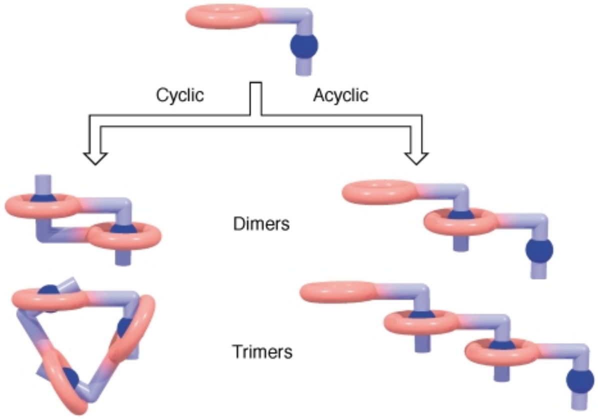


Fig. 41 Some of the possible superstructures into which such a plerotopic monomer may self-assemble.

Finally, we report on our efforts to uncover a very strong recognition motif that could be employed in the construction of novel supramolecular polymers, which can propagate by virtue of threading interactions. We have seen that the formation of bundles is possible if we use crown ethers that possess more than one site capable of binding an $R_2NH_2^+$ ion. To date, this requirement has prevented us from using the parent system—namely the DB24C8/$R_2NH_2^+$ ion recognition motif. However, if we are able to display *n* DB24C8 macrocycles about a core in a controlled fashion, and do likewise with *n* DBA^+ cations, the formation of superbundles is certainly possible. Already in hand was the trifurcated tris(ammonium) salt **8**·3PF_6, and so all that was required[63] was for us to design and synthesise

Fig. 42 The solid-state superstructure of a head-to-tail dimer formed by the hybrid crown ether/ammonium ion molecule.

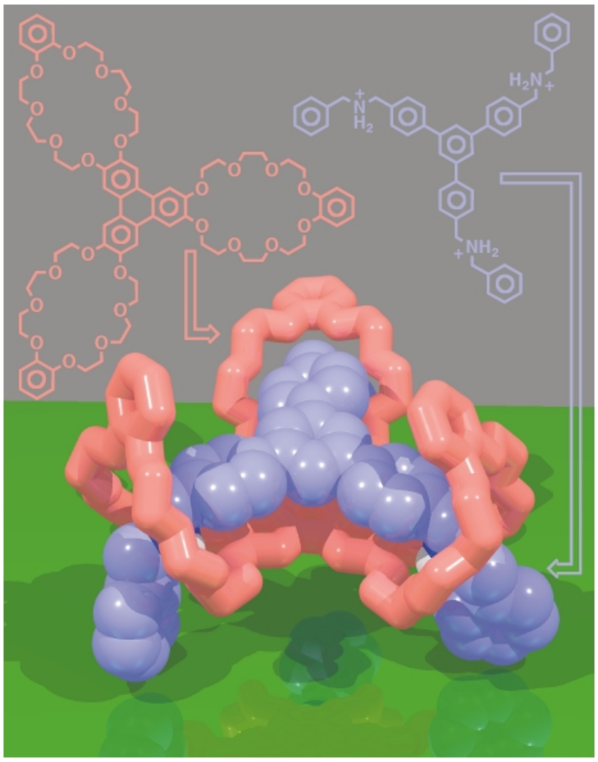


Fig. 43 The solid-state superstructure of a *triple-threaded* 1 : 1 complex formed between a trifurcated tris(ammonium) thread and a complementary triphenylene-based tris(DB24C8) derivative.

a complementary tris(DB24C8) derivative. We decided to base our crown ether system upon a triphenylene core, and produced the tritopic receptor **11** in which three DB24C8 rings are displayed in a trigonal fashion. The X-ray crystallographic analysis of the 1 : 1 complex formed between the tris(crown ether) **11** and **8**·3PF$_6$ revealed (Fig. 43) the formation of the *triple-threaded* two component superbundle. The noncovalent synthesis of this discrete superstructure presumably occurs as a consequence of the highly complementary nature of the two building blocks. Not only is complex stabilisation achieved through the formation of N$^+$–H···O hydrogen bonds, but also by a π–π stacking of the aromatic cores (centroid–centroid separation = 3.6 Å). The solid-state behaviour of these two components is mirrored in solution, wherein a very stable 1 : 1 complex—the triple-threaded superbundle—is observed. Our next goal involves the synthesis of two complementary monomer units that will polymerise *via* the formation of triple-threaded superbundles. One monomer unit will be constructed from two tris(DB24C8) units that are linked by a short, rigid, covalent spacer and the other monomer will possess two trifurcated tris(ammonium) cation clusters linked in a similar fashion. On mixing these two monomers, we can reasonably expect (Fig. 44) superbundle formation leading to supramolecular polymerisation.[60]

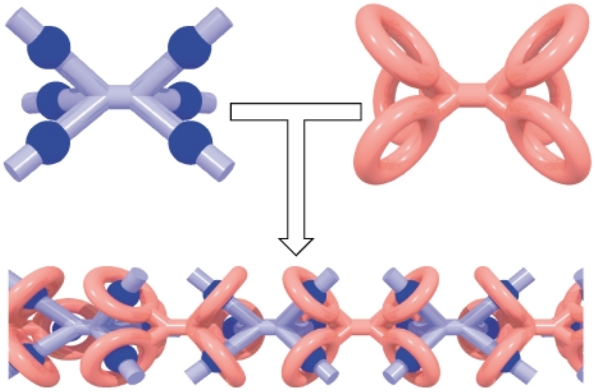


Fig. 44 A schematic representation of supramolecular polymer formation anticipated upon mixing a monomer containing two tris(DB24C8) units with another that contains two trifurcated tris(ammonium) cation clusters.

Statistically speaking

To date, a total of 25 unique crystal structures of R$_2$NH$_2$$^+$/DB24C8 pseudorotaxanes and rotaxanes have been published. Here, we report a statistical survey of the EPSRC's Chemical Database Service at Daresbury.[64] As noted in the many examples above, the principal means of association is by N$^+$–H···O hydrogen bonding. Depending on the substituents on the benzyl groups, there may be from two to four such bonds (mean = 3.06 per structure) with N$^+$–H···O distances[65] ≤2.5 Å (range, 1.91–2.49; mean 2.26 Å). The bonding always involves both phenolic and nonphenolic oxygen sites, and the modes vary between (i) bifurcated phenolic plus bifurcated nonphenolic (four hydrogen bonds), (ii) phenolic plus bifurcated nonphenolic (three hydrogen bonds), (iii) nonphenolic plus bifurcated phenolic (three hydrogen bonds), and (iv) phenolic plus nonphenolic (two hydrogen bonds). No cases of mixed bifurcation (to both types of oxygen atom) are observed. Hydrogen bonds to nonphenolic oxygen atoms are shorter on average than those to their phenolic counterparts (2.21 *vs*. 2.31 Å), while the mean N$^+$–H···O angles are comparable (149.8 *vs*. 150.3°, respectively). The mean distributions can be broken down further into (i) nonbifurcated nonphenolic (2.13 Å, 166.4°), (ii) bifurcated nonphenolic (2.26 Å, 142.1°), (iii) nonbifurcated phenolic (2.28 Å, 158.2°), and (iv) bifurcated phenolic (2.33 Å, 143.9°).

As noted, complex assembly also benefits from a number of C–H···O contacts, which are directly observable in the solid state. Even when a strict limiting C–H···O distance of ≤2.5 Å is imposed—*i.e.*, the same as for N$^+$–H···O contact—most superstructures exhibit at least one and up to three such interactions (mean = 1.32 Å per structure), with an average C–H···O distance of 2.40 Å and C–H···O angle of 150.0°. In this case, however, poor correlation between the hydrogen bonding angle and distance suggests a lower quality interaction than is the case for the N$^+$–H···O bond (Fig. 45). This observation is undoubtedly a consequence of the geometric requirements of the more dominant N$^+$–H···O interactions, coupled with the limited conformational mobility of the macrocycle.

Of the crystal superstructures investigated, 15 are single-threaded pseudorotaxane systems involving a series of simple

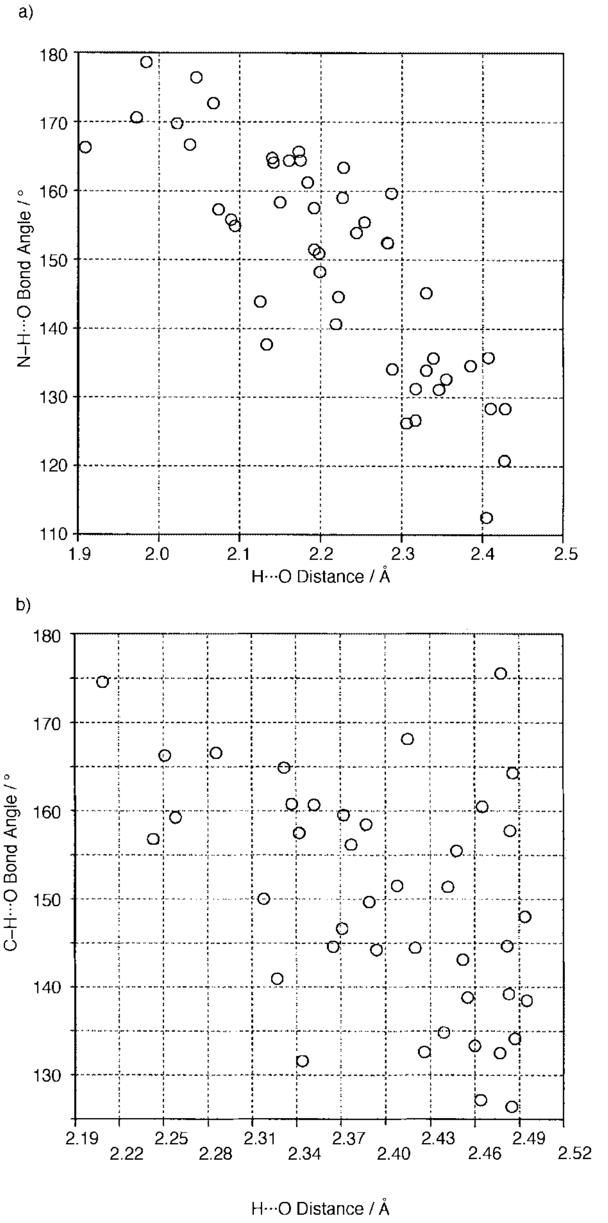


Fig. 45 a) Scatterplot of N^+–H···O bond angles and H···O bond distances observed in the solid state for all DB24C8-derived ammonium-based rotaxanes and pseudorotaxanes; b) a similar scatterplot relating the C–H···O bond angles and H···O bond distances observed in the solid state.

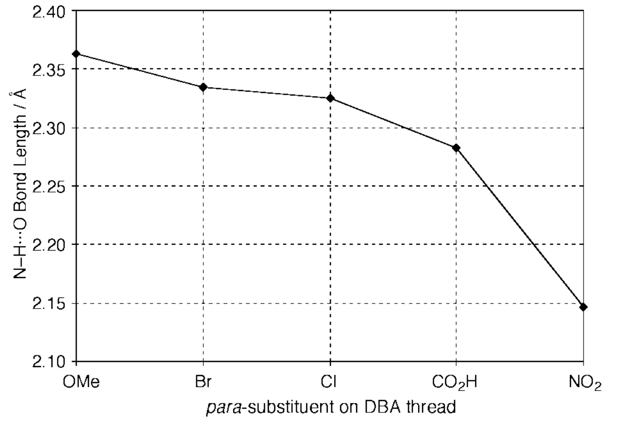


Fig. 46 A graph showing how N^+–H···O hydrogen bond distance decreases as the DBA^+ benzyl group is functionalised with increasingly electron-withdrawing substituents.

dibenzylammonium cations substituted with electron donating or withdrawing substituents in the *meta* or *para* positions. Although a subtle interplay of electronic and steric influences dictates the mode of assembly in this series, some correlation between the electronic nature of the substituent on the benzyl ring and N^+–H···O hydrogen bonding distances is apparent. For example, the *meta*-OMe, -Br, -Cl, and -CO_2H substituted dibenzylammonium salt/DB24C8 complexes all have comparable crystal superstructures exhibiting the maximum number (four) of hydrogen bonds. The mean contact distance decreases in this series with increasing electron demand of the aromatic substituent (Fig. 46). The *meta*-NO_2 dibenzylammonium donor has an even shorter mean hydrogen bonding distance (2.15 Å) but does not have an analogous crystal superstructure (two nonbifurcated hydrogen bonds) and hence this data point must be interpreted with caution. The apparent improvement in hydrogen bond quality seen in Fig. 46 agrees with published[66] Hammett correlations between dibenzylammonium salt/DB24C8 association constants and σ. In the unsubstituted and *para*-substituted series, three different types of crystal superstructure appear which makes a statistical analysis of these data impractical. Indeed it seems remarkable that, despite the similarities of the components, the crystal superstructures share little in common.

Conclusions

It has been possible, during much less than a decade, to assemble a molecular meccano kit, based on some well-known recognition motifs, that relies primarily upon the ability of neutral macrocyclic polyethers—with [24]crown-8 constitutions and larger—to thread onto chains containing, for the most part, benzylic functions and secondary dialkylammonium centres. With the help of other edge-to-edge (*e.g.*, the carboxylic acid hydrogen-bonded dimer) and face-to-face (*e.g.*, π–π stacking of aromatic ring systems) interactions, supermolecules and supramolecular arrays can be formed that, in some instances, exist both in solution and the solid state—and in other instances exist only in solution. There are also a few cases where the supramolecular architectures differ in the solid and solution states. The recognition of hexafluorophosphate anions by the positively-charged supermolecules appears to be one factor that can appreciably influence the adoption of a particular supramolecular architecture in the solid state that is not necessarily seen at all in the solution state.

Acknowledgements

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