

The Solid-state Self-organisation of a Self-assembled [2]Catenane

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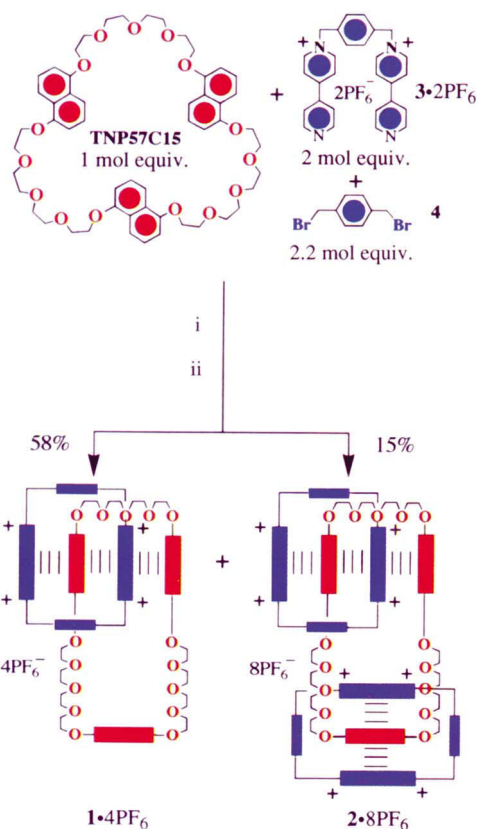
The reluctance of a [2]catenane, comprised of macrocycles incorporating π -donors and π -acceptors, to be catenated further to form a [3]catenane may be explained by the molecular arrangement revealed in the solid-state structure of the [2]catenane, which shows all aromatic units to be involved in *intramolecular* π - π stacking interactions; moreover, the molecules self-organise in the solid-state to form a quilt-like two-dimensional array by virtue of *intermolecular* π - π stacking interactions.

The control of noncovalent bonding interactions is central to the development of molecules capable of self-organising¹ in the solid state and self-assembling² in the solution state. The field of so-called crystal engineering³ has spawned several fascinating supramolecular structures which rely upon hydrogen bonding⁴ for their self-organisation. Successful self-assembling systems are often engendered as a result of information—often unexpected—obtained in the solid state.⁵ As one of the key components for the construction of oligo- and poly-catenanes,⁶ we have investigated a range of macrocyclic polyethers containing π -electron rich aromatic residues.⁷ The macrocyclic polyether, tris(1,5-naphthalene)-57-crown-15 (TNP57C15), has a sufficiently large ring size to permit the accommodation simultaneously of two threaded 4,4'-bipyridinium units, whilst also possessing three powerful templating units inducing the formation of tetracationic cyclophanes that incorporate these π -electron deficient units. However, the efficacy of these templating units was somewhat less than had been anticipated at the outset.⁸ This communication, in addition to providing a possible explanation for the shortcomings in our original design strategy of the self-assembling system, relays an important message about the self-organisa-

tion of catenated derivatives of TNP57C15 in the solid state. We report (i) the self-assembly in one pot of a [2]- and [3]-catenane incorporating, respectively, one and two cyclobis(paraquat-*p*-phenylene) cyclophanes around a single TNP57C15 macrocycle, (ii) the structure of the self-organised [2]catenane in the solid state,[†] and reflect upon (iii) the consequences of this supramolecular structure for the design of a new genre of superstructures incorporating similar building blocks.

The [2]catenane **1**·4PF₆ and the [3]catenane **2**·8PF₆ were self-assembled (Scheme 1) by reacting the template TNP57C15 with two molar equivalents of **3**·2PF₆ and 1,4-bis(bromomethyl)benzene **4** in DMF at ambient temperature and pressure. The [2]- and [3]-catenanes were isolated as purple solids in 58 and 15% yields, respectively, after silica column chromatography (MeOH–DMF–2 mol dm⁻³ NH₄Cl–MeNO₂) and counterion exchange (NH₄PF₆, H₂O). They were subsequently characterised^{‡,§} by FAB-MS, ¹H and ¹³C NMR spectroscopies, and—in the case of the [2]catenane—by X-ray crystallography.[†]

Single crystals of **1**·4PF₆, suitable for X-ray crystallography, were grown by vapour diffusion of Pr₂O into a solution of the [2]catenane in MeCN. The solid-state structure reveals (Fig. 1) a highly ordered molecular arrangement in which one naphthalene unit is sandwiched between the two bipyridinium moieties of the cyclobis(paraquat-*p*-phenylene) component. The other two naphthalene units are positioned with one unit 'alongside' one of the bipyridinium moieties, and the other unit adjacent to one of the *para*-xylyl spacers in the tetracationic cyclophane. In all three cases, near parallel alignments of the aromatic rings with respect to their nearest neighbours in the molecule are observed. The molecular structure is further stabilised by aromatic [C–H \cdots π] interactions⁹ and a



Scheme 1 Self-assembly of the [2]catenane **1**·4PF₆ and the [3]catenane **2**·8PF₆ from the macrocyclic polyether TNP57C15. *Reagents and conditions:* i, DMF, 10 d, room temp., atmospheric pressure; ii, column chromatography, then NH₄PF₆, H₂O.



Fig. 1 The structure of **1**⁴⁺ in the solid state, showing the [C–H \cdots π] and [C–H \cdots O] stabilising interactions. The [H \cdots ring centroid] distances are both 2.53 Å and the [C–H \cdots O] distances are 2.35, 2.44 and 2.34 Å for the a, b and c hydrogen atoms, respectively.

series of [C–H...O] hydrogen bonds between both methine and methylene hydrogen atoms in the tetracationic cyclophane and oxygen atoms in the tetraethylene glycol spacer residue in the macrocyclic polyether. The π -donor/ π -acceptor interactions[¶] present within the molecule extend in two directions in the crystal to form a two-dimensional quilt-like array (Fig. 2) of [2]catenanes involving all of the aromatic rings. The quilt-like packing of the [2]catenanes in the crystals of **1-4PF₆** is remarkably similar to the packing observed in the solid-state structure of a [2]pseudorotaxane,¹⁰ comprised of cyclobis(paraquat-*p*-phenylene) and a thread-like molecule incorporating three 1,5-dioxynaphthalene residues. Each two-dimensional sheet consists of repeating arrays of seven aromatic residues held in line by six π - π stacking interactions,¹¹ with the molecules arranged orthogonally with respect

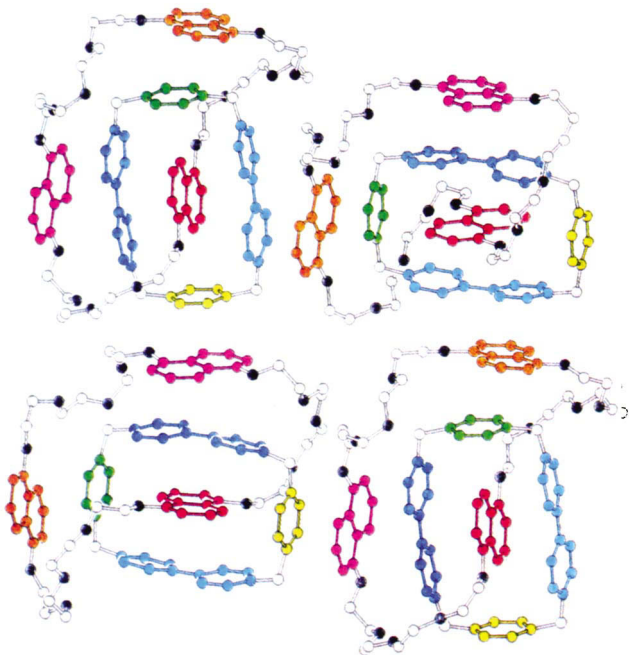


Fig. 2 Part of the continuous two-dimensional 'molecular quilt' formed by the [2]catenane **1-4PF₆** in the crystal, illustrating the sequences of π -electron deficient and π -electron rich aromatic moieties

to each other. There is, however, a subtle conceptual difference between the [2]pseudorotaxane and [2]catenane arrays in their respective crystals. The [2]pseudorotaxane has two different interacting exterior faces in each complex supermolecule, one of which is a naphthalene residue, and the other, a *para*-xylyl residue (Fig. 3). The [2]catenane molecules, on the other hand, have four different interacting exterior faces—(i) a naphthalene residue alongside a *para*-xylyl spacer, (ii) a naphthalene residue alongside a bipyridinium unit, (iii) a *para*-xylyl spacer, and (iv) a bipyridinium moiety.

In the knowledge of the structure of the [2]catenane in the solid state, we sought to establish if a similar 'secondary structure' exists predominantly in the solution state. The ¹H NMR spectrum (400 MHz, CD₃CN) of **1-4PF₆** at room temperature reflects a dynamic situation (Fig. 4) in which one of the 1,5-dioxynaphthalene residues resides in the cavity of the tetracationic cyclophane. The appearance of two resonances for each of the constitutionally equivalent protons in the tetracationic cyclophane component as a result of the imposed local *C*_{2h} symmetry of the π -electron rich guest, which has chemical shifts for H-4/8, H-3/7, H-2/6 at δ 2.11, 5.68, and 5.97, respectively, is in accord with the gross structure **A** for **1-4PF₆**, *i.e.* the process involving circumrotation of the neutral component through the charged cyclophane component is slow on the ¹H NMR timescale in this [2]catenane. The free energy of activation (ΔG^\ddagger) required to dislodge the π -electron rich unit from the tetracationic cyclophane was calculated^{||} to be 15.3 kcal mol⁻¹ (1 cal = 4.184 J).^{**} The ¹H NMR spectra show no temperature dependent behaviour on cooling the CD₃CN solution down from room temperature to -30 °C. However, when the [2]catenane was dissolved in a mixture of CD₃COCD₃–CD₃CN (70:30) and the solution cooled down even further, significant changes in the ¹H NMR spectra resulted. Most notably, one of the resonances (δ 7.44) arising from the protons associated with the 'outside' π -electron rich unit and one (δ 7.87) of the two resonances arising from the *para*-xylyl spacer in the tetracationic cyclophane component are shifted to higher field (Fig. 5), perhaps as a result of the intramolecular stacking of the π -faces of these aromatic systems. Below -70 °C, all the resonances for **1-4PF₆** broaden dramatically, whilst the signals arising from the solvent remain well resolved. This observation is consistent with a slowing

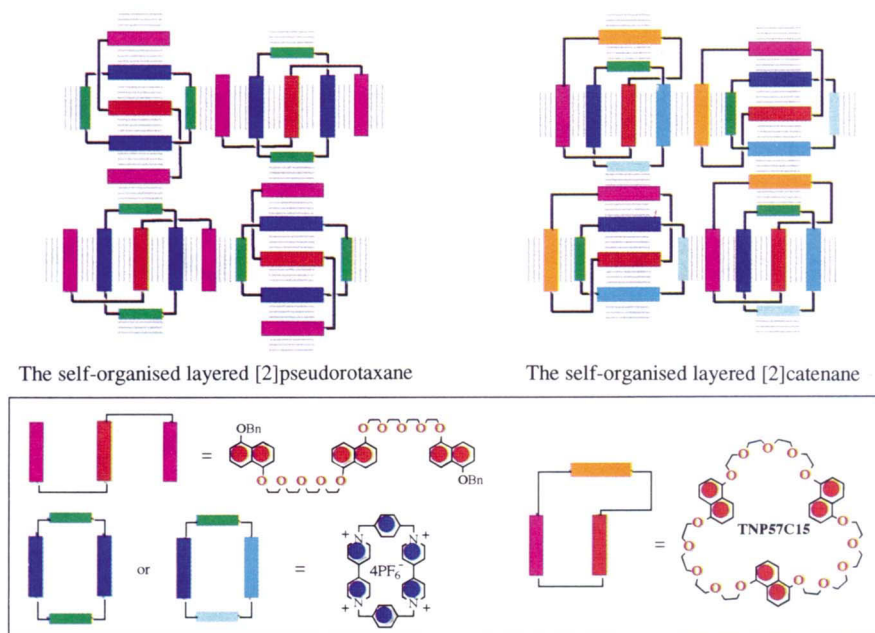


Fig. 3 A schematic comparison of the packing in crystals of a [2]pseudorotaxane, and the packing observed in crystals of **1-4PF₆**

down the rate of equilibration (Fig. 4) between the enantiomeric compacted conformations **B** and $\bar{\mathbf{B}}$, involving the intermediate 'open' conformation **A**. It is hardly surprising for a system in which aggregation could be occurring in solution for line broadening to be evident in the ^1H NMR spectrum at -90°C .

In the [2]catenane **1**·4PF₆, the ability of the 'outside' 1,5-dioxynaphthalene residues to act as templates for the formation of cyclobis(paraquat-*p*-phenylene), thereby affording the [3]catenane **2**·8PF₆, is diminished substantially over that for these same residues in free **TNP57C15**. The reason for this observation may be that the positively charged cyclophane renders unlikely the self-assembly of a second tetracationic cyclophane through the same macrocyclic polyether because of either steric factors or charge–charge repulsions. Alterna-

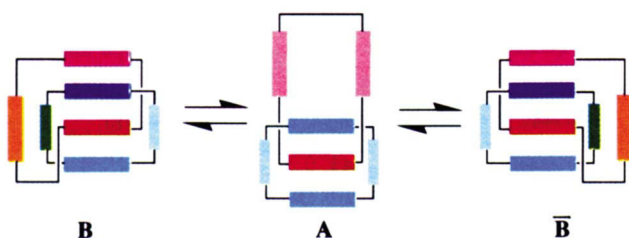


Fig. 4 Schematic representation of the equilibrium of **1**·4PF₆ between enantiomeric 'compacted' (**B** and $\bar{\mathbf{B}}$) conformations via the 'open' conformation (**A**) in solution. (The cartoons used in this diagram are defined in Fig. 3).

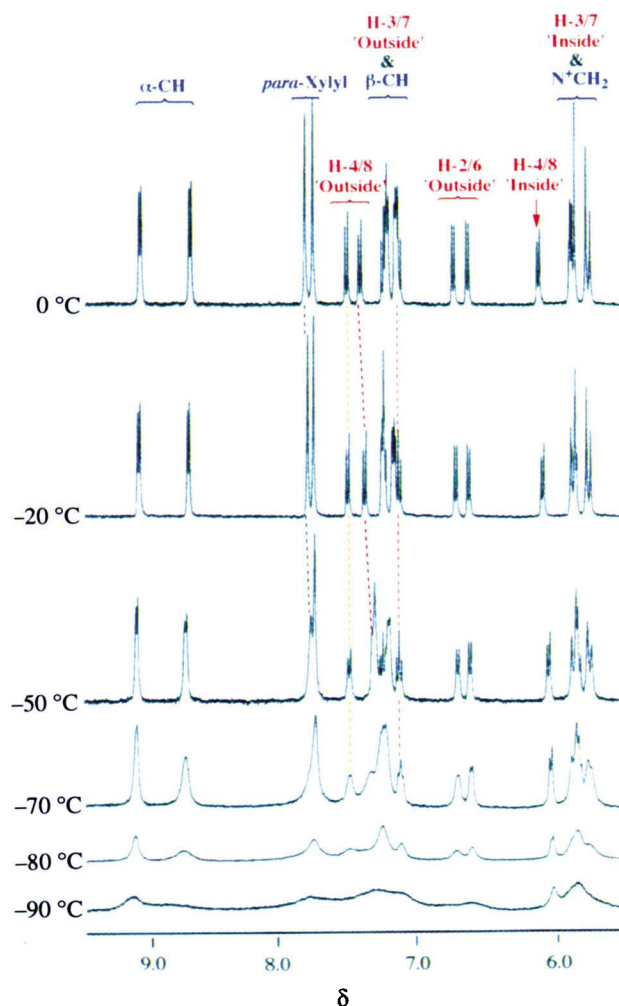


Fig. 5 The temperature variation in the partial ^1H NMR spectra [400 MHz, CD_3COCD_3 – CD_3CN (70:30)] of **1**·4PF₆. Resonances arising from residual solvent remained well resolved over the whole temperature range.

tively, an equilibrium favouring structure **B** (Fig. 4), similar to that observed in the solid state, is tantamount to introducing a negative allosteric effect, thus inhibiting the formation of the [3]catenane. Although solution-state studies do not permit us to conclude categorically that the observed solid-state structure—in which all the π -electron rich units in the macrocyclic polyether are utilised in π – π stacking interactions within the molecule—corresponds to the predominant form in solution, the relatively low yield of the [3]catenane lends support to this conclusion. The differences in the crystal structures of the [2]pseudorotaxane and the [2]catenane show how the 'programming' of molecular compounds can be exploited for the 'engineering' of related superstructures¹² in the solid state. These crystal structures provide valuable glimpses of how complementary moieties recognise each other in arrays and assemblies that respectively self-organise in the solid state and self-assemble in the solution state.

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Footnotes

† *Crystal data* for **1**·4PF₆: $\text{C}_{90}\text{H}_{98}\text{N}_4\text{O}_{15}\cdot 4\text{PF}_6\cdot 1.5\text{MeCN}$, $M = 2117.2$, orthorhombic, $a = 22.209(8)$, $b = 21.375(6)$, $c = 43.38(2)$ Å, $U = 20592(14)$ Å³, space group $Pbca$, $Z = 8$, $D_c = 1.37$ g cm⁻³, $\mu = 16.1$ cm⁻¹, $F(000) = 8760$. 12937 independent reflections ($2\theta < 110^\circ$) were measured on a Siemens P4 rotating anode diffractometer with Cu-K α radiation (graphite monochromator) using ω -scans. 5637 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by direct methods. There is severe disorder in all four PF₆⁻ counterions; in one of these, this was resolved into two partial occupancy orientations. Because of the shortage of observed data, all the six-membered aromatic rings in the structure were refined as rigid bodies. All atoms, with the exception of the aromatic units within the tetracationic cyclophane (which were kept isotropic), were refined anisotropically. The final R values are consequently somewhat high with $R = 0.111$, $R_w = 0.116$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. Computations were carried out on a Silicon Graphics Iris Indigo Computer using the SHELXTL-IRIS program system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Spectroscopic data* for **1**·4PF₆: FAB-MS: m/z 2055, 1910, 1764 and 1629, corresponding to $[\text{M}]^+$, $[\text{M} - \text{PF}_6]^+$, $[\text{M} - 2\text{PF}_6]^+$ and $[\text{M} - 3\text{PF}_6]^+$, respectively; ^1H NMR (CD_3CN , 400 MHz, 0°C) δ 2.11 (d, J 8.5 Hz, 2H), 3.64–3.82 (m, 20H), 3.83–3.97 (m, 16H), 3.98–4.03 (m, 4H), 4.04–4.17 (m, 8H), 5.48 (d, J_{AB} 14 Hz, 4H), 5.63 (d, J_{AB} 14 Hz, 4H), 5.68 (t, J 8.5 Hz, 2H), 5.97 (d, J 8.5 Hz, 2H), 6.56 (d, J 8.5 Hz, 2H), 6.75 (dd, J 2, 7 Hz, 4H), 6.80 (d, J 8.5 Hz, 2H), 6.86 (dd, J 2, 7 Hz, 4H), 7.18 (t, J 8.5 Hz, 2H), 7.33 (t, J 8.5 Hz, 2H), 7.44 (d, J 8.5 Hz, 2H), 7.52 (d, J 8.5 Hz, 2H), 7.59 (s, 4H), 7.61 (s, 4H), 8.32 (d, J 7 Hz, 4H), 8.77 (d, J 7 Hz, 4H); ^{13}C NMR (CD_3CN , 101 MHz) δ 66.0, 69.1, 70.2, 70.4, 70.6, 70.8, 71.0, 71.3, 71.4, 71.6, 72.2, 104.9, 107.1, 107.2, 109.1, 115.0, 115.1, 124.8, 125.1, 126.2, 126.5, 126.7, 127.2, 128.9, 131.7, 131.9, 137.1, 144.8, 145.1, 151.8, 155.0.

§ *Spectroscopic data* for **2**·8PF₆: FAB-MS: m/z 3010, 2866, 2720 and 2574, corresponding to $[\text{M} - \text{PF}_6]^+$, $[\text{M} - 2\text{PF}_6]^+$, $[\text{M} - 3\text{PF}_6]^+$ and $[\text{M} - 4\text{PF}_6]^+$, respectively; ^1H NMR (CD_3CN , 400 MHz, -5°C) δ 1.96 (d, partially obscured by CD_3CN) 2.27 (d, J 7.5 Hz, 2H), 3.43–3.51 (m, 4H), 3.54–3.64 (m, 8H), 3.70–3.78 (m, 4H), 3.85–4.08 (m, 20H), 4.10–4.25 (m, 12H), 5.39 (d, J_{AB} 13.5 Hz, 4H), 5.56 (d, J_{AB} 13.5 Hz, 4H), 5.66 (d, J_{AB} 13.5 Hz, 4H), 5.72 (d, J_{AB} 13.5 Hz, 4H), 5.77 (t, J 7.5 Hz, 2H), 5.89 (t, J 7.5 Hz, 2H), 6.08–6.17 (m, 4H), 6.35–6.41 (m, 2H), 6.85–6.90 (m, 4H), 6.97–7.01 (m, 4H), 7.04–7.15 (m, 12H), 7.65 (s, 4H), 7.83 (s, 4H), 7.90 (s, 4H), 7.98 (s, 4H), 8.36 (d, J 6 Hz, 4H), 8.54 (d, J 6 Hz, 4H), 8.68 (d, J 6 Hz, 4H), 9.04 (d, J 6 Hz, 4H).

¶ The mean interplanar separations *intramolecularly* between both the 'inside' and 'alongside' naphthalene π -donors and the bipyridinium π -acceptors are *ca.* 3.46 Å within each [2]catenane. The

intermolecular π - π stacking distances between the naphthalene and the *para*-xylyl rings are 3.56 Å, whilst those between the naphthalene rings and the bipyridinium moieties are 3.37 Å.

|| A value of $k_c = 398 \text{ s}^{-1}$ was obtained (I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, 1971, **4**, 71) by using the approximate expression $k_c = \pi(\Delta\nu)/(2)^{1/2}$ (the limiting chemical shift difference, $\Delta\nu = 179 \text{ Hz}$) and the Eyring equation was then employed to calculate the ΔG_c^\ddagger value at the coalescence temperature ($T_c = 53.4^\circ\text{C}$) for the signals associated with the α -CH protons of the tetracationic cyclophane component in **1**·4PF₆.

** This value compares with a $\Delta G_c^\ddagger = 15.8 \text{ kcal mol}^{-1}$ for a catenane incorporating the smaller bis(1,5-naphthalene)-38-crown-10 (P. R. Ashton, C. L. Brown, E. J. T. Chrystal, T. T. Goodnow, A. E. Kaifer, K. P. Parry, D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 634).

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