A Self-organised Layered Superstructure of Arrayed [2]Pseudorotaxanes

Peter R. Ashton,[a] Douglas Philp,[a] Neil Spencer,[a] J. Fraser Stoddart[a] and David J. Williams[b]

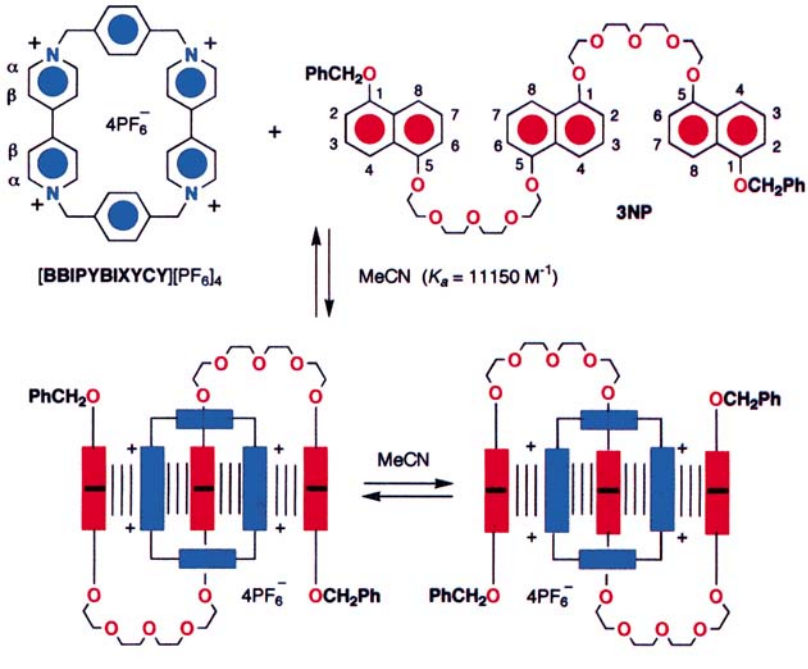
[a] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT*
[b] *Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY*

A [2]pseudorotaxane, built up from a macrocyclic cyclophane containing two aromatic π-acceptors and an acyclic molecule containing three aromatic π-donors, has the ability to undergo self-organisation on crystallisation to form a layered superstructure of arrayed [2]pseudorotaxanes.

The recent surge of interest in the control of molecular arrangements in the solid state—often referred to as crystal engineering[1]—has led researchers to take cognisance of the importance of weak non-covalent intermolecular forces. This facet of supramolecular chemistry[2] has so far centred principally upon the hydrogen bond[3] as the mediator of intermolecular recognition and organisation. These interactions have permitted the assembly of one-[4], two-[5] and three-[6] dimensional networks. Here, we describe the self-assembly[7] in solution of a [2]pseudorotaxane,† which, upon crystallisation, undergoes self-organisation to give an extended two-dimensional network of π-donors and π-acceptors, oriented by both aromatic face-to-face[8] and edge-to-face[9] interactions. This discovery adds a further dimension to the extensively characterised π–π stacking motifs we have observed (Fig. 1) in (*a*) a molecular complex,[10] (*b*) a [3]catenane[11] and (*c*) two [2]catenanes[12,13] and a [2]pseudorotaxane.[14]

When the multi-π-donor guest **3NP**,‡ incorporating three 1,5-dioxynaphthalene residues, was mixed (Scheme 1) in equimolar proportions with the tetracationic host[15] [**BBIPYBIXYCY**][PF_6]$_4$ in MeCN solution, an intense purple colour developed immediately.§ A spectrophotometric titration confirmed the formation of the 1:1 complex [**BBIPYBIXYCY.3NP**][PF_6]$_4$, the stability constant being 11 000 ± 200 mol dm^{-3}, *i.e.* corresponding to a $-\Delta G°$ value of 5.6 kcal mol^{-1} (1 cal = 4.184 J). Evaporation of the MeCN afforded a purple-coloured powder, which, on analysis by FABMS, revealed peaks at *m/z* 1932 and 1787, corresponding to the loss of one and two hexafluorophosphate counterions, respectively, from the intact [2]pseudorotaxane, [**BBIPYBIXYCY·3NP**][PF_6]$_4$. Vapour diffusion of Pr^i_2O into a solution of the [2]pseudorotaxane in MeCN yielded crystals suitable for X-ray structural analysis.¶ In the solid state [Fig. 2(*a*)], **3NP** is not only inserted through the centre of the [**BBIPYBIXYCY**]$^{4+}$ tetracation, such that the middle 1,5-dioxynaphthalene unit is encircled, but its polyether chains also curl back on themselves around the cyclophane, enabling the other two π-donors to stack against the sides of the π-accepting bipyridinium residues; the [2]pseudorotaxane has crystallographic C_i symmetry. In the crystal lattice [Fig. 2(*b*)], the [2]pseudorotaxanes are arranged to form infinite two-dimensional sheets sustained by a combination of π–π stacking and aromatic [CH···π] interactions‖ that extend to create a grid-like pattern [Fig. 1(*d*)]. The sheets are in register with respect to the crystallographic *a* direction which is perpendicular to the sheet plane. The PF_6^- counterions are located between the sheets.

Although the 400 MHz ^{1}H NMR spectrum of [**BBIPYBIXYCY·3NP**][PF_6]$_4$, recorded in CD_3CN solution at room temperature, exhibits some line broadening as a result of exchange processes (*vide infra*), on cooling the solution down to −30 °C, the signals become well-resolved and can be interpreted in terms of only *one* translational isomer, undergoing a degenerate equilibration process involving switching of the 'alongside' 1,5-dioxynaphthalene units, as shown in Scheme 1. Aside from this dynamic property, it is analogous in its gross features to the superstructure observed [Fig. 2(*a*)] in the solid state. An ^{1}H–^{1}H COSY experiment, performed under the same conditions, allowed the assignments of signals listed in Table 1 to the protons, other than the OCH_2 protons,



Scheme 1

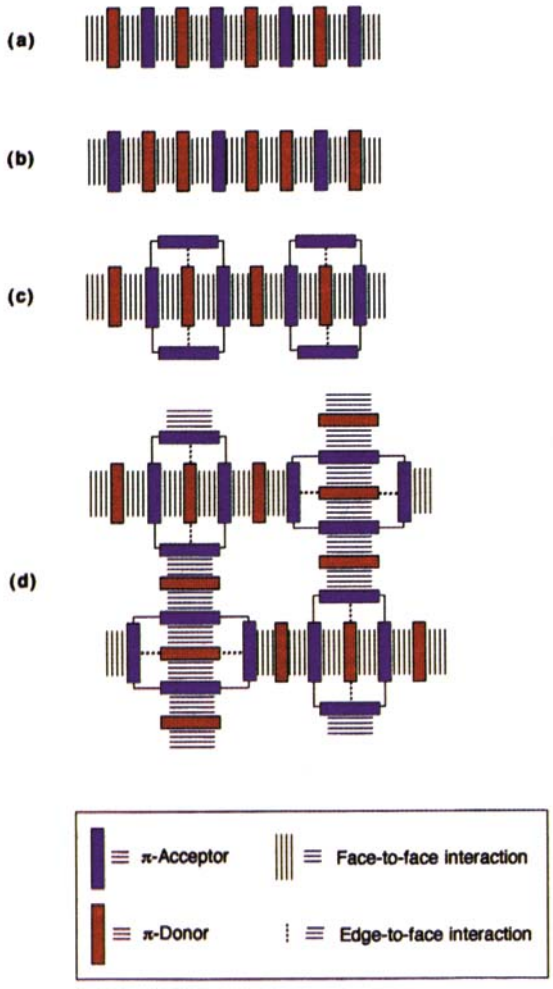


Fig. 1 Schematic representation of the arrangements of π-donors and π-acceptors so far observed in (*a*) a molecular complex, (*b*) a [3]catenane, (*c*) two [2]catenanes and a [2]pseudorotaxane, and (*d*) in the [2]pseudorotaxane, [**BBIPYBIXYCY·3NP**]$^{4+}$

in the [2]pseudorotaxane to be deduced for the numerous and, in some cases, overlapping resonances. The appearance of two resonances in each case for the bipyridinium α-CH and β-CH, aromatic C_6H_4 and NCH_2 protons of the [**BBIPYBIXYCY**]$^{4+}$ component of the [2]pseudorotaxane can be rationalised by the inclusion of the central 1,5-dioxynaphthalene residue within the cavity of the macrocycle such that this residue in the guest imparts its averaged C_{2h} symmetry on the host component of the superstructure. Large upfield shifts are observed for the signals for the bipyridinium α-CH (Δδ −0.18 and −0.74 ppm) and NCH_2 (Δδ −0.19 and −0.31 ppm) protons, reflecting the powerful ring current shielding effect of the naphthalene rings in the 'alongside' positions of the [2]pseudorotaxane. The even more dramatic upfield shifts of the resonances for the β-CH protons (Δδ −1.53 and −1.59 ppm) are commensurate with the positioning of these protons between the π-surfaces of the 'alongside' and included naphthalene rings of **3NP** within the [2]pseudorotaxane. The chemical shift changes observed (Table 1) from the proton resonances of the **3NP** component are also indicative of the π–π stacked superstructure proposed (Scheme 1) for the [2]pseudorotaxane in solution. By far the largest shift changes are observed for the H-4/8 protons (Δδ −5.41 ppm) of the included naphthalene ring. This large Δδ value is consistent with the location of these protons considerably less than 3.0 Å from the mean planes of the *para*-xylyl units in the [**BBIPYBIXYCY**]$^{4+}$ component. The observation of cross-peaks arising from *meta*-couplings between the pairs of α-CH and

Table 1 Partial ^{1}H NMR chemical shift data for compounds or components in CD_3CN at 400 MHz

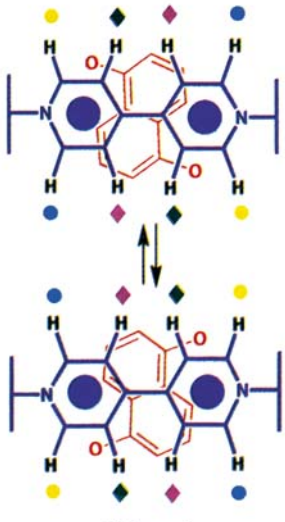
Compound or component	Proton	δ_{uc}[a]	$\delta_c(-30\,°C)$[b]	Δδ[c]
BBIPYBIXYCY^{4+}	α-CH[d]	8.86	8.68	−0.18
			8.12	−0.74
	β-CH[d]	8.16	6.63	−1.53
			6.57	−1.59
	C_6H_4	7.52	7.84	+0.32
			7.71	+0.19
	CH_2N^+	5.74	5.53	−0.21
			5.43	−0.31
3NP	'Alongside' H-4[e]	7.77	7.32	−0.45
	'Alongside' H-8[e]	7.79	7.33	−0.46
	'Alongside' H-7[e]	7.34	7.16	−0.18
	'Alongside' H-3[e]	7.32	7.07	−0.25
	'Alongside' H-6[e]	6.88	6.69	−0.19
	'Alongside' H-2[e]	6.82	6.40	−0.42
	Included H-2/H-6	6.95	5.90	−1.05
	Included H-3/H-7	7.34	5.60	−1.74
	Included H-4/H-8	7.82	2.41	−5.41

[a] δ_{UC} is the chemical shift in the ^{1}H NMR spectrum of the resonances for each component (*ca.* 4×10^{-3} mol dm^{-3}) in the uncomplexed state. [b] $\delta_c(-30\,°C)$ is the chemical shift in the ^{1}H NMR spectrum of the resonances for the 1 : 1 complex [**BBIPYBIXYCY·3NP**][PF_6]$_4$ (*ca.* 4×10^{-3} mol dm^{-3}). [c] $\Delta\delta = \delta_c(-30\,°C) - \delta_{uc}$. Although the δ_{uc} values are quoted at ambient temperature, it has been shown that they are close to invariant (±0.01 ppm) at temperatures as low as −40 °C for [**BBIPYBIXYCY**][PF_6]$_4$ and down to −20 °C for **3NP**, where this component starts to become insoluble in CD_3CN. [d] Relative to the bipyridinium ring nitrogen atoms (see Scheme 1). [e] The assignments (Scheme 1) of the resonances of the 'alongside' naphthalene protons follow from the identification of H-2 at δ 6.40 by an NOE difference experiment in which the benzylic methylene protons of **3NP** resonating at δ 4.89 were irradiated.

Table 2 Kinetic and thermodynamic parameters obtained from the temperature-dependent ^{1}H NMR spectra recorded on [**BBIPYBIXYCY·3NP**][PF_6]$_4$ in CD_3CN

β-CH	24.0	53	+30	15.4
C_6H_4	52.0	116	+41	15.5

[a] Undergoing site exchange in the [**BBIPYBIXYCY**]$^{4+}$ component. [b] Calculated from the approximate expression, $k_c = \pi(\Delta\nu)/2^{1/2}$. [c] Temperature measured using an electronic thermometer and thermocouple. [d] Calculated using the Eyring equation.



Scheme 2

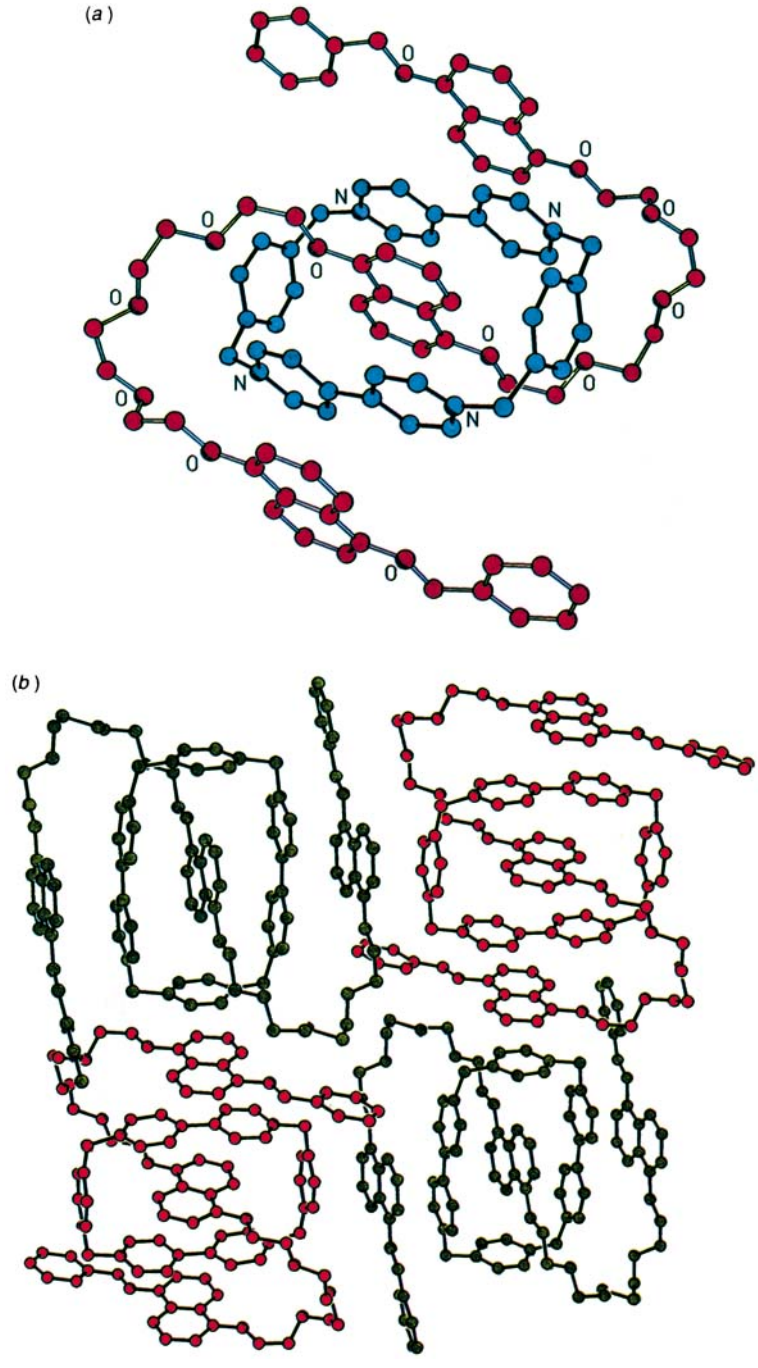


Fig. 2 The X-ray crystal structure of (*a*) the [2]pseudorotaxane, [**BBIPYBIXYCY·3NP**]$^{4+}$, and (*b*) the arrangement of the tetracations in the crystalline state

β-CH protons within the bipyridinium rings of this component in the ^{1}H–^{1}H COSY experiment provides further evidence for the enforcement of averaged C_{2h} symmetry upon the superstructure of the [2]pseudorotaxane.** The averaged symmetry of the superstructure is increased if the central naphthalene unit of the **3NP** component is ejected from the cavity of the [**BBIPYBIXYCY**]$^{4+}$ component and then returned to the cavity such that it assumes the alternative orientation (Scheme 2). Observation (Table 2) of the coalescence of the signals, arising from the bipyridinium β-CH and the C_6H_4 protons of the [**BBIPYBIXYCY**]$^{4+}$ component, has afforded a $\Delta G^{\ddagger}$ value of 15.45 kcal mol^{-1} for this reorientation process.

A [2]pseudorotaxane, which not only exhibits a high stability and a remarkable degree of internal organisation but also provides the ingredients in the form of appropriately sited π-acceptors and π-donors to generate supramolecular order on the nanometre scale in the crystalline state, has thus been identified. Two-dimensional arrays in which the molecules and ions of an aromatic nature form continuous networks, could ultimately play a rôle in the construction of nanosystems containing molecular machinery.[16]

We thank the SERC in the UK for financial support.

Received, 4th August 1993; Com. 3/04707E

Footnotes

† The name *rotaxane* derives (G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, 1971) from the Latin *rota*

meaning wheel and *axis* meaning axle. The addition of the prefix *pseudo* indicates that the wheels are free to dissociate from the axle as in a more conventional type of complex.

‡ **3NP** (mp 122–125 °C) was obtained by alkylating (NaH–THF) 1,5-bis-[2,(2-hydroxyethoxy)ethoxy]naphthalene, prepared from reacting (K_2CO_3–DMF) 1,5-dihydroxynaphthalene with 2-(2-chloroethoxy)ethanol, with 2 molar equivalents of 1-{2-[2-(*p*-tolylsulfonyl) ethoxy]ethoxy}-5-benzyloxynaphthalene, prepared from 1,5-dihydroxynaphthalene in a sequence of reactions which involves (*i*) monobenzylation ($PhCH_2Br$–K_2CO_3–Me_2CO), (*ii*) reaction (K_2CO_3–MeCN) of 1-benzyloxy-5-hydroxynaphthalene with 2-(2-chloroethoxy)ethanol, and (*iii*) tosylation ($TsCl$–Et_3N–CH_2Cl_2) of the alcohol to afford the required tosylate (*vide supra*).

§ For an explanation of the acronym employed for the tetracationic cyclophane, see ref. 12(*b*). The descriptor **3NP** indicates an acyclic polyether incorporating three naphthalene units.

¶ *Crystal Data*: $C_{96}H_{96}N_4O_{12}\cdot 4PF_6\cdot 7(MeCN)$, M = 2365.0. Monoclinic, a = 13.822(2), b = 21.517(4), c = 20.288(3) Å, β = 101.23(2)°, U = 5918(2) Å^3, space group $P2_1/n$, Z = 2, D_c = 1.33 g cm^{-3}, μ = 14.5 cm^{-1}, $F(000)$ = 2452, 7450 independent reflections ($\theta < 55°$) were measured on a Siemens P3/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. 3832 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 the PF_6^- counterions. This disorder was resolved into two partial occupancy orientations in one case, but could not be resolved in the other. There is also disorder in the polyether linkages and in the chain OCH_2Ph termini. Two acetonitrile solvent molecules are also disordered. Refinement was by full-matrix least-squares. Because of the shortage of observed data, only the major occupancy counterions and the major occupancy atoms of the polyether chain were refined anisotropically. The remaining atoms were refined isotropically; the tetracationic cyclophane is comparatively rigid and does not usually display appreciable anisotropy. The final R-values are consequently somewhat high with R = 0.125, R_w = 0.129 [$w^{-1} = \sigma^2(F) + 0.0005\ F^2$]. Computations were carried out on a 486 PC using the SHELXTL-PC program system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‖ The mean interplanar separations between the naphthalene π-donors and bipyridinium π-acceptors are 3.4 Å within each [2]pseudorotaxane. In addition, there are pairs of [CH···π] interactions (H···ring centroid distance, 2.54 Å) between H-4/8 and the *para*-xylyl bridging units of the cyclophane. A π–π stacking interaction also exists (mean planar separation, 3.5 Å) between the 'alongside' naphthalene rings of one [2]pseudorotaxane and the *para*-xylyl bridging units of a symmetry-related [2]pseudorotaxane. These interactions extend in two essentially perpendicular directions in the crystals.

** A 2D-NOESY experiment, likewise performed in CD_3CN at −30 °C, also revealed the presence of cross peaks arising from through-space correlations between H-2 and H-6 on the 'alongside' naphthalene rings in the **3NP** component and the two resonances of the **[BBIPYBIXYCY]**$^{4+}$ component, providing yet more evidence for the existence of a π–π stacked superstructure for the [2]pseudorotaxane in solution.

References

1 G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, 1989.

2 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; 1990, **29**, 1304; *Science* 1992, **260**, 1762.

3 (*a*) G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco, 1960; (*b*) G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer-Verlag, Berlin, 1991.

4 (*a*) H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 487; (*b*) J.-M. Lehn, M. Mascal, A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1990, 479; (*c*) M. C. Etter and D. A. Adsmond, *J. Chem. Soc., Chem. Commun.*, 1990, 589; (*d*) C. Fouquey, J.-M. Lehn and A. M. Levelut, *Adv. Mater.*, 1990, **2**, 254; (*e*) J. A. Zerkowski, C. T. Seto, D. A. Wierda and G. M. Whitesides, *J. Am. Chem. Soc.*, 1990, **112**, 9025; (*f*) F. Garcia-Tellado, S. J. Geib, S. Goswami and A. D. Hamilton, *J. Am. Chem. Soc.*, 1991, **113**, 9265; (*g*) S. J. Geib, S. C. Hirst, C. Vicent and A. D. Hamilton, *J. Chem. Soc., Chem. Commun.*, 1991, 1283; (*h*) C. V. K. Sharma, K. Panneerselvam, R. Pilati and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1992, 832; (*i*) C. B. Aakeröy, G. S. Bahra, P. B. Hitchcock, Y. Patell and K. R. Seddon, *J. Chem. Soc., Chem. Copmmun.*, 1993, 152; (*j*) J. Yang, E. Fan, S. J. Geib and A. D. Hamilton, *J. Am. Chem. Soc.*, 1993, **115**, 5314.

5 (*a*) C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1993, **115**, 905; (*b*) C. T. Seto, J. P. Mathias and G. M. Whitesides, *J. Am. Chem. Soc.*, 1993, **115**, 1321; (*c*) C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.*, 1993, **115**, 1330; (*d*) N. M. Stainton, K. D. M. Harris and R. A. Howie, *J. Chem. Soc., Chem. Commun.*, 1991, 1781.

6 (*a*) M. Simard, D. Su and J. D. Wuest, *J. Am. Chem. Soc.*, 1991, **113**, 4696; (*b*) S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8719; *J. Chem. Soc., Chem. Commun.*, 1993, 1078; (*c*) A. T. Ung, R. Bishop, D. C. Craig, I. G. Dance and M. L. Scudder, *J. Chem. Soc., Chem. Commun.*, 1993, 322.

7 (*a*) J. F. Stoddart, in *Host-Guest Molecular Interactions: From Chemistry to Biology*, Ciba Foundation Symposium 158, Wiley, Chichester 1991, pp. 5–22; (*b*) J. S. Lindsey, *New. J. Chem.*, 1991, **15**, 153; (*c*) G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312.

8 (*a*) W. L. Jorgensen and D. L. Severance, *J. Am. Chem. Soc.*, 1990, **112**, 4768 and references cited therein; (*b*) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525, and references cited therein.

9 M. Nishio and M. Hirota, *Tetrahedron*, 1989, **45**, 7201 and references cited therein.

10 J. Y. Ortholand, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1394.

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

12 (*a*) P. R. Ashton, T. T. Goodnow, A. E. Kaifer, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1396; (*b*) P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 193.

13 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.

14 P. L. Anelli, P. R. Ashton, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1036.

15 (*a*) B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1547; (*b*) P. R. Ashton, B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1550.

16 K. E. Drexler, *Nanosystems, Molecular Machinery, Manufacturing and Computation*, Wiley, New York, 1992.