The self-assembly of some novel [2]rotaxanes and their alkali metal cation complexation

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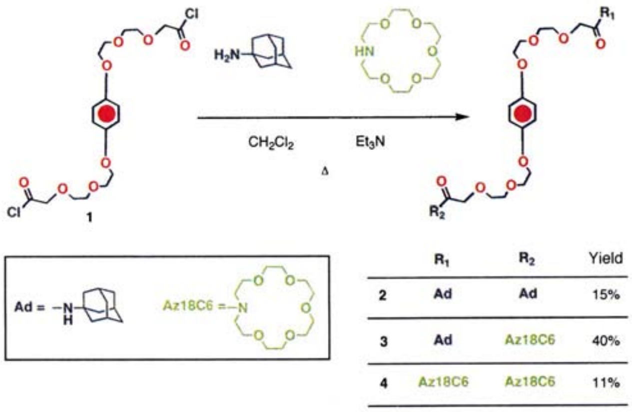
[2]Rotaxanes, in which cyclobis(paraquat-*p*-phenylene) encircles multi-topic dumbbell components wherein a polyether chain is intercepted by a hydroquinone ring and terminated by amide functions attached to either adamantyl groups or monoaza-18-crown-6 macrocycles, can be self-assembled by slippage in acetonitrile solution at +50 °C, provided alkali metal cations, such as Na^+ and K^+, are absent: furthermore, the X-ray crystal structure of a novel bis(monoaza-18-crown-6)-containing [2]rotaxane has also been obtained.

Self-assembly[1] processes are widely used in the biological world for the construction of large and complex three-dimensional supramolecular architectures. Striking examples of the beauty and efficiency of self-assembly are illustrated by the building-up of thermodynamically-stable entities, such as the tobacco mosaic virus, DNA and the enzyme ribonuclease. Recently, the self-assembly and control of mechanically-interlocked molecules such as catenanes[2] and rotaxanes[3] have been investigated in order to develop smart systems which could have implications in a world of advanced materials and new technologies.

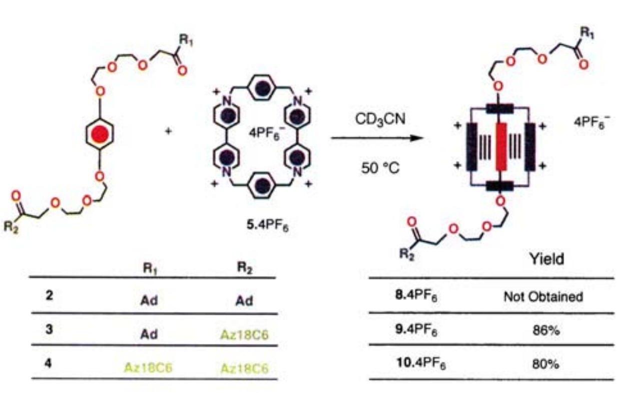
Here, we describe: (i) the syntheses of dumbbell-shaped compounds and [2]rotaxanes containing one and two monoaza-18-crown-6† macrocycles at their termini by slippage,[4] together with a dumbbell-shaped compound and [2]rotaxane containing two aminoadamantane† groups at their termini by a clipping[5] method, (ii) their characterisation by ^{1}H NMR spectroscopy and liquid secondary ion mass spectrometry (LSIMS), (iii) their alkali metal cation binding properties, and (iv) the X-ray crystal structure of a [2]rotaxane bearing two monoaza-18-crown-6 macrocycles at its termini. Monoaza-18-crown-6 was selected as the slippage stopper for the dumbbell-shaped component for three reasons. Firstly, the size complementarity between the tetracationic cyclophane and monoaza-18-crown-6 as the stopper is such that slippage of the cyclophane over them is possible as suggested by the inspection of CPK space-filling molecular models and by previous studies.‡ Secondly, monoaza-18-crown-6 is known[6] to exhibit a high affinity towards the binding of alkali metal cations such as Na^+ and K^+ ions. Thirdly, monoaza-18-crown-6 can be protonated, thus affecting the cation binding affinity of the macrocycle.

The dumbbell-shaped compounds **2**, **3** and **4** were prepared (Scheme 1) in 15, 40 and 11% yields, respectively, from a one-pot reaction of the diacid chloride **1**§ with equimolar mixtures of 1-aminoadamantane† and monoaza-18-crown-6 in dichloromethane for 24 h. Heating 3 equiv. of the dumbbell-shaped compound **2** containing the two adamantyl groups at the termini with the tetracationic cyclophane **5**.$4PF_6$ in a CD_3CN solution at 50 °C for 14 d (Scheme 2) does not result in the formation of the [2]rotaxane **8**.$4PF_6$¶ since the adamantyl groups are sufficiently large to prevent the slippage of the tetracationic cyclophane **5**.$4PF_6$ over them. However, this [2]rotaxane **8**.$4PF_6$ can be synthesised in 6% yield by employing the clipping methodology using **6**.$2PF_6$ and the dibromide **7** (Scheme 3).[5] By contrast, the mono and bis crown ether-containing [2]rotaxanes **9**.$4PF_6$¶ and **10**.$4PF_6$¶ (Scheme 2) can be obtained in yields of 86 and 80%, respectively, using the slippage methodology.[4] Their formation



	R_1	R_2	Yield
2	Ad	Ad	15%
3	Ad	Az18C6	40%
4	Az18C6	Az18C6	11%

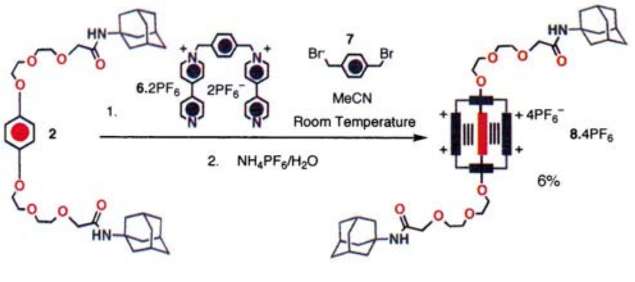
Scheme 1 The synthesis of dumbbell compounds **2**, **3** and **4**



	R_1	R_2
2	Ad	Ad
3	Ad	Az18C6
4	Az18C6	Az18C6

	Yield
8.$4PF_6$	Not Obtained
9.$4PF_6$	86%
10.$4PF_6$	80%

Scheme 2 Self-assembly of **9**.$4PF_6$ and **10**.$4PF_6$ using the slippage method



Scheme 3 Self-assembly of **8**.$4PF_6$ using the clipping approach

can be monitored by ^{1}H NMR spectroscopy.|| The α-bipyridinium, β-bipyridinium and *para*-phenylene protons can all be used as probes to study the progress of the reaction. They can be purified easily by preparative thin layer chromatography** on silica gel [eluent: MeOH–MeNO$_2$–2 M NH$_4$Cl$_{(aq)}$]. As the reaction progresses, the signals corresponding to the free cyclophane **5**.4PF$_6$ decrease and signals corresponding to [2]rotaxane **10**.4PF$_6$ become apparent (Fig. 1). Under the conditions employed to promote slippage of the tetracationic cyclophane **5**.4PF$_6$ (*i.e.* 50 °C, in MeCN) over the monoaza-18-crown-6 stoppers of the dumbbell-shaped compounds **3** and **4**, the equilibrium of the reaction is such that we see no evidence for the unthreading or 'slipping off' (*i.e.* the reverse reaction) by ^{1}H NMR spectroscopy. In fact, even heating the bis(monoaza-18-crown-6)-containing [2]rotaxane **10**.4PF$_6$ in MeCN at 80 °C for 16 h does not result in the extrusion of the tetracationic cyclophane **5**.4PF$_6$ from the dumbbell-shaped compound **4**. We propose that, once slippage of the tetracationic cyclophane **5**.4PF$_6$ over the aza-18-crown-6 macrocycles occurs, the resulting complexation of the π-electron rich hydroquinone ring on the dumbbell-shaped components by the tetracationic cyclophane **5**.4PF$_6$ provides a *thermodynamic trap* for the tetracationic cyclophane **5**.4PF$_6$, raising the activation energy for the extrusion process relative to that for slippage. The [2]rotaxane structures which arise are stabilised by a multitude of dispersive forces, such as charge transfer interactions, π–π stacking interactions, T-type interactions, and hydrogen bonding.[7] Hence, the self-assembled [2]rotaxanes **9**.4PF$_6$ and **10**.4PF$_6$ are very stable compounds.

Addition of alkali metal cations to the dumbbell-shaped compounds **3** and **4**, prior to carrying out the slippage experiment with the tetracationic cyclophane **5**.4PF$_6$ in MeCN at 50 °C, inhibits the formation of the [2]rotaxanes **9**.4PF$_6$ and **10**.4PF$_6$. It is proposed that, the increase in size of the monoaza-18-crown-6 macrocyclic termini, which occurs as a result of them complexing alkali metal cations, is sufficient to prevent the slippage of the tetracationic cyclophane **5**.4PF$_6$ over them.

The X-ray crystal structural analysis†† of **10**.4PF$_6$ reveals (Figs. 2 and 3) an elegant structural arrangement wherein the (monoaza-18-crown-6)-terminated dumbbell-shaped component is threaded centrosymmetrically through the middle of the tetracationic cyclophane,‡‡ the OC$_6$H$_4$O axis of the hydroquinone rings being inclined by 45° to the plane of the cyclophane. In addition to the π–π stacking interaction between the electron rich hydroquinone ring and the electron deficient bipyridinium units, there are (i) T-type edge-to-face interactions between the hydroquinone ring of the dumbbell-shaped component and the *p*-xylyl residues of the tetracationic cyclophane component [(H···π) distance, 2.87 Å; (C–H···π) angle, 157°], (ii) (C–H···O) hydrogen bonds between pairs of α-bipyridinium hydrogen atoms in the dumbbell-shaped component [(C···O) distance, 3.36 Å; (H···O) distance, 2.47 Å (C–H···O) angle, 154°], and (iii) a pair of strong electrostatic interactions between the carbonyl oxygen atoms of the amide functions in the dumbbell-shaped component and their proximal bipyridinium carbon atoms in the cyclophane component: the (C···O) distances are 2.81 Å.§§ The only supramolecular feature to note is a parallel and overlapping alignment between the *p*-xylyl residue in adjacent [2]rotaxanes. The associated interplanar and centroid–centroid separations are 4.03 and 4.17 Å, respectively, indicating an absence of any appreciable π-π stacking interactions.

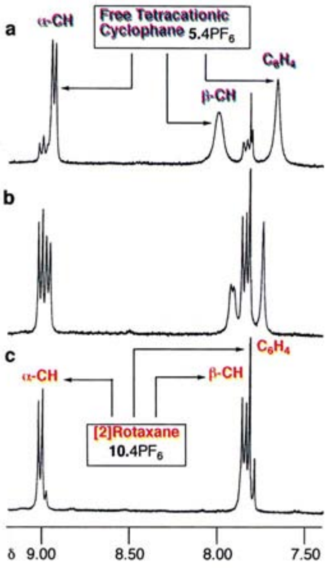


Fig. 1 Partial ^{1}H NMR spectra showing the self-assembly of the [2]rotaxane **10**.4PF$_6$ from **5**.4PF$_6$ and **4** in CD$_3$CN at 50 °C (*a*) at the beginning, (*b*) after 5 d and (*c*) after 14 d. The labels α-CH and β-CH refer to pyridinium ring protons α and β to the nitrogen atoms and the label C$_6$H$_4$ refer to the *p*-xylyl residue units of the tetaracationic cyclophane **5**.4PF$_6$.

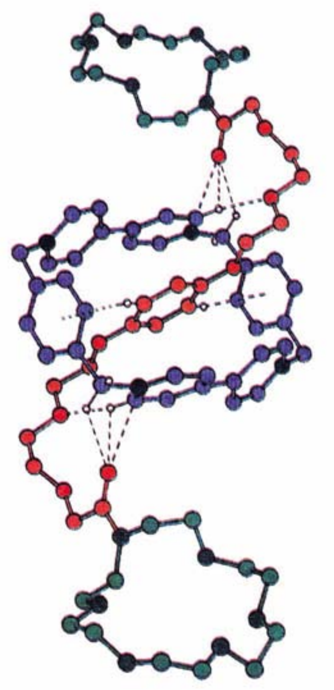


Fig. 2 A ball-and-stick representation of the solid state structure of the [2]rotaxane **10**.4PF$_6$. The tetracationic cyclophane component is shaded in blues. The dumbbell-shaped component is portrayed with the thread portion coloured in shades of red and the monoaza-18-crown-6 stoppers in shades of green.

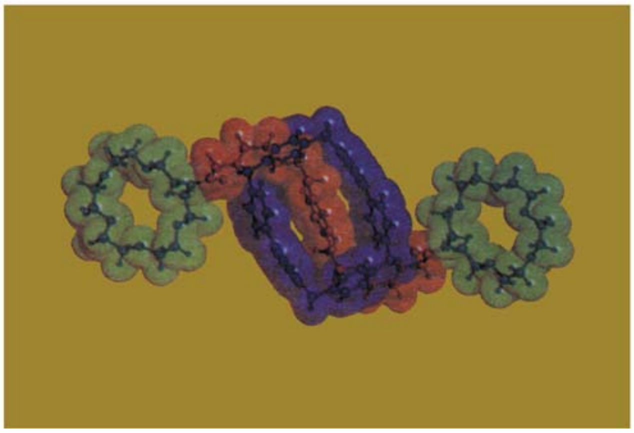
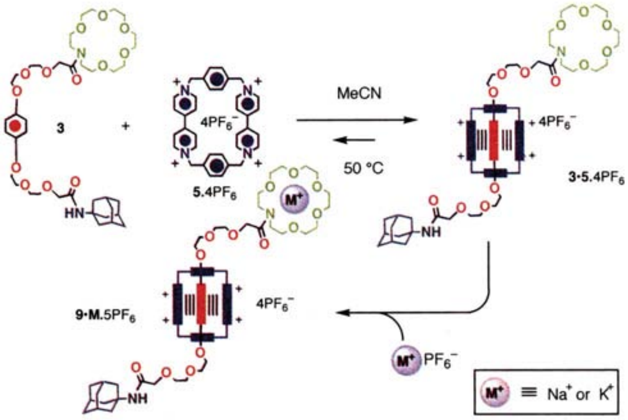


Fig. 3 Ball-and-stick representation of the solid state structure of the [2]rotaxane **10**.4PF$_6$, superimposed upon a space-filling version

The Liquid Secondary Ion Mass Spectra (LSIMS) of the two [2]rotaxanes **9**.4PF$_6$ and **10**.4PF$_6$ shows peaks at *m/z* 1881 and 1993, which correspond to their respective molecular ions [M]$^+$. Additionally, peaks arising from the successive loss of three hexafluorophosphate counterions are significant features of the spectra. Following the addition of NaPF$_6$ (5×10^{-3} mol dm^{-3} in MeCN) to a solution of the [2]rotaxane **9**.4PF$_6$ (5×10^{-3} mol dm^{-3} in MeCN) the LSIMS now shows a molecular ion at *m/z* 2049 which corresponds to a 1 : 1 adduct between the [2]rotaxane **9**.4PF$_6$ and NaPF$_6$ along with the successive loss of hexafluorophosphate counterions (Scheme 4). The treatment of a solution of the bis(monoaza-18-crown-6)-containing [2]rotaxane **10**.4PF$_6$ with NaPF$_6$, however, produces a spectrum which now shows a molecular ion at *m/z* 2329 for a 1 : 2 adduct between the [2]rotaxane **10**.4PF$_6$ and NaPF$_6$ and the usual losses of hexafluorophosphate counterions as major fragments (Table 1). Experiments using KPF$_6$ instead of NaPF$_6$ produced complementary spectra for the [2]rotaxanes **9**.4PF$_6$ and **10**.4PF$_6$. The number of alkali metal cations bound within the [2]rotaxanes appears to correspond to the number of monoaza-18-crown-6-macrocycles available for binding on a 1 : 1 molar basis. Furthermore, unthreading of the [2]rotaxanes **9**.4PF$_6$ and **10**.4PF$_6$ does not occur^8 readily upon addition of alkali metal cations as observed in similar systems.

The self-assembly of a new class of [2]rotaxanes **9**.4PF$_6$ and **10**.4PF$_6$, bearing monoaza-18-crown-6 macrocycles at their termini by employing a slippage methodology, has been demonstrated. Hence, an efficient method to synthesise [2]rotaxanes from dumbbell-shaped compounds capable of recognising alkali metal and organic cations has been established. We have also shown that the size of the stoppers can be modified by the addition of alkali metal cations to inhibit the slippage of the tetracationic cyclophane **5**.4PF$_6$ over the monoaza-18-crown-6-macrocyclic termini.



Scheme 4 The self-assembly and complexation **9**.4PF$_6$ with NaPF$_6$ and KPF$_6$

Table 1 LSIMS^a data for [2]rotaxanes **9**.4PF$_6$ and **10**.4PF$_6$ and their alkali metal complexes with NaPF$_6$ and KPF$_6$

Compound	[M]$^+$	[M − PF$_6$]$^+$	[M − 2PF$_6$]$^+$	[M − 3PF$_6$]$^+$
9.4PF$_6$	1881	1735	1590	1445
9·Na.5PF$_6$	2049	1903	1758	1613
9·K.5PF$_6$	2065	1919	1775	1630
10.4PF$_6$	1993	1848	1703	1558
10·2Na.6PF$_6$	2329	2183	2038	1893
10·2K.6PF$_6$	2361	2216	2071	1926

^{a} LSIMS were obtained from a VG Zabspec mass spectrometer operating at 8 kV and 2500 resolution and samples were dissolved in 1–2 μl of *m*-nitrobenzyl alcohol which had previously been coated onto a stainless steel probe. Spectra were recorded in the positive ion mode at a scan speed of 5 s per decade.

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Footnotes

† Monoaza-18-crown-6 macrocycle and 1-aminoadamantane were purchased from the Aldrich Chemical Company.

‡ A series of dumbbell-shaped compounds containing carbon-pivoted 12-crown-4, 15-crown-5, and 18-crown-6 macrocycles have been investigated to assess their abilities to act as slippage stoppers for the tetracationic cyclophane **5**.4PF$_6$. It was found that 12-crown-4 and 15-crown-5 derivatives are too small and hence [2]pseudorotaxanes result instantaneously upon addition of the tetracationic cyclophane, whereas the 18-crown-6 derivative was found to be too large to allow slippage to occur. The monoaza-18-crown-6 macrocycle was identified as the slippage stopper for the dumbbell-shaped component since it is slightly larger in size than the 15-crown-5 macrocycle and slightly smaller in size than the 18-crown-6 macrocycle.

§ The diacid chloride **1** was synthesised by reaction of the corresponding diacid with oxalyl chloride in toluene at room temperature.

¶ *Selected data* for **8**.4PF$_6$: $C_{74}H_{88}N_6O_8P_4F_{24}$ requires [M$^+$] 1769. Found (positive ion LSIMS) [M − PF$_6$]$^+$ 1623, [M − 2PF$_6$]$^+$ 1479 and [M − 3PF$_6$]$^+$ 1334; δ_H (300 MHz, CD$_3$CN) 8.94 (8 H, d, *J* 6.5 Hz), 7.86 (8 H, d, *J* 6.5 Hz), 7.83 (8 H, s), 6.26 (2 H, br s), 5.72 (8 H, s), 3.97–3.99 (4 H, m), 3.96 (4 H, s), 3.88–3.90 (8 H, m), 3.62–3.65 (4 H, m), 3.56 (4 H, s), 2.24 (12 H, br s), 1.80–1.90 (6 H, m) and 1.60–1.63 (12 H, m); δ_C (75 MHz, CD$_3$CN) 169.5, 151.1, 147.7, 145.8, 137.7, 132.0, 127.1, 114.0, 72.0, 71.8, 71.6, 70.7, 67.9, 65.8, 52.5, 42.2, 37.0 and 30.4. For **9**.4PF$_6$: $C_{76}H_{96}N_6O_{13}P_4F_{24}$ requires [M]$^+$ 1881. Found (positive ion LSIMS) [M − PF$_6$]$^+$ 1736, [M − 2PF$_6$]$^+$ 1590 and [M − 3PF$_6$]$^+$ 1445; δ_H (300 MHz, CD$_3$CN) 8.97 (8 H, d, *J* 6.5 Hz), 7.86 (8 H, d, *J* 6.5 Hz), 7.83 (8 H, s), 6.26 (1 H, s), 5.75 (8 H, s), 4.01–3.86 (8 H, m), 3.68–3.42 (40 H, m), 2.24 (6 H, br s), 1.80–1.90 (3 H, m) and 1.60–1.63 (6 H, m); δ_C (75 MHz, CD$_3$CN) 171.0, 169.9, 151.1, 151.0, 147.7, 145.7, 137.7, 131.9, 127.0, 114.0, 113.9, 72.0, 71.9, 71.7, 71.5, 71.3, 71.1, 70.7, 70.4, 70.3, 69.9, 69.7, 67.5, 65.0, 64.1, 52.5, 42.1, 42.0, 36.9, 36.9, 30.3 and 30.3. For **10**.4PF$_6$: $C_{78}H_{104}N_6O_{18}P_4F_{24}$ requires [M]$^+$ 1993. Found (positive ion LSIMS) [M − PF$_6$]$^+$ 1848, [M − 2PF$_6$]$^+$ 1703, [M − 3PF$_6$]$^+$ 1558 and [M − 4PF$_6$]$^+$ 1413; δ_H (300 MHz, CD$_3$CN) 8.98 (8 H, d, *J* 6.5 Hz), 7.87 (8 H, d, *J* 6.5 Hz), 7.84 (8 H, s), 6.00 (4 H, br s), 5.74 (8 H, s), 4.38 (4 H, s), 3.96–3.98 (4 H, m), 3.89–3.93 (8 H, m), 3.64–3.68 (4 H, m), 3.44–3.54 (48 H, m); δ_C (75 MHz, CD$_3$CN) 170.6, 151.0, 147.6, 145.9, 137.8, 131.9, 127.1, 126.9, 113.9, 72.1, 71.9, 71.0, 70.9, 70.8, 70.6, 69.8, 67.9, 66.3, 65.6 and 31.3.

‖ The value $k_a = 1.3 \times 10^{-4}$ mol dm^{-3} s^{-1} of the second-order rate constant for the formation of the [2]rotaxane **10**.4PF$_6$, was obtained from ^{1}H NMR spectroscopy at 50 °C in CD$_3$CN. The second-order rate constant was calculated by a non-linear curve-fitting procedure (K. J. Laidler, *Chemical Kinetics*, 3rd edn., Harper Collins Publishers, New York, 1987).

** Kieselgel 60 F$_{254}$ preparative thin layer chromatography (TLC) plates were purchased from Merck.

†† *Crystal data* for [**10**.4PF$_6$].2MeCN: $C_{78}H_{104}N_6O_{18}F_{24}P_4$.2MeCN, M = 2075.66, triclinic, a = 12.236(2), b = 14.172(3), c = 14.474(3) Å, α = 90.74(2), β = 103.45(2), γ = 99.96(2)°, V = 2400.4(8) Å^3, space group $P\bar{1}$, Z = 1 (the rotaxane has crystallographic C_i symmetry), D_c = 1.436 g cm^{-3}, μ(Cu-Kα) = 17.4 cm^{-1}, $F(000)$ = 1078. An orange–yellow block of dimensions 0.40 × 0.27 × 0.20 mm was used. 7130 Independent reflections ($2\theta \leq 120°$) were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically by full-matrix least-squares (based on F^2) to give R_1 = 0.088 and wR_2 = 0.2321 for 4921 independently observed reflections [$|F_0| > 4\sigma(|F_0|)$, ($2\theta \leq 120°$)] and 622 parameters. 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.

‡‡ The tetracationic cyclophane displays characteristic twisting and bowing distortions within the bipyridinium units, the twist angle between the two pyridnium rings being 26° whilst the two NCH$_2$ bonds subtend an angle of 27°.

§§ The shortest (H...O) contacts to these carbonyl oxygen atoms are from α-bipyridinium hydrogen atoms (2.52 Å) and from one of the methylene hydrogen atoms (2.53 Å) within the cyclophane component as illustrated in Fig. 2.

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