The Self-assembly of [*n*]Pseudorotaxanes

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An acyclic oligomeric polyether in which four tetraethylene glycol units are located between five hydroquinol rings, with the two terminal rings carrying benzyl ether groups, self-assembles in solution with one and two molar equivalents of a tetracationic cyclobis(paraquat-*p*-phenylene) macrocycle to afford, respectively and selectively, a [2]pseudorotaxane and a [3]pseudorotaxane.

In Nature, large, ordered, and structured molecular assemblies are constructed with remarkable ease and accuracy as a result of the operation of various kinds of self-assembly processes.[1] In the realm of wholly-synthetic systems,[2] examples of superstructures assembled in this manner are still relatively rare. Recently, we reported[3] the formation (Scheme 1) of the [2]pseudorotaxane‡ $[\mathbf{1}\cdot\mathbf{3HQ}]^{4+}$ from its molecular components $\mathbf{1}^{4+}$ and **3HQ** by a self-assembly process. Furthermore, X-ray crystallography revealed that this 1 : 1 complex displays a remarkable degree of self-ordering in the solid state. In order to investigate further the range and generality of the self-assembly process evident in the construction of $[\mathbf{1}\cdot\mathbf{3HQ}]^{4+}$, we have now synthesised[4] the larger, acyclic polyether homologue **5HQ** containing five π-electron-rich hydroquinol rings. We envisaged that molecules of this higher oligomer (**5HQ**) of **3HQ** might self-assemble in the first instance with one—and then with two—molecules of the cyclobis(paraquat-*p*-phenylene) tetracation[5–9] $\mathbf{1}^{4+}$, yielding (Scheme 2), firstly a [2]pseudorotaxane $[\mathbf{1}\cdot\mathbf{5HQ}]^{4+}$, and then subsequently a [3]pseudorotaxane $[\mathbf{1}_2\cdot\mathbf{5HQ}]^{8+}$. Here, we report that this expectation has been fulfilled.

When **5HQ** is mixed in acetone with $\mathbf{1}\cdot4\mathrm{PF}_6$ in equimolar proportions, a deep orange coloured solution results. When the solvent is removed *in vacuo*, the residual solid is reddish-orange in colour. Analysis of this solid by FABMS§ revealed two peaks at *m*/*z* 2317 and 2172 corresponding to $[\mathrm{M} - \mathrm{PF}_6]^+$ and $[\mathrm{M} - 2\mathrm{PF}_6]^+$ as a result of the loss of one and two counterions respectively from a [2]pseudorotaxane $[\mathbf{1}\cdot\mathbf{5HQ}][\mathrm{PF}_6]_4$ formed between $\mathbf{1}\cdot4\mathrm{PF}_6$ and **5HQ**. In addition, a lower intensity peak is evident at *m*/*z* 2484 for $[\mathrm{M} + \mathrm{Na}]^+$. When this experiment was repeated with two molar equivalents of $\mathbf{1}\cdot4\mathrm{PF}_6$ with respect to **5HQ**, the residual solid was red in colour. Although the positive-ion FABMS revealed only peaks for the [2]pseudorotaxane $[\mathbf{1}\cdot\mathbf{5HQ}][\mathrm{PF}_6]_4$, ^{1}H NMR spectroscopy at 400 MHz confirmed the existence of the [3]pseudorotaxane $[\mathbf{1}_2\cdot\mathbf{5HQ}][\mathrm{PF}_6]_8$ as predominantly one 2 : 1

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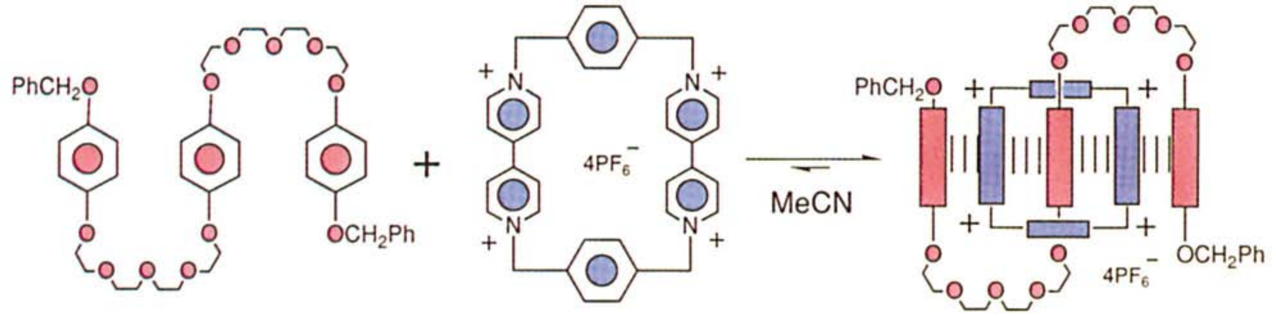
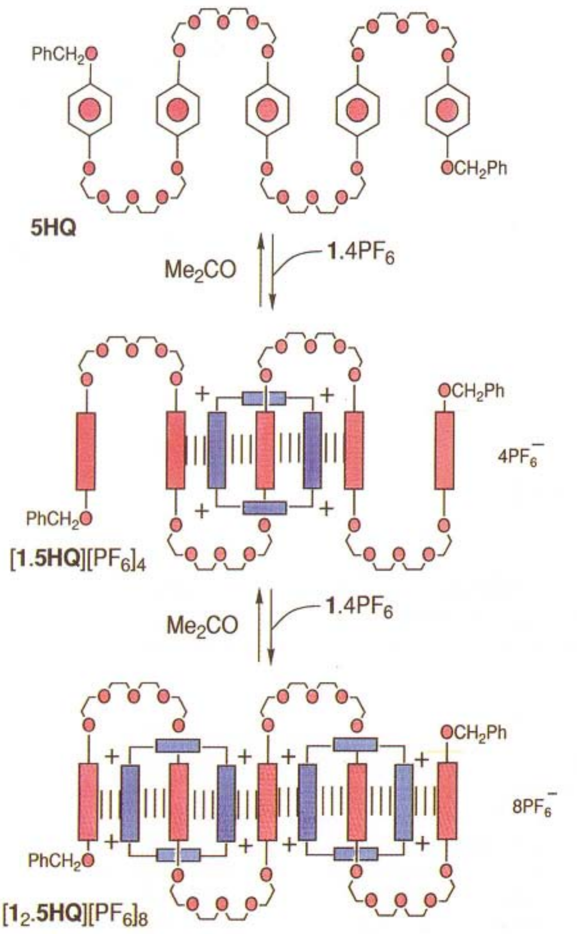
‡ The name *rotaxane* derives (G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, 1971) from the Latin *rota* meaning wheel and *axis* meaning axle. The addition of the prefix *pseudo* indicates (ref. 10) that the wheels are free to dissociate from the axle as in a more conventional type of complex. In chemical terms, this means that molecular components of the *pseudorotaxane* are held together only by their mutual noncovalent bonding attraction and not (also) by a mechanical feature as in a genuine rotaxane.

§ FABMS was carried out on a Kratos MS80RF mass spectrometer (accelerating voltage, 3 kV; resolution 1500) coupled to a DS90 data system. The atom gun was an adapted saddle field source (Ion Tech Ltd.) operated at *ca.* 7 keV with a tube current of *ca.* 2 mA. Xenon was used to provide a primary beam of atoms. The samples were dissolved in a small volume of 3-nitrobenzyl alcohol which had been previously coated on to a stainless steel probe tip. Spectra were recorded in the positive-ion mode at scan speed of 30 s per decade.



Scheme 1 The self-assembly of the [2]pseudorotaxane [**1·3HQ**]$[PF_6]_4$ from **3HQ** and **1**·$4PF_6$ in acetonitrile. Red rectangles refer to hydroquinol rings. Large and small blue rectangles refer to 4,4′-bipyridinium and *p*-phenylene rings, respectively.



Scheme 2 The step-wise self-assembly of the [2]pseudorotaxane [**1·5HQ**]$[PF_6]_4$ and the [3]pseudorotaxane [**1**$_2$·**5HQ**]$(PF_6)_8$ from **5HQ** and **1**·$4PF_6$ in acetone. Red rectangles refer to hydroquinol rings. Large and small blue rectangles refer to 4,4′-bipyridinium and *p*-phenylene rings, respectively.

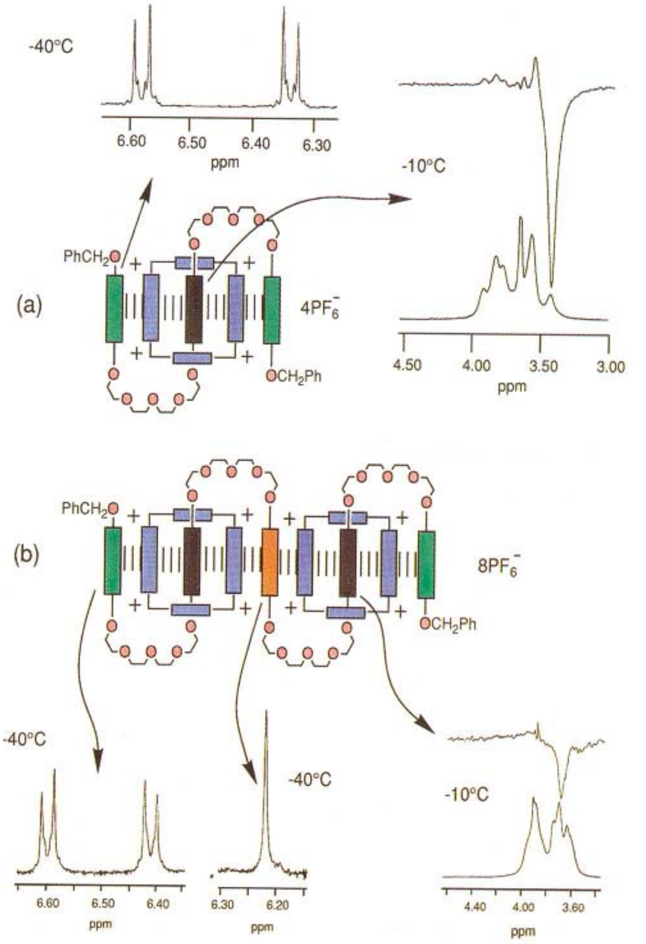


Fig. 1 ^{1}H NMR spectra recorded at −10 and −40 °C for (*a*) [**1·3HQ**]$[PF_6]_4$ in CD_3CN and for (*b*) [**1**$_2$·**5HQ**]$[PF_6]_8$ in CD_3COCD_3. Black, green and orange rectangles refer to hydroquinol rings. Large and small blue rectangles refer to 4,4′-bipyridinium and *p*-phenylene rings, respectively.

complex. The resonances for the hydroquinol protons in the ^{1}H NMR spectrum of this complex in CD_3COCD_3 at room temperature are quite broad. However, at −40 °C, in addition to a singlet resonating at δ 6.22 for the protons on the orange hydroquinol ring, an AA′BB′ system is observed (Fig. 1) in the range δ 6.39–6.62 for the protons on the green hydroquinol rings. This assignment was confirmed by carrying out an NOE difference experiment at −10 °C: irradiation of the AA′ portion of the AA′BB′ system resulted in an enhancement of the signal at δ 4.85 for the benzylic methylene protons located on the benzyl groups at the ends of the **5HQ** oligomer. This experiment also allowed us to identify a resonance at δ 3.70 for the protons on the black hydroquinol rings: some saturation transfer was observed between the protons on the green and black hydroquinol rings whilst performing the NOE difference experiment. The signal pattern displayed for these protons is almost identical to that observed in CD_3CN at low temperatures for the smaller [2]pseudorotaxane[3] [**1·3HQ**]$[PF_6]_4$. The protons on the black hydroquinol ring of this 1 : 1 complex were identified (δ 3.43) as a result of some saturation transfer which was observed during an NOE difference experiment performed at −10 °C. At −40 °C, the protons on the green hydroquinol rings of the [2]pseudorotaxane [**1·3HQ**]$[PF_6]_4$ resonate as an AA′BB′ system spanning the range δ 6.33 to δ 6.60. The relative simplicity of these ^{1}H NMR spectra suggests that both these pseudorotaxanes exist

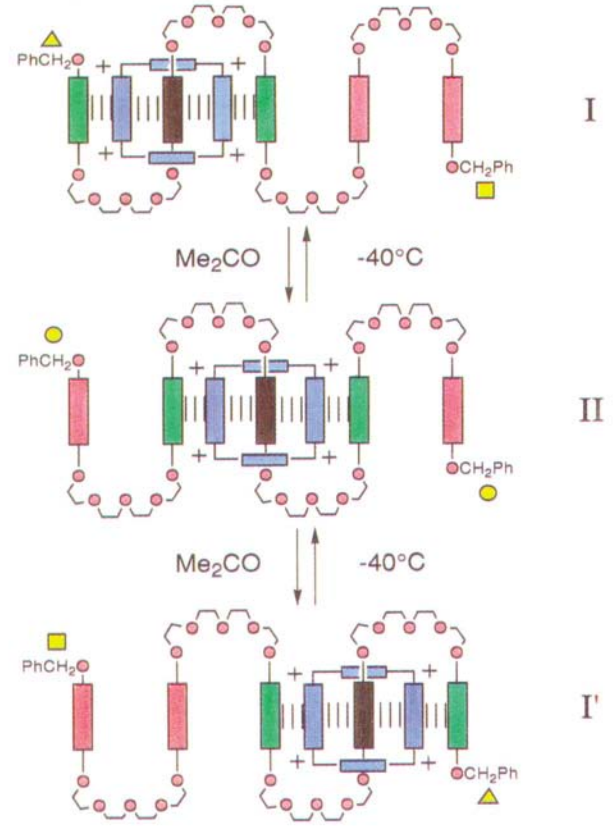


Fig. 2 The equilibration process in the [2]pseudorotaxane $[\mathbf{1}\cdot\mathbf{5HQ}]^{4+}$ between species **I**, **I'**, and **II** in solution. Black, green and red rectangles refer to hydroquinol rings. Large and small blue rectangles refer to 4,4'-bipyridinium and *p*-phenylene rings, respectively.

predominantly as one superstructure in solution at low temperatures. Further evidence for the superstructure shown in Fig. 1 for $[\mathbf{1}_2\cdot\mathbf{5HQ}][PF_6]_8$ is present in the ^1H NMR spectrum recorded at −80 °C. In addition to an upfield shift of 0.22 ppm for the protons on the orange hydroquinol ring, indicative of a stronger dynamic interaction between this π-electron-rich aromatic ring and the two adjacent π-electron-deficient bipyridinium (bipy) rings of the $\mathbf{1}^{4+}$ tetracations, the α- and β-bipy-CH protons (α and β with respect to N) *each* resonate as *two* doublets.¶

In the ^1H NMR spectrum of the [2]pseudorotaxane $[\mathbf{1}\cdot\mathbf{5HQ}][PF_6]_4$ recorded in CD_3COCD_3 at room temperature, the resonances for the hydroquinol ring protons in the **5HQ** component are very broad, indicating that the intramolecular and/or intermolecular exchange processes are occurring slowly on the ^1H NMR time-scale. On cooling the solution down to −40 °C, the singlet observed (δ 4.98) at room temperature for the benzylic methylene protons in the **5HQ** component separates into two singlets at δ 4.86 and δ 5.00 with a relative intensity of 1 : 2. This temperature-dependent behaviour may be rationalised in terms of the equilibrium shown in Fig. 2 between the degenerate complexes **I** and **I'** and the translational isomer **II**. The high field signal (δ 4.86) can be assigned to the benzylic methylene protons associated with the yellow triangles and the lower field one (δ 5.00) associated with the yellow circles and squares. A saturation transfer experiment (*vide supra*) allowed us to locate signals for the black and green hydroquinol ring protons at δ 3.65 and in the range δ 6.20 to δ 6.60, respectively. Lower field signals in the region δ 6.70 to δ6.90 can be assigned to protons on the red hydroquinol rings. The relative intensities of 1 : 2 : 2 from high to low field for these signals equates well with the proportion of black : green : red hydroquinol rings arising from an equimolar mixture of **I**, **I'** and **II** present in the equilibrium shown in Fig. 2. This interpretation is also consistent with the temperature dependent behaviour of the benzylic methylene protons in the ^1H NMR spectrum discussed above.

Both $[\mathbf{1}\cdot\mathbf{3HQ}][PF_6]_4$ and $[\mathbf{1}\cdot\mathbf{5HQ}][PF_6]_4$ exhibit charge-transfer bands centred on 468 nm. Spectrophotometric titrations performed at this wavelength at 27 °C afforded K_a values of 2800 and 2900 dm^3 mol^{-1}, respectively, for the 1 : 1 complex formed between (*i*) $\mathbf{1}\cdot 4PF_6$ and **3HQ** and (*ii*) $\mathbf{1}\cdot 4PF_6$ and **5HQ**. The free energy of complexation (4.75 kcal mol^{-1}; 1 cal = 4.184 J) is very similar for both these [2]pseudorotaxanes. This observation was not unexpected.

With the spontaneous formation of the [3]pseudorotaxane $[\mathbf{1}_2\cdot\mathbf{5HQ}]^{8+}$, we have demonstrated that it is possible to self-assemble a superstructure which is reasonably large at a termolecular level simply by employing two different molecular components which, by virtue of their mutual recognition properties, are capable of self-organising themselves in a delicately controlled and stepwise manner. Assuming a tightly packed π–π stacked structure for $[\mathbf{1}_2\cdot\mathbf{5HQ}]^{8+}$, the [3]pseudorotaxane is *ca.* 30 Å long with a diameter of around 15 Å. In general, tertiary structures assembled by this kind of modular approach may be viewed[10,11] as prototypes for the construction of large, ordered polymolecular arrays capable of functioning as information storing and processing devices.[12]

We thank SERC in the UK and NEDO in Japan for financial support.

Received, 23rd July 1991; Com. 1/03756K

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¶ This observation implies that one of two possible reorganisations within the superstructure of $[\mathbf{1}_2\cdot\mathbf{5HQ}]^{8+}$ is slow at −70 °C on the ^1H NMR time-scale either (*i*) the pirouetting simultaneously of both the tetracationic macrocycles $\mathbf{1}^{4+}$ about the O· · · ·O axis of the black hydroquinol rings, or (*ii*) the conrotatory oscillation of the tetracation macrocycles $\mathbf{1}^{4+}$ about their long axis such that, in both cases, the bipyridinium units between green and black, and black and orange hydroquinol rings are undergoing slow exchange. Further experiments are required in order to eludicate which of these two exchange processes is being observed in the temperature range −60 to −80 °C at 400 MHz.