A supramolecular poly[3]pseudorotaxane by self-assembly of a homoditopic cylindrical bis(crown ether) host and a bisparaquat derivative†

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A supramolecular poly[3]pseudorotaxane was prepared by self-assembly of a homoditopic cylindrical bis(crown ether) host and a bisparaquat derivative in solution by host–guest complexation.

Supramolecular polymers have currently attracted great interest.[1,2] Recent examples include discotic liquid crystals driven by hydrogen-bonding,[2a] bipyridine metal-coordination polymers,[2b] dye aggregation driven by dipolar interactions,[2c] poly(pseudorotaxane) on gold using host-stabilized charge-transfer interactions,[2d] and an aqueous amphiphilic perylene polymer driven by hydrophobic–hydrophilic interactions.[2e] Interlocked macromolecules, including polyrotaxanes[3] and polycatenanes,[4] have been widely studied because of their unique mechanically interlocked structures and potential functions.[5] Here we report the formation of a supramolecular poly[3]pseudorotaxane from self-assembly of a homoditopic cylindrical bis(crown ether) host and a bisparaquat derivative in solution by host–guest complexation. When appropriate stoppers are introduced, this poly[3]pseudorotaxane can be transformed into a poly[3]rotaxane interlocked macromolecule.

Recently we found that cylindrical bis(crown ether) host **1** forms a [3]pseudorotaxane with paraquat **2** (Fig. 1); the interactions of the two guests with the host are independent of each other.[6] Therefore, a supramolecular poly[3]pseudorotaxane **4** can form when a bisparaquat derivative **3**[7] complexes **1** (Scheme 1). The directional requirements for the formation of the [3]pseudorotaxane structure and the rigid natures of **1** and **3** make it unfavorable to form cyclic species as deduced from CPK model studies. The proton NMR spectra of equimolar solutions of **1** and **3** (Fig. 2) are concentration dependent, reflecting the involvement of fast-exchanging noncovalent interactions in solution. When the initial concentrations of **1** and **3** increased, a larger chemical shift change was observed for H_1 on **3**. This demonstrated that the percentage of complexed paraquat moieties increased with increasing initial concentrations of **1** and **3**, showing the formation of supramolecular poly[3]pseudorotaxane **4**. Values of the fraction *p* of

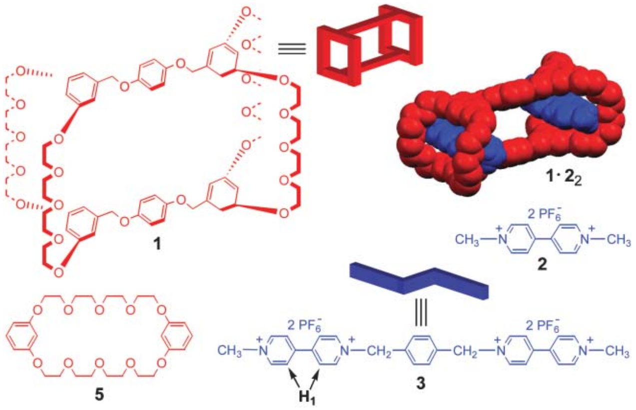
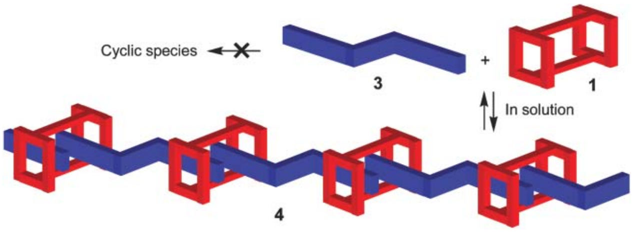


Fig. 1 Compounds used in this study and a space-filling diagram[6] of the [3]pseudorotaxane **1**·**2**$_2$.



Scheme 1 Schematic illustration of the formation of a supramolecular poly[3]pseudorotaxane **4** based on the self-assembly of the complementary homoditopic host **1** and guest **3**.

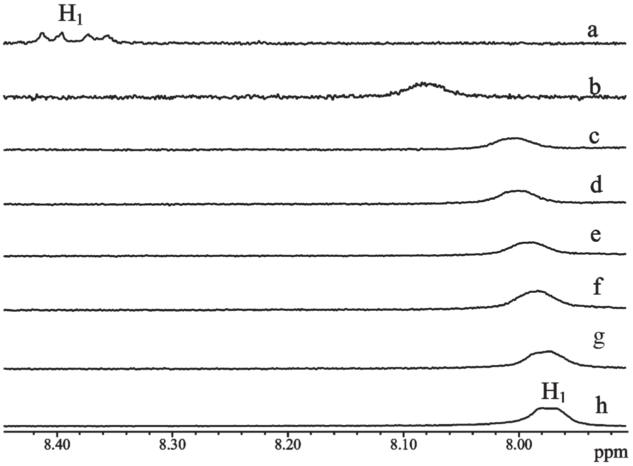


Fig. 2 Partial proton NMR spectra (400 MHz, 1 : 1 acetonitrile-d_3 : chloroform-*d*, RT) of **3** (a) and the mixture of **1** and **3** (molar ratio 1 : 1) at different concentrations: (b) 0.438, (c) 1.90, (d) 2.22, (e) 2.67, (f) 3.33, (g) 4.44, and (h) 6.67 mM.

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† Electronic supplementary information (ESI) available: Other parts of the MALDI-TOF mass spectrum of **4** and details on the determination of Δ_0 of H_1 on **3**. See http://www.rsc.org/suppdata/cc/b4/b417966h/
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Table 1 Δ, p, and n at different initial concentrations of **1** and **3**

$[\mathbf{1}]_0 = [\mathbf{3}]_0$ (mM)	Δ (ppm)	p	n
1.90	0.381	0.903	10.3
3.33	0.396	0.938	16.1
6.67	0.410	0.972	35.7

complexed paraquat moieties and the degree n of polymerization at different initial concentrations of **1** and **3** were estimated (Table 1) according to the value of the maximum chemical shift change Δ_0, determined to be 0.421 ppm by extrapolation of a plot of $\Delta = \delta - \delta_u$ *vs.* $1/[\mathbf{1}]_0$ in the high initial concentration range of **1**.[8] As the initial concentrations increase the calculated size of the supramolecular polymeric aggregrate increases. For example, at $[\mathbf{1}]_0 = 6.67$ mM, $n = 35.7$, corresponding to a polymer molar mass of 8.44×10^4 g mole^{-1}.

The MALDI-TOF mass spectrum (Fig. 3) provided support for the formation of the supramolecular poly[3]pseudorotaxane **4**. The base peak was found at *m/z* 172.91 (100%), which is from 4-[4′-(*N*-methylpyridinium)]pyridine, $[C_{11}H_{11}N_2 + 2H]^+$. Six peaks were found for **3·1·3**: *m/z* 2783.17 $[\mathbf{3{\cdot}1{\cdot}3} - 4PF_6 - 2CH_3]^+$ (2.0%), 2640.65 $[\mathbf{3{\cdot}1{\cdot}3} - C_{11}H_{11}N_2 - 4PF_6]^+$ (1.9%), 2496.36 $[\mathbf{3{\cdot}1{\cdot}3} - C_{11}H_{11}N_2 - 5PF_6]^+$ (2.0%), 2325.90 $[\mathbf{3{\cdot}1{\cdot}3} - 2C_{11}H_{11}N_2 - 5PF_6]^+$ (1.9%), 2181.09 $[\mathbf{3{\cdot}1{\cdot}3} - 2C_{11}H_{11}N_2 - 6PF_6]^+$ (2.5%), and 2036.12 $[\mathbf{3{\cdot}1{\cdot}3} - 2C_{11}H_{11}N_2 - 7PF_6]^+$ (2.0%). Four peaks correspond to **1·3·1**: *m/z* 3349.56 $[\mathbf{1{\cdot}3{\cdot}1} - 2PF_6 - C_7H_6O + K]^+$ (1.5%), 3220.23 $[\mathbf{1{\cdot}3{\cdot}1} - 3PF_6 - C_6H_4O + K + H]^+$ (1.6%), 3061.05 $[\mathbf{1{\cdot}3{\cdot}1} - 4PF_6 - C_7H_6O + K + H]^+$ (1.6%), and 2931.68 $[\mathbf{1{\cdot}3{\cdot}1} - 4PF_6 - C_7H_6O - C_6H_4O + 2H]^+$ (1.8%). Three peaks correspond to $(\mathbf{1{\cdot}3})_2$: *m/z* 3805.37 $[(\mathbf{1{\cdot}3})_2 - C_{11}H_{11}N_2 - 3PF_6 - 2HPF_6 - 2CH_3]^+$ (1.4%), 3665.47 $[(\mathbf{1{\cdot}3})_2 - C_{11}H_{11}N_2 - 5PF_6 - C_7H_6 - C_7H_6O_2 + K + H]^+$ (1.4%), and 3519.45 $[(\mathbf{1{\cdot}3})_2 - C_{11}H_{11}N_2 - 6PF_6 - C_7H_6 - C_7H_6O_2 + K]^+$ (1.6%). Weaker peaks in higher mass ranges were found up to tetramers, corresponding to a polymer molecule weight of about 10,000 g mole^{-1}. However, the intensity of the peaks diminish as the molecular weight increases. Since the MALDI-TOF spectra depend on the ability of the molecule to "fly" under the experimental conditions, the possibility of the presence of still higher units in the polymer cannot be ruled out.

Further support came from viscosity studies (Fig. 4).[10] Under the same bisparaquat molar concentration, the 1 : 1 CH_3CN : $CHCl_3$ solutions of **4** have higher viscosity than the solutions of a model system containing simple crown ether **5**[11] and bisparaquat **3** (molar ratio 2 : 1). The relationship between the reduced viscosity of solutions of **4** and the concentration has the typical feature of some traditional covalent polyelectrolytes, that is, a maximum viscosity peak at low concentrations.[12] Under the existence of an added electrolyte, this maximum peak disappeared (line b in Fig. 4).[13] When monotopic crown ether **5** was added into solutions of **4**, an expected reduction of viscosity was observed.

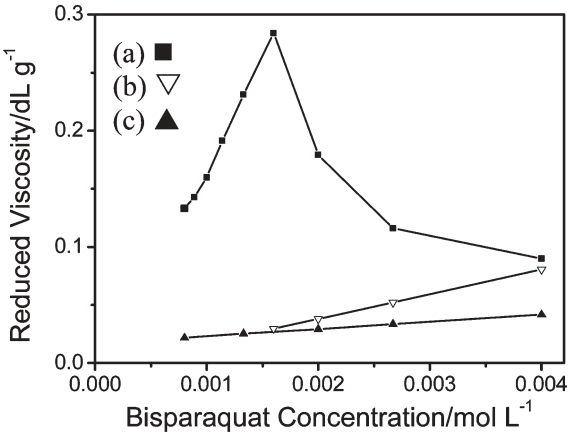

Fig. 4 Reduced viscosity as a function of bisparaquat concentration (solutions at RT): (a) **1** and **3** (molar ratio 1 : 1) in 1 : 1 CH_3CN : $CHCl_3$, (b) **1** and **3** (molar ratio 1 : 1) in a 1 : 1 CH_3CN : $CHCl_3$ solution of 0.0500 M tetrabutylammonium hexafluorophsphate, (c) **5** and **3** (molar ratio 2 : 1) in 1 : 1 CH_3CN : $CHCl_3$.

In summary, we have demonstrated that a supramolecular poly[3]pseudorotaxane can be prepared from a homoditopic cylindrical bis(crown ether) host and a bisparaquat derivative in solution. The trapping of the paraquat moieties in these polymers by introducing appropriate blocking groups will produce a poly[3]rotaxane interlocked macromolecule. This new method of preparing one-dimensional supramolecular polymers can easily be extended to similiar supramolecular polymers based on other well-established recognition motifs.

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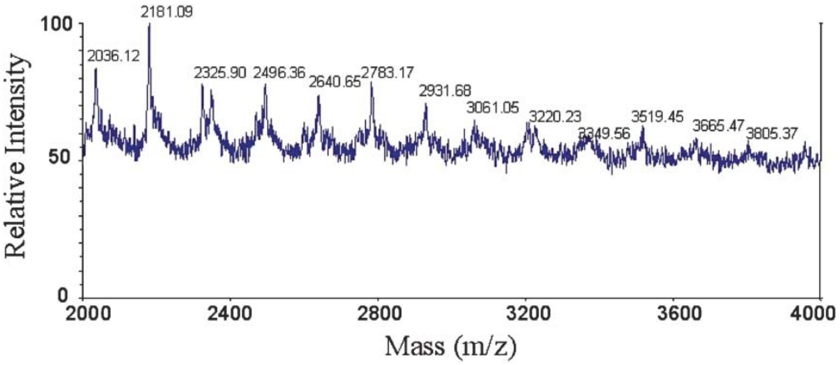

Fig. 3 The partial MALDI-TOF mass spectrum of the supramolecular poly[3]pseudorotaxane **4** formed from **1** and **3**. The spectrum was measured in the positive-ion mode using 2,5-dihydroxbenzoic acid as the matrix and acetone as the solvent.

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