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Pseudo-polyrotaxanes based on a protonated version of the 1,2-bis(4,4′-bipyridinium)ethane–24-crown-8 ether motif

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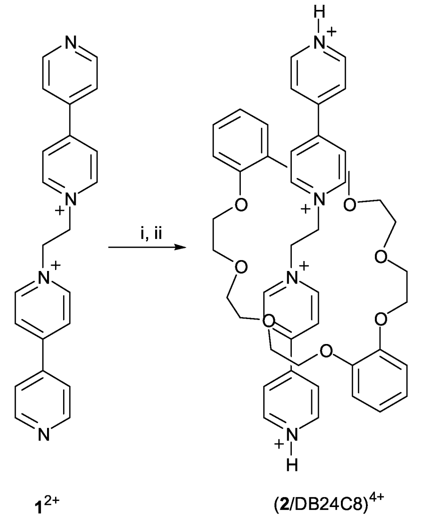
Protonated 1,2-bis(4,4′-bipyridinium)ethane axles and dibenzo-24-crown-8 ether wheels thread to form [2]pseudorotaxanes which associate in the solid state to form pseudo-polyrotaxanes by hydrogen bonding or π-stacking.

The systematic preparation of solid-state materials which contain mechanical linkages combines the ideas of molecular machinery and crystal engineering and has the potential to produce compounds with tuneable and controllable properties.[1–6] We have recently begun to investigate the application of our 1,2-bis(bipyridinium)ethane–24-crown-8 pseudorotaxane motif to this concept. In particular, we have shown that 1,2-bis(4,4-bipyridinium)ethane axles, **1**$^{2+}$, can be linked by coordination chemistry.[7,8] Herein we report the use of the diprotonated form of this axle, **2**$^{4+}$, to form an analogous [2]pseudorotaxane [**2**/DB24C8]$^{4+}$ which can be extended into polymeric systems *via* hydrogen bonding and π-stacking interactions (Scheme 1).

Treatment of [**1**][OTf]$_2$ with CF_3SO_3H in MeCN led to protonation of the terminal N-atoms and formation of [**2**][OTf]$_4$ in 82% yield. Mixing [(**2**)][OTf]$_4$ with 2 equiv. of DB24C8 in MeCN at room temperature resulted in a yellow solution indicative of [2]pseudorotaxane formation. Slow evaporation of this solution deposited an orange–red solid and two sets of different X-ray quality crystals (**3** and **4**) were isolated.†

X-Ray diffraction studies showed **3** to have formulation [(**2**/DB24C8)((H_2O)$_2$/DB24C8)][OTf]$_4$·4H_2O. The structure is a one-dimensional polymer in which the two distinct components [**2**/DB24C8]$^{4+}$, (A) and [(H_2O)$_2$/DB24C8], (B) are hydrogen bonded in a linear (A-B)$_n$ pattern. In the (A) unit of this material, the protonated axle, **2**$^{4+}$, is threaded through an S-shaped DB24C8 ring to form a [2]pseudorotaxane in exactly the same manner as found for (**1**/DB24C8)$^{2+}$.[8] In the (B) portion, two water molecules are hydrogen-bonded inside an identical S-shaped DB24C8 molecule. The connection between the two components is H-bonding between the NH$^+$ group of the axle in (A) and the water oxygen atoms in (B). A section of the 1D polyrotaxane showing one [(H_2O)$_2$/DB24C8] (B) unit bridging two [**2**/DB24C8]$^{4+}$ (A) units is shown in Fig. 1.



Scheme 1 *Reagents and conditions*: i, 2 equiv. CF_3SO_3H, MeCN (82%). ii, 2 equiv. DB24C8 in MeCN at room temperature.

X-Ray diffraction studies showed **4** to have formulation [(**2**/DB24C8)(DB24C8)$_2$][OTf]$_4$·4H_2O (Fig. 2). As in **3**, the central component is a [2]pseudorotaxane, [**2**/DB24C8]$^{4+}$, (A) but in this material both terminal NH$^+$ groups of the axle are capped by H-bonding into the centre of a DB24C8 molecule (B) which has adopted a rare C-shaped conformation.[9–11] These [2]rotaxane-like (BAB) units are then arranged in a network by

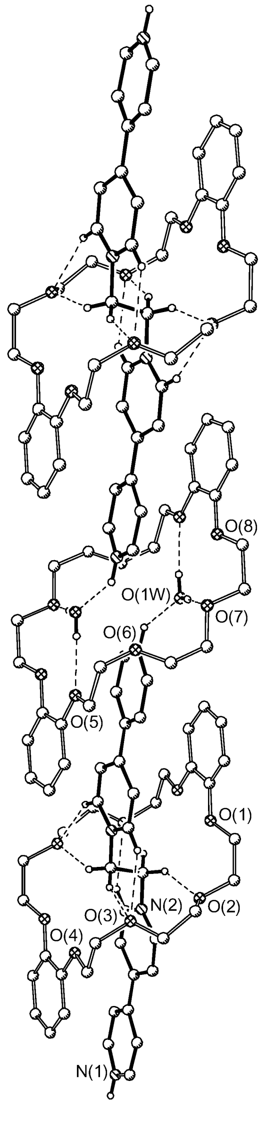


Fig. 1 A ball-and-stick representation of the X-ray crystal structure of **3** showing the basic numbering scheme. One [(H_2O)$_2$/DB24C8] (B) unit is shown bridging two [**2**/DB24C8]$^{4+}$ (A) units.

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π-stacking between the electron-rich aromatic groups of the capping DB24C8 units and the electron-poor aromatic rings of the bipyridinium axle.

Figs. 3 and 4 show how these [2]pseudorotaxane components of **3** and **4** are arranged in the solid state to form polyrotaxanes and how these 1D polymers are packed. Both materials are organized such that the interpenetrating components of the [2]pseudorotaxane [**2**/DB24C8]$^{4+}$, which have been extended through non-covalent bonding (H-bonding for **3** and π-stacking for **4**), are aligned in alternating rows with the anions.

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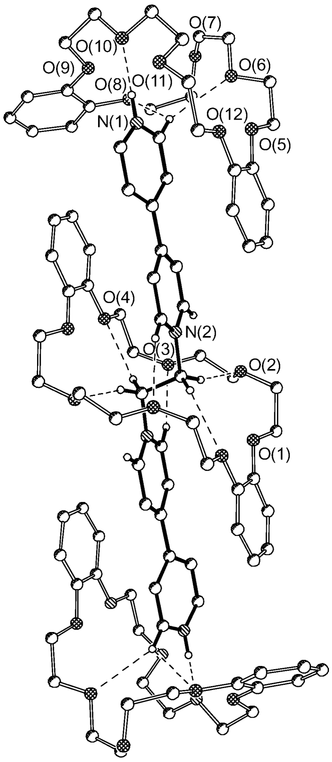

Fig. 2 A ball-and-stick representation of the X-ray crystal structure of **4** showing the basic numbering scheme. One [**2**/DB24C8]$^{2+}$ (A) unit is shown capped by two DB24C8 (B) units.

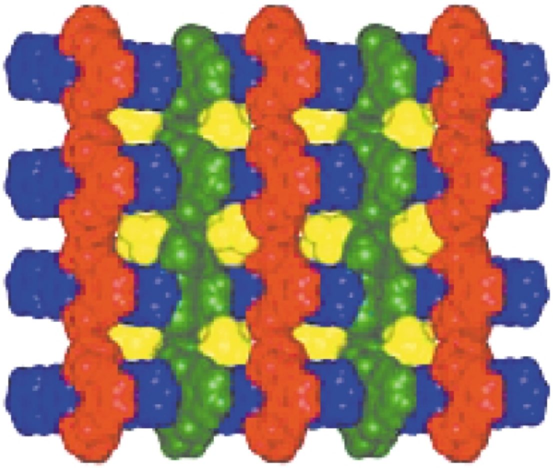

Fig. 3 A space-filling model of **3** showing the hydrogen-bonded pyridinium axles (blue) with alternating penetrated (red) and capping (green) molecules of DB24C8; triflate anions (yellow) are shown in layers between the strands of polyrotaxane.

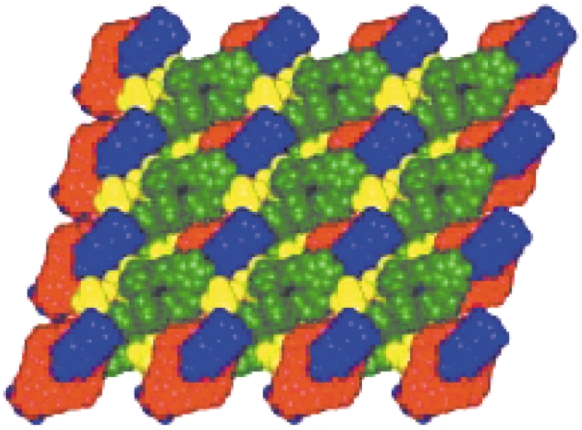

Fig. 4 A space-filling model of **4** showing the hydrogen-bonded pyridinium axles (blue) with alternating penetrated (red) and capping (green) molecules of DB24C8; triflate anions (yellow) are shown in layers between the strands of polyrotaxane.

Notes and references

† *Crystal data*, **3**: $C_{74}H_{98}F_{12}N_4O_{34}S_4$, M = 1943.8, monoclinic, space group $P2_1/c$, a = 17.322(3), b = 20.385(3), c = 12.300(2) Å, β = 92.332(3)°, U = 4341.9(12) Å^3, T = 293(2) K, Z = 2, μ = 0.223 mm^{-1}, 4649 independent reflections (R_{int} = 0.0590). $R1$ = 0.1163, $wR1$ = 0.1815, (2497 reflections, $I > 2\sigma I$), $R2$ = 0.2865, $wR2$ = 0.3337, (all data), Goodness-of-fit ($F2$) = 1.050. **4**: $C_{98}H_{126}F_{12}N_4O_{40}S_4$, M = 2356.3, triclinic, space group $P1$, a = 11.653(4), b = 14.953(5), c = 17.266(6) Å, α = 98.355(7), β = 93.107(6), γ = 110.818(7)°, U = 2764.2(17) Å^3, T = 293(2) K, Z = 1, μ = 0.193 mm^{-1}, 7890 independent reflections (R_{int} = 0.0229). $R1$ = 0.0873, $wR1$ = 0.1350, (4361 reflections, $I > 2\sigma I$), $R2$ = 0.2482, $wR2$ = 0.2867, (all data), Goodness-of-fit ($F2$) = 1.019. Data were collected on a Bruker APEX CCD instrument and solutions performed using the SHELXTL 5.03 Program Library, Siemens Analytical Instrument Division, Madison, WI, USA, 1997. CCDC 181512 and 181513. See http://www.rsc.org/suppdata/cc/b2/b201664h/ for crystallographic files in .cif or other electronic format. It was estimated the isolated solid comprised **3** and **4** in a 9:1 ratio.

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