# A New Motif for the Self-Assembly of [2]Pseudorotaxanes; 1,2-Bis(pyridinium)ethane Axles and [24]Crown-8 Ether Wheels**

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The threading of the paraquat dication PQT^{2+} through the cavity of bis(paraphenylene)[34]crown-10 (BPP34C10) to form the [2]pseudorotaxane [(BPP34C10)(PQT)]$^{2+}$ (**1**) was the genesis of a diverse range of molecules that contain mechanical linkages (rotaxanes, catenanes, molecular shuttles, and switches) derived from this basic interaction, and stands as a landmark discovery in the area of supramolecular chemistry (Scheme 1).[1] Many examples of rotaxanes have
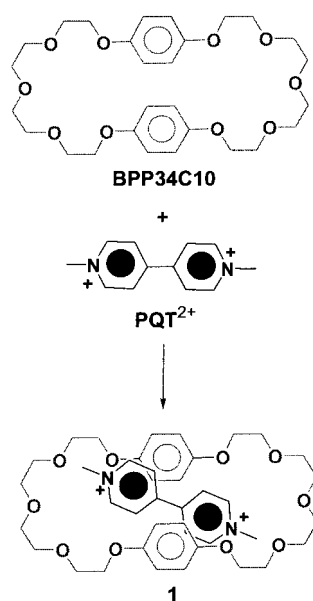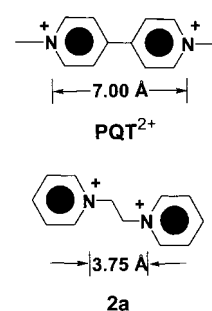

Scheme 1. Formation of the [2]pseudorotaxane **1** by insertion of the linear dicationic axle PQT^{2+} through the cavity of the neutral crown ether wheel BPP34C10.

now been reported involving π stacking between electron-rich and electron-poor aromatic rings,[2] hydrogen bonding between secondary dialkylammonium ions and crown ethers[3] or between amides and large ring lactams,[4] hydrophobic interactions within the cavity of a cyclodextrin,[5, 6] and metal–ligand interactions between transition metal ions and cyclic ligands.[7–9] In many of these systems the ion–dipole interaction between positively charged atoms of one component and the Lewis basic atoms of the other component makes a significant contribution to the binding. Although these electrostatic interactions are not directional and predictable in the same manner as hydrogen bonds or metal–ligand

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bonds, they are nonetheless extremely important. For example, the PQT^{2+} ion in **1** is tilted away from perpendicular by 62° so as to maximize the N$^+$···O interactions and also form weak CH···O hydrogen bonds along with the major π-stacking components.[1]

Herein, we present a new motif for the design of [2]pseudorotaxanes based on the simple concept of optimizing N$^+$···O interactions between pyridinium ions and simple crown ethers.[10] The N$^+$–N$^+$ distance in PQT^{2+} is about 7.00 Å while in the isomeric 1,2-bis(pyridinium)ethane dication **2a** it is only about 3.75 Å (Scheme 2). Although Stoddart et al. have reported that the interaction between dibenzylparaquat and DB24C8 is negligible,[11, 12] an examination of CPK and computer models suggested a good match between **2a** (the "axle") and the 24-membered crown ethers (wheels) 24C8, B24C8, and DB24C8 (Scheme 3) that should

Scheme 2. Comparison of the intramolecular N$^+$–N$^+$ distances in the isomeric pyridinium ions PQT^{2+} and [pyCH$_2$CH$_2$py]$^{2+}$ (**2a**).
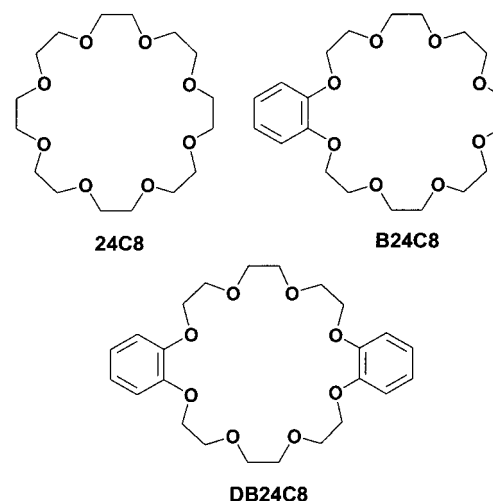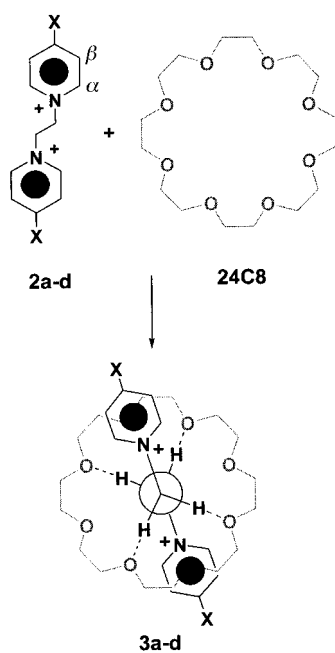

Scheme 3. Formation of [2]pseudorotaxanes from 24C8, B24C8, and DB24C8.

optimize the N$^+$···O interactions. Scheme 4 shows how two sets of N$^+$···O interactions might be accompanied by a series of four C–H···O hydrogen bonds that are formed with alternate oxygen atoms in the crown ether. The question remains as to whether these interactions are sufficient to produce a stable [2]pseudorotaxane in the absence of the π-stacking interactions found in **1** and related molecules.

The addition of one equivalent of 24C8 to a solution of one equivalent of **2a**(BF$_4$)$_2$ in MeCN gave the [2]pseudorotaxane **5a**. An association constant K_a of 165 M^{-1} was measured for this interaction by ^{1}H NMR titration in MeCN at 298 K. By variation of the substitutuent X on the pyridinium ring other axles can be incorporated and a more detailed understanding of the overall interaction can be obtained. The strength of the interaction can be controlled by varying X as shown in Table 1. In particular, the introduction of the electron-with-

2a-d + **24C8**

↓

3a-d

Scheme 4. Newman projection along the C–C vector of the $N^+CH_2CH_2N^+$ portion of the dication $[XpyCH_2CH_2pyX]^{2+}$, **2a–d**, (X = H, Me, Ph, CO_2Et,). This combination of $N^+\cdots O$ ion–dipole interactions and $C-H\cdots O$ hydrogen bonds might stabilize the formation of [2]pseudorotaxanes with 24C8.

drawing group CO_2Et results in the largest association constant for the interactions with each of the three crown ethers.

Incorporation of aromatic groups into the crown ether provides the possibility of π stacking between the pyridinium rings and the catechol rings of the crown ether. In the ^1H NMR spectra of the two pseudorotaxanes derived from **2a** (X = CO_2Et) with B24C8 (**4d**) and DB24C8 (**5d**) π stacking in solution is clearly evident: the signals for the β protons of the pyridine group shift upfield ($\delta = 8.56$, 8.36, and 8.14 for the pseudorotaxanes with 24C8, B24C8, and DB24C8, respectively). This trend is mirrored by a uniform increase in K_a from 320 to 740 to 1200 M^{-1} and an increase in the intensity of a charge transfer absorption band at about 370 nm (Figure 1). In addition, **3d–5d** show significant downfield shifts ($\delta = $

0.20–0.31) for the α and NCH_2 protons, which is indicative of the formation of $C-H\cdots O$ hydrogen bonds to the oxygen atoms of the crown ether.

These results and the threading conformation proposed in Scheme 4 are supported by the solid-state structure of $[(EtO_2CpyCH_2CH_2pyCO_2Et)(DB24C8)]^{2+}$ (**5d**; py = $C_5H_4N^+$).[13] Figures 2 and 3 show different views of the threading of the dicationic axle through the cavity of the DB24C8 macrocycle. The [2]pseudorotaxane is stabilized by 1) eight $N^+\cdots O$ interactions (N–O 3.76–4.88 Å), 2) eight $C-H\cdots O$ hydrogen bonds (the four predicted ones between the bridging ethane unit and alternate ether oxygen atoms as well as four others between α-pyridinium hydrogen atoms and symmetry related O5 atoms
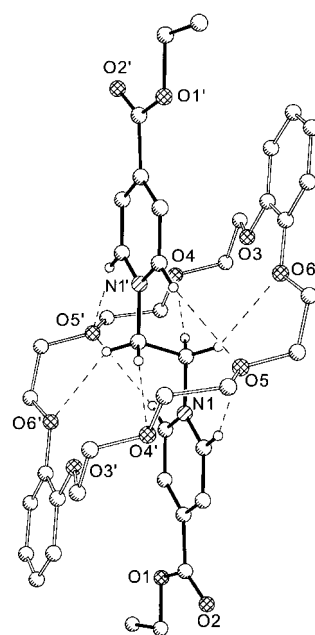
Figure 2. A ball-and-stick representation of the crystal structure of **5d**, formed from $[EtO_2CpyCH_2CH_2pyCO_2Et]^{2+}$ (**2d**) and DB24C8.

Figure 3. A ball-and-stick representation of the crystal structure of **5d**, shown along the C9–C9′ bond. This view corresponds to the Newman projection show schematically in Scheme 4. N^+–O distances: $N1^+$–O3 4.88, $N1^+$–O4 4.43, $N1^+$–O5 3.76, $N1^+$–O6 4.66 Å. $C-H\cdots O$ hydrogen bonds (lengths [Å] and angles [°]): H9A–O4′ 2.54, H9B–O6′ 2.66, H6A–O5 2.36, H7A–O5′ 2.54; C9-H9A-O4′ 165.0, C7-H7A-O5′ 141.0, C6-H6A-O5 154.2, C9-H9B-O6′ 150.0.
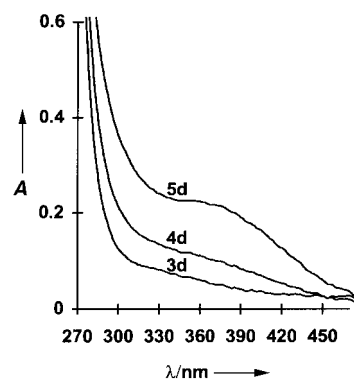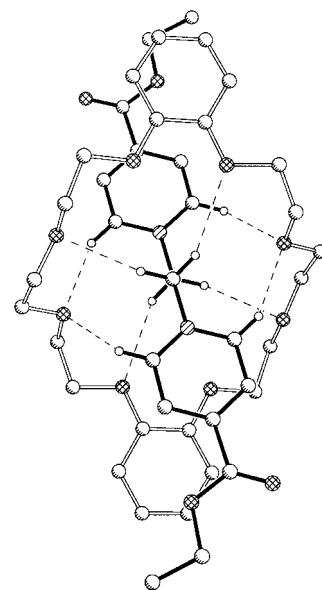

Figure 1. UV absorption spectra of **3d, 4d,** and **5d**. The intensity of the charge-transfer band in the region 270–470 nm increases with increased capacity for π-stacking interactions.

Table 1. Association constants (K_a) and free energies of complexation (ΔG) for **3a–d**, **4a–d**, and **5a–d** formed from $[X-pyCH_2CH_2py-X]^{2+}$, **2a–d**, and 24C8, B24C8, or DB24C8 in MeCN at 298 K.[a]

	24C8		B24C8		DB24C8	
X	K_a [M^{-1}]	$-\Delta G$ [kJ mol^{-1}]	K_a [M^{-1}]	$-\Delta G$ [kJ mol^{-1}]	K_a [M^{-1}]	$-\Delta G$ [kJ mol^{-1}]
H (**a**)	165	12.7	195	13.1	180	12.9
Me (**b**)	105	11.6	205	13.2	230	13.5
Ph[b] (**c**)	160	12.6	300	14.2	320	14.3
CO_2Et[b] (**d**)	320	14.3	740	16.4	1200	17.6

[a] Sample concentrations $2.0 \times 10^{-3} - 5.0 \times 10^{-3}$ M. [b] Chemical exchange was slow on the NMR time scale and peaks were observed for both complexed and uncomplexed species. K_a was determined by integration from a 1:1 mixture. All other K_a values were determined by NMR titration experiments by using the program EQNMR.[16] Estimated errors: < 10% for $K_a > 100$.

(C–O 2.36–2.66 Å), and 3) π-stacking interactions between the electron-rich catechol rings of the crown ether and the electron-poor aromatic rings and ester group of the pyridinium salt.

The new binding motif for the formation of [2]pseudorotaxanes presented herein demonstrates for the first time that simple crown ethers can be used to form [2]pseudorotaxanes. The ability to easily tune the interaction strength and the availability of these simple components bodes well for the extension of this motif to more complex supramolecular systems with interlocked [n]rotaxanes and [n]catenanes.

Experimental Section

All pyridinium bromide salts were prepared by the literature method.[14] The BF_4^- salts were precipitated from water by the addition of $NaBF_4$ or NH_4BF_4 and recrystallized before use. DB24C8 was purchased from Aldrich and used as received. B24C8 and 24C8 were prepared by literature methods.[15] In a typical experiment, [2]pseudorotaxanes were formed in solution by mixing equimolar solutions of $2a(BF_4)_2$–$d(BF_4)_2$ and crown ether in MeCN. Typical data for [2]pseudorotaxanes in which X = CO_2Et: **3d**: ^1H NMR (300 MHz, CD_3CN, 298 K): δ = 9.27 (d, 4H, $J = 5.3$ Hz; α-pyH), 8.56 (d, 4H, $J = 5.3$ Hz; β-pyH), 5.40 (s, 4H; NCH_2), 4.50 (q, 4H, $J = 7.1$ Hz; $C(O)OCH_2$), 3.50 (s, 32H; OCH_2), 1.44 (t, 6H, $J = 7.1$ Hz; CH_3); ES-MS m/z (%): 770 (5) $[M − BF_4]^+$, 341 (100) $[M − 2BF_4]^{2+}$. **4d**: ^1H NMR (300 MHz, CD_3CN, 298 K): δ = 9.24 (d, 4H, $J = 6.4$ Hz; α-pyH), 8.36 (d, 4H, $J = 6.4$ Hz; β-pyH), 6.80 (m, 4H; Ar), 5.46 (s, 4H; NCH_2), 4.47 (q, 4H, $J = 7.1$ Hz; $C(O)OCH_2$), 4.02 (m, 4H; $ArOCH_2$), 3.94 (m, 4H; OCH_2), 4.83 (m, 8H; OCH_2), 3.63 (m, 4H; OCH_2), 3.43 (m, 4H; OCH_2), 3.18 (m, 4H; OCH_2), 1.44 (t, 6H, $J = 7.1$ Hz; CH_3); ES-MS m/z (%): 818 (7) $[M − BF_4]^+$, 365 (100) $[M − 2BF_4]^{2+}$. **5d**: ^1H NMR (300 MHz, CD_3CN, 298 K): δ = 9.24 (d, 4H, $J = 6.7$ Hz; α-pyH), 8.14 (d, 4H, $J = 6.7$ Hz; β-pyH), 6.74 (m, 8H; Ar), 5.58 (s, 4H; NCH_2), 4.40 (q, 4H, $J = 7.1$ Hz; $C(O)OCH_2$), 4.00 (m, 24H; OCH_2) 1.44 (t, 6H, $J = 7.1$ Hz; CH_3); ES-MS m/z (%): 865 (12) $[M − BF_4]^+$, 389 (100) $[M − 2BF_4]^{2+}$.

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[13] Crystal structure data for $5d(BF_4)_2$: monoclinic, space group $P2_1/c$, $a = 13.2421(4)$, $b = 15.7037(5)$, $c = 12.1739(4)$ Å, $\beta = 94.909(1)°$, $V = 2522.3(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.308$ g cm^{-3}, $2\theta_{max} = 45.0°$, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 296$ K. A pale yellow crystal with dimensions $0.2 \times 0.2 \times 0.3$ mm was grown by vapor diffusion of isopropyl ether into a solution of **5d** in MeCN and mounted on a fibre. The 3280 unique reflections ($R_{int} = 0.0715$) were integrated from frame data obtained from programmed hemisphere scan routine on a Siemens SMART CCD diffractometer. Decay ($< 1\%$) was monitored by 50 standard data frames measured at the beginning and end of data collection. Systematic absences in the diffraction data and determined unit-cell parameters were consistent with the space group $P2_1/c$. Lorentzian-polarization correction and semi-empirical absorption correction, based on redundant data at varying effective azimuthal angles, were applied to the data ($\mu = 0.112$ cm^{-1}, min./max. transmission = 0.221/0.492). The structure was solved by direct methods, with Fourier syntheses, and refined with full-matrix least-squares methods against $|F^2|$ data to give $R(F) = 0.0815$, $wR(F^2) = 0.2271$, GOF = 1.033, $N_o/N_v = 3275/354$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison, WI). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101459. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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$[Te_6N_8(TeCl_4)_4]$—Tellurium Nitride Stabilized by Tellurium Tetrachloride

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Exactly 100 years ago tellurium nitride was first obtained by the reaction of tellurium tetrabromide with liquid ammonia.[1] The composition TeN was ascribed to this yellow, extremely poorly soluble, and highly exlosive substance. Considering the analogy to the crystallographically well characterized homologues S_4N_4[2] and Se_4N_4,[3] this assignment has not been entirely ruled out to this day.[4] However, later analytical work made the composition Te_3N_4 with tetravalent tellurium probable.[5–7] The tellurium compounds with nitride functionalities which were characterized in recent years also derive from tellurium(+IV). Among these are the complexes of type **1** with X = Cl[8] and F,[9] which correspond to the structure motif **A** with pyramidal nitride functionality, and the nitride

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