Remarkably improved complexation of a bisparaquat by formation of a pseudocryptand-based [3]pseudorotaxane

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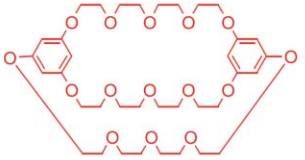
Significant improvement of complexation of a bisparaquat guest was achieved by the formation of a pseudocryptand-based [3]pseudorotaxane.

The field of host–guest chemistry is a topic of great current interest.[1] Bisparaquat derivatives, linear and cyclic, have been widely used in the construction of pseudorotaxanes, catenanes, and rotaxanes with potential applications in electronics.[2] Cryptands have been shown to be much better hosts for paraquat derivatives than corresponding simple crown ethers.[3] Recently we reported a [3]pseudorotaxane by cooperative complexation between cryptand host **1** and bisparaquat guest **2a**.[4] We have also found that improved complexation can be achieved by the chelation of 32-crown-10 diol **3** to form pseudocryptands.[5,6] Here we report significant improvement of the complexation of a bisparaquat guest by the formation of a [3]pseudorotaxane based on a new pseudocryptand host, which is even better than the covalent cryptand host **1**.



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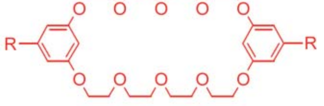
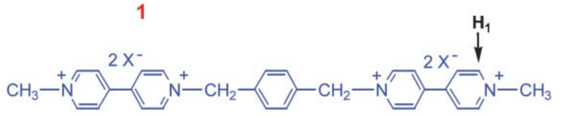


3: R = CH$_2$OH; **4**: R = OH



2a: X = PF$_6$; **2b**: X = CF$_3$COO

Solutions of 32-crown-10 bisphenol **4**[3a] and bisparaquat **2a** are yellow due to charge transfer between the electron-rich aromatic rings of the host **4** and the electron-poor pyridinium rings of the guest **2a**. Proton NMR characterizations were done on a series of acetone solutions of **4** and **2a** at 22 °C; the initial concentration of **2a** was kept constant at 0.500 mM, while the initial concentration of **4** was systematically varied. The stoichiometry of the complex between **4** and **2a** was determined to be 1:1 by a mole ratio plot[7] (Fig. 1). Electrospray ionization mass spectrometry (ESIMS) confirmed this stoichiometry. The base peak was at *m/z* 570.13, corresponding to $[\mathbf{4} + 2H]^+$. Three relevant peaks were found for **4·2a**: *m/z* 1141.40 $[\mathbf{4{\cdot}2a} - 3PF_6 - H_2O]^+$ (1%), 993.46 $[\mathbf{4{\cdot}2a} - PF_6 - 3HPF_6 - H_2O]^+$ (1%) and 285.13 $[\mathbf{4{\cdot}2a} - 3PF_6 - H_2O + H]^{4+}$ (4%). No peaks related to other stoichiometries were found. The value of Δ_0, the difference in δ values for H$_1$ in the uncomplexed and fully complexed species, was determined to be 0.183 ppm by extrapolation of a plot of $\Delta = \delta - \delta_u$ *vs.* 1/[**4**]$_0$ (Fig. 2) in the high initial concentration range of **4**. The complexed fraction, p, of the paraquat units can be calculated from $p = \Delta/\Delta_0$. At 1.00 mM initial concentrations of **4** and **2a** the association constant, K_a, was calculated from $K_a = p/\{(1 - p)^2[\mathbf{4}]_0\}$ to be 388 (±152) M^{-1}.

When 1.13 mM tetraethylammonium trifluoroacetate (TEATFA) was added into a CD$_3$COCD$_3$ solution of 0.500 mM **2a** and 1.00 mM **4**, in anticipation of forming a pseudocryptand by chelation of **4**, the color of the solution changed from pale yellow

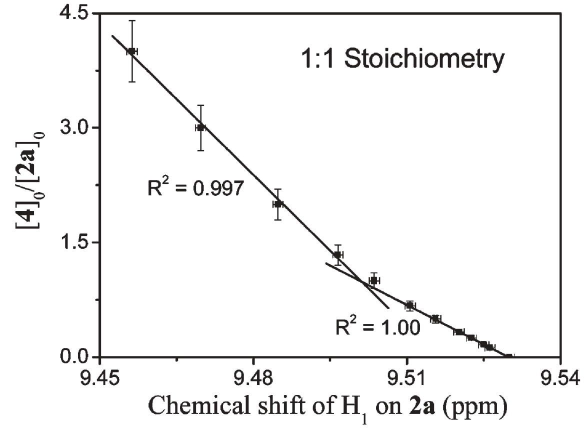


Fig. 1 Mole ratio plot showing 1:1 stoichiometry for the complexation between **4** and **2a**, 22 °C. The solvent is CD$_3$COCD$_3$. [**4**]$_0$ and [**2a**]$_0$ are initial concentrations of **4** and **2a**. [**2a**]$_0$ is constant at 0.500 mM.

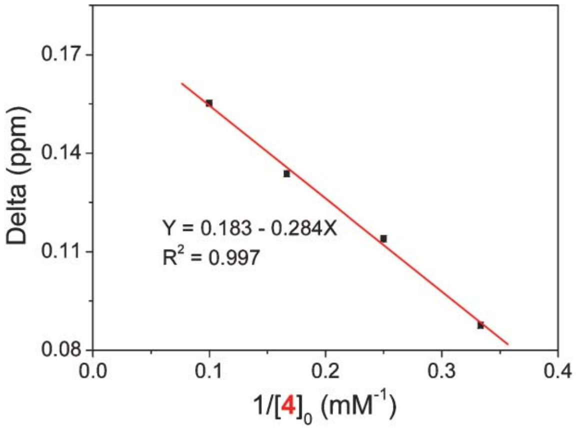


Fig. 2 Relationship between Δ for H$_1$ of **2a** and 1/[**4**]$_0$ for the complexation between **4** and **2a** in CD$_3$COCD$_3$, 22 °C.

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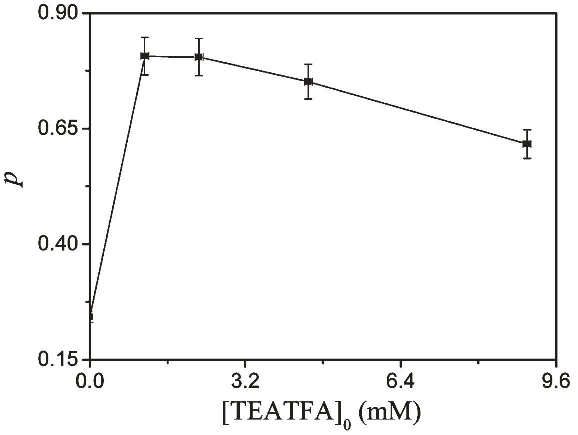

Fig. 3 The influence of added TEATFA on the fraction p of complexed paraquat units; $[\mathbf{2a}]_0$ = 0.500 mM and $[\mathbf{4}]_0$ = 1.00 mM in CD_3COCD_3, 22 °C.

to bright yellow. Correspondingly, p increased from 24.3 to 80.7%![8] Remarkably this value exceeds the complexed fraction, 79.2%, of the paraquat units in a solution of 0.500 mM **2a** and 1.00 mM covalent cryptand host **1**.[4] The complex $\mathbf{1}_2\cdot\mathbf{2a}$ from the covalent cryptand is formed in a cooperative manner with $K_1 = 1.2 \times 10^3\ M^{-1}$ and $K_2 = 2.0 \times 10^4\ M^{-1}$. By comparison then, the purported pseudocryptand host is slightly superior to the covalent cryptand **1** and vastly superior to the bisphenolic crown ether **4** in the absence of a chelating anion; these results indicate cooperative formation of $\mathbf{4}_2\cdot\mathbf{2b}$.

When the concentration of added TEATFA was increased further, however, p decreased, but still exceeded that in the absence of TEATFA (Fig. 3). These results can be easily understood in terms of H-bonding of the TFA anion to the phenolic groups of host **4**. At low concentrations of TEATFA, chelation of a single TFA anion to the two phenolic groups of host **4** is favored, leading to the formation of the pseudocryptand, so p increases.[9] At higher concentrations of TEATFA, the complexation of two moles of TFA with each mole of diphenol reduces the fraction of pseudocryptand that forms, so p decreases somewhat.

Gratifyingly the formation of the proposed pseudocrystand structure was confirmed by X-ray analysis (Fig. 4).‡ Though the quality of the crystal structure of this first pseudocryptand-based [3]pseudorotaxane $\mathbf{4}_2\cdot\mathbf{2b}\cdot 2H_2O$ is not high because of the disorder of **4** and TFA counterions, the remarkable result is that a total of seven species are self-assembled. The two hydroxy groups of each host **4** are connected *via* a TFA counterion and a water molecule by hydrogen bonding to form a new pseudocryptand and two of these enshroud the guest in a face-to-face orientation. This structure is similar to the [3]pseudorotaxane based on the covalent cryptand host **1** and the bisparaquat guest **2a**.[4] No PF_6 counterions were found in the crystal structure. It is interesting that the supramolecular bridge of the pseudocryptand host includes 9 atoms and 10 total covalent and noncovalent bonds, the same as in a reported pseudocryptand-based [2]pseudorotaxane from diol **3**.[5a] This suggests an optimal length for the supramolecular bridge of such hosts, useful information in the design of efficient cryptand and pseudocryptand hosts for paraquat derivatives.

Further support for the formation of the pseudocryptand-based [3]pseudorotaxane structure was obtained from the ESIMS characterization of a solution of **4**, **2a** and TEATFA (molar ratio 4:1:4). The base peak was at m/z 570.27, corresponding to $[\mathbf{4} + 2H]^+$. Four relevant peaks were found for $\mathbf{4}_2\cdot\mathbf{2b}\cdot 2H_2O$: m/z 1883.8 $[\mathbf{4}_2\cdot\mathbf{2b}\cdot 2H_2O - 4H_2O - 2TFA]^+$ (0.5%), 1571.40 $[\mathbf{4}_2\cdot\mathbf{2b}\cdot 2H_2O - 2H_2O - 4TFA - 2OH + Na]^+$ (1%), 971.73 $[\mathbf{4}_2\cdot\mathbf{2b}\cdot 2H_2O - 2H_2O - TFA + Na]^{2+}$ (3%) and 781.80 $[\mathbf{4}_2\cdot\mathbf{2b}\cdot 2H_2O - 3H_2O - 2TFA - TFA - HTFA]^{2+}$ (7%).

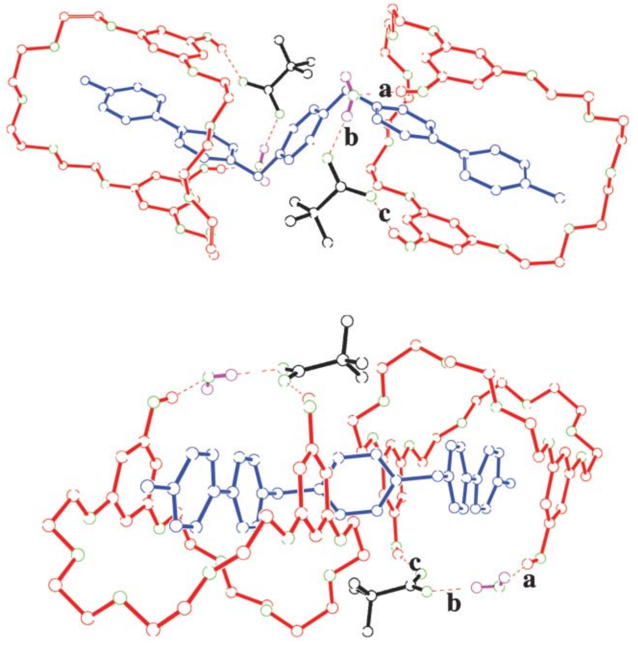

Fig. 4 Two views of the X-ray structure of $\mathbf{4}_2\cdot\mathbf{2b}\cdot 2H_2O$. Oxygens are green, **2b** is blue, **4** molecules are red, water molecules are magenta, and trifluoroacetate counterions are black. Solvent molecules, two trifluoroacetate couterions and hydrogens except those on phenol groups and water molecules have been omitted for clarity. Selected hydrogen-bond parameters: O···O distances (Å): **a** = 2.64, **b** = 2.78, **c** = 2.68; H···O distances (Å): **a** = 1.82, **b** = 1.90, **c** = 1.89; O–H···O angles (°): **a** = 167, **b** = 172, **c** = 156.

In summary, a pseudocryptand-based [3]pseudorotaxane was prepared by self-assembly of seven components. We demonstrated that a facile method for greatly improving the complexation between suitably functionalized bis(m-phenylene)-32-crown-10 hosts and bisparaquat guests is by the formation of the pseudocryptand structure through chelation. Our current efforts are focused on extending this motif to the preparation of novel supramolecular systems based on other crown ethers and appropriate guests, certainly including bisparaquat derivatives.

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Notes and references

‡ *Crystal data*: prism, orange, prepared by the vapor diffusion of pentane into an acetone solution of **4**, **2a** and TEATFA, 0.43 × 0.32 × 0.26 mm, $C_{102}H_{138}O_{34}N_4F_{12}$, M_r = 2192.16, triclinic, space group $P\bar{1}$, a = 11.1544(19), b = 15.267(3), c = 16.196(3) Å, α = 106.345(3), β = 93.511(3), γ = 106.790(3)°, V = 2503.2(7) $Å^3$, Z = 1, D_c = 1.454 g cm^{-3}, T = 100 K, μ = 1.22 cm^{-1}, 19629 measured reflections, 9769 independent reflections, 670 parameters, $F(000)$ = 1158, R_{int} = 0.0476, $R1$ = 0.1854, $wR2$ = 0.3924 [$I > 2\sigma(I)$], maximum residual density 0.930 e $Å^{-3}$, and GooF(F^2) = 1.247. The structure was solved by SHELXS-97[10] and refined by SHELXL-97.[11] CCDC 218876. See http://www.rsc.org/suppdata/cc/b4/b417661h/ for crystallographic data in .cif or other electronic format.

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8 Within experimental error Δ_0 of H_1 does not change with the addition of TEATFA, *e.g.*, in a solution of 0.500 mM **2a**, 15.0 mM **4**, and 16.1 mM TEATFA Δ = 0.171 ppm, in good agreement with Fig. 2.

9 When 1.00 mM **4** was mixed with 1.00 mM TEATFA, signals corresponding to the aromatic hydrogens on **4** changed from a multiplet to a doublet and triplet and shifted downfield and upfield, respectively. This is presumably due to the formation of the pseudocryptand. No obvious interactions were observed when the less acidic **3** was mixed with TEATFA.[5a]

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