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Contrasting biscryptand/dimethyl paraquat [3]pseudorotaxanes: statistical *vs.* anticooperative complexation behavior†

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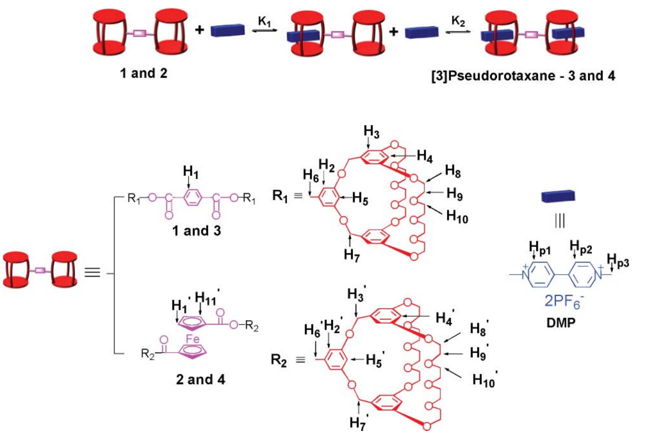
***Via* the self-assembly of two bis(*meta*-phenylene)-32-crown-10-based cryptands, bearing covalent and metal complex (ferrocene) linkages, with dimethyl paraquat, novel [3]pseudorotaxanes were formed statistically and anticooperatively, respectively.**

In supramolecular chemistry, pseudorotaxanes,[1] which consist of a linear molecular component ("guest") encircled by a macrocyclic component ("host"), have been topics of great interest due to their topological importance and potential applications as fundamental building blocks for construction of advanced supramolecular species, such as rotaxanes, catenanes, polypseudorotaxanes, polyrotaxanes and polycatenanes.[2] Paraquat (*N*,*N*′-dialkyl-4,4′-bipyridinium) derivatives[3] are commonly used guests with crown ether hosts to prepare pseudorotaxanes.[4] Compared with simple crown ethers, cryptands,[5] multidentate hosts bearing more than two bridges in the molecule, have proved to be much better hosts for paraquat derivatives and cryptand/bispraquat based [3]pseudorotaxanes formed *via* cooperative complexation have been found.[5b,5f] Here, for the first time, we report two novel biscryptand/dimethyl paraquat (DMP) based [3]pseudorotaxanes, one self-assembled *via* statistical complexation and the other in an anticooperative fashion.

The biscryptands **1** and **2** (Scheme 1) were prepared according to the published procedure.[2j] Although the individual solutions of biscryptand **1** and **DMP** ($CDCl_3/(CD_3)_2CO$ = 1/3 <v/v>) were colorless, a solution of biscryptand **1** and **DMP** was yellow due to the charge-transfer between the electron-rich aromatic rings of the biscryptand and the electron-poor pyridinium rings of the **DMP**. ^{1}H-NMR spectra of solutions of biscryptand **1** and **DMP** displayed only one set of peaks, indicating fast-exchange complexation (Fig. 1). After complexation, peaks corresponding to pyridine protons (H_{P1}, H_{P2} and H_{P3}) of **DMP** and aromatic proton H_4, ethyleneoxy protons H_8 and H_9 on biscryptand **1** moved upfield. Furthermore, peaks corresponding to H_1, H_2, H_5 and H_6 moved downfield, as normally observed in such complexes.[4,5]

The stoichiometry of the complex between biscryptand **1** and **DMP** was determined to be 1 : 2 in solution by a mole ratio plot[6] (Fig. 2). Electrospray Ionization Mass Spectrometry (ESI-MS) confirmed this stoichiometry. Three relevant peaks were found for $\mathbf{1{\cdot}DMP_2}$: *m/z* 1096.39 $[\mathbf{1{\cdot}DMP_2} - 2PF_6]^{2+}$, 1031.34 $[\mathbf{1{\cdot}DMP_2} - 3PF_6 + OH]^{2+}$, 475.88 $[\mathbf{1{\cdot}DMP_2} - 4PF_6]^{4+}$; The value of Δ_0, the chemical shift difference for H_4 between the uncomplexed and fully complexed species, was determined to be 0.631 ppm by extrapolation of a plot of Δ, the chemical shift difference for H_4 between the uncomplexed and partially complexed species, *versus* $1/[\mathbf{DMP}]_0$ in the high initial concentration range of **DMP**. The complexed fraction, *p*, of the biscryptand **1** can be calculated from $p = \Delta/\Delta_0$ based on data for H_4. The linear nature of the Scatchard plot (Fig. 3) demonstrated that the complexation between biscryptand **1** and **DMP** was statistical,[7] indicating that the two cryptand binding sites behave independently. The average association constant was determined to be $K_{av} = 4.3 \pm 0.3 \times 10^3$ M^{-1}, $K_1 = 6.9 \pm 0.5 \times 10^3$ M^{-1} and $K_2 = 1.7 \pm 0.1 \times 10^3$ M^{-1}.



Scheme 1 Schematic illustration of the formation of [3]pseudorotaxanes **3** and **4** *via* the self-assembly of bicryptands **1** and **2** with DMP.

Solutions of biscryptand **2** and **DMP** were dark red due to the red color of biscryptand **2** and it was hard to see any color change caused by the charge-transfer between the electron-rich aromatic rings of the biscryptand and the electron-poor pyridinium rings of the **DMP**. ^{1}H-NMR spectra of solutions of biscryptand **2** and **DMP** contained only one set of peaks, indicating fast-exchange complexation (Fig. 1). After complexation, peaks corresponding to pyridine protons (H_{P1}, H_{P2} and H_{P3}) on **DMP** and aromatic proton $H_4{}'$, ethyleneoxy protons $H_8{}'$ and $H_9{}'$ on biscryptand **2** (bf) moved upfield, while peaks corresponding to $H_1{}'$, $H_2{}'$, $H_5{}'$ and

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† Electronic supplementary information (ESI) available: ESI-MS spectra and determination of Δ_0 of $\mathbf{1{\cdot}DMP_2}$ and $\mathbf{2{\cdot}DMP_2}$. See DOI: 10.1039/c1ob06299a

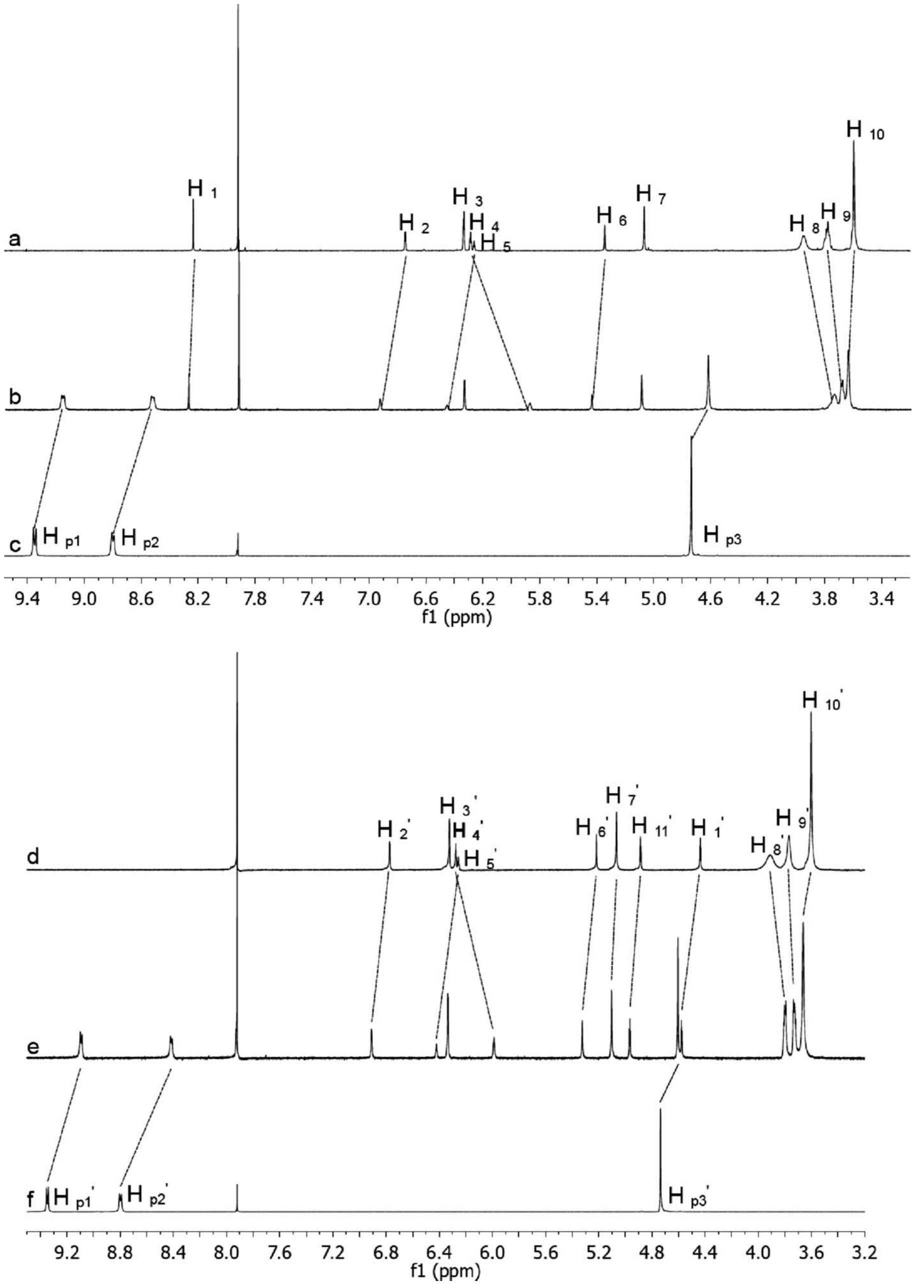

Fig. 1 Partial ^{1}H-NMR spectra (500 MHz, $CDCl_3/(CD_3)_2CO = 1/3$ <v/v>, 22 °C) of: (a) Pure biscryptand **1**; (b) **1** and **DMP** (1/3, mol/mol); (c) Pure **DMP**; (d) Pure biscryptand **2**; (e) **2** and **DMP** (1/2, mol/mol); (f) Pure **DMP**.

$H_6{}'$ moved downfield, as normally observed in such complexes.[4,5] A mole ratio plot showed that the stoichiometry of the complex between biscryptand **2** and **DMP** was 1 : 2 in solution (Fig. 2). ESI-MS confirmed this stoichiometry. Three relevant peaks were found for **2**·**DMP**$_2$: m/z 1138.84 [**2**·**DMP**$_2 - 3PF_6 - 3CH_2 + H_2O]^{2+}$, 1076.64 [**2**·**DMP**$_2 - 3PF_6 - 2H]^{2+}$ and 718.16 [**2**·**DMP**$_2 - 3PF_6]^{3+}$.

The value of Δ_0, the chemical shift difference for $H_4{}'$ between the uncomplexed and fully complexed species, was determined to be 0.657 ppm by extrapolation of a plot of Δ, the chemical shift difference for $H_4{}'$ between the uncomplexed and partially complexed species, *versus* 1/[**DMP**]$_0$ in the high initial concentration range of **DMP**. The complexed fraction, p, of the biscryptand **2** can be calculated from $p = \Delta/\Delta_0$ based on data for H_4. The nonlinear nature of the Scatchard plot (Fig. 3) demonstrated that the complexation of biscryptand **2** and **DMP** was anticooperative,[7,8] indicating that the threading of the first **DMP** into biscryptand **2** disfavored the threading of the second **DMP**. Based on the Scatchard plot, the K_1 was estimated to be $1.1 \pm 0.7 \times 10^4$ M^{-1}, and $K_2 = 0.8 \pm 0.1 \times 10^3$ M^{-1}.[9] The ratio of $K_2/K_1 = 0.07$ is much lower than the value of 0.25 expected for statistical complexation,[7] confirming that the complexation behavior is anticooperative. The anticooperative behavior is possibly due to the relatively flexible ferrocene linkage,[10] which can rotate in turnstile-fashion in solution. The first threaded paraquat species may interact with both cryptand units, due to this flexibility, thus disfavoring the threading of the second paraquat species.

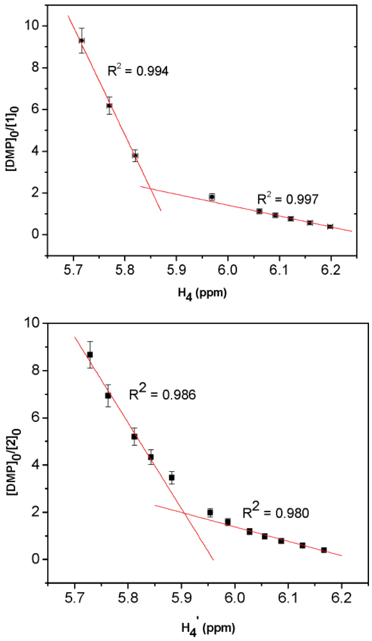

Fig. 2 Mole ratio plots for **1** and **DMP** (upper) and **2** and **DMP** (lower). The solvent was $CDCl_3/(CD_3)_2CO = 1/3$ <v/v>.

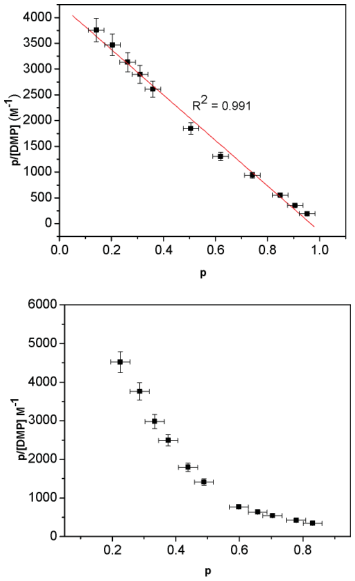

Fig. 3 Scatchard plots for complexation of **DMP** with: biscryptand **1** (upper) and biscryptand **2** (lower) in $CDCl_3/(CD_3)_2CO = 1/3$ <v/v> at 22 °C. p = fraction of biscryptand units complexed. Error bars in p: ± 0.03 absolute. Error bars in p/[**DMP**]: ±0.06 relative.

In summary, two biscryptands were used to prepare novel [3]pseudorotaxanes with a paraquat derivative. In one system the complexation behavior is statistical and the other behaves in an anticooperative manner. This is the first time that anticooperative behavior has been observed in such complexation processes with biscryptands and paraquats. Our future work is focused on preparation of biscryptands for application to polymeric systems.

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9 K_1 = **[DMP·2]**/{**[DMP][2]**} and K_2 = **[DMP$_2$·2]**/{**[DMP][DMP·2]**}. The intercept of the linear fit straight line based on the first four data points for low p (Fig. 3, lower plot) gave the value of K_1, while the slope of the last five data points for high p (Fig. 3) gave the value of $-2K_2$.[7] Errors of the two apparent association constants were calculated on the basis of errors of the slopes.

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