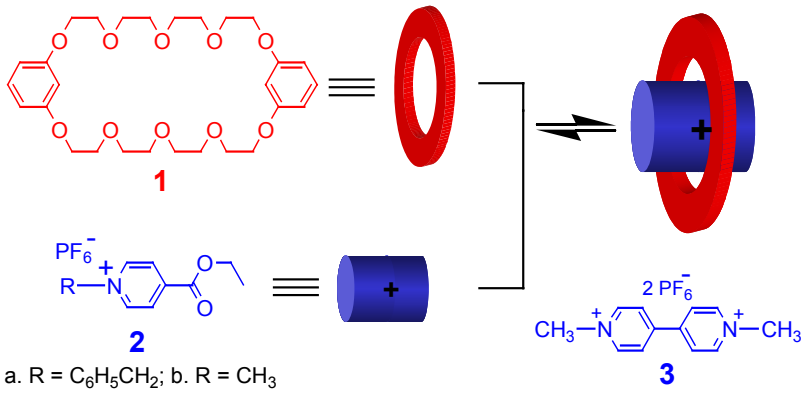
Chapter 13

Bis(*m*-phenylene)-32-crown-10/Monopyridinium [2]Pseudorotaxanes

13.1. INTRODUCUTION

Threaded structures, including psedurotoaxanes, rotaxanes, and catenanes, are attractive to scientists all over the world not only because of their topological importance but also their potential applications in preparation of nanoscale devices.[1] Crown ethers have been widely used in preparing threaded structures as hosts of organic salts, such as paraquat derivatives[2] and secondary ammonium compounds.[3] Monopyridinium salts have also been widely studied in chemistry due to their easy availability.[4] Though Beer et al. used monopyridinium salts in fabrication of some threaded structures based on ion-pair recognition by ditopic hosts[5] and we reported some cryptand/monopyridinium [2]pseudorotaxanes,[6] threaded structures based on crown ether/monopyridinium recognition motifs have not been reported up to now. Here we report a new recognition motif for preparing threaded structures which is based on bis(*m*-phenylene)-32-crown-10 and monopyridinium salts.



13.2. RESULTS AND DISCUSSION

The yellow color of solutions of crown ether **1**[7] and monopyridinium salt **2**[6] is much weaker than solutions of **1** and paraquat **3**, indicating that the charge transfer between **1** and **2** is weaker. Partial proton NMR spectra of **1**, **2a**, and an equimolar solution of **1** and **2a** are shown in Figure 1. Only one set of peaks was found in the proton NMR spectrum of the solution of **1** and **2**, indicating fast-exchange complexation. After complexation, peaks corresponding to pyridinium protons (H_7 and H_8) on **2a** and aromatic protons H_2 and α-ethyleneoxy protons H_3 of **1** moved upfield. Furthermore, phenyl protons (H_{10} and H_{11}) on **2a** and γ-ethyleneoxy protons H_4 of **1** moved downfield, while aromatic protons H_1 and β-ethyleneoxy protons H_5 of **1** and benzyl protons H_9 and ethyl ester methylene protons H_6 of **2a** moved upfield. The stoichiometries of the complexes between **1** and **2** were determined to be 1:1 in solution by Job plots[8] using proton NMR data (e.g., Figure 2). The association constants for the complexation between **1** and **2a** and between **1** and **2b** are 95 (± 11) and 78 (± 14) M^{-1} in 1:1 $CDCl_3$:CD_3COCD_3, respectively,[9] showing that the N-benzyl group is better for complexation than the N-methyl group as we observed in the study of cryptand/monopyridinium [2]pseudorotaxanes.[6]

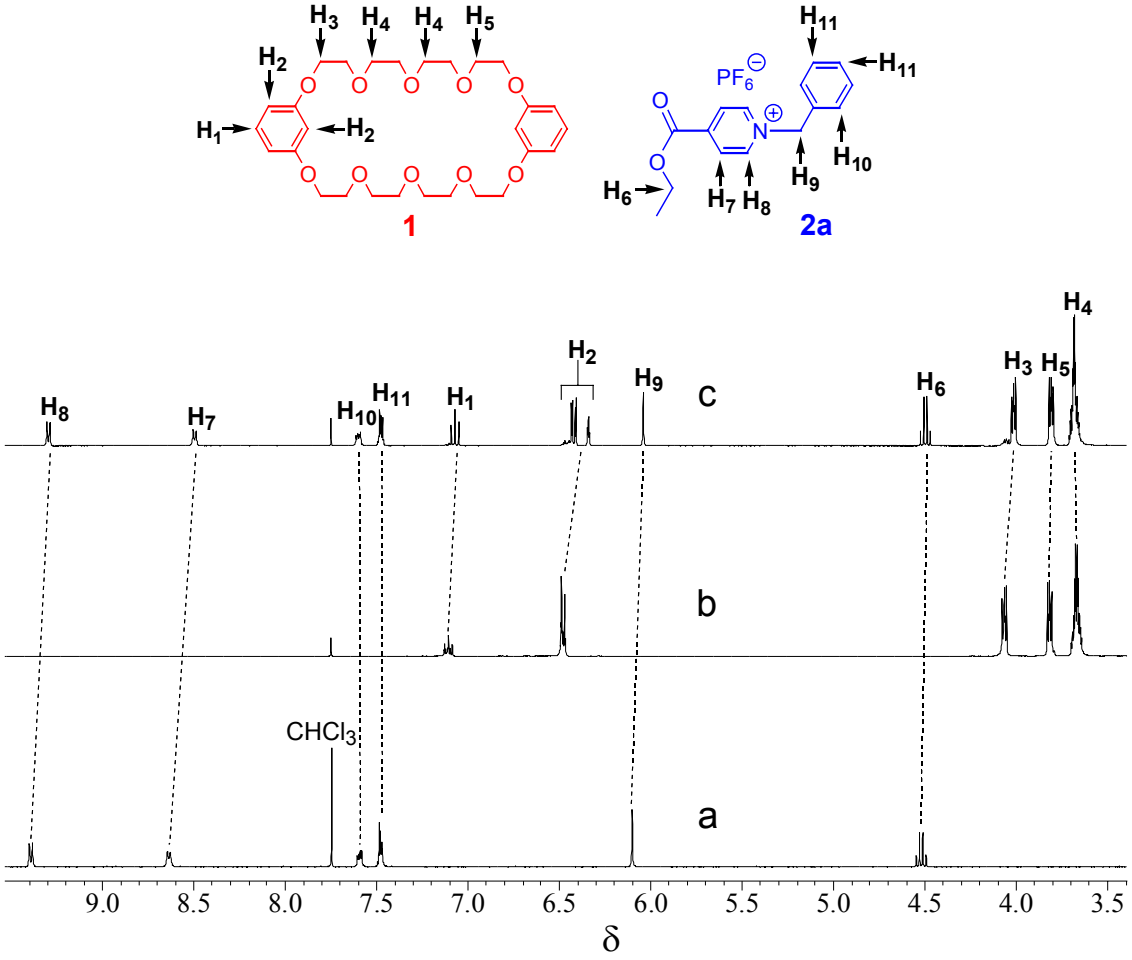


Figure 1. Partial proton NMR spectra (400 MHz, 1:1 $CDCl_3$:CD_3COCD_3, 22 °C) of monopyridinium salt **2a** (a, bottom), crown ether **1** (b, middle), and 30.0 mM **1** and **2a** (c, top).

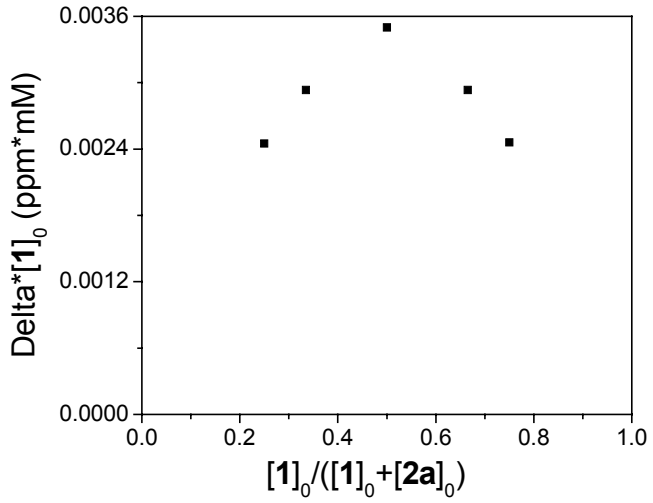


Figure 2. Job plot showing the 1:1 stoichiometry of the complex between crown ether **1** and monopyridinium **2a** in 1:1 $CDCl_3$:CD_3COCD_3. $[\mathbf{1}]_0 + [\mathbf{2a}]_0$ = 2.00 mM. Delta = the chemical shift change of H_1.

Electrospray ionization mass spectra of solutions of **1** and **2** in 4:1 acetonitrile:chloroform confirmed the 1:1 stoichiometry of the complexes. For the mass spectrum of a solution of **1** and **2a** with molar ratio 3:1, the base peak was at *m*/*z* 559.4, corresponding to $[\mathbf{1} + Na]^+$. Three peaks were found for **1•2a**: *m*/*z* 946.4 (4%) $[\mathbf{1{\bullet}2a} + Na]^+$, 778.2 (9%) $[\mathbf{1{\bullet}2a} - PF_6]^+$, and 750.3 (8%) $[\mathbf{1{\bullet}2a} - PF_6 - C_2H_4]^+$. For the mass spectrum of a solution of **1** and **2a** with molar ratio 1:5, the base peak was at *m*/*z* 629.2, corresponding to "triple ion"[10] $[\mathbf{2a}_2 - PF_6]^+$. Two peaks were found for **1•2a**: *m*/*z* 912.4 (4%) $[\mathbf{1{\bullet}2a} - C_2H_5 + H_2O]^+$ and 778.3 (82%) $[\mathbf{1{\bullet}2a} - PF_6]^+$. For the mass spectrum of a solution of **1** and **2b** with molar ratio 3:1, the base peak was at *m*/*z* 559.4, corresponding to $[\mathbf{1} + Na]^+$. Four peaks were found for **1•2b**: *m*/*z* 870.4 (7%) $[\mathbf{1{\bullet}2b} + Na]^+$, 702.5 (31%) $[\mathbf{1{\bullet}2b} - PF_6]^+$, 674.3 (37%) $[\mathbf{1{\bullet}2b} - PF_6 - C_2H_4]^+$, and 658.3 (25%) $[\mathbf{1{\bullet}2b} - PF_6 - OC_2H_4]^+$.

X-ray analysis was done on a yellow crystal of **1•2a**[11] grown by vapor diffusion of pentane into an equimolar acetone solution of crown ether **1** and monopyridinium salt **2a**. The crystal structure (Figure 3) demonstrated that the crown/monopyridinium complex **1•2a** is a pseudorotaxane because the linear molecule **2a** is threaded through the

cavity of the cyclic host. For this pseudorotaxane the main stabilization interactions in the solid state are hydrogen bonding, face-to-face π-stacking, and charge transfer interactions. One α-pyridinium proton of **2a** is hydrogen bonded (**A**) to an oxygen atom on an ethyleneoxy chain of the crown ether host, while the other α-pyridinium proton is connected indirectly to the other ethyleneoxy chain by a water bridge (**B**, **C**, and **D**). The other protons of **2a** are not involved in interactions with the crown ether host. The centroid-centroid distances, 4.02 and 4.19 Å, between the electron-poor pyridinium ring of **2a** and the electron-rich phenylene rings of the crown ether host are about equal to each other, presumably in order to maximize face-to-face π-stacking. The dihedral angle and centroid-centroid distance between the phenylene rings of the crown ether host in **1•2a** are 4.3° and 7.03 Å, while the corresponding values are 3.2° and 6.90 Å in a complex between **1** and a paraquat derivative.[2b] These results indicate that charge transfer interactions between the crown ether host **1** and monopyridinium guest **2a** in **1•2a** are weaker than those in **1•**paraquat complexes, consistent with the weaker yellow color of crystals of **1•2a** vs. the yellow-orange of crystals of **1•**paraquat complexes.

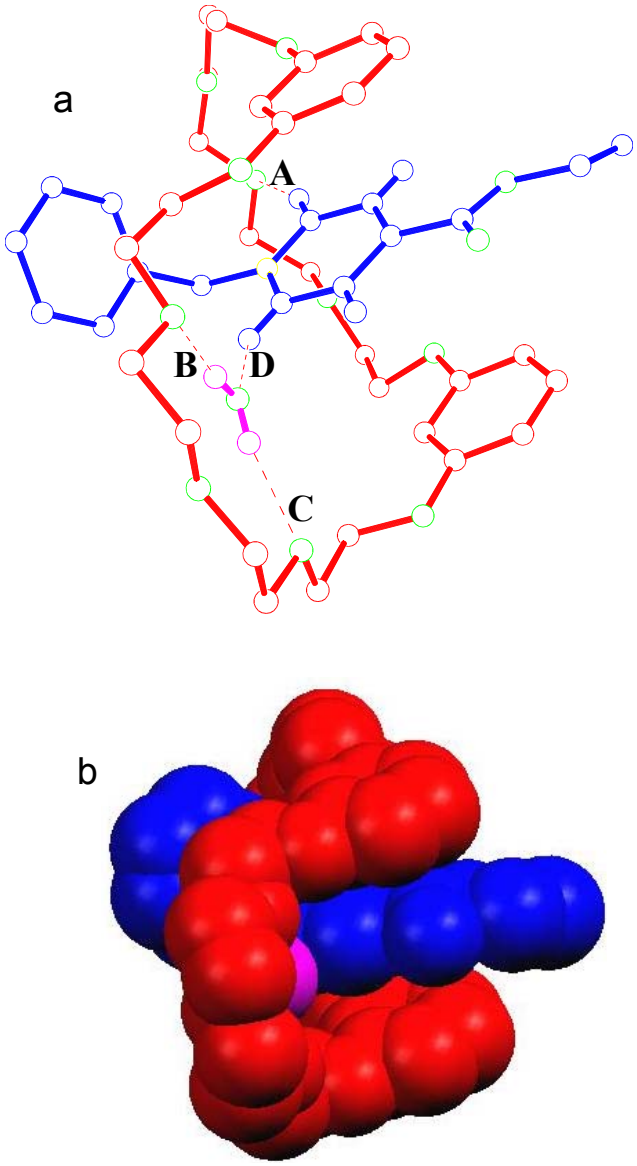


Figure 3. Two views of the X-ray structure of **1•2a**. Solvent molecules, a PF_6 counterion, and hydrogens except pyridinium protons on **2a** and protons on the water molecule have been omitted for clarity. (a) Oxygens are green, **1** is red, **2a** is blue, the water molecule is magenta, and nitrogen is yellow. Hydrogen-bond parameters: C(O)···O distances (Å), H···O distances (Å), C(O)-H···O angles (deg) **A**, 3.45, 2.53, 162; **B**, 2.85, 1.99, 174; **C**, 2.90, 2.08, 166; **D**, 3.00, 2.29, 131. Face-to-face π-stacking parameters: centroid-centroid distances (Å) 4.02, 4.19; ring plane/ring plane inclinations (deg): 7.6, 3.9. (b) All protons have been omitted.

13.3. CONCLUSIONS

In summary, though bis(*m*-phenylene)-32-crown-10 derivatives form 1:1 taco complexes with paraquat derivatives (N,N'-dialkyl-4,4'-biyridinium) in the solid state,[2a,b] pseudorotaxanes can be made based on the new bis(*m*-phenylene)-32-crown-10/monopyridinium recognition motif. Considering the ready availabilities of bis(*m*-phenylene)-32-crown-10 and pyridinium derivatives, this new recognition motif should be easily extended to preparation of other supramolecular threaded structures. Once interlocked structures (rotaxanes or catenanes) based on monopyridinium salts are made, they have the potential to be reduced in order to prepare neutral interlocked structures.[12] The study presented here may stimulate further studies on complexation of other crown ethers with monopyridinium salts. We are focusing on such projects now.

13.4. ACKNOWLEDGEMENTS

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13.5. SUPPORTING INFORMATION

*Job plot for Complexation between **1** and **2b***

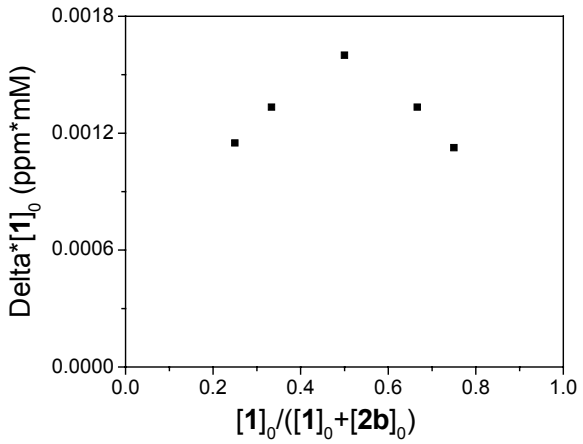

Figure S1. Job plot showing the 1:1 stoichiometry of the complex between crown ether **1** and monopyridinium **2b** in 1:1 acetone-d_6:chloroform-*d*. $[\mathbf{1}]_0$ and $[\mathbf{2b}]_0$ are initial concentrations of **1** and **2b**. $[\mathbf{1}]_0 + [\mathbf{2b}]_0 = 2.00$ mM. Delta = the chemical shift change of H_1.

*Determination of Δ_0 of H_1 for Complexation between **1** and **2a** in 1:1 Acetone-d_6:Chloroform-d*

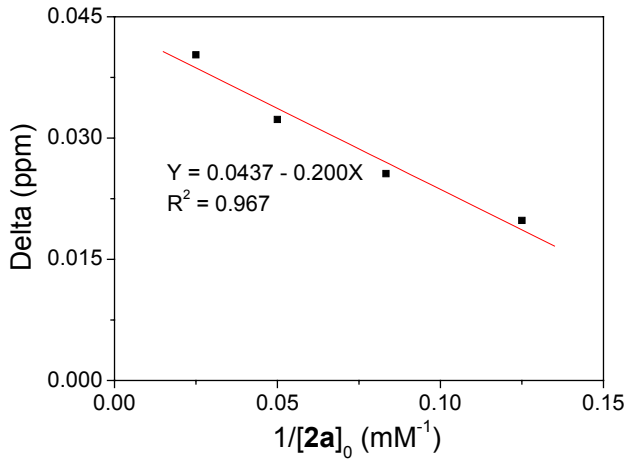

Figure S2. Relationship between Δ and 1/[**2a**]$_0$ for the complexation between **1** and **2a** in 1:1 acetone-d_6:chloroform-*d* at 22°C. [**1**]$_0$ and [**2a**]$_0$ are initial concentrations of **1** and **2a**. [**1**]$_0$ is constant at 0.250 mM.

*Determination of Δ_0 of H_1 for Complexation between **1** and **2b** in 1:1 Acetone-d_6:Chloroform-d*

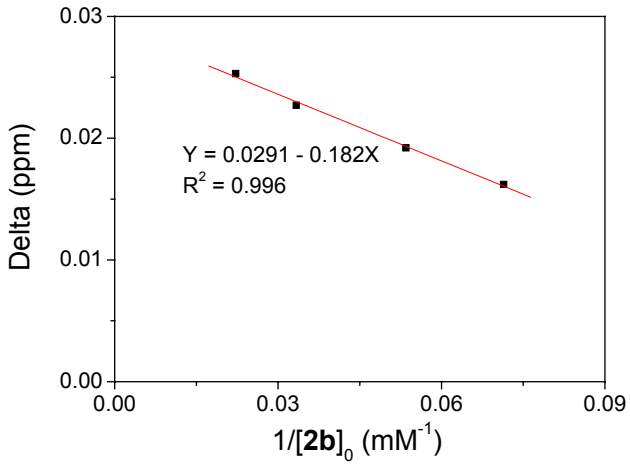

Figure S3. Relationship between Δ and 1/[**2b**]$_0$ for the complexation between **1** and **2b** in 1:1 acetone-d_6:chloroform-*d* at 22°C. [**1**]$_0$ and [**2b**]$_0$ are initial concentrations of **1** and **2b**. [**1**]$_0$ is constant at 0.333 mM.

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Chem. Soc. **2004**, *126*, 9682-9872. Zhao, D.; Fei, Z.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 15876-15882. Pittelkow, M.; Christensen, J. B.; Meijer, E. W. *J. Polym. Sci., Pol. Chem.* **2004**, *42*, 3792-3799.

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8. Job, P. *Ann. Chim*. **1928**, *9*, 113-203.
9. ^{1}H NMR characterizations were done on solutions with constant $[\mathbf{1}]_0$ and varied $[\mathbf{2}]_0$. Based on these NMR data, $\Delta_{0,\mathbf{1}}$, the difference in δ values for H_1 of **1** in the uncomplexed and fully complexed species, was determined as the y-intercept of a plot of $\Delta = \delta - \delta_u$ vs. $1/[\mathbf{2}]_0$ in the high initial concentration range of **2**. Then $K_{a,\mathbf{1\bullet 2}}$ values at different $[\mathbf{1}]_0$ and $[\mathbf{2}]_0$ were calculated from $K_{a,\mathbf{1\bullet 2}} = (\Delta_{\mathbf{1}}/\Delta_{0,\mathbf{1}})/\{1 - (\Delta_{\mathbf{1}}/\Delta_{0,\mathbf{1}})\}\{[\mathbf{2}]_0 - (\Delta_{\mathbf{1}}/\Delta_{0,\mathbf{1}})[\mathbf{1}]_0\}$. The values and errors of $K_{a,\mathbf{1\bullet 2}}$ are the means and standard derivations from seven or nine data points with different $[\mathbf{1}]_0$ and $[\mathbf{2}]_0$ and $0.1 < \Delta_{\mathbf{1}}/\Delta_{0,\mathbf{1}} < 0.9$.
10. Examples: Buchner, R.; Chen, T.; Hefter, G. *J. Phys. Chem. B* **2004**, *108*, 2365-2375. Huang, F.; Zakharov, L. N.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, *70*, in press.
11. Crystal data of **1•2a**: prism, yellow, $C_{43}H_{58}F_6NO_{13}P$, FW 941.87, monoclinic, space group $P2_1/n$, a = 13.5444(10), b = 19.5351(13), c = 17.0637(14) Å; β = 92.206(6)º; V = 4511.6(6) Å^3, Z = 4, T = 100 K, μ = 1.50 cm^{-1}, 21258 measured reflections, 7986 independent reflections[R(int) = 0.0462], 586 parameters, $F(000)$ = 1984, R_1 = 0.0947, wR_2 = 0.0773 (all data), R_1 = 0.0438, wR_2 = 0.0647 [$I > 2\sigma(I)$], and GooF (F^2) = 0.0939. CCDC 257731.
12. For example, quaternized monopyridinium nuclei can be easily reduced by sodium borohydride to the neutral tetrahydro derivatives. See: *Pyridine and Its Derivatives*, E. N. Shaw, and E. Klingsberg Eds.: Interscience: New York, **1960**;

Part 2, pp 47-55. L. A. Paquette, *Modern Heterocyclic Chemistry*; W. A. Benjamin: New York, **1968**; pp 240-241.

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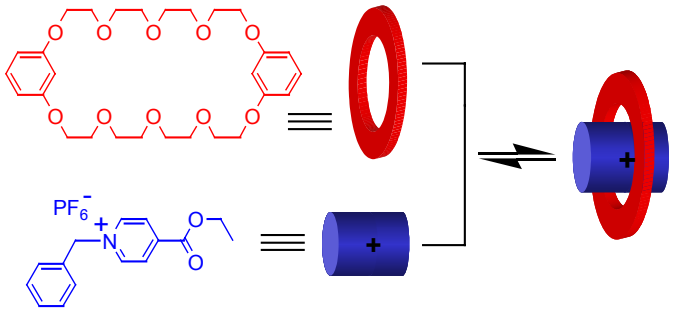

Abstract: Some crown ether/monopyridinium pseudorotaxanes were successfully prepared based on the new bis(*m*-phenylene)-32-crown-10/monopyridinium recognition motif as confirmed by proton NMR spectroscopy, electrospray ionization mass spectrometry and X-ray analysis.