ORGANIC LETTERS

2006
Vol. 8, No. 6
1069−1072

A Triptycene-Based Bis(crown ether) Host: Complexation with Both Paraquat Derivatives and Dibenzylammonium Salts

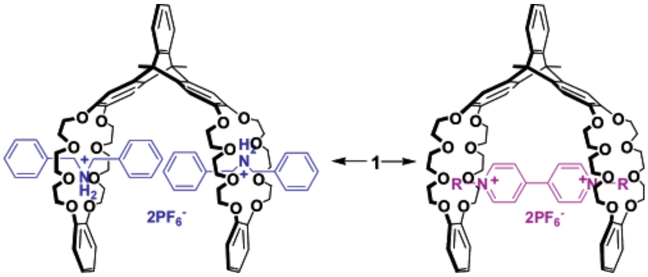
Tao Han[†,‡] and Chuan-Feng Chen[*,†]

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080, China, and Graduate School, Chinese Academy of Sciences,
Beijing 100049, China

cchen@iccas.ac.cn

Received December 12, 2005

ABSTRACT



A novel triptycene-based bis(crown ether) host (1) incorporating two dibenzo-24-crown-8 ether moieties has been synthesized. It can form not only a new bis[2]pseudorotaxane with dibenzylammonium salts but also stable clip-shaped complexes with paraquat derivatives. Moreover, the complexation process between 1 and the two classes of guests can be chemically controlled.

Since Stoddart et al. first reported the complexation of paraquat by the bisparaphenylene-34-crown-10 in the late 1980s,[1] paraquats (*N*,*N*′-dialkyl-4,4′-bipyridinium salts) have been extensively studied as guests in host−guest chemistry. In particular, a variety of interlocked molecules, such as pseudorotaxanes, rotaxanes, and catenanes, have been constructed by the complexation of the paraquats with crown ethers,[2] cryptands,[3] and other hosts.[4]

Triptycene, for its three-dimensional rigid structure, was found to be a useful building block for the construction of supramolecular systems with unique structures and properties.[5] Inspired by the fact that dibenzo-24-crown-8 (DB24C8) can be threaded by secondary ammonium ions to form [2]-pseudorotaxanes,[6] we recently reported that the complexation of a triptycene-based homotritopic host with dibenzylam-

---

[†] Institute of Chemistry, Chinese Academy of Sciences.

[‡] Graduate School, Chinese Academy of Sciences.

(1) Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1064−1066.

(2) For recent examples on crown ether/paraquat complexes, see: (a) Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845−1849. (b) Badjic, J. D.; Cantrill, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 2288−2289. (c) Huang, F.; Fronczek, F. R.; Gibson, H. W. *Chem. Commun.* **2003**, 1480−1481. (d) Long, B.; Nikitin, K.; Fitzmaurice, D. *J. Am. Chem. Soc.* **2003**, *125*, 15490−15498.

(3) For recent examples on cryptand/paraquat complexes, see: (a) Huang, F.; Fronczek, F. R.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 9272−9273. (b) Huang, F.; Gibson, H. W.; Bryant, W. S.; Nagvekar, D. S.; Fronczek, F. R. *J. Am. Chem. Soc.* **2003**, *125*, 9367−9371. (c) Huang, F.; Switek, K. A.; Zakharov, L. N.; Fronczek, F. R.; Slebodnick, C.; Lam, M.; Golen, J. A.; Bryant, W. S.; Mason, P. E.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, *70*, 3231−3241.

(4) For some recent examples, see: (a) Huang, F.; Zakharov, L. N.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, *70*, 809−813. (b) Huang, F.; Gibson, H. W. *Chem. Commun.* **2005**, 1696−1698. (c) Kwangyul, M.; Grindstaff, J.; Sobransingh, D.; Kaifer, A. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 5496−5499. (d) Kwangyul, M.; Kaifer, A. E. *Org. Lett.* **2004**, *6*, 185−188. (e) Arduini, A.; Calzavacca, F.; Pochini, A.; Secchi, A. *Chem. Eur. J.* **2003**, *9*, 793−799. (f) Credi, A.; Dumas, S.; Silvi, S.; Venturi, M.; Arduini, A.; Pochini, A.; Secchi, A. *J. Org. Chem.* **2004**, *69*, 5881−5887. (g) Arduini, A.; Ciesa, F.; Fragassi, M.; Pochini, A.; Secchi, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 278−281.

10.1021/ol053008s CCC: $33.50

monium salts formed a tris[2]pseudorotaxane that could further be transferred into [4]pseudocatenanes.[7] Here, we report a novel triptycene-based host **1** containing two DB24C8 moieties, which show the complexation not only with dibenzylammonium salts to result in a bis[2]pseudorotaxane but also with paraquats[8] to form stable clip-shaped complexes in solution and in the solid state (Figure 1). Moreover, the complexation process between **1** and guests **3** and **4** can be chemically controlled.

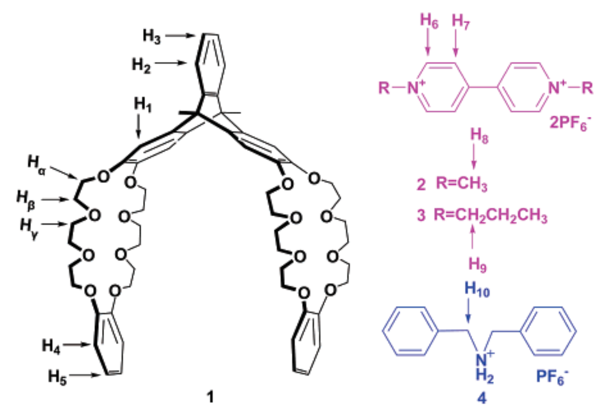
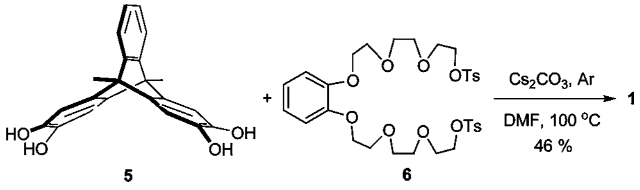


Figure 1. Structure and proton designations of the host **1** and guests **2**−**4**.

Synthesis of host **1** is depicted in Scheme 1. Reaction of the triptycene derivative **5**[5d] and 2 equiv of 1,2-bis[2-[2-(2-tosyloxyethoxy)ethoxy]ethoxy]benzene **6**[7] under high dilution conditions afforded **1** in 46% yield. Host **1** was characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analysis.[9]

Scheme 1. Synthesis of Host **1**



When host **1** and paraquat **2** (2 mM each) were mixed in acetonitrile, they gave a deep orange solution immediately due to charge transfer between the electron-rich aromatic rings of the host **1** and the electron-poor pyridinium rings of the guest **2**. Similarly, the mixed solution of **1** and **3** also showed typical charge-transfer features but the color is yellow. As shown in Figure 2, the ^{1}H NMR spectrum of a 1:1 mixture of **1** and **2** in CD_3CN showed a great difference with those for host **1** and guest **2**. Consequently, the proton H_7 of paraquat ring showed a significant upfield shift ($\Delta\delta = 0.901$ ppm), which may be due to the strong shielding effect of the aromatic rings in **1**. Similarly, the H_1−H_5 proton signals of **1** also shifted upfield. In contrast, a considerable downfield shift of the methyl protons in guest **2** was observed, which is attributed to the hydrogen bond interactions and its position in the deshielding region of the aromatic rings of **1**. These observations suggested that a stable complex between **1** and guest **2** was formed. Furthermore, ^{1}H NMR spectroscopic titrations afforded a quantitative estimate for the complex of **1** and **2** by monitoring the changes of the chemical shift of the proton H_7 in the paraquat ring. The results showed that a 1:1 complex **1·2** was formed by a mole ratio plot.[10] Accordingly, the apparent association constant between **1** and paraquat **2** was calculated to be $K_{a,exp,\mathbf{1}\cdot\mathbf{2}} = 1.63(\pm 0.3) \times 10^{4}$ M^{-1}.[11] Similarly, **1** and the paraquat derivative **3** also formed a 1:1 complex, and the apparent association constant ($K_{a,exp,\mathbf{1}\cdot\mathbf{3}}$) was determined to be 136 (±22) M^{-1}. The big $K_{a,exp}$ difference between **1·2** and **1·3** presumably results from the different bonding manner of host **1** with guests **2** and **3**. For complex **1·2**, there exist strong NOE effects between *N*-methyl protons, pyridinium protons (H_6) of the guest, and crown ether protons

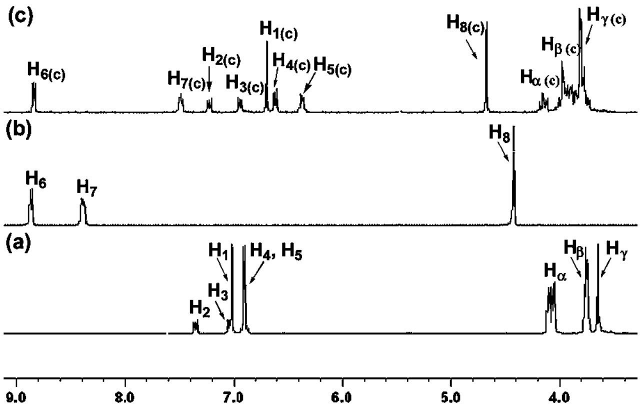


Figure 2. Partial ^{1}H NMR spectra (300 MHz, CD_3CN, 295 K) of (a) free host **1**, (b) free guest **2**, and (c) **1** and 1.0 equiv of **2**. $[\mathbf{1}]_0 = 2$ mM.

---

[5] (a) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303−1324. (b) Corbett, P. T.; Tong, L. H.; Sanders, J. K. M.; Otto, S. *J. Am. Chem. Soc.* **2005**, 127, 8902−8903. (c) Zhu, X. Z.; Chen, C. F. *J. Org. Chem.* **2005**, *70*, 917−924. (d) Zong, Q. S.; Chen, C. F. *Org. Lett.* **2006**, *8*, 211−214.

[6] Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Peter, T. G.; Menzer, S.; Phlip, D.; Sepencer, N.; Stoddart, J. F.; Tasher, P. A.; Willams, D. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 1865−1869.

[7] Zhu, X. Z.; Chen, C. F. *J. Am. Chem. Soc.* **2005**, *127*, 13158−13159.

[8] Gibson et al. recently mentioned in a paper that DB24C8 can form a 1:1 complex with the paraquat in solution, but a 2:1 complex in the solid state. Huang, F.; Jones, J. W.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 14458−14464.

[9] See the Supporting Information.

[10] Tsukube, H.; Furuta, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtleand, F., Lehn, J. M., Eds.; Elsevier: New York, 1996.

[11] Complexation between **1** and **2** was determined to be non-concentration dependent, which is in contrast with the complex formed by DB24C8 and **2**.[8] This result indicated that complexation of **2** with the host **1** occurred in a way different from the complexation of DB24C8. For the determination of the $K_{a,exp}$, see the Supporting Information.

of the host. However, such short distance contacts were not observed for complex **1·3** under the same conditions.[9]

The electrospray ionization mass spectrum (ESI MS) provided more evidence for the formation of complexes **1·2** and **1·3**.[9] As a result, a strong peak at *m*/*z* 604.8 for $[\mathbf{1{\cdot}2} - 2PF_6^-]^{2+}$ was observed, which indicated that the 1:1 stable complex between **1** and guest **2** formed. For **1·3**, the relevant peak was observed at *m*/*z* 632.5, corresponding to $[\mathbf{1{\cdot}3} - 2PF_6^-]^{2+}$.

Further support for formation of the complex **1·2** came from its X-ray diffraction results.[12] As shown in Figure 3, in the solid state the paraquat is included in the center of the host **1** while the two *N*-methyl groups are positioned in the two DB24C8 cavities, which results in a pseudorotaxane-like structure. Due to multiple CH···O hydrogen bonds between the *N*-methyl protons and proton H_6 of the paraquat unit and ether oxygen atoms in **1**, and the face to face π-stacking interactions between paraquat ring and aromatic rings of the crown units, the complex **1·2** exhibits a high stability. This result is consistent with that of **1·2** in solution.

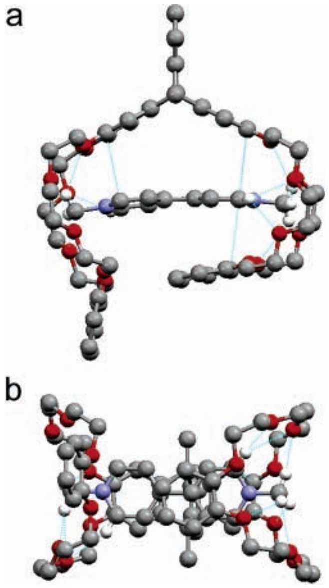


Figure 3. Top view (a) and side view (b) of the crystal structure of the complex **1·2**. Hydrogen atoms not involved in the interactions, and counterions are omitted for clarity.

Complexation between host **1** and dibenzylammonium salt **4** was studied by ^1H NMR spectroscopic titrations (Figure 4). As expected, the host **1** binds two of the guest **4** to form a bis[2]pseudorotaxane-type complex $\mathbf{1{\cdot}4_2}$, and the complexation of **4** with host **1** occurs under a slow exchange process. When the ion-pairing effect was considered, the association constants[13] for $\mathbf{1{\cdot}4_2}$, $K_{ap,1}$, and $K_{ap,2}$ in an acetonitrile solution were determined to be 720 ± 180 and 77 ± 22 M^{-1}, respectively. These values suggested that **1** binds to the dibenzylammonium salts with a similar strength as the DB24C8 does.[14] Formation of the complex $\mathbf{1{\cdot}4_2}$ was further confirmed by its ESI MS. As a result, two relevant peaks were observed for $\mathbf{1{\cdot}4_2}$ at *m*/*z* 619.9 (100) for $[\mathbf{1{\cdot}4_2} - PF_6^- + H_3^+O]^{2+}$ and 709.7 (91%) for $[\mathbf{1{\cdot}4_2} - 2PF_6^-]^{2+}$.[9]

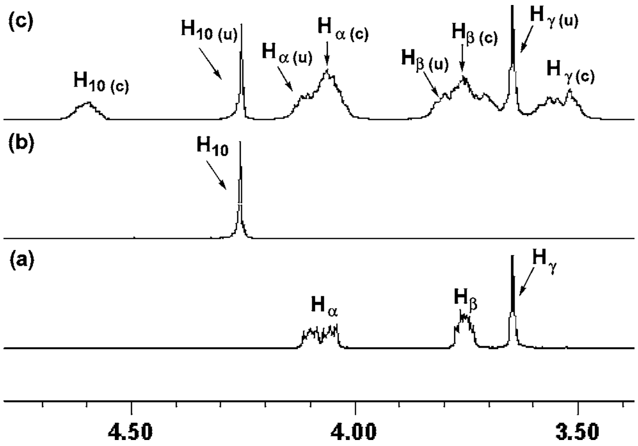


Figure 4. Partial ^1H NMR spectra (300 MHz, CD_3CN, 295 K) of (a) free host **1**, (b) free guest **4**, and (c) **1** and 2.0 equiv of **4**. $[\mathbf{1}]_0$ = 5 mM.

It was known that the association and disassociation of the complex between DB24C8 and secondary ammonium salts could be chemically controlled by pH, which inspired us to further examine the competitive bonding ability of the host **1** toward different guests. Consequently, a series of ^1H NMR experiments were carried out. As shown in Figure 5b, the host **1** and 1 equiv of the guest **3** formed a stable complex **1·3**. When 2 equiv of the guest **4** was added into the solution of **1·3** in CD_3CN, proton H_7 of guest **3** shifted downfield almost to the original position (Figure 5c), which indicates that the complex **1·3** disassociated. Meanwhile, the more stable complex $\mathbf{1{\cdot}4_2}$ formed. To the above solution was added 1.6 μL of tributylamine,[15] and it was found that protons on guest **4** were peeled off, which showed that the complex $\mathbf{1{\cdot}4_2}$ disassociated while **1·3** recovered (Figure 5d). Furthermore, when 1.0 μL of trifluoroacetic acid was added, the complex **1·3** disassociated while the complex $\mathbf{1{\cdot}4_2}$ formed again (Figure 5e). These observations suggested that the host **1** exhibited a pH-controllable guest-exchange process.

In summary, we have synthesized a novel triptycene-based bis(crown ether) and demonstrated that it could form not only bis[2]pseudorotaxane-type complex with dibenzylammonium

---

(12) Crystal data for complex **1·2**: $C_{70}H_{84}F_{12}N_2{\cdot}O_{16}P_2$, M_r = 1499.33, triclinic, space group *P*-1, *a* =15.069(3) Å, *b* =24.790(6) Å, *c*=25.460(6) Å; α = 114.553(4)°, β = 91.187(4)°, γ = 102.178 (5)°; *V* = 8393 (3) Å^3, *Z* = 4, *T* = 294(2) K, R_1 = 0.2371, wR_2 = 0.3210 (all data); R_1 = 0.1056, wR_2 = 0.2819 [$I > 2\sigma(I)$].

(13) Elizarov, A. M.; Chiu, S. H.; Glink, P. T.; Stoddart, J. F. *Org. Lett.* **2002**, *4*, 679−682.

(14) When PF_6^- counterion was considered, the asscociation constant for the 1:1 complex between DB24C8 and **4** was determined to be 560 ± 60 M^{-1} in $CDCl_3/CD_3CN$ (3/2).

(15) Tributylamine was usually used as a base to deprotonate the NH_2^+ center. See: Ashton, P. R.; Ballardine, R.; Balzani, V.; Baxter, I.; Credi, A.; Fyfe, M. C. T.; Gandolfi, M. T.; Gómez-López, M.; Martínez-Díaz, M. V.; Piersanti, A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 11932−11942.

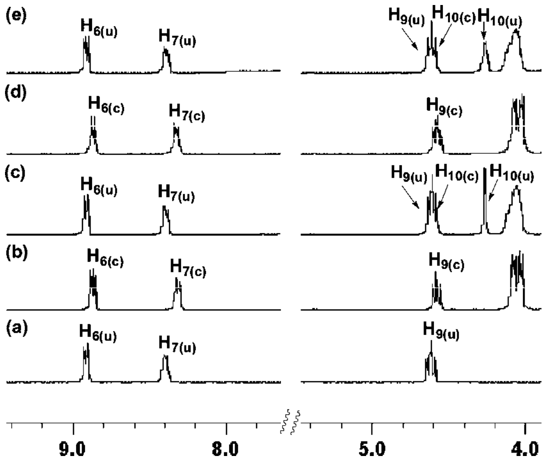


Figure 5. Partial ^{1}H NMR spectra (300 MHz, CD_3CN, 295 K) of (a) $\mathbf{[3]}_0$ (5 mM), (b) $\mathbf{[1]}_0/\mathbf{[3]}_0 = 5$ mM/5 mM, (c) $\mathbf{[1]}_0/\mathbf{[4]}_0/\mathbf{[3]}_0 =$ 5 mM/10 mM/5 mM, (d) to the solution of c was added 1.6 μL of tributylamine, and (e) to the solution of d was added 1 μL of trifluoroacetic acid.

salts but also clip-shaped complexes with paraquat derivatives in solution and in the solid state. Moreover, we found that the complex processes between host **1** and the guests **3** and **4** could be controlled by changing the solution pH, which would be useful for the design of chemically controlled molecular machines, such as molecular muscles.[16] Further work on the fabrication of a rotaxane-based molecular muscle is being done.

Acknowledgment. We thank the Chinese Academy of Sciences and the National Natural Science Foundation of China for financial support. We also thank Dr. H. B. Song for determining the crystal structure of the complex.

Supporting Information Available: Experimental procedure and characterization for the host and the complexes. Determination of the association constants for the complexes. The crystal structure for **1·2** and its CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL053008S

---

(16) (a) Jiménez, M. C.; Dietrich-Buchecker, C.; Sauvage, J. P. *Angew. Chem., Int. Ed*. **2000**, *39*, 3284−3287. (b) Yi, L.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H. R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C. M.; Stoddart, J. F. *J. Am. Chem. Soc*. **2005**, *127*, 9745−9759.