

Novel Triptycene-Based Cylindrical Macrotricyclic Host: Synthesis and Complexation with Paraquat Derivatives

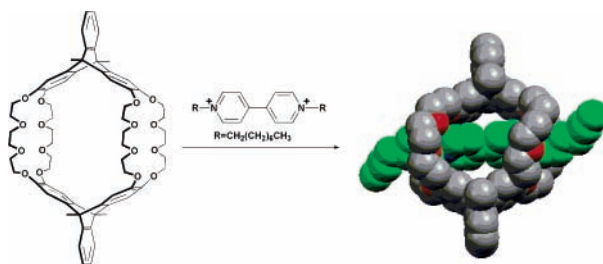
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ABSTRACT



A novel triptycene-based cylindrical macrotricyclic polyether containing two dibenzo[24]crown-8 cavities has been synthesized and proved to be a highly efficient host for the complexation with paraquat derivatives. Consequently, a new kind of very stable pseudorotaxane-type complex was formed in solution and in the solid state.

Host–guest chemistry¹ has attracted great interest since Pedersen first reported² the synthesis and cation-complexing characteristics of the crown ethers. One particular interest in this regard came from complexation of paraquat derivatives by bisarylene crown ethers,³ which resulted in a variety of interlocked supramolecular assemblies⁴ such as pseudorotaxanes, rotaxanes, and catenanes. Consequently, paraquat derivatives have become some of the most common guests,

and crown ethers,⁵ cryptands,⁶ cylindrical bis(crown ether),⁷ cucurbit[*n*]uril,⁸ and calix[6]arene derivatives⁹ have been used as hosts for formation of the interlocked complexes.

(5) 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.

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A permanent and challenging topic in host–guest chemistry is the design and synthesis of novel macrocyclic hosts which are capable of binding substrate species strongly and selectively. Cylindrical macrotricyclic polyethers consist of one central cavity and two lateral circular cavities, which have new topological features with respect to the macromono- and macrobicyclic ligands.¹⁰ Owing to their architectural and functional plasticity, cylindrical macrotricyclic hosts are especially attractive for designing both biomimetic and abiotic receptor molecules for guests.^{7,11} However, the previously reported cylindrical macrotricyclic hosts are all formed by linking two macrocycles together through single point (two bridges), which makes the structures so flexible that their complexation with guests may be influenced to a certain extent. We reasoned that a cylindrical macrotricyclic polyether formed by incorporating a rigid substituent and linking through double points (four bridges) could show enhanced and coordinated complexation abilities toward substrates such as paraquat derivatives. For this purpose, triptycene,¹² an interesting class of compounds with a unique propeller-like three-dimensional rigid structure, was used as the building block for constructing cylindrical hosts considering that it can act not only as a spacer and a cavity-forming unit but also as a potential donor for π -stacking interactions. Herein, we report the synthesis of the first triptycene-based cylindrical macrotricyclic host **1** containing two dibenzo[24]crown-8 moieties¹³ (Figure 1), which shows excellent complexation abilities toward paraquat derivatives and consequently self-assembles into stable pseudorotaxane-type complexes in solution and in the solid state.

Synthesis of the host **1** is depicted in Scheme 1. Triptycene derivative **6** was synthesized in 85% yield by the reaction of 9,10-dimethyl-2,3,6,7-tetramethoxy-anthracene **5**^{12e} and benzenediazonium-2-carboxylate in the presence of propylene oxide. Demethylation of **6** with tribromoborane afforded compound **7**, which reacted with 8-tosyloxy-3,6-dioxaoctanol in the presence of K_2CO_3 , followed by reaction with *p*-toluenesulfonyl chloride, to give **8** as an oil. Compound **8** was further reacted with **7** under a high dilution condition in the presence of cesium carbonate to give **1** in 20% yield. Host **1** was characterized on the basis of NMR data, mass

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(13) Gibson et al. recently reported that dibenzo[24]crown-8 and paraquat form a 1:1 complex in solution but form a 2:1 complex in the solid state. Huang, F.; Jones, J. W.; Slobodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 14458–14464.

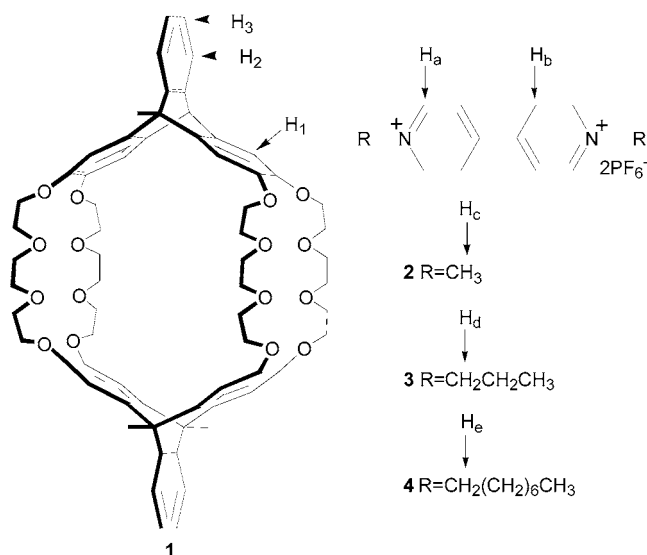
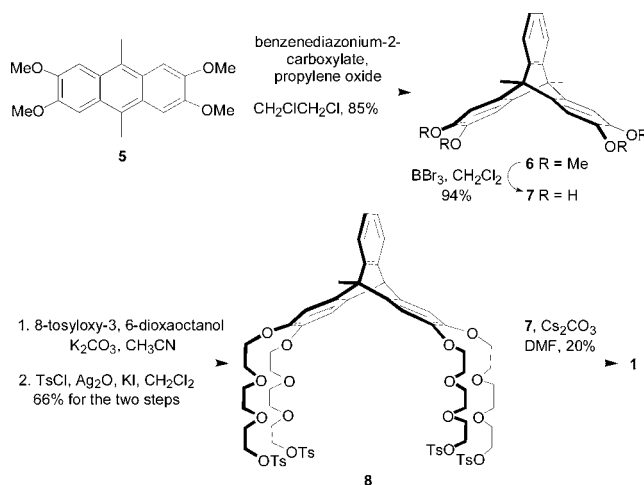


Figure 1. Structure and proton designations of the host **1** and guests **2–4**.

spectrometry, and X-ray crystallography.¹⁴ The crystal structure of **1** shows that two triptycene units are linked with four tri(ethylene glycol) bridges to form two lateral dibenzo[24]crown-8 cavities and one beltlike central cavity with a size of ca. $10.2 \times 13.9 \text{ \AA}$ (see Supporting Information). The dihedral angle and centroid–centroid distance between the phenylene rings of each crown unit are 59.3° and 8.56 \AA , respectively.

Scheme 1. Synthesis of **1**



When host **1** and paraquat **2** (6 mM each) were mixed in 1:1 chloroform/acetonitrile, they gave a bright red solution

(14) Crystal data for $1 \cdot 2CH_3CN \cdot 4CHCl_3$: $C_{76}H_{86}Cl_{12}N_2O_{16}$; $M_r = 1708.87$; monoclinic; space group $P2(1)/c$; $a = 12.410(12) \text{ \AA}$, $b = 12.837(12) \text{ \AA}$, $c = 25.498(2) \text{ \AA}$; $\beta = 92.490(2)^\circ$; $V = 4058.2(7) \text{ \AA}^3$; $Z = 2$; $d = 1.398 \text{ g cm}^{-3}$; $T = 294(2) \text{ K}$; $R1 = 0.1314$, $wR2 = 0.3070$ (all data); $R1 = 0.0873$, $wR2 = 0.2583$ [$I > 2\sigma(I)$].

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, mixed solutions of **1** and **3** or **4** also showed typical charge-transfer features but lighter color changes than that of **1** and **2**. Complex studies of host **1** with paraquat derivatives were carried out in a 1:1 CDCl₃/CD₃CN solution by monitoring the changes in the chemical shift of the hydrogen atom (H₁) during ¹H NMR spectroscopic titrations. Although Gibson et al. recently reported that dibenzo[24]crown-8 and the paraquat form a 1:1 complex in acetone solution,¹³ we found that the complexes between the host **1** containing two dibenzo[24]-crown-8 moieties and the paraquat derivatives **2–4** also had 1:1 complex stoichiometries in 1:1 chloroform and acetonitrile, which were determined by the molecular ratio plot based on NMR data.¹⁵ As shown in Figure 2, when 1.0 equiv

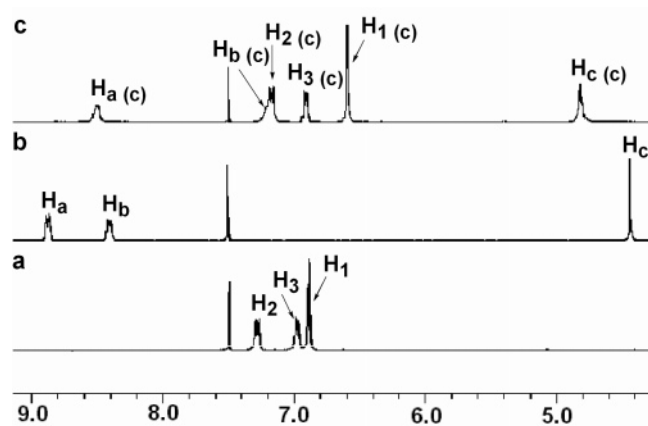


Figure 2. Partial ¹H NMR spectra (300 MHz, CD₃CN/CDCl₃ = 1:1, 295 K) of (a) free host **1**, (b) free guest **2**, and (c) **1** and 1.0 equiv of **2**. [**1**]₀ = 6 mM.

of guest **2** was added to a solution of the host **1**, only one set of resonances for the complex **1•2** was observed (Figure 2c). However, if either the host or the guest is excess, the spectrum shows one set of resonances for the host **1** or the guest **2** besides those for the complex¹⁶ (see Supporting Information). These observations suggested that the complex **1•2** was very stable, and the rates of complexation and decomplexation were both slow at room temperature. Accordingly, the association constant (K_{a1-2}) for 1:1 complex **1•2** was determined by a competitive method¹⁷ to be $4 \times 10^5 \text{ M}^{-1}$ ($\Delta G = -3 \times 10^2 \text{ kJ/mol}$).

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(16) The resonances of the complex were assigned by the ¹H–¹H COSY and ¹H NMR titration experiments (Supporting Information).

(17) Bis(5-hydroxymethyl-*m*-phenylene)-32-crown-10 (BMP32C10-diol) (**R**_{ref}) was used as the reference host. In a 4.0 mM equimolar solution of **1**, **2**, and BMP34C10-diol, the concentration of complexed BMP34C10-diol, [**R**_{ref}]_c, was 0.385 mM. The K_a for **1•2** was calculated from it. The error is based on errors of [**R**_{ref}]_c and K_a for **R**_{ref}•**2** (Supporting Information). Heath, R. E.; Dykes, G. M.; Fish, H.; Smith, D. K. *Chem.–Eur. J.* **2003**, *9*, 850–855.

Moreover, the 1:1 complex **1•2** was directly detected by electrospray ionization mass spectrum (see Supporting Information), in which the strongest (base) peak at m/z 667.9 for [**1•2**–2PF₆[−]]²⁺ was observed. At the same time, it was also found that the complex **1•2** was not decomposed even in DMSO-*d*₆ (see Supporting Information).

It is different from the complexation between **1** and **2** that **1** and the guest **3** or **4** belong to the fast-exchange complexation system. A plausible explanation¹⁸ for the different complexation dynamics may be that the dimethyl compound initially forms a 2:1 complex with **1**, and then this slowly rearranges to the 1:1 complex. The larger dialkyl viologens are not able to form 2:1 complexes and, hence, exhibit fast exchange. Consequently, the association constants (K_{a1-3} , K_{a1-4}) for the 1:1 complexation between **1** and **3** or **4** were determined to be $2 \times 10^3 \text{ M}^{-1}$ ($\Delta G = -2 \times 10^2 \text{ kJ/mol}$) and $2 \times 10^3 \text{ M}^{-1}$ ($\Delta G = -2 \times 10^2 \text{ kJ/mol}$) by using the Scatchard plots.¹⁹ The electrospray ionization mass spectra of the solutions of **1•3** and **1•4** also showed their 1:1 complexation (see Supporting Information). Correspondingly, the strongest (base) peaks at m/z 695.8 for [**1•3**–2PF₆[−]]²⁺ and 765.6 for [**1•4**–2PF₆[−]]²⁺, respectively, were observed.

The formation of the 1:1 complex between **1** and **2** was further confirmed by X-ray analysis (Figure 3).²⁰ It was noted

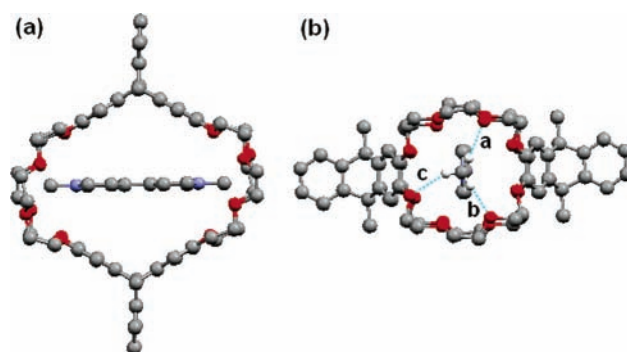


Figure 3. (a) Top view and (b) side view of the crystal structure of the complex **1•2**. Solvent molecules, two PF₆[−] counterions, and hydrogen atoms are omitted for clarity. Hydrogen-bonding parameters: H⋯O distances (Å) and C–H⋯O angles (deg). $a = 2.47$, 177; $b = 2.47$, 171; $c = 2.69$, 130.

that the structural feature of the complex **1•2** is completely different from those of paraquat-based complexes reported previously.^{5–7} In the complex **1•2**, the paraquat is included in the center of the macrotricyclic host and the two *N*-methyl groups are positioned in the two dibenzo[24]crown-8 cavities, which results in a pseudorotaxane-like structure. Compared with the crystal structure of **1**, its conformation in the

(18) We thank one of the reviewers for the valuable suggestions.

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(20) Crystal data for **1•2**•0.5CH₃CN•0.5CH₂Cl₂•C₂H₅OC₂H₅: C_{85.5}H_{102.5}ClF₁₂N_{2.5}O₁₇P₂; $M_r = 1762.59$; monoclinic; space group $P2(1)/n$; $a = 15.303(2) \text{ \AA}$, $b = 16.558(2) \text{ \AA}$, $c = 19.187(3) \text{ \AA}$; $\beta = 97.376(2)^\circ$; $V = 4821.9(11) \text{ \AA}^3$; $Z = 2$; $T = 294(2) \text{ K}$; $R1 = 0.1912$, $wR2 = 0.3641$ (all data); $R1 = 0.0996$, $wR2 = 0.2858$ [$I > 2\sigma(I)$].

complex **1**·**2** is a more symmetrical one, in which the two dibenzo[24]crown-8 moieties are almost the same. In addition, it was also found that the bipyridinium unit was slightly distorted with 6.8° of the dihedral angle between two pyridinium rings. Because multiple hydrogen-bonding interactions²¹ between the *N*-methyl protons of the paraquat unit and the ether oxygen atoms and the face–face π -stacking interactions between paraquat rings and aromatic rings of the triptycene skeletons exist, the complex **1**·**2** shows a high stability which is consistent with the result in solution. Thus, about a 1.2 ppm upfield shift of H_b is attributed to the strong shielding effect of the aromatic rings of **1**. The significant downfield shift of the methyl protons in the guest **2** is due to the hydrogen-bond interactions and its position in the deshielding region of the aromatic rings of **1**. Moreover, proton H_1 of **1** and proton H_a of **2** are in the shielding region of the paraquat **2** and in the aromatic rings of the host **1**, respectively, which results in their upfield shifts.

We further obtained the crystals of the complex **1**·**4** suitable for X-ray analysis by diffusion of ether into an equimolar mixture of the two components in $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1:1) solution.²² As shown in Figure 4, the host **1** and the guest **4** also formed a 1:1 complex in the solid state, which is consistent with that in solution. In the complex **1**·**4**, the dihedral angles/centroid–centroid distances between the phenylene rings of each crown unit are $63.36^\circ/9.30 \text{ \AA}$ (A and C) and $63.36^\circ/9.48 \text{ \AA}$ (B and D), whereas the two pyridinium rings are well coplanar, which is different from that in **1**·**2**. Similar to the complex **1**·**2**, the complex **1**·**4** is also stabilized by the multiple hydrogen bonds²⁰ among the *N*-methylene protons and the proton H_c of **4** and the ether oxygen atoms and by the π -stacking interactions between the aromatic rings of **1** and the pyridinium rings of **4**. Interestingly, it was found that the two *N*-octyl groups in the guest **4** are threaded out from the two lateral crown-8 cavities of **1** to form a new kind of pseudorotaxane.

(21) There also exist multiple hydrogen-bonding interactions between the PF_6^- counterions and either the host or the guest, which may play an important role in the complex's stability (Supporting Information).¹³

(22) Crystal data for **1**·**4**· CH_2Cl_2 : $\text{C}_{95}\text{H}_{120}\text{Cl}_2\text{F}_{12}\text{N}_2\text{O}_{16}\text{P}_2$; $M_r = 1906.77$; triclinic; space group $P\bar{1}$; $a = 13.944(3) \text{ \AA}$, $b = 14.295(4) \text{ \AA}$, $c = 15.300(4) \text{ \AA}$; $\alpha = 82.786(5)^\circ$, $\beta = 66.607(4)^\circ$, $\gamma = 63.871(4)^\circ$; $V = 2508.6(11) \text{ \AA}^3$; $Z = 1$; $T = 294(2) \text{ K}$; $R_1 = 0.2023$, $wR_2 = 0.3954$ (all data); $R_1 = 0.1113$, $wR_2 = 0.3250$ [$I > 2\sigma(I)$].

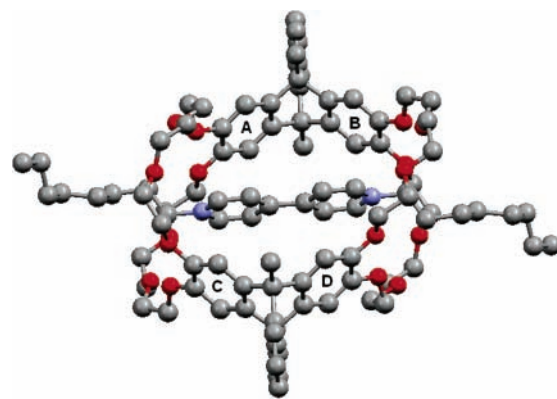


Figure 4. Crystal structure of the complex **1**·**4**. Solvent molecules, two PF_6^- counterions, and hydrogen atoms are omitted for clarity.

In summary, we have presented a novel triptycene-based cylindrical macrotricyclic polyether, which proved to be a highly efficient host for the complexation with paraquat derivatives. Consequently, a new kind of very stable pseudorotaxane-type complex has been constructed in solution and in the solid state. The results presented here provide us many opportunities for developing complex supramolecular assemblies such as supramolecular polymers,²³ which are now in progress.

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Supporting Information Available: Experimental procedures and characterization data for the host and the complexes. The crystal structures for **1**, **1**·**2**, and **1**·**4** and their CIF data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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