

Synthesis of Triptycene-Derived Macrotricyclic Host Containing Two Dibenzo-[18]-crown-6 Moieties and Its Complexation with Paraquat Derivatives: Li⁺-Ion-Controlled Binding and Release of the Guests in the Complexes

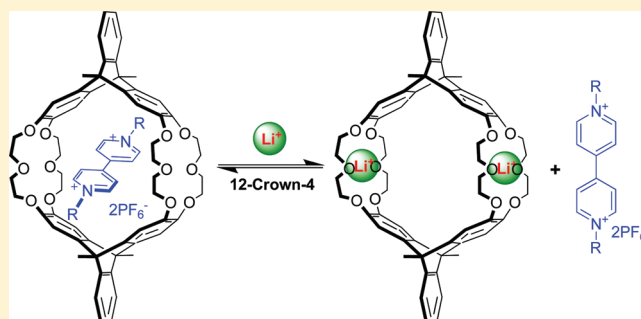
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S Supporting Information

ABSTRACT: A new triptycene-derived macrotricyclic host containing two dibenzo-[18]-crown-6 moieties was synthesized and shown to form 1:1 complexes with paraquat derivatives in solution, in which the guests all thread the central cavity of the host. However, it was interestingly found that, depending on the paraquat derivatives with different functional groups, the host can form stable 1:1 or 1:2 complexes in different complexation modes in the solid state, which is significantly different from those of the macrotricyclic host containing two dibenzo-[24]-crown-8 moieties. The formation of the complexes was also proved by the ESI MS and electrochemical experiments. Moreover, it was found that the binding and release of the guests in the complexes could be easily controlled by the addition and removal of lithium ions.



INTRODUCTION

Since Pedersen first reported¹ the cation-complexing properties of the crown ethers, host–guest chemistry² has been a topic of great interest during the past decades. One particular interest in this research area came from the complexation between paraquat derivatives and bisarylene crown ethers reported by Stoddart and his co-workers in 1987,³ which have resulted in a variety of interlocked supramolecular assemblies,⁴ such as pseudorotaxanes, rotaxanes, and catenanes. Consequently, paraquat derivatives have become some of the most common guests, and crown ethers,⁵ cryptands,⁶ cylindrical macrotricyclic polyethers,⁷ cucurbit[*n*]uril,⁸ calix[6]arene derivatives,⁹ and other macrocycles¹⁰ have been utilized as the hosts for formation of the host–guest complexes with specific structures and properties.

In host–guest chemistry, macrocyclic hosts have undoubtedly played key roles in constructing different kinds of complexes, and the development of novel macrocyclic hosts with the capability of binding substrate species strongly and selectively is also a permanent and challenging topic in this research area.¹¹ Recently, we reported a novel triptycene-derived cylindrical macrotricyclic host containing two dibenzo-[24]-crown-8 lateral cavities^{12a} (**1a**) and found that host **1a** showed guest-dependent complexation with different functional paraquat derivatives, which resulted in formation of a series of stable complexes with specific structures in both solution and the solid state.^{12b} In this paper, we report the synthesis of a new

triptycene-derived macrotricyclic host **1b** containing two dibenzo-18-crown-6 moieties¹³ (Figure 1) and its complexation with different functional paraquat derivatives in solution and in the solid state, which shows significantly different complexation modes with those ones between **1a** and the paraquat derivatives. Moreover, Li⁺-ion-controlled binding and release of the guests in the complexes is also described.

RESULTS AND DISCUSSION

Synthesis of Host 1b. According to the same method as described previously,^{12a} host **1b** was synthesized via three steps starting from triptycene derivative **11**. As shown in Scheme 1, reaction of **11** and 2-(2-hydroxyethoxy)ethyl 4-methylbenzenesulfonate in the presence of K₂CO₃, followed by reaction with *p*-toluenesulfonyl chloride, gave triptycene derivative **12** as a yellow oil in 50% total yield for the two steps. Compound **12** was then reacted with **11** under a high dilution condition in the presence of K₂CO₃ to give **1b** in 22% yield. The structure of **1b** was confirmed by ¹H NMR, ¹³C NMR, MALDI-TOF MS, and elemental analysis.

Complexation Between Host 1b and Paraquat Derivatives in Solution. Complexation between host **1b** and the paraquat derivatives **2–10** was first studied in solution by the ¹H NMR spectroscopic method. When we mixed the

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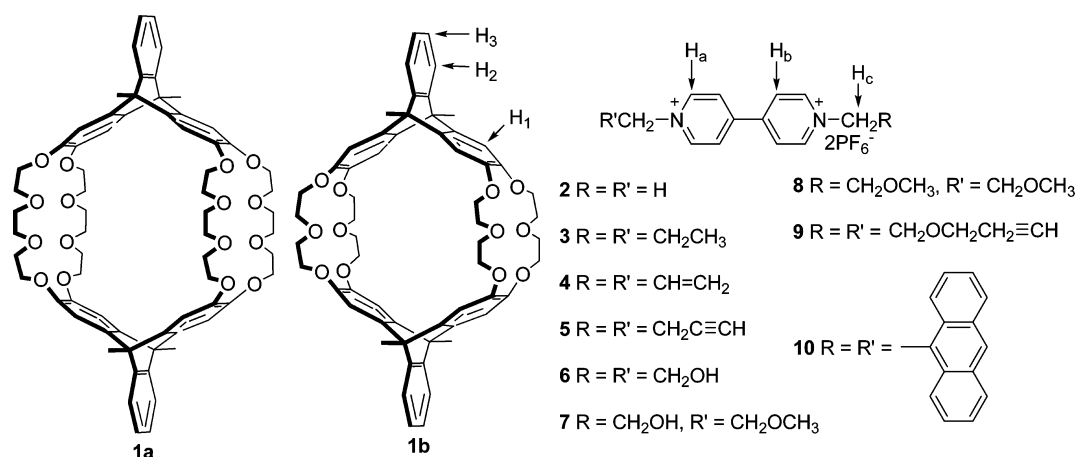


Figure 1. Chemical structures and proton designations of the hosts **1a** and **1b**, and the guests **2**–**10**.

Scheme 1. Synthesis of Host **1b**

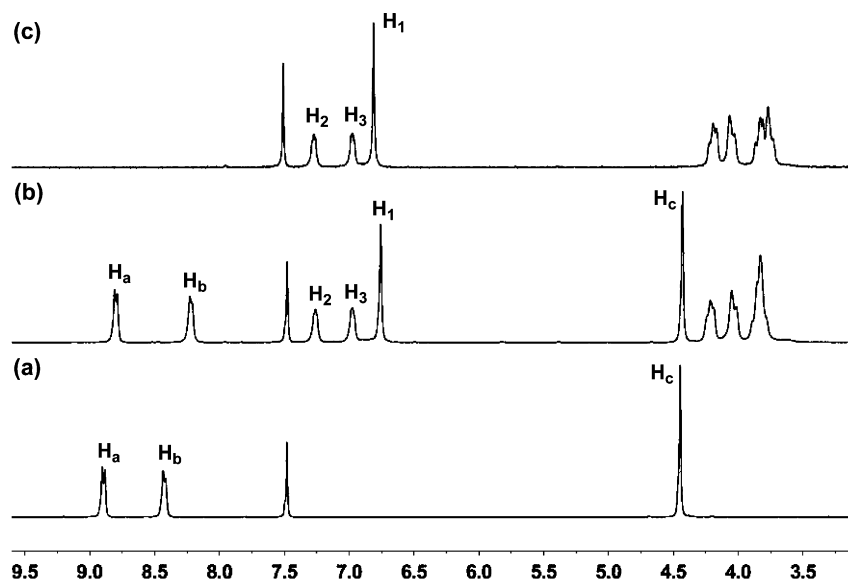
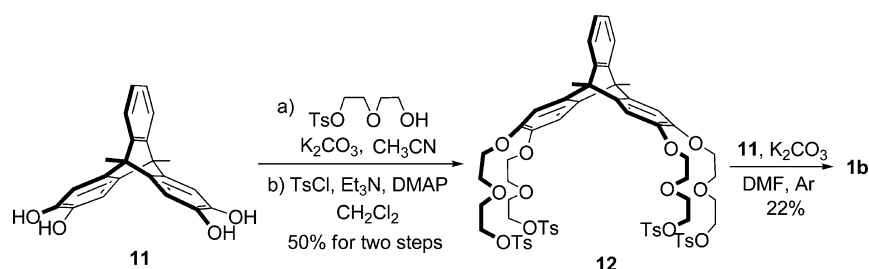


Figure 2. Partial ¹H NMR spectra (300 MHz, CD₃CN/CDCl₃ = 2:3, v/v, 295 K) of (a) free guest **2**, (b) **1b** and 1.0 equiv of **2**, and (c) free host **1b**. [**1b**]₀ = 4.0 mM.

host **1b** (4.0 mM) and 1.0 equiv of **2** in 2:3 (v/v) CD₃CN/CDCl₃, a deep orange solution formed immediately because of charge transfer between the electron-rich aromatic rings of the host and the electron-poor pyridinium rings of the guest. As shown in Figure 2, the ¹H NMR spectrum of a 1:1 mixture of **1b** and **2** showed only one set of different signals from those of the separated host and guest, which suggested that a new complex **1b**·**2** was formed, and the complexation between **1b** and **2** was a fast exchange process. Especially, it was found that the proton H_b of the paraquat ring showed an upfield shift ($\Delta\delta =$

0.21 ppm) due to the shielding effect of aromatic rings in **1b**, and H₁ and H_a proton signals also shifted upfield. The ¹H NMR spectroscopic titrations further afforded a quantitative estimate for the complexation between host **1b** and guest **2** by monitoring the changes of the chemical shift of the proton H₁ of **2**. The results showed that a 1:1 complex between **1b** and **2** was formed by a mole ratio plot. Accordingly, the apparent association constant $K_{a,exp}$ was calculated to be $4.0(\pm 0.1) \times 10^2 \text{ M}^{-1}$ by the Scatchard plot.^{14,15} Previously, we found that the triptycene-derived macrotricyclic host containing two dibenzo-

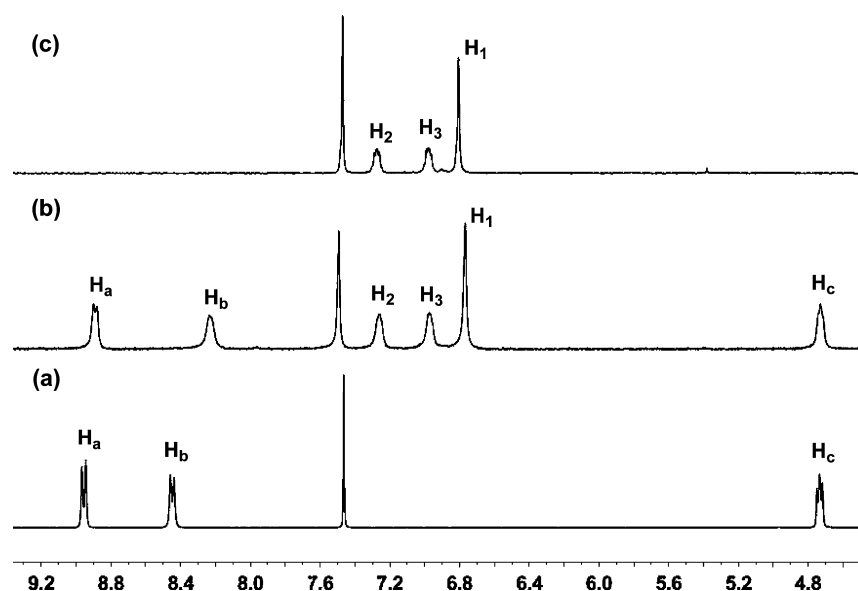


Figure 3. Partial ^1H NMR spectra (300 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3 = 2:3$, v/v, 295 K) of (a) free host **1b**, (b) **1b** and 1.0 equiv of **6**, and (c) free guest **6**. $[\mathbf{1b}]_0 = 4.0$ mM.

[24]-crown-8 moieties (**1a**) could also form a 1:1 stable complex with the paraquat **2**, but the complexation between host **1a** and **2** was a slow exchange process. Especially, the methyl groups in **2** are all positioned at the two lateral crown-8 cavities of the host **1a**, which was proved by the ^1H - ^1H NOESY spectrum.^{12a} However, in the case of complex **1b**·**2**, its ROESY 2D NMR spectrum showed no intermolecular cross-signals for the methyl proton H_c and the crown ether protons in host **1b**,¹⁴ which implied that the paraquat **2** might thread the central cavity of the host **1b** to form a 1:1 complex. This different complexation mode might be attributed to the smaller cavity of **1b** than that of the macrocycle **1a**.

Similarly, we found that the complexation between host **1b** and guest **6** was also a fast exchange process. Correspondingly, the proton H_b of the paraquat ring showed an upfield shift ($\Delta\delta = 0.22$ ppm) due to the shielding effect of aromatic rings in **1b**, while H_1 and H_a proton signals also shifted upfield (Figure 3). Moreover, the stoichiometry of the complex was determined to be 1:1 by a mole ratio plot, and the association constant K_a for the complex was calculated to be $4.0(\pm 0.1) \times 10^2 \text{ M}^{-1}$ by the Scatchard plot. The 2D ROESY spectral experiment¹⁴ of complex **1b**·**6** was further carried out to investigate the complexation between the host and the guest. The results showed that the cross-peaks between proton H_a in the bipyridinium ring of **6** and the protons in crown ether units of **1b** were found, which suggested that the guest could thread the central cavity of host **1b** to form a 1:1 complex. This result is similar to the complexation between **2** and **1b**, but different from that case between **6** and **1a** in which two guests of **6** were included in the central cavity of the host **1a** to form a 1:2 complex.^{12b} Formation of a 1:1, not a 1:2, complex between **1b** and **6** is also attributed to the small cavity of **1b**.

We also tested the complexation between host **1b** and other paraquat derivatives with different functional groups in solution by NMR spectroscopy. The results showed that, similar to the complexation modes between host **1b** and **2**, and **1b** and **6**, the guests **3**–**5** and **7**–**10** could all thread the central cavity of host **1b** to form 1:1 complexes. Moreover, the association constants for the complexes were all calculated by the Scatchard plot, and

the results are summarized in Table 1. It was found that the association constant of 1:1 complex **1b**·**10** is the biggest among

Table 1. Summary of the Stoichiometries and Association Constants of the Complexes

complex	stoichiometry (H/G)	K_a [M^{-1}] ^a
1b · 2	1:1	$4.0(\pm 0.1) \times 10^2$
1b · 3	1:1	$2.0(\pm 0.1) \times 10^2$
1b · 4	1:1	$9.0(\pm 0.1) \times 10^2$
1b · 5	1:1	$3.0(\pm 0.1) \times 10^2$
1b · 6	1:1	$4.0(\pm 0.1) \times 10^2$
1b · 7	1:1	$4.0(\pm 0.1) \times 10^2$
1b · 8	1:1	$2.0(\pm 0.1) \times 10^2$
1b · 9	1:1	$3.0(\pm 0.1) \times 10^2$
1b · 10	1:1	$1.4(\pm 0.1) \times 10^3$

^aFrom the ^1H NMR titration experiments in $\text{CD}_3\text{CN}/\text{CDCl}_3$ (2:3, v/v).

those of the tested complexes, which might be due to significant intermolecular interactions between the host and the anthracyl groups in the guest.

Complexation Between Host **1b and Paraquat Derivatives in the Solid State.** By vapor diffusion of diisopropyl ether into a solution of **1b** and **3** in CH_3CN and CHCl_3 (2:3, v/v), we obtained a rodlike single crystal suitable for X-ray diffraction analysis. The crystal structure showed that the host **1b** formed 1:2 complex **1b**·**3**₂ with two guests of **3** (Figure 4), in which one bipyridinium guest (**A**) threaded symmetrically through the central cavity of the host, while another bipyridinium guest (**B**) was located at a pseudo cavity formed by the crown rings of two adjacent macrocycles of **1b**. The two bipyridinium guests in the complex are almost vertical. This complexation mode of complex **1b**·**3**₂ in the solid state is different from that in solution, and also obviously different from that of the host **1a** with the *N*-alkyl substituted paraquats, in which the two *N*-alkyl groups in the guest were threaded out from the two lateral crown-8 cavities of the host to form a 1:1 complex.

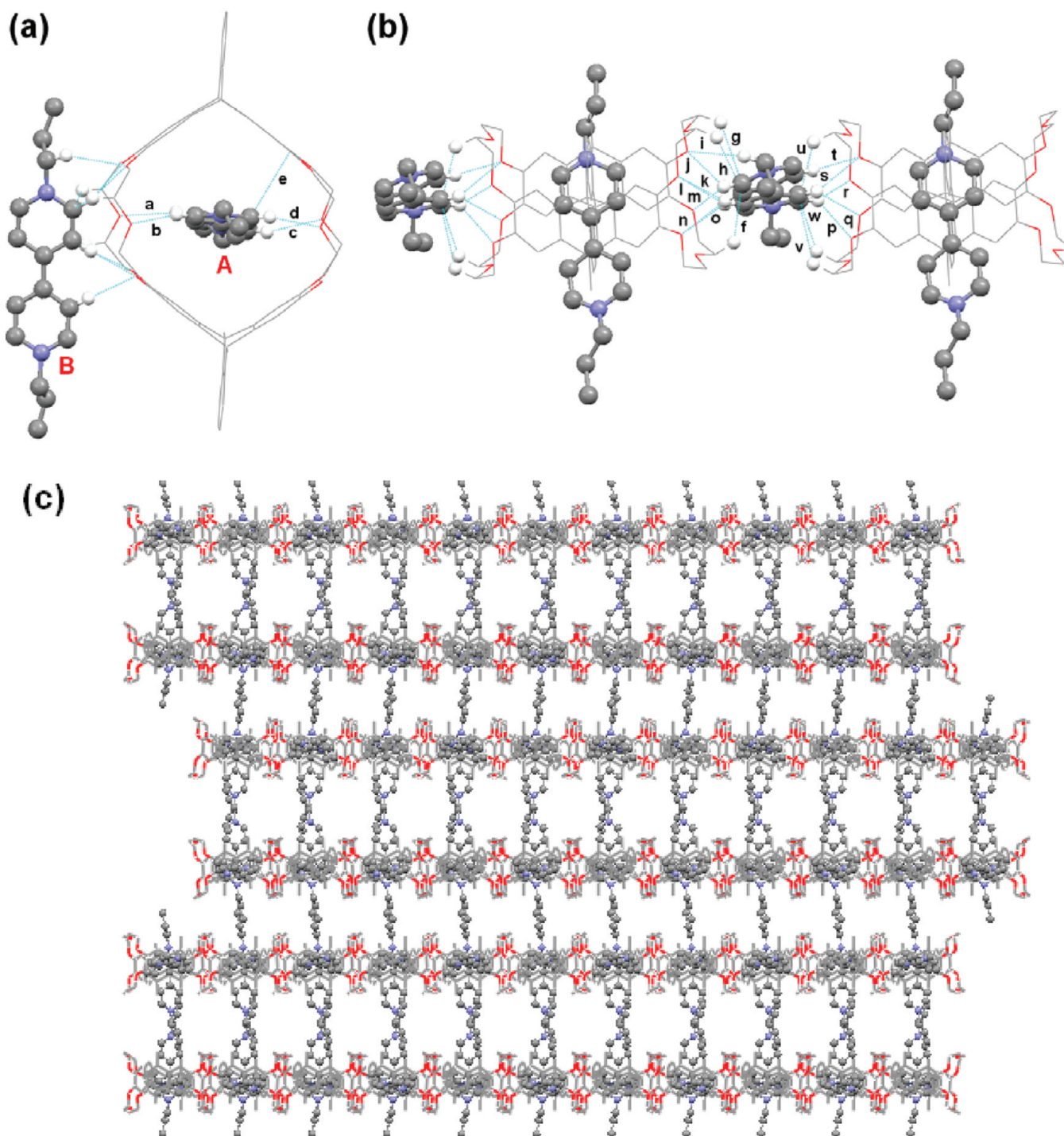


Figure 4. Top view (a) and side view (b) of the crystal structure of complex $1b \cdot 3_2$. Blue lines denote the noncovalent interactions between the host and the guests. The C–H...O hydrogen bond distances (Å): $i = 2.53$, $j = 2.51$, $k = 2.65$, $l = 2.49$, $m = 2.39$, $n = 2.50$, $o = 2.65$, $p = 2.23$, $q = 2.46$, $r = 2.40$, $s = 2.50$, $t = 2.39$. (c) Packing of complex $1b \cdot 3_2$ viewed along the a axis. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

As shown in Figure 4a, it was found that the guests **A** and **B** were distorted by the dihedral angles between the pyridinium rings of 9.74° and 8.82° , respectively. For the guest **A**, there existed multiple C–H...O hydrogen bonding interactions between the protons of the bipyridinium ring and ether oxygen atoms of the host with the distances of 2.38 \AA for a , 2.45 \AA for b , 2.46 \AA for c , and 2.47 \AA for d , and also the π – π stacking interaction between the paraquat ring and one aromatic ring of the triptycene skeleton with the distance of 3.28 \AA (e). For the

guest **B** positioned at the pseudo cavity formed by the crown ether rings of the two adjacent macrocycles of **1b**, besides the multiple C–H...O hydrogen bonding interactions between the protons of the bipyridinium ring and ether oxygen atoms of the adjacent macrocycles, there also existed multiple CH... π interactions between the methylene protons of the crown ethers and the bipyridinium ring with the distances of 2.82 \AA for f , 2.83 \AA for g , 2.82 \AA for h , 2.88 \AA for u , 2.75 \AA for v , and 2.85 \AA for w , respectively. These multiple noncovalent

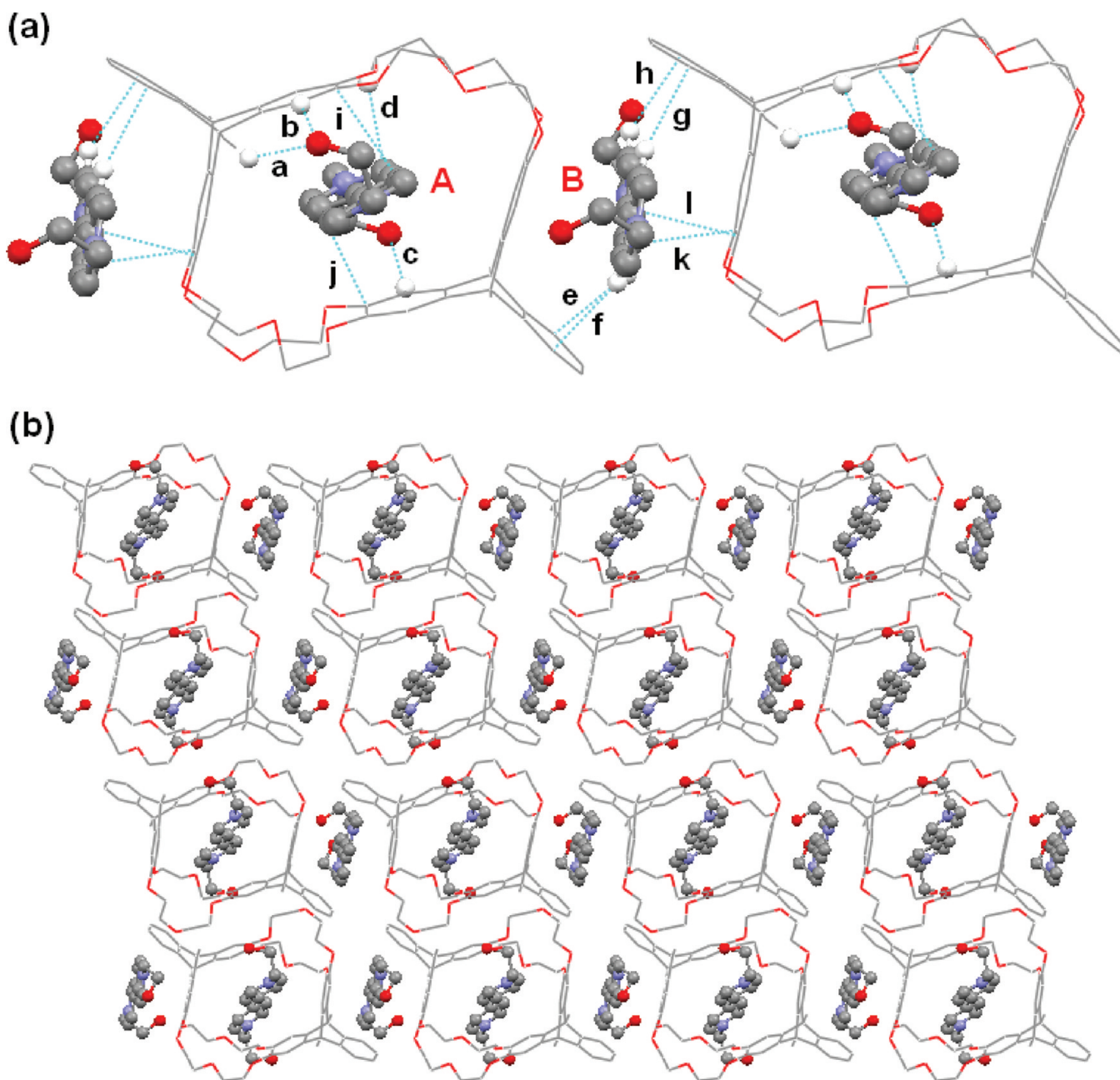


Figure 5. (a) The crystal structure of complex $1b \cdot 6_2$. Blue lines denote the noncovalent interactions between the host and the guests. (b) Packing of the complex $1b \cdot 6_2$, viewed along the a axis. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

interactions between the host and the guest play an important role in the stability of complex $1b \cdot 3_2$. Moreover, it was also found that complex $1b \cdot 3_2$ can self-assemble into a linear supramolecular array, which further results in a 2D layer viewed along the a axis and a 3D microporous network (Figure 4c).

Similarly, we obtained the single crystals suitable for X-ray diffraction analysis from the $CH_3CN/CHCl_3$ mixture solution of $1b$ and 6 . As shown in Figure 5a, it was found that the host $1b$ also formed 1:2 complex $1b \cdot 6_2$ with two guests of 6 in the solid state, in which one bipyridinium guest (A) threaded through the central cavity of the host, while another bipyridinium guest (B) was located at a pseudo cavity formed by two adjacent triptycene moieties. The two bipyridinium guests in complex $1b \cdot 6_2$ are at the same position. Formation of

1:2 complex $1b \cdot 6_2$ in the solid state was not consistent with the 1:1 complex in solution, and also obviously different from the complex formed by the host $1a$ with the guest 6 , in which the two guests of 6 threaded the central cavity of host $1a$ to form 1:2 complex $1a \cdot 6_2$ in both solution and the solid state. Moreover, the complexation mode of complex $1b \cdot 6_2$ is different from that of $1b \cdot 3_2$, which might be due to the repulsion between the hydroxyl groups of the guest 6 and the oxygen atoms of the crown ethers. These results suggested that a small structural change in the host or the guest could result in the formation of a complex with a different structure and a different complexation mode, which might provide a new opportunity to develop supramolecular systems with specific structures and properties.

For the guest **A** in the cavity of the host, the dihedral angle between the two pyridinium rings is 8.32° . There existed multiple π - π stacking interactions between the bipyridinium ring and one aromatic ring of the triptycene skeleton with the distances of 3.36 (i), and 3.29 Å (j), respectively. Moreover, C-H...O hydrogen bonds (2.61 Å for a, 2.68 Å for b, and 2.54 Å for c) between the protons of the paraquat ring and ether oxygen atoms of the host were also observed. For the guest **B** outside the cavity of the host, there also existed the π - π stacking interactions (3.28 Å for k and 3.33 Å for l) between the bipyridinium ring and the aromatic rings of the triptycene moieties, and CH... π interactions (2.80 Å for e, 2.86 Å for f, 2.89 Å for j, and 2.88 Å for h) between the protons of the bipyridinium ring and the aromatic rings of the triptycene moieties. By virtue of a pair of C-H... π ($d_{\text{C-H}\cdots\pi}$ 2.78 Å) interactions between the protons of the crown ether moiety and the aromatic ring of the adjacent triptycene, the complex **1b**·**6**₂ could further form a 2D gridlike viewed along the *a* axis (Figure 5b), in which there was one guest in each grid while the bipyridinium ring outside the cavity of the host connected the two adjacent hosts.

By vapor diffusion of diisopropyl ether into a CH₃CN/CHCl₃ (2:3, v/v) mixture solution, we also obtained the single crystals of complex **1b**·**8** suitable for X-ray diffraction analysis. As shown in Figure 6, the guest **8** threaded symmetrically the

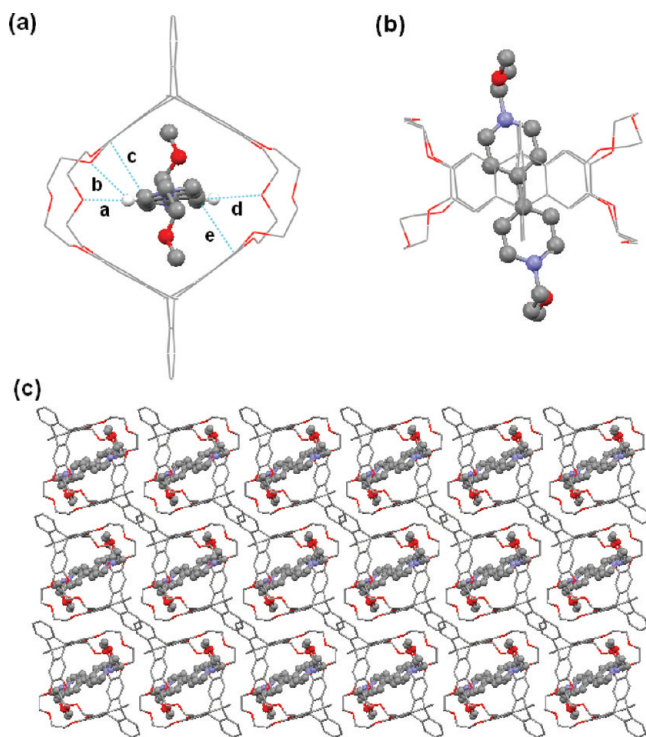


Figure 6. (a) Top view and (b) side view of the crystal structure of complex **1b**·**8**. Blue lines denote the noncovalent interactions between the host and the guests. (c) Packing of the complex **1b**·**8** viewed along the *a* axis. Solvent molecules, PF₆⁻ counterions, and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

central cavity of the host **1b** to form 1:1 complex **1b**·**8**. The two β -methoxyethyl groups in **8** were located outside the cavity and nearly vertical with the pyridinium rings, which resulted in a “Z”-like structure of the guest. The complexation mode of complex **1b**·**8** in the solid state is different from those between the host **1b** and the guests **3** and **6**, which might be due to the

small “pseudo cavity” formed by the adjacent triptycene moieties that could not include the guest **8** with big terminal groups. There existed π - π stacking interactions between the paraquat ring and one aromatic ring of the triptycene skeleton with the distances of 3.38 Å (c) and 3.36 Å (e), respectively. Moreover, there existed C-H...O hydrogen bonding interactions between the protons of the paraquat ring and ether oxygen atoms of the host with the distances of 2.30 Å for a, 2.62 Å for b, and 2.29 Å for d, respectively. These multiple noncovalent interactions between the host and the guest also played an important role in the stability of the complex. In addition, **1**·**8** could also self-assemble into a linear supramolecular array by virtue of a pair of C-H... π ($d_{\text{C-H}\cdots\pi}$ 2.78 Å) interactions between the protons of the crown ether moiety and the aromatic ring of the adjacent triptycene, which further resulted in a 2D layer viewed along the *a* axis.

ESI MS Studies on Formation of the Complexes. The electrospray ionization (ESI) mass spectrometry was also used to characterize the complexes between host **1b** and the guests. Consequently, the strongest peak at m/z 579.6 for [**1b**·**2**-2PF₆]²⁺ was found by using the solution of **1b** and **2** in 3:2 (v/v) chloroform and acetonitrile, which provided another evidence for formation of a 1:1 stable complex between host **1b** and the paraquat derivative **2**. Similarly, formation of the 1:1 complexes between host **1b** and the paraquat derivatives **3**–**10** was also evidenced by the ESI mass spectra, in which the strong peaks at m/z 607.9, 605.8, 618.0, 609.7, 616.8, 624.0, 648.1, and 756.0 for [**1b**·**3**-2PF₆]²⁺, [**1b**·**4**-2PF₆]²⁺, [**1b**·**5**-2PF₆]²⁺, [**1b**·**6**-2PF₆]²⁺, [**1b**·**7**-2PF₆]²⁺, [**1b**·**8**-2PF₆]²⁺, [**1b**·**9**-2PF₆]²⁺, and [**1b**·**10**-2PF₆]²⁺, respectively, were all observed.¹⁴

Electrochemical Studies on Formation of the Complexes. Since the paraquat derivatives are organic redox-active molecules, their electrochemical behaviors in the absence and presence of host **1b** were also studied. As shown in Figure 7,

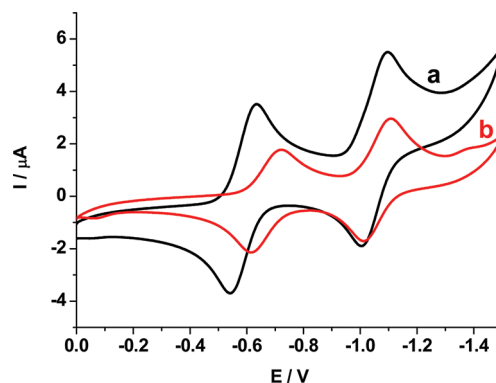


Figure 7. CV curves for a solution of [**10**-2PF₆]²⁺ (1×10^{-3} M) in CH₃CN/CHCl₃ (2:3, v/v) with (NBu₄)PF₆ (0.1 M) as the supporting electrolyte in the absence (black line, a) and the presence (red line, b) of **1b** (3.0×10^{-3} M). Working electrode: Pt. Scan rate: 0.1 V s⁻¹.

the [**10**-2PF₆]²⁺ showed two reversible one-electron reduction processes¹⁶ corresponding to the successive reduction of the 4,4'-bipyridinium core with the half-wave potential values [$E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$] at -0.589 and -1.050 V vs Ag/AgNO₃, respectively.¹⁷ Upon the addition of **1b** to the CH₃CN and CHCl₃ (2:3, v/v) solution of **10**, both the cathodic and the anodic peaks of the first one-electron reduction process significantly moved to the more negative values while the peaks corresponding to the second one-electron reduction process slightly moved to the more negative values. These

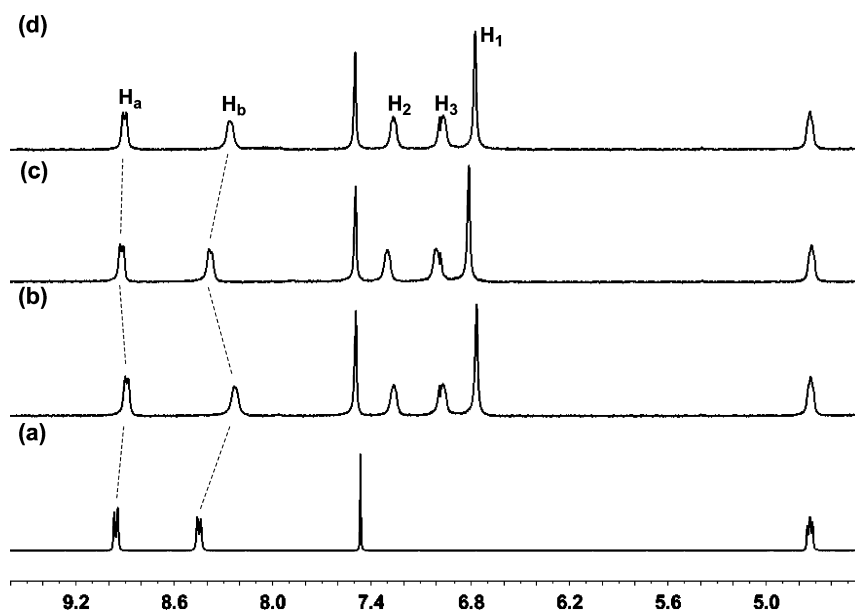


Figure 8. Partial ^1H NMR spectra (300 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3 = 1:1$, v/v, 295 K) of (a) free guest **6**, (b) **1b** and 1.0 equiv of **6**, (c) to the solution of (b) was added 4.0 equiv of LiClO_4 , and (d) to the solution of (c) was added 6.0 equiv of 12-crown-4. $[\mathbf{1b}]_0 = 3.0$ mM.

observations suggested that the stable host–guest complex formed, and formation of the complex was caused by a charge-transfer interaction and the complex might dissociate upon two one-electron reductions of the bipyridinium ring. Under the same conditions as above, it was found that, upon the addition of host **1b** to the solution of guests **2–9**, both the cathodic and the anodic peaks corresponding to the first and the second one-electron reduction processes of the bipyridinium core all moved to the more negative values,¹⁴ but they are smaller than those in the cases of guest **10**. The results implied that, compared with guest **10**, the guests **2–9** showed the smaller complexation, but similar complexation mode with the host **1b**, which are consistent with the results of ^1H NMR experiments.

Li^+ -Ion-Controlled Binding and Release of the Guests in the Complexes. The host containing two dibenzo-18-crown-6 moieties could form a complex with cations, such as lithium ions, and the consequent complexation of cations would introduce extra electrostatic repellent force to the cationic organic guest molecules and dissociate the previously formed host–guest complex. Moreover, it was known that 12-crown-4 is a strong sequestering agent¹⁸ for lithium ions. Thus, a series of ^1H NMR experiments were carried out for investigating the ion-controlled binding and release of the guest molecules in the complexes. As shown in Figure 8, spectrum c, when 4.0 equiv of LiClO_4 was added into the solution of complex **1b•6**, the proton signals of the complex disappeared, while the proton signals of the deprotonated guest **6** and **1b** were observed. These observations suggested that decomplexation of the complex occurred due to the complexation of the crown cavities with lithium ions. However, when 6.0 equiv of 12-crown-4 ether was added into the above system, it was found that the proton signals of complex **1b•6** recovered (Figure 8, spectrum d), which suggested that complex **1b•6** formed again. Thus, the ion-controlled binding and release of guest **6** in the complex could be easily performed by adding and removing the lithium ions. Similarly, Li^+ -ion-controlled binding and releasing of guest **3** in complex **1b•3** was also found.¹⁴

CONCLUSION

In conclusion, we have synthesized a new triptycene-derived macrotricyclic host containing two dibenzo-[18]-crown-6 moieties and proved that paraquat derivatives with different functional groups can all thread the cavity of the host to form 1:1 stable complexes in solution. Interestingly, it was found that the host could form 1:2 complexes with propyl and hydroxyethyl substituted paraquat derivatives in different complexation modes, while the host formed a 1:1 complex with a methoxyethyl substituted paraquat derivative in the solid state. The formation of these complexes was also proved by the ESI MS and electrochemical experiments. Furthermore, it was found that the binding and release of the guests in the complexes could be easily controlled by the addition and removal of Li^+ ions. The results presented here suggested that a small structural change in the host or the guest could result in the formation of the complex with different structures and different complexation modes. Consequently, it will provide us with a new opportunity to develop supramolecular systems with specific structures and properties, which is underway in our laboratory.

EXPERIMENTAL SECTION

The guests **2–10**^{12b,19,20} and compound **11**^{12a} were prepared according to the published procedures.

Compound 12. To a stirred solution of **11** (2.2 g, 6.3 mmol) and 2-(2-hydroxyethoxy)ethyl 4-methylbenzenesulfonate (7.5 g, 28.8 mmol) in dried CH_3CN (120 mL) was added K_2CO_3 (7.9 g, 57.2 mmol). The reaction mixture was stirred at reflux for 30 h, cooled to room temperature, and then filtered. The filtrate was concentrated under reduced pressure. The residue was dissolved in dried CH_2Cl_2 (100 mL), and TsCl (6.5 g, 34.0 mmol), Et_3N (6 mL, 43.2 mmol), and DMAP (0.2 g, 1.66 mmol) were added. The reaction mixture was stirred at reflux temperature for 12 h. The solution was washed with H_2O and dried over anhydrous sodium sulfate. Evaporation of the solvent, followed by column chromatography (SiO_2 : 100:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$), gave **12** (4.2 g, 50%) as a pale yellow sticky oil. ^1H NMR (300 MHz, CDCl_3) δ 2.27 (s, 18H), 3.61–3.64 (m, 16H), 3.92–3.95 (m, 8H), 4.04–4.08 (m, 8H), 6.87 (s, 4H), 6.90–6.94 (m, 2H), 7.15–7.18 (m, 8H), 7.21–7.24 (m, 2H), 7.66–7.68 (m, 8H); ^{13}C NMR (75

MHz, CDCl₃) δ 12.8, 20.5, 46.9, 67.8, 68.3, 68.8, 69.0, 108.9, 119.0, 123.6, 126.9, 128.8, 131.9, 141.6, 143.7, 144.8, 147.7; MALDI-TOF MS m/z 1314.7 (M⁺). Anal. Calcd for C₆₆H₇₄O₂₀S₄·H₂O: C, 59.44; H, 5.74. Found: C, 59.33; H, 5.75.

Compound 1b. A suspension of potassium carbonate (492 mg, 3.56 mmol) in anhydrous DMF (50 mL) under an argon atmosphere was stirred and then heated to 100 °C. To the mixture was added dropwise a solution of **11** (154 mg, 0.445 mmol) and **12** (585 mg, 0.445 mmol) in anhydrous DMF (50 mL) over 12 h. The reaction mixture was stirred at 110 °C for another 3 days. After cooling down to ambient temperature, the mixture was filtered and washed with DMF. The filtrate was concentrated under reduced pressure, and the residue was dissolved in CHCl₃ (100 mL) and washed with H₂O. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the resulting oil was subjected to successive column chromatography (SiO₂: 50:1 CH₂Cl₂/MeOH) to yield **1b** (103 mg, 22%) as a white solid. mp > 300 °C. ¹H NMR (300 MHz, CD₃CN/CDCl₃ = 2:3, v/v) δ 2.25 (s, 12H), 3.73–3.86 (m, 16H), 4.02–4.06 (m, 8H), 4.17–4.22 (m, 8H), 6.81 (s, 8H), 6.96–6.99 (m, 4H), 7.26–7.28 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 13.7, 47.8, 69.5, 69.9, 107.5, 119.9, 124.6, 141.8, 145.0, 148.6; MALDI-TOF MS m/z 973.6 (M⁺). Anal. Calcd for C₆₀H₆₀O₁₂·CH₂Cl₂: C, 69.25; H, 5.91. Found: C, 69.53; H, 6.23.

■ ASSOCIATED CONTENT

● Supporting Information

Copies of ¹H and ¹³C NMR spectra for new compounds, ¹H–¹H COSY spectra and ROESY spectra for the complexes, determination of the association constants, ESI-MS for the complexes, and X-ray crystallographic files (CIF) for the complexes **1b**·**3**₂, **1b**·**6**₂, and **1b**·**8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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