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Guest-Dependent Complexation of Triptycene-Based Macrotricyclic Host with Paraquat Derivatives and Secondary Ammonium Salts: A Chemically Controlled Complexation Process

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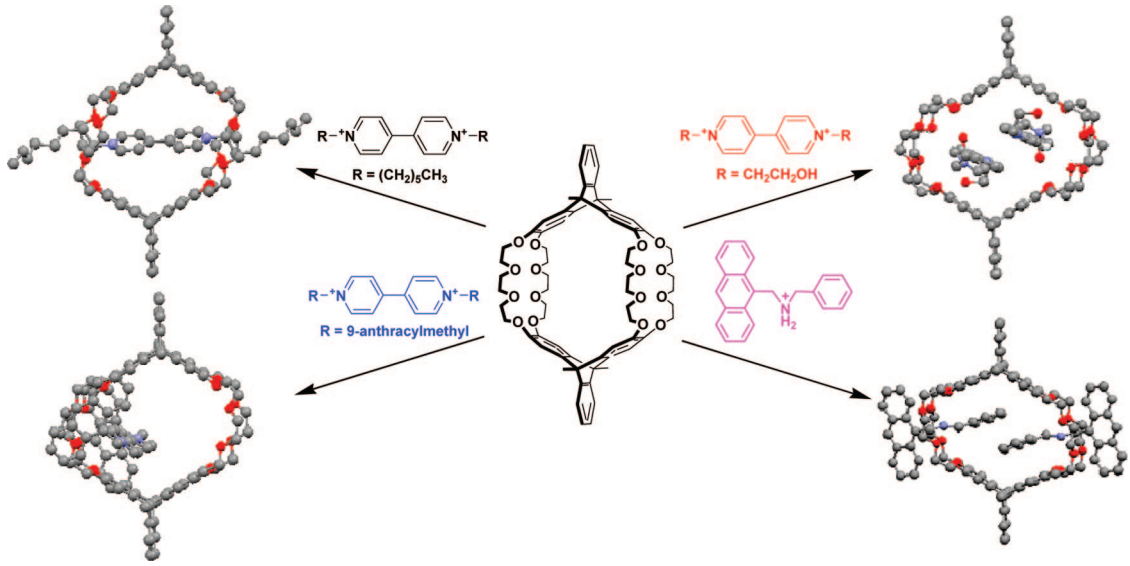
Received May 29, 2008



The triptycene-based macrotricyclic host containing two dibenzo-[24]-crown-8 moieties has been found to form stable 1:1 or 1:2 complexes in different complexation modes with different functional paraquat derivatives and secondary ammonium salts in solution and in the solid state. Consequently, the alkyl-substituted paraquat derivatives thread the lateral crown cavities of the host to form 1:1 complexes. It was interestingly found that the paraquat derivatives containing two β-hydroxyethyl or γ-hydroxypropyl groups form 1:2 complexes, in which two guests thread the central cavity of the host. Other paraquat derivatives containing terminal hydroxy, methoxy, 9-anthracylmethyl, and amide groups were included in the cavity of the host to form 1:1 complexes. Moreover, the host also forms a 1:2 complex with two 9-anthracylmethylbenzylammonium salts, in which the 9-anthracyl groups were selectively positioned outside the lateral crown cavities. The competition complexation process between the host and two different guests (the propyl-substituted paraquat derivative and a dibenzylammonium salt) could be chemically controlled.

Introduction

Since Pedersen first reported[1] the cation-complexing characteristics of the crown ethers, host−guest chemistry[2] has been a topic of great interest during the past decades. One particular interest in this field was that paraquat and its derivatives became some of the most common guests, and crown ethers,[3] cryptands,[4] cucurbit[*n*]urils,[5] calixarenes,[6] and others[7] have been used as hosts for formation of host−guest complexes with them. Another interest came from the complexation of secondary dialkylammonium ions by dibenzo-[24]-crown-8 (DB24C8),[8] which resulted in [2]pseudorotaxane-type complexes.

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10.1021/jo801170t CCC: $40.75 © 2008 American Chemical Society
Published on Web 08/02/2008

In host−guest chemistry, macrocyclic hosts have undoubtedly played key roles in constructing different kinds of complexes with specific structures and properties. Consequently, numerous hosts have been hitherto designed and synthesized.[2] However, few of them are capable of binding different organic guests in different complexation modes, which could provide many opportunities for developing new specific supramolecular systems.

Recently, we[9] became interested in synthesis and properties of novel receptors based on triptycene[10] with unique 3D rigid structures. As a result, a novel triptycene-based cylindrical macrotricyclic polyether[11] containing two dibenzo-[24]-crown-8 lateral cavities and a central macrocyclic cavity (Figure 1) has been synthesized, and it showed a highly efficient complexation not only with some alkyl-substituted paraquat derivatives to form 1:1 complexes,[12a] but also with two dibenzylammonium ions to form 1:2 complexes in solution and in the solid state.[12b] With specific structural characteristics, we deduced that this macrocyclic host could exhibit interesting complexation properties toward many guests. Consequently, some host−guest complexes with specific structures and properties could be obtained. Herein, we report the guest-dependent complexation of the box-like macrotricyclic host **H** with different functional paraquat derivatives and secondary ammonium salts (Figure 1),

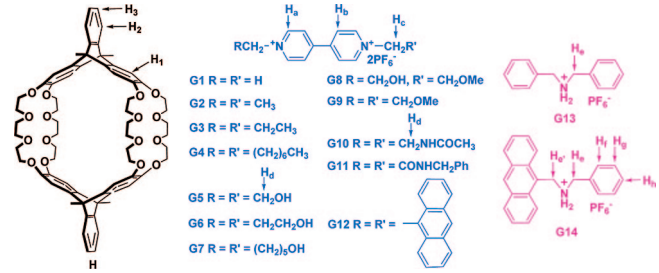

FIGURE 1. Structure and proton designations of the host and the guests.

which results in formation of a series of stable complexes with specific structures in solution and in the solid state. Moreover, a chemically controlled complexation process between the host and a propyl-substituted paraquat derivative and a dibenzylammonium salt is also described.

Results and Discussion

Formation of the Complexes between the Host and Paraquat Derivatives. In the previous communication,[12a] we have shown that the host was highly efficient for the complexation with the alkyl-substituted paraquat derivatives **G1**, **G3**, and **G4**. Consequently, a new kind of stable 1:1 pseudorotaxane-type complexes in which the two alkyl groups of paraquats thread the two lateral crown-8 cavities of the host were formed in solution and in the solid state. The ROESY or NOESY 2D NMR spectra all showed the intermolecular cross-signals for the proton H_c adjacent to dipyridinium rings and crown ether protons in the host, which provided further evidence for the complexation mode in solution.[13] Similarly, the host also forms a 1:1 complex with **G2** in the same complexation mode as above, which was proved by the $^1H-^1H$ NOESY spectrum of a solution of H and 1 equiv of **G2**.[13] Because the complexation between **H** and **G2** is a fast exchange process, according to ^1H NMR spectroscopic titrations, the association constant between **H** and **G2** was calculated to be $4.0(\pm0.2) \times 10^3$ M^{-1} by a Scatchard plot,[14] which is almost the same as those for **H·G3** and **H·G4** but only one-hundredth of that for the complex **H·G1**.[12a]

When we further tested the complexation between the host **H** and the paraquat derivative **G5** containing two β-hydroxyethyl groups, it was interestingly found that the complexation was totally different from the cases of the alkyl-substituted paraquat derivatives. Initially, when **H** (4.0 mM) and 2 equiv of **G5** were mixed in 1:1 chloroform/acetonitrile, they gave a deep orange solution immediately due to charge transfer between the electron-rich aromatic rings of the host and the electron-poor pyridinium rings of the guest. A complexation study of the host with **G5** was carried out in a 1:1 $CDCl_3/CD_3CN$ solution by monitoring the change in the chemical shift of proton H_1 during ^1H NMR spectroscopic titration. The results showed that the complex between **H** and **G5** had 1:2 complex stoichiometry, which was determined by the molar ratio plot based on NMR data. As shown in Figure 2, the ^1H NMR spectrum of a 1:2 mixture of **H** and **G5** showed a great difference from those for free host and free **G5**. Consequently, the proton H_b of the paraquat ring showed a significant upfield shift ($\Delta\delta = 0.65$ ppm), which might be due to the strong shielding effect of the

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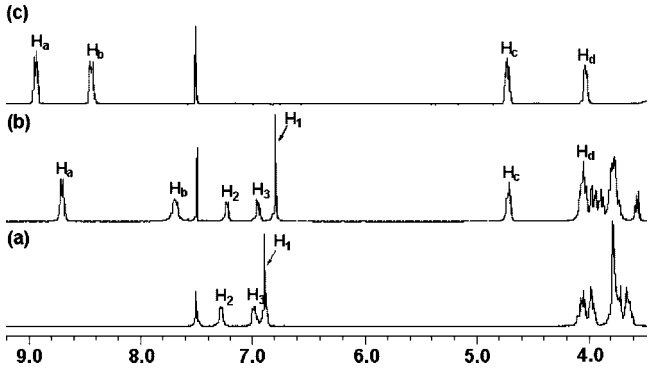

FIGURE 2. Partial ^{1}H NMR spectra (300 MHz, 295 K) of (a) free host, (b) **H** and 2.0 equiv of **G5**, and (c) free guest **G5** in CD_3CN:$CDCl_3$ (1:1, v:v). $[\mathbf{H}]_0 = 4.0$ mM.

aromatic rings in **H**. Similarly, H_1 and H_a proton signals also shifted upfield. However, no shifts of H_c and H_d proton signals in **G5** occurred. These observations indicated that **G5** did not take the same complexation mode as those of complexes between **H** and alkyl-substituted paraquat derivatives, but two **G5**s could be included in the central cavity of the host to form a 1:2 complex. Furthermore, ^{1}H NMR spectroscopic titrations showed that the rates of complexation and decomplexation were fast-exchange at room temperature. Accordingly, the average association constant (K_{av})[7a] for 1:2 complex $\mathbf{H}\cdot\mathbf{G5}_2$ was calculated to be $4.2(\pm0.2) \times 10^3$ M^{-1}.

In the electrospray ionization mass spectrum (ESI MS), a strong peak at *m*/*z* 595.0 for $[\mathbf{H}\cdot\mathbf{G5}_2\text{-}3PF_6^-]^{3+}$ was observed.[13] Formation of the 1:2 complex between **H** and **G5** was further confirmed by its X-ray crystal structure (Figure 3). It was noteworthy that the structure of the complex $\mathbf{H}\cdot\mathbf{G5}_2$ is totally different from those of dialkyl paraquat-based complexes reported previously. In $\mathbf{H}\cdot\mathbf{G5}_2$, two guest molecules do not thread the lateral crown cavities but are included in the central cavity of the host, and the two *N*-β-hydroxyethyl groups are located outside the cavity of **H** to result in an interesting[3] pseudorotaxane-type complex, which is consistent with the result in solution. It was found that two bipyridinium units were distorted with 20.92° and 20.87°, respectively, of the dihedral angle between two pyridinium rings. Moreover, there existed not only C−H···O hydrogen bonding ($d_{H\cdots O} = 2.53$ Å for b and 2.57 Å for c) between the aromatic protons of paraquat rings and ether oxygen atoms of **H**, but also a $\pi-\pi$ stacking interaction between the host and the guest with a distance of 3.21 Å (for d). C−H···O hydrogen bonding interaction between the two guests with a distance of 2.70 Å (a) was also observed, which plays an important role in the formation of the 1:2 stable complex.

Similarly, it was found that **H** and **G6** containing two *N*-γ-hydroxypropyl groups also form a 1:2 complex under the same conditions as above, and the average association constant (K_{av}) for $\mathbf{H}\cdot\mathbf{G6}_2$ was calculated to be $3.6(\pm0.2) \times 10^3$ M^{-1}. Formation of the 1:2 complex between **H** and **G6** was further proved by its ESI MS, in which the peak at *m*/*z* 613.6 for $[\mathbf{H}\cdot\mathbf{G6}_2\text{-}3PF_6^-]^{3+}$ was found. However, when we tested the complexation between **H** and **G7** with two *N*-ω-hydroxyhexyl groups, the result showed that they only formed a 1:1 host−guest complex. Moreover, we found that when the two hydroxyl groups in **G5** were substituted by one (**G8**) or two methoxyl groups (**G9**), they also did not form 1:2 complexes but 1:1 complexes. Formation of the 1:1 complexes between **H** and **G7** to **G9** was further proved by ESI MS,[13] peaks at *m*/*z* 754.4 for $[\mathbf{H}\cdot\mathbf{G7}\text{-}2PF_6^-]^{2+}$, *m*/*z* 704.4 for $[\mathbf{H}\cdot\mathbf{G8}\text{-}2PF_6^-]^{2+}$, *m*/*z* 712.0 for $[\mathbf{H}\cdot\mathbf{G9}\text{-}2PF_6^-]^{2+}$ were observed, respectively. On the basis of the ^{1}H NMR titrations, the association constants between the host and guests **G7**−**G9** were calculated to be $2.6(\pm0.2) \times 10^3$, $4.7(\pm0.2) \times 10^3$, and $8.2(\pm0.4) \times 10^3$ M^{-1}, respectively, by the Scatchard plots.[14]

Furthermore, we studied the complexation modes between the host and the guests **G7**−**G9** by the ^{1}H−^{1}H NOESY 2D NMR spectra[13] and X-ray crystallographic analysis. Consequently, no intermolecular cross-peaks between proton H_c adjacent to bipyridinium ring in guest **G7** and crown ether protons in **H** were observed. Moreover, the H_a and H_b proton signals of bipyridinium rings shifted upfield, while no obvious signal changes of protons in the substituent groups of guest **G7** were observed. In the case of guests **G8** and **G9**, phenomena similar to guest **G7** were also shown. These observations implied that the guests **G7**−**G9** could thread through the central cavity of the host. Fortunately, we also obtained single crystals of complex $\mathbf{H}\cdot\mathbf{G8}$ suitable for X-ray analysis by diffusion of isopropyl ether into an equimolar mixture of the two components in CH_2Cl_2/CH_3CN (1:1, v:v) solution. As expected, the crystal structure of $\mathbf{H}\cdot\mathbf{G8}$ showed that the guest **G8** threaded the central cavity of **H** (Figure 4), which is consistent with the result in solution. Moreover, it was also found that there exist not only $\pi-\pi$ stacking interactions between the host and the guest with the distances of 3.19 (A) and 3.29 Å (B), but also multiple C−H···O hydrogen bonding interactions between the host and the guest with the distances of 2.52 (a), 2.63 (b), 2.48 (c), 2.10 (d), 2.70 (e), 2.43 (f), and 2.70 Å (g). These multiple noncovalent interactions might play an important role in the formation of the complex and its stability. Interestingly, it was further found that the guest **G8** was only positioned in one side of the cavity, which implied that the host would have free volume available for another guest to result in ternary complexes.[5a,15]

To test if the hydrogen bonding between the guests could promote 1:2 complexes as $\mathbf{H}\cdot\mathbf{G5}_2$ and $\mathbf{H}\cdot\mathbf{G6}_2$, we also synthesized two new paraquat derivatives **G10** and **G11** containing amide groups, and tested their complexation with the host by the ^{1}H NMR titrations, ESI MS, and X-ray crystallographic analysis. The results showed that **G10** and **G11** formed only 1:1 complexes with **H**, which are different from those of **G5** and **G6** with terminal hydroxyl groups. On the basis of the ^{1}H NMR titrations, the association constants between **H** and the guests **G10** and **G11** were calculated to be $1.2(\pm0.1) \times 10^3$, and $9.6(\pm0.5) \times 10^3$ M^{-1}, respectively, by Scatchard plots.[14] Moreover, we also studied the complexation modes of complexes $\mathbf{H}\cdot\mathbf{G10}$ and $\mathbf{H}\cdot\mathbf{G11}$ in solution and in the solid state. Similar to the complexes $\mathbf{H}\cdot\mathbf{G7}$, $\mathbf{H}\cdot\mathbf{G8}$, and $\mathbf{H}\cdot\mathbf{G9}$, we found that the H_a and H_b proton signals of bipyridinium rings in **G10** shifted upfield, while protons H_c and H_d and the amide protons showed no obvious signal changes (Figure 5). Moreover, the ^{1}H−^{1}H NOESY 2D NMR spectrum of a solution of **H** and 1 equiv of **G10** also showed no intermolecular cross signals between proton H_c adjacent to bipyridinium ring and crown ether protons in **H**. These observations suggested that **G10** could thread through the central cavity of the host. Fortunately, we further obtained the crystal structure of complex $\mathbf{H}\cdot\mathbf{G10}$, which

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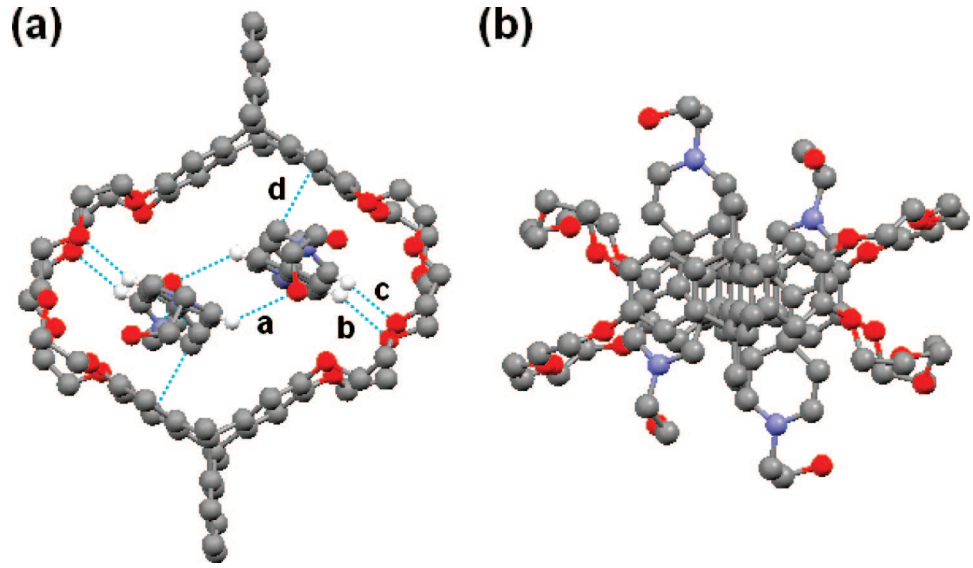

FIGURE 3. (a) Top view and (b) side view of the crystal structure of the complex **H**·**G5**$_2$. Blue lines denote the noncovalent interactions between **H** and **G5** and the two guests. Solvent molecules, the four PF_6^- counterions, and hydrogen atoms not involved in the interactions are omitted for clarity.

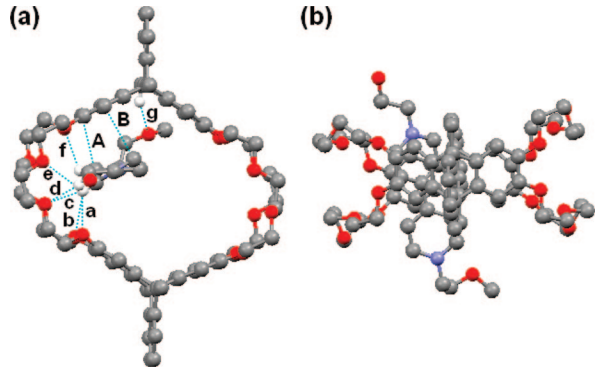

FIGURE 4. (a) Top view and (b) side view of crystal structure of the complex **H**·**G8**. Blue lines denote the noncovalent interactions between **H** and **G8**. Solvent molecules, four PF_6^- counterions, and hydrogen atoms not involved in the interactions are omitted for clarity.

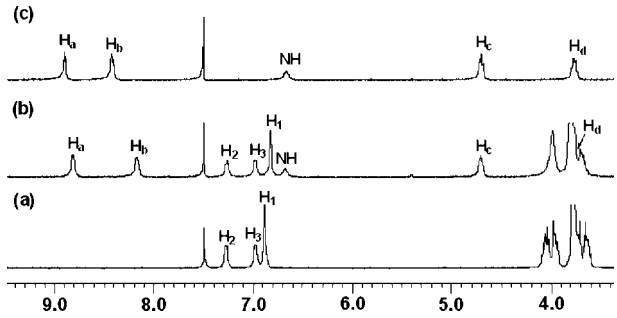

FIGURE 5. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3/CD_3CN$ (1:1, v:v), 295 K) of (a) free host **H**, (b) **H** and 1.0 equiv of **G10**, and (c) free guest **G10**. $[\mathbf{H}]_0 = 4.0$ mM.

provided direct evident for the 1:1 complex. As shown in Figure 6, the guest was included in the central cavity of **H**, and the amide groups were all positioned outside the cavity, which is consistent with the results in solution. In the case of **G11**, the ^{1}H−^{1}H NOESY 2D NMR spectrum[13] showed that the intermolecular cross signals not only between proton H_c adjacent to bipyridinium ring and crown ether protons in **H**, but also between the amide proton and benzylic protons in the guest and crown ether protons in the host were observed, which implied that the guest did not thread through the lateral crown cavities of the host, but was positioned inside the central cavity of **H** and close to the crown ether moiety to form a sandwich-like structure.

We also studied the complexation of the host with paraquat derivative **G12** containing two anthracene groups. It is different from the complexation between the host and alkyl substituted paraquat derivatives, **G12** did not thread through the crown cavities of the host to form a 1:1 complex. However, when **H** and **G12** (4.0 mM each) were mixed in 1:1 chloroform/acetonitrile, they gave a deep orange solution immediately due to the charge transfer between the host and the guest, which implied that a stable host−guest complex was formed. Consequently, we carried out the ^{1}H NMR titrations in 1:1 chloroform and acetonitrile. As shown in Figure 7, the ^{1}H NMR spectrum of a 1:1 mixture of **H** and **G12** showed a great difference from those for free host and guest **G12**. Consequently, the protons H_a ($\Delta\delta = -0.16$ ppm) and H_b ($\Delta\delta = -0.55$ ppm) of the paraquat ring showed significant upfield shifts due to the strong shielding effect of the aromatic rings in **H**. Moreover, the signal of the aromatic proton H_1 ($\Delta\delta = -0.32$ ppm) and the protons of crown ether units of **H** also exhibited upfield shift. These observations suggested that a 1:1 stable complex between **H** and guest **G12** formed. However, no significant change for the proton H_c signal was observed, which implied that the guest is included in the central cavity of **H** and the methylene protons in **G12** are positioned out of the cavity. Moreover, the rates of complexation and decomplexation between **H** and **G12** were found to be fast-exchange at room temperature. Accordingly, the association constant for 1:1 complex **H**·**G12** was calculated to be $5.8(\pm 0.2) \times 10^3$ M^{-1} by the Scatchard plot.[14]

ESI mass spectrometry was also used to characterize the complex between **H** and **G12**, a peak at *m*/*z* 843.4 for $[\mathbf{H}\cdot\mathbf{G12}\text{-}2PF_6^-]^{2+}$ gave evidence for the 1:1 complex **H**·**G12**.[13] X-ray crystallographic analysis (Figure 8) shows that the guest **G12** threaded the central cavity of **H** while the two *N*-(9-anthracyl) methyl groups were located outside the cavity, which resulted in a sandwich-like structure similar to that of complex **H**·**G11**. It was found that the bipyridinium unit in the complex **H**·**G12** was distorted by a −19.68° dihedral angle between the pyri-

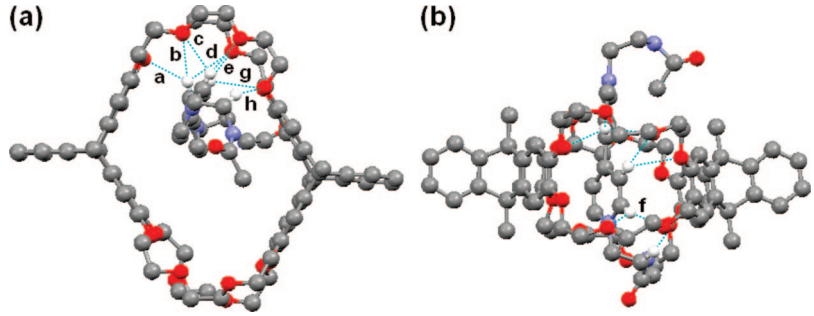

FIGURE 6. (a) Top view and (b) side view of crystal structure of the complex **H·G10**. Blue lines denote the hydrogen bonding between H and G10. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the interactions are omitted for clarity. Hydrogen bond distances (Å): $a = 2.59$, $b = 2.58$, $c = 2.49$, $d = 2.65$, $e = 2.47$, $f = 2.37$, $g = 2.72$, $h = 2.47$ for C−H···O.

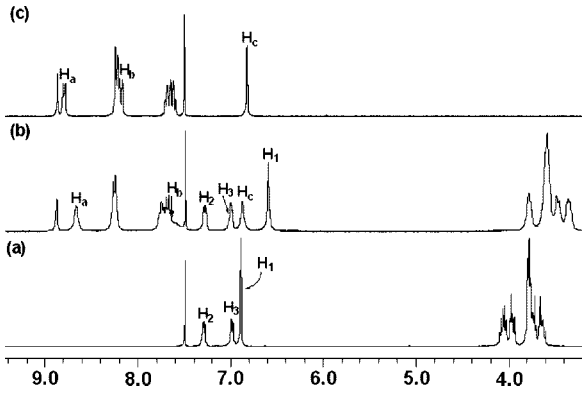

FIGURE 7. Partial ^{1}H NMR spectra (300 MHz, CD_3CN:$CDCl_3$ (1:1, v:v), 295K) of (a) free host **H**, (b) **H** and 1.0 equiv of **G12**, and (c) free guest **G12**. $[\mathbf{H}]_0 = 5.0$ mM.

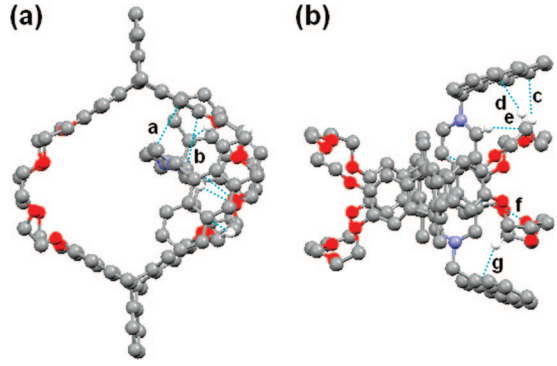

FIGURE 8. (a) Top view and (b) side view of crystal structure of complex **H·G12**. Blue lines denote the noncovalent interactions between **H** and **G12**. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the interactions are omitted for clarity.

dinium rings. A couple of $\pi-\pi$ stacking interactions between the paraquat ring and one aromatic ring of the triptycene skeleton with distances of 3.30 (a) and 3.38 Å (b) were observed. Moreover, there also existed not only two C−H···O hydrogen bonds ($d_{H\cdots O} = 2.29$ Å for e, and 2.26 Å for f) between the protons of paraquat ring and ether oxygen atoms of the host, but also C−H···π interactions ($d_{H\cdots\pi} = 2.85$ Å for c, 2.68 Å for d, and 2.61 Å for g) between the methylene protons of the host and anthracene rings of the guest. These multiple noncovalent interactions between the host and the guest play an important role in the stability of the complex **H·G12**. Similar to the complex **H·G8**, the guest **G12** in complex **H·G12** was also found to be positioned in one side of the cavity, which

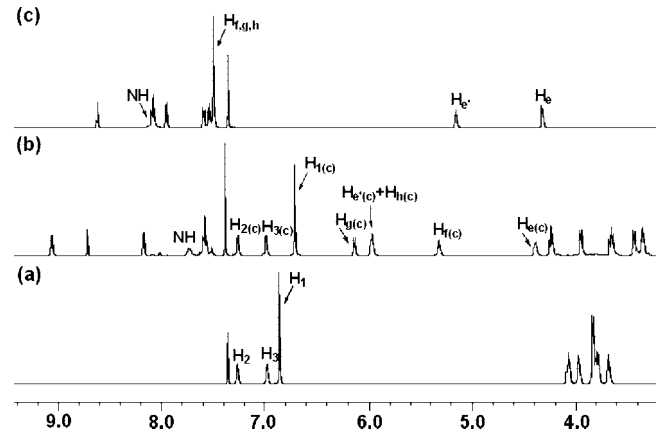

FIGURE 9. Partial ^{1}H NMR spectra (600 MHz, CD_3CN: $CDCl_3$ (1:5, v:v), 295 K) of (a) free host **H**, (b) **H** and 2.0 equiv of **G14**, and (c) free guest **G14**. $[\mathbf{H}]_0 = 5.0$ mM.

implied that the host has free volume available for another guest to form ternary complexes.

Complexation of the Host with the Secondary Ammonium Salts. It has been found that the host self-assembles with two dibenzylammonium salts to form a stable 1:2 complex **H·G13$_2$** in solution and in the solid state, in which multiple hydrogen bonding and $\pi-\pi$ stacking interactions between the host and the guest played an important role.[12b] Similar to the complex **H·G13$_2$**, the host also formed a 1:2 complex **H·G14$_2$**. But it was noted that in the complex the two 9-anthracyl groups were selectively positioned outside the cavity of the host. We investigated the formation of the complex between **H** and **G14** in solution by ^{1}H NMR experiments. As shown in Figure 9b, the ^{1}H NMR spectrum of a 1:2 mixture of **H** and **G14**, recorded in $CDCl_3$/CD_3CN (5:1, v:v), revealed a dispersed array of well-defined resonances and great difference with those for host **H** (Figure 9a) and guest **G14** (Figure 9c). The signal of the outer methylene proton $H_{e'}$ adjacent to the NH_2^+ center exhibited a large downfield shift ($\Delta\delta = 0.78$ ppm), which was attributed to hydrogen bonding interactions and the deshielding effect of the aromatic rings in **H**. Particularly, it was found that the inner phenyl protons (H_f-H_h) showed striking upfield shifts ($\Delta\delta = -1.32$ to -2.30 ppm) due to the strong shielding effect of the macrocycle. Moreover, an upfield shift for the aromatic proton H_1 ($\Delta\delta = -0.13$ ppm) of **H** and significant changes in the chemical shifts of the protons in the anthracene rings and crown rings were also observed. These observations suggested that a new stable 1:2 complex **H·G14$_2$** in which the anthracyl groups were positioned outside the cavity was selectively formed. Since host−guest exchange was slow on the ^{1}H NMR time scale at

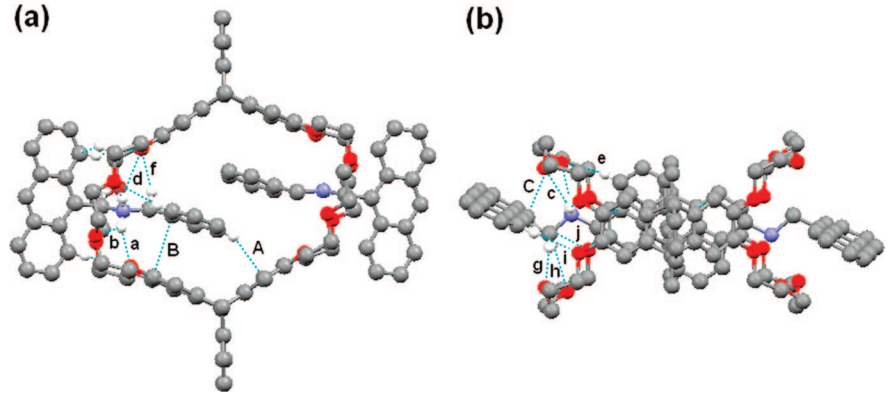

FIGURE 10. (a) Top view and (b) side view of the crystal structure of the complex **H**·**G14**$_2$. Blue lines denote the noncovalent interactions between **H** and one of the guests. Solvent molecules, two PF_6^- counterions, and hydrogen atoms not involved in interactions are omitted for clarity. Hydrogen bond distances (Å): $a = 2.95$, $b = 2.49$, $c = 2.04$, $d = 2.71$ for N−H···O; $e = 2.51$, $f = 2.46$, $g = 2.21$, $h = 2.58$, $i = 2.61$, $j = 2.63$ for C−H···O.

room temperature, the association constants K_1 and K_2, for the first and second binding events, were calculated to be 8.0(±0.4) × 10^3 and 1.6(±0.2) × 10^3 M^{-1}, respectively.

In the ESI mass spectrum of a solution of **H** and **G14**, the strongest (base) peak was found at *m*/*z* 872.9 for [**H**·**G14**$_2$-2PF_6^-]$^{2+}$.[13] Furthermore, formation of the 1:2 complex **H**·**G14**$_2$ was confirmed by its X-ray crystal structure. As shown in Figure 10, both of the secondary ammonium ions were threaded symmetrically through the crown cavities, and the anthracyl groups were all positioned outside the central cavity of **H**, which resulted in a [3]pseudorotaxane-type structure with a "gull-wing" conformation. The planes of two phenyl rings inside the cavity are almost parallel, and the centroid−centroid distance between the two planes was found to be 4.00 Å. There existed multiple C−H···O and N−H···O hydrogen bonds between the host and the guest. Moreover, a couple of C−H···O interactions between the host and the guest with distances of 2.89 (A) and 2.65 Å (C), and a $\pi-\pi$ stacking interaction between the phenyl ring of the guest and the adjacent aromatic ring of the host with a distance of 3.27 Å (B) were also observed. These multiple noncovalent interactions played important roles in the stability of the complex.

A Competition Complexation Process Controlled by Acid and Base. It was known that the association and disassociation of the complex between DB24C8 and secondary ammonium salt could be chemically controlled by pH,[16] which inspired us to examine the competitive binding abilities of the host toward different kinds of guests. As shown in Figure 11b, the host and 1 equiv of the guest **G3** formed a stable complex **H**·**G3**. When 2 equiv of the guest **G13** was added into the solution of **H**·**G3** in 1:1 chloroform/acetonitrile solution, proton H_a, H_b of guest **G3** shifted downfield almost to the original position (Figure 11c), which indicates that the complex **H**·**G3** disassociated. Meanwhile, the more stable complex **H**·**G13**$_2$ formed. To the above solution was added 3.6 μL (6 equiv of **H**) of tributylamine, and guest **G13** was deprotonated. Consequently, the complex **H**·**G13**$_2$ disassociated while **H**·**G3** reformed (Figure 11d). Furthermore, when 10 μL (52 equiv of **H**) of trifluoroacetic acid was added, the complex **H**·**G3** disassociated while the complex **H**·**G13**$_2$ formed again (Figure 11e). These observations show that the guest-exchange process between the host and two different guests can be controlled by acid and base.

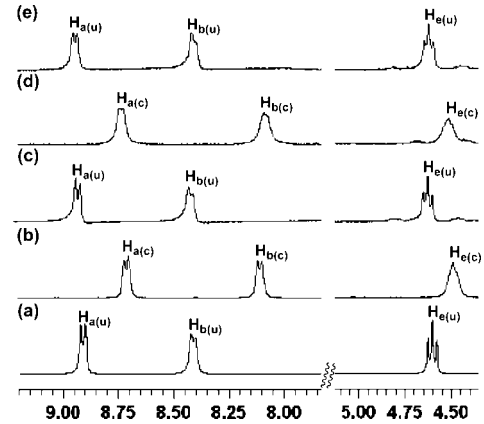

FIGURE 11. Partial ^{1}H NMR spectra (300 MHz, CD_3CN:$CDCl_3$ (1:1 v:v), 295 K) of (a) **H** (5.0 mM), (b) complex **H**·**G13** (5.0 mM), (c) 2.0 equiv of **G13** added to the solution of b, (d) 3.6 μL (6.0 equiv of **H**) of tributylamine added to the solution of c, and (e) 10 μL (52 equiv of **H**) of trifluoroacetic acid added to the solution of d.

Conclusion

In conclusion, we have proved that the triptycene-based macrotricyclic host containing two dibenzo-[24]-crown-8 moieties selectively forms stable 1:1 or 1:2 complexes with different functional paraquat derivatives and secondary ammonium salts in solution and in the solid state. In particular, the host showed guest-dependent complexation modes (Table 1), which have been proved by ^{1}H NMR, NOSEY, or ROSEY 2D NMR spectra and X-ray crystallographic analysis. Consequently, the alkyl-substituted paraquat derivatives thread the lateral crown cavities of the host to form 1:1 complexes. Interestingly, it was found that the host and the paraquat derivatives containing two β-hydroxyethyl or γ-hydroxypropyl groups form 1:2 complexes, in which two guests threaded the central cavity of the host. Other functional paraquat derivatives containing terminal hydroxyl, methoxyl, 9-anthracylmethyl, and amide groups were included in the cavity of the host to form 1:1 complexes. Moreover, we also found that the host could form an 1:2 complex with two 9-anthracylmethylbenzylammonium salts, in which the two 9-anthracyl groups were selectively positioned outside the

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TABLE 1. Summary of the Nature of the Complexes and the Association Constants

guest	stoichiometry (H/G)	binding geometry	association constant[a] K_a (M^{-1})
G1	1:1	lateral cavities	$3.4(\pm0.6) \times 10^5$
G2	1:1	lateral cavities	$4.0(\pm0.2) \times 10^3$
G3	1:1	lateral cavities	$2.3(\pm0.2) \times 10^3$
G4	1:1	lateral cavities	$2.4(\pm0.3) \times 10^3$
G5	1:2	central cavity	$4.2(\pm0.2) \times 10^3$
G6	1:2	central cavity	$3.6(\pm0.2) \times 10^3$
G7	1:1	central cavity	$2.6(\pm0.2) \times 10^3$
G8	1:1	central cavity	$4.7(\pm0.2) \times 10^3$
G9	1:1	central cavity	$8.2(\pm0.4) \times 10^3$
G10	1:1	central cavity	$1.2(\pm0.1) \times 10^3$
G11	1:1	central cavity	$9.6(\pm0.5) \times 10^3$
G12	1:1	central cavity	$5.8(\pm0.2) \times 10^3$
G13	1:2	lateral cavities	$1.2(\pm0.2) \times 10^4$
			$2.4(\pm0.3) \times 10^3$
G14	1:2	lateral cavities	$8.0(\pm0.4) \times 10^3$
			$1.6(\pm0.2) \times 10^3$

[a] For **G5** and **G6**, the values are the average association constants (K_{av}) for 1:2 complexes. For **G13** and **G14**, the values are the first and second association constants K_1 and K_2, respectively.

central cavity of the host. Furthermore, a competition complexation process between the host and two different guests (the propyl-substituted paraquat derivative and a dibenzylammonium salt) could be chemically controlled by acid and base. We believe that this macrotricyclic host and its guest-dependent complexation presented here can provide many opportunities to develop new supramolecular systems with specific structures and properties, which are underway in our laboratory.

Experimental Section

The guests **G2**,[3f] **G5**,[3f] **G6**,[17] **G7**,[18] **G12**,[3f] and **G14**[19] were prepared according to published procedures.

Synthesis of G8. A mixture of 2-methoxyethyl 4-methylbenzenesulfonate (230 mg, 1 mmol) and 4,4′-bipyridine in dry acetonitrile (10 mL) was refluxed for 24 h. The resulting mixture was concentrated, and then purified by column chromatography on silica gel (MeOH/MeCN/2 M NH_4Cl = 4:1:0.2). A white solid was obtained, which was dissolved in H_2O and treated with NH_4PF_6, and then the solution was stirred for 30 min at ambient temperature. The solid precipitated and was collected by filtration and dried under vacuum to yield 160 mg (44%) of 1-(2-methoxyethyl)-4,4′-bipyridine hexafluorophosphate (**G8′**) as a white solid. Mp 159−160 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.23 (d, J = 6.9 Hz, 2H), 8.88 (m, 2H), 8.67 (d, J = 6.9 Hz, 2H), 8.00 (m, 2H), 5.07 (t, J = 9.7 Hz, 4H), 4.04 (t, J = 9.7 Hz, 4H), 3.37 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6) δ 59.1, 62.1, 71.1, 122.6, 126.5, 142.1, 146.7, 152.1, 155.3. ESI MS m/z 215.3 [M − PF_6^-]$^+$. Anal. Calcd for $C_{13}H_{15}F_6N_2OP$: C 43.34, H 4.20, N 7.78. Found: C 43.37, H 4.13, N 7.81.

A solution of 1-iodoethanol (114.6 mg, 0.67 mmol) and **G8′** (120 mg, 0.33 mmol) in dry acetonitrile (8 mL) was refluxed for 1 day. The resulting mixture was filtered to give a solid residue, which was washed with acetonitrile (5 mL) and dissolved in H_2O (10 mL), then NH_4PF_6 was added. The mixture was stirred for 30 min at ambient temperature, and then filtered to give a solid residue, which was washed with H_2O (5 mL) and crystallized from EtOH (5 mL) to give **G8** (146 mg, 80%) as a white solid. Mp 146−147 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.33 (t, J = 5.2 Hz, 4H), 8.81 (d, J = 5.2 Hz, 4H), 5.10 (t, J = 9.4 Hz, 4H), 5.03 (t, J = 9.4 Hz, 4H), 4.21 (t, J = 9.0 Hz, 4H), 4.04 (t, J = 9.0 Hz, 4H), 3.37 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6) δ 59.1, 61.5, 62.6, 65.2, 80.0, 127.8, 127.8, 147.3, 151.1, 151.3. ESI MS m/z 405.1 [M − PF_6^-]$^+$, 130.1 [M − $2PF_6^-$]$^{2+}$. Anal. Calcd for $C_{15}H_{20}F_{12}N_2O_2P_2\cdot0.5H_2O$: C, 32.21; H, 3.78; N, 5.01. Found: C, 32.13; H, 3.69; N, 5.05.

Synthesis of G9. A solution of 1-iodo-2-methoxyethane (697 mg, 3.7 mmol) and 4,4′-bipyridine (243 mg, 1.56 mmol) in dry acetonitrile (20 mL) was refluxed for 18 h. The resulting mixture was filtered and washed with acetonitrile (5 mL). The solid residue was dissolved in H_2O (10 mL). After addition of NH_4PF_6 and stirring for 30 min at ambient temperature, the mixture was filtered. The solid residue was washed with H_2O (5 mL) and then crystallized from EtOH (5 mL) to give **G9** (560 mg, 64%) as a white solid. Mp 196−198 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.35 (d, J = 6.7 Hz, 4H), 8.82 (d, J = 6.7 Hz, 4H), 5.12 (t, J = 9.4 Hz, 4H), 4.05 (t, J = 9.4 Hz, 4H), 3.37 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6) δ 59.1, 62.7, 71.0, 127.9, 147.4, 151.3. ESI-MS m/z 419.2 [M − PF_6]$^+$. Anal. Calcd for $C_{16}H_{22}F_{12}N_2O_2P_2$: C, 34.06; H, 3.93; N, 4.96. Found: C, 34.25; H, 4.00; N, 5.10.

Synthesis of G10. A mixture of *N*-(2-chloroethyl) acetamide (845 mg, 6.9 mmol) and 4,4′-bipyridine (258 mg, 1.62 mmol) in dry acetonitrile (50 mL) was refluxed for 24 h. The resulting mixture was filtrated and washed with acetonitrile (5 mL) to give a solid residue, which was dissolved in H_2O (10 mL), then NH_4PF_6 was added. The mixture was then stirred for 30 min at ambient temperature and filtered. The solid residue was washed with H_2O (5 mL) and crystallized from EtOH (5 mL) to give **G10** (420 mg, 42%) as a white solid. Mp 215−216 °C. ^{1}H NMR (300 MHz, CH_3CN:$CDCl_3$ = 1:1) δ 8.88 (d, J = 5.9 Hz, 4H), 8.40 (d, J = 5.9 Hz, 4H), 6.66 (br s, 2H, NH), 4.65−4.76 (m, 2H), 3.70−3.85 (m, 2H), 1.83 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6) δ 22.5, 40.8, 63.1, 127.8, 147.5, 150.9, 171.4. ESI MS m/z 473.2 [M − PF_6]$^+$. Anal. Calcd for $C_{18}H_{24}F_{12}N_4O_2P_2$: C, 34.96; H, 3.91; N, 9.06. Found: C, 34.34; H, 3.87; N, 8.96.

Synthesis of G11. A mixture of *N*-benzyl-2-chloroacetamide (145 mg, 0.79 mmol), 4,4′-bipyridine (50 mg, 0.32 mmol), and NaI (140 mg, 0.93 mmol) in dry acetonitrile (20 mL) was refluxed for 24 h. The resulting mixture was filtered and washed with acetonitrile (5 mL). The solid residue was dissolved in H_2O (10 mL). After addition of NH_4PF_6 and stirring for 30 min at ambient temperature, the mixture was filtered to give a solid residue, which was washed with H_2O (5 mL) and then crystallized from EtOH (5 mL) to give **G11** (95 mg, 40%) as a pale-yellow solid. Mp 234−236 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.40 (d, J = 7.0 Hz, 4H), 8.94 (d, J = 7.0 Hz, 4H), 8.34 (br s, 2H, NH), 7.25−7.39 (m, 10H), 5.91 (s, 4H), 4.53 (d, J = 5.8 Hz, 4H). ^{13}C NMR (75 MHz, acetone-d_6) δ 44.4, 63.3, 127.7, 128.2, 128.6, 129.4, 139.1, 148.4, 151.7, 164.6. ESI MS m/z 597.2 [M − PF_6]$^+$, 226.0 [M − $2PF_6$]$^+$. Anal. Calcd for $C_{18}H_{24}F_{12}N_4O_2P_2\cdot H_2O$: C, 44.22; H, 3.98; N, 7.37. Found: C, 43.91; H, 3.66; N, 7.49.

Acknowledgment. We thank the National Natural Science Foundation of China (20372063, 20532030, 20625206), the National Basic Research Program (2007CB808004, 2008CB617-501), and the Chinese Academy of Sciences for financial support. We also thank Dr. H. B. Song at Nankai University for determining the crystal structures.

Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR spectra of new compounds, ^{1}H−^{1}H COSY, NOESY, ROESY, and ^{1}H NMR titration experiments, determination of the association constants, ESI MS spectra of the host−guest complexes, and X-ray crystallographic files (CIF) for complexes **H·G5$_2$**, **H·G8**, **H·G10**, **H·G12**, and **H·G14$_2$**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO801170T

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