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Selective Templated Complexation of a Cylindrical Macrotricyclic Host with Neutral Guests: Three Cation-Controlled Switchable Processes

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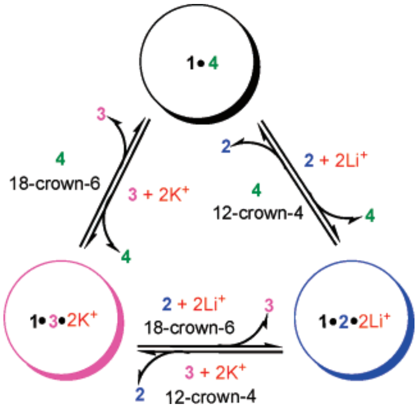

A novel triptycene-based cylindrical macrotricyclic host **1** containing an anthracene unit and two dibenzo [24]crown-8 moieties was synthesized, and its cation binding properties were studied. It was found that the host could not only form complex with the paraquat derivative **4**, but also show selective templated complexation with pyromellitic diimide **2** and anthraquinone **3** in the presence of lithium and potassium ions, respectively. Consequently, two novel cascade complexes with neutral molecules as bridging species were formed in solution and in the solid state, which were structurally studied by NMR, MS spectra, and X-ray methods. Moreover, we also found that the association and dissociation of the complexes could be easily achieved by the addition and removal of lithium or potassium ions, which resulted in three cation-controlled switchable processes.

Introduction

The discovery[1] of cation recognition by crown ethers has led to myriads of host−guest systems, in which the design and synthesis of novel hosts[2] with specific structures and properties played a decisive role. Cylindrical macrotricyclic hosts[3] consisting of one central cavity and two lateral circular cavities have new topological features with respect to the mono- and bicyclic hosts. Consequently, they are especially attractive for designing both biomimetic and abiotic receptor molecules for inorganic and organic cation guests.[4] However, little is so far known about the cylindrical macrocyclic hosts designed for binding neutral

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[1] (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495−2496. (b) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017−7036.

[2] (a) *Functional Synthetic Receptors*; Schrader, T., Hamilton, A. D., Eds.; Wiley-VCH: Weinheim, Germany, 2005. (b) *Macrocyclic Chemistry—Current Trends and Future Perspectives*; Gloe, K., Ed.; Springer: New York, 2005.

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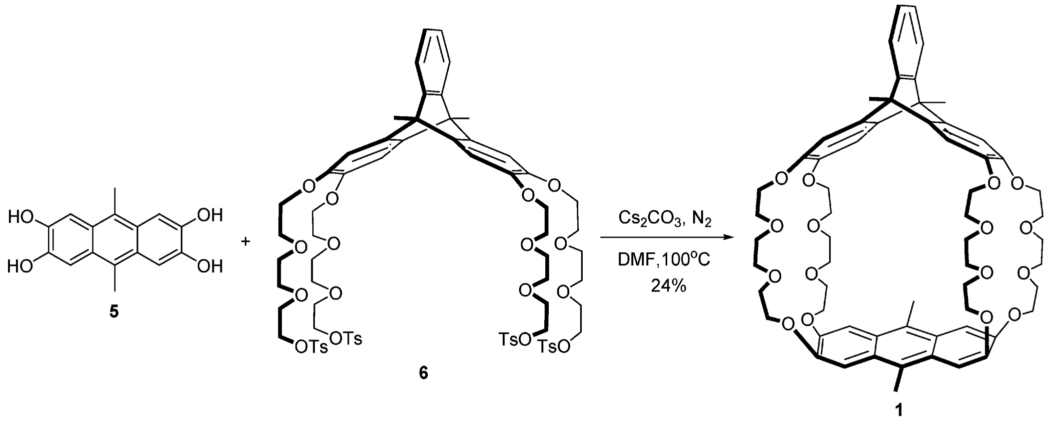
SCHEME 1. Synthesis of the Host 1



organic guests such as pyromellitic diimide[5] and anthraquinone,[6] which were intensively studied for their interesting photophysical and electrochemical properties. Moreover, the previously reported cylindrical hosts were almost formed by linking two macrocycles together through two bridges, which could also make the structures so flexible that their complexation with guests might be influenced to a certain extent.

Recently, we[7] became interested in the development of new supramolecular systems based on triptycene with unique three-dimensional rigid structure. As a result, we reported a novel triptycene-based cylindrical macrotricyclic host[7b] formed by incorporating two rigid triptycenes and linking two macrocycles through four bridges, which showed enhanced and coordinated complexation abilities toward paraquat derivatives. Because the triptycene-based cylindrical macrotricyclic host or its analogues contained not only one electron-rich central cavity but also two lateral crown cavities, we deduced that they could bind two metal ions efficiently to form a new "host" with a long intercationic distance, which could further bind neutral electron-deficient guests with coordinated sites for the two cations. Consequently, novel cascade complexes[8] would be formed, and new supramolecular systems with specific structures and properties would be developed. Herein, we report (1) the synthesis and its cation binding properties of a novel triptycene-based cylindrical macrotricyclic host **1** (Figure 1) containing an anthracene unit, which may provide a strong $\pi-\pi$ interaction between host and guest molecules, (2) selective templated complexation of the host **1** with pyromellitic diimide **2** and anthraquinone **3** in the presence of lithium and potassium ions, respectively, which results in the formation of two novel cascade complexes, and (3) three cation-controlled switchable processes between host **1** and guests **2**–**4**.

Results and Discussion

Synthesis and Cation Binding Properties of the Host. According to a similar method as described before,[7b] the host **1** was easily synthesized in a 24% yield by the reaction of 9,10-dimethyl-2,3,6,7-tetrahydroxyanthracene **5** and compound **6** under a high dilution condition in the presence of cesium carbonate (Scheme 1). The structure of **1** was confirmed by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analysis.[9]

The host **1** contains two dibenzo[24]crown-8 cavities, which have been demonstrated to efficiently bind different alkaline and alkaline-earth metal ions.[10] The further evaluation of binding abilities of host **1** toward different metal ions including Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} was carried out by electrospray ionization mass spectrometry.[9,11] As a result, the strongest peaks at 543.6 nm for $[\mathbf{1}\cdot 2Li]^{2+}$, 559.6 nm for $[\mathbf{1}\cdot 2Na]^{2+}$, and 575.6 nm for $[\mathbf{1}\cdot 2K]^{2+}$ were observed. These results indicated that host **1** could form 1:2 stable complexes with Li^+, Na^+, and K^+ ions, which could provide us opportunities to construct novel cascade complexes and further develop new supramolecular systems. In the cases of Mg^{2+} and Ca^{2+}, it was found that the strongest peaks showed at 548.7 nm for $[\mathbf{1}\cdot Mg]^{2+}$ and 556.8 nm for $[\mathbf{1}\cdot Ca]^{2+}$, which implied that **1** might form 1:1 stable complexes with Mg^{2+} and Ca^{2+}.

Lithium-Templated Complexation of Host 1 with Pyromellitic Diimide 2. We first investigated the complexation between host **1** and pyromellitic diimide **2** in solution and found that the mixture of **1** and **2** (each 3 mM concentration) in 1:1 chloroform/acetonitrile solution at room temperature showed little color change. However, it was found that the addition of solid LiBr into the mixture gave a bright blue solution (Figure 2) with a CT band at 579 nm,[9] which implied that a strong

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[9] See the Supporting Information.

[10] Cation-binding properties of dibenzo-24-crown-8; see: (a) Poonia, N. S.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2062–2065. (b) Willey, R.; Meehan, P. R.; Rudd, M. D.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1995**, 811–817. (c) Lin, C. F.; Liu, Y. H.; Lai, C. C.; Peng, S. M.; Chiu, S. H. *Chem. Eur. J.* **2006**, *12*, 4594–4599.

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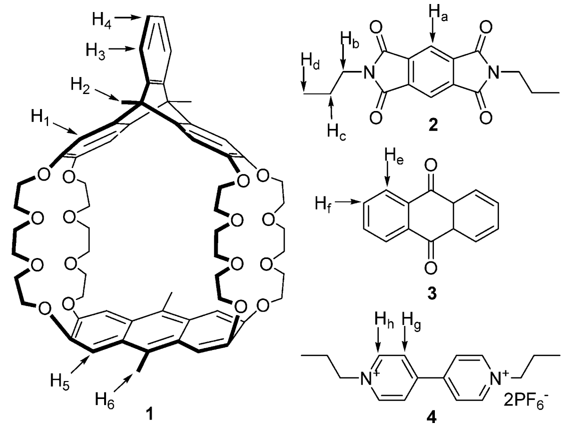

FIGURE 1. Structure and proton designations of host **1** and guests **2**−**4**.

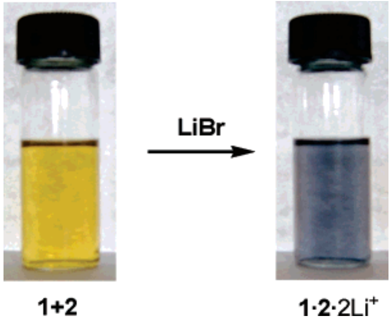

FIGURE 2. Observed color change after the addition of an excess of lithium bromide to a 1:1 chloroform/acetonitrile solution of **1** (3 mM) and **2** (3 mM).

lithium-templated complexation between **1** and **2** might occur.[12] More direct evidence for the complexation came from the ^1H NMR spectral studies. Consequently, it was found that the ^1H NMR spectrum of the 1:1 mixture is essentially the sum of the two components, except that proton H_a showed a little shift to upfield (Figure 3c), which indicated that no obvious complexation between **1** and **2** existed. But when LiBr was added to the 1:1 mixture of **1** and **2**, a dispersed array of well-defined resonances (Figure 3d) and great differences with those for **1** (Figure 3a) and **2** (Figure 3b) were observed. Especially, the proton signal of H_a shifted dramatically to upfield and broadened, which might be due to the strong shielding effect of the aromatic rings in **1** and the fast waggle of the threaded guest molecule relative to host **1**. Similarly, the upfield shifts of the signals for protons H_1−H_6 were also observed. These observations are consistent with the formation of a novel complex between **1** and **2** in the presence of lithium salts.

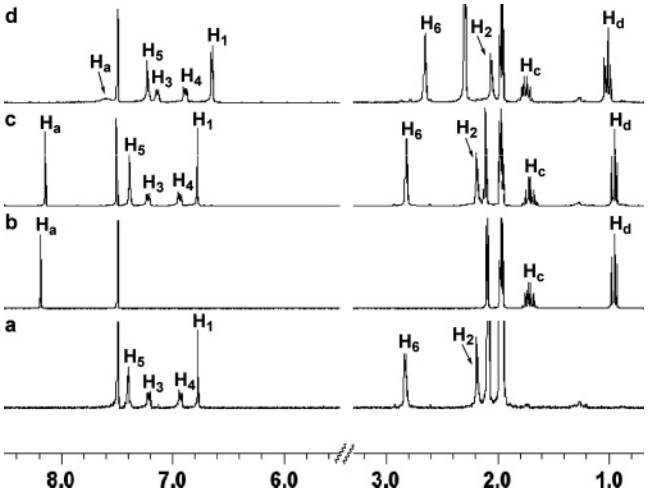

FIGURE 3. Partial ^1H NMR spectra (300 MHz, CD_3CN:$CDCl_3$ = 1:1, 295 K) of (a) **1**, (b) **2**, (c) **1** and 1.0 equiv of **2**, $[\mathbf{1}]_0 = 3$ mM, and (d) the mixture obtained after adding LiBr (4 equiv) to the solution from c.

The low-temperature ^1H NMR experiment showed that the guest proton resonances of H_a−H_d split into two sets of signals at 233 K.[9] In particular, it was found that compared with the H_a signal of free guest, the complexed H_a signal showed a striking upfield shift ($\Delta\delta = -2.2$ ppm). These observations suggested that the complexation between **1** and **2** in the presence of lithium salts became a slow exchange on the chemical shift time scale at 233 K. Although the binding process is complex since a tetracomponent complex was formed, we have chosen to titrate **2** into a solution of **1** containing a large excess of lithium salts, and under these conditions it is reasonable to assume that bonding of Li^+ to **1** is essentially complete.[13] The ^1H NMR spectroscopic titrations afforded a quantitative estimate for the complex of **1** and **2** in the presence of 20 equiv of LiBr by monitoring the changes of the chemical shift of the proton H_1 of the host. The results showed that a 1:1 complex between **1** and **2** was formed by a mole ratio plot.[14] Accordingly, the apparent equilibrium constant was determined to be $9.1(\pm1.3) \times 10^3$ M^{-1} by the Scatchard plot.[15]

Furthermore, a light purple crystal from an acetone solution of a 1:1 mixture of host **1** and pyromellitic diimide **2** was obtained, and its X-ray diffraction result confirmed the observations in solution. As shown in Figure 4, the guest **2** was outside of the cavity of host **1**, and formed an interesting sandwich structure with two host molecules. The centroid−centroid distance between the pyromellitic ring (A) and the anthracene ring (B) is about 3.43 Å, which may indicate the existence of an intermolecular face-to-face π-stacking interaction.

The situation was totally different when lithium salts were used in the process of growing single crystals. Consequently, deep purple crystals of complex **1**·**2**·$2LiClO_4$ were obtained by slow ether diffusion into an equimolar mixture of **1** and **2** in 1:1 chloroform/acetonitrile solution in the presence of $LiClO_4$.[16] As shown in Figure 5, the guest **2** was included in the cavity of **1** to form a novel cascade complex in the solid state, and two lithium ions were found to act as templates in the formation of the complex, which is consistent with the result in solution. In the complex **1**·**2**·$2LiClO_4$, both of the lithium ions are five-

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[12] Sodium and potassium ions were found to show weaker template effects on the complexation between **1** and **2** than lithium ions did.[9]

[13] The use of a large excess of LiBr ensured the elimination of complications arising in the determination of the dissociation constant for the ion pair. The apparent equilibrium constants are actually the measurements of the bonding ability of the pre-formed [**1**·$2Li^+$] with guest **2**: (a) Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 7001−7004. (b) Pascu, S. I.; Jarrosson, T.; Naumann, C.; Otto, S.; Kaiser, G.; Sanders, J. K. M. *New J. Chem.* **2005**, *29*, 80−89.

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[15] Connors, K. A. *Binding Constants*; J. Wiley and Sons: New York, 1987.

[16] The ^1H NMR spectrum of a 1:1 mixture of **1** and **2** in the presence of $LiClO_4$ displayed similar shifts of the signals to those of LiBr.[9]

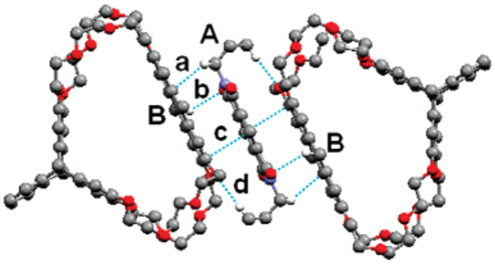

FIGURE 4. Crystal structure of **1**·**2**·**1**. Solvent molecules and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity. The short contact distances (Å): $a = 2.77$, $b = 2.68$, $c = 3.37$, $d = 2.70$.

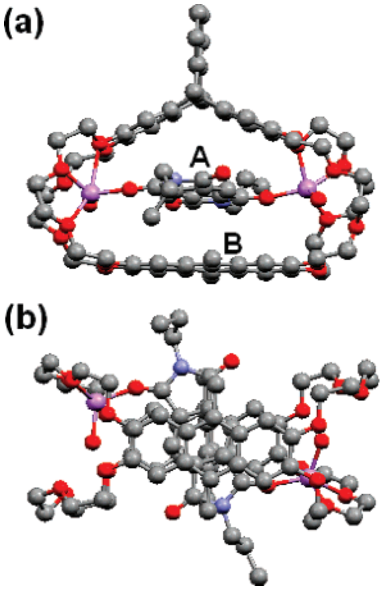

FIGURE 5. (a) Top view and (b) side view of the crystal structure of **1**·**2**·2LiClO$_4$. Solvent molecules, ClO$_4^-$ counterions, and hydrogen atoms are omitted for clarity.

coordinate with a distorted trigonal bipyramidal arrangement, in which three glycol oxygen atoms and one pyromellitic diimide carbonyl group are bound to each lithium ion, while water takes the fifth coordination site. Interestingly, it was also found that the two water molecules acted as a bridge and had hydrogen bonding interactions with the glycol chains. Moreover, the dihedral angle and the centroid−centroid distance between the pyromellitic ring (A) and the anthracene ring (B) were found to be 2.84° and 3.55 Å, respectively, and the intercationic distance between the two complexed lithium ions was 10.44 Å.

We further tested the template effect of other cations on the complexation between host **1** and guest **2** by the NMR approach. The results showed that Na$^+$ and K$^+$ ions caused smaller upfield shifts of the aromatic proton H$_1$ and H$_a$ signals than the Li$^+$ ion did,[9] while no obvious proton signal change of **2** was observed upon the addition of Mg^{2+} and Ca^{2+} ions into the 1:1 mixture of **1** and **2**. These observations suggested that Na$^+$ and K$^+$ ions had template effects on the complexation between host **1** and guest **2**, but they are weaker than that of Li$^+$ ion. For Mg^{2+} and Ca^{2+} ions, they had little influence on the formation of the complex.

Potassium-Templated Complexation of Host 1 with Anthraquinone 3. Similarly, Li$^+$, Na$^+$, Mg^{2+}, and Ca^{2+} ions also showed little or no template effects on the complexation between host **1** and anthraquinone **3**.[9] However, it was found that under the same conditions, the guest **3** could form a stable complex with host **1** in the presence of potassium ions. Consequently, a remarkable color change[17] could be observed when KPF$_6$ was added into a solution of host **1** and guest **3** in chloroform/acetonitrile (1:1 v/v). Moreover, the ESI-MS spectrum showed a strong peak at *m/z* 737.6 for **1**·**3**·2K$^+$, which provided more evidence for formation of the complex.

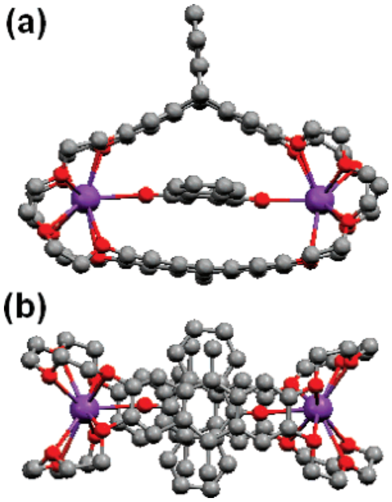

FIGURE 6. (a) Top view and (b) side view of crystal structure of **1**·**3**·2KPF$_6$. Solvent molecules, PF$_6^-$ counterions, and hydrogen atoms are omitted for clarity.

Similar to the case of host **1** and guest **2**, the ^{1}H NMR spectrum of a 1:1 mixture of **1** and **3** in 1:1 chloroform/acetonitrile solution is essentially the sum of the two components, which suggests that there is insufficient complexation to be detected by NMR. However, the addition of solid KPF$_6$ caused a significant change of the spectrum. The signals of protons H$_1$−H$_6$, H$_e$, and H$_f$ all shifted upfield, which might be due to the stacking of the aromatic rings of **1** and **3**. In the presence of 20 equiv of KPF$_6$, ^{1}H NMR spectroscopic titrations were also performed by monitoring the changes of the chemical shift of the proton H$_1$ of the host. The results showed that a 1:1 complex between **1** and **3** was formed by a mole ratio plot, and the apparent equilibrium constant was determined to be 2.8(±0.4) × 10^4 M^{-1}.

Furthermore, we obtained the deep red crystals of the complex **1**·**3**·2KPF$_6$ suitable for X-ray analysis by slow diffusion of ether into an equimolar mixture of **1** and **3** in a 1:1 chloroform/acetonitrile solution in the presence of excess KPF$_6$. As shown in Figure 6, both of the potassium ions are all nine-coordinate, in which one is from the oxygen atom of the anthraquinone, and the others are from the oxygen atoms of the glycol chains. The anthraquinone ring is threaded into the host cavity to result in a new cascade complex structure. The intercationic distance between two potassium ions was 10.80 Å, a little longer than the distance between two lithium ions in **1**·**2**·2LiClO$_4$. The centroid−centroid distance between the anthracene ring and the anthraquinone ring is 3.44 Å. Interestingly, it was also found that there exist π-stacking and C−H···π interactions between the anthracene rings of two adjacent host molecules[9] and the interplanar separation between the central rings of two anthracenes is 3.36 Å.

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(17) The color changed from light yellow to deep red.

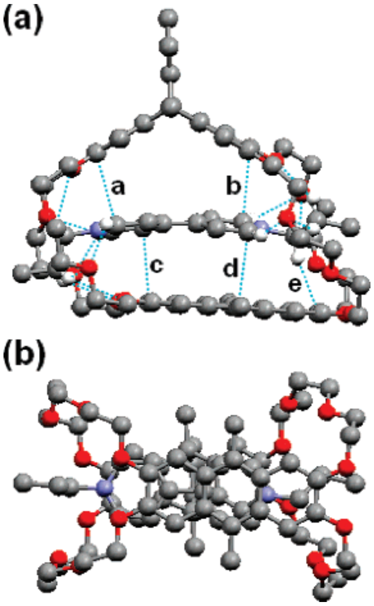

FIGURE 7. (a) Top view and (b) side view of the crystal structure of the complex **1·4**. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

Complex Formation between Host 1 and the Paraquat Derivative 4. Similar to the complexation of the triptycene-based cylindrical macrotricyclic polyether with paraquat derivatives reported by us previously,[7b] we found that the host **1** could also form a 1:1 stable complex with the paraquat derivative **4**. Formation of the complex **1·4** was confirmed by the ^{1}H NMR and ESI MS spectrum. ^{1}H NMR spectroscopic titrations have been done to quantitatively estimate the bonding property of the host **1** toward guest **4**. Accordingly, the apparent equilibrium constant[18] of a 1:1 complex between **1** and **4** was determined to be $4.4(\pm 0.7) \times 10^3$ M^{-1} by the Scatchard plot,[15] which is almost twice as much as the K_a of the complex between the triptycene-based cylindrical host we reported before and guest **4**. This result indicated that there existed a stronger $\pi-\pi$ interaction between host **1** and the paraquat derivative.

The crystal structure of the complex **1·4** (Figure 7) further revealed that the guest **4** is threaded out from the two lateral crown-8 cavities of **1** to form a new pseudorotaxane. The complex was stabilized by the multiple hydrogen bonds between the *N*-methylene protons and the aromatic protons of guest **4** and the ether oxygen atoms, π-stacking interactions between the aromatic rings of **1** and the pyridinium rings of **4** with distances of 3.27 (a), 3.39 (b), 3.31 (c), and 3.33 Å (d), and a C−H···π interaction between the *N*-methylene proton and the anthracene ring with distance of 2.59 Å (e).

Three Cation-Controlled Switchable Processes. Since both Li^+ and K^+ ions were key components in the formation of the two cascade complexes, removal of the metal ions could dissociate the previously formed complexes. It was also known that 18-crown-6 and 12-crown-4 were very strong sequestering agents for K^+ and Li^+ ions, respectively.[19] Therefore, the facts that the host **1** could selectively complex with three different kinds of guests **2**−**4** in different modes would provide us an opportunity to further study the switchable features between the different complexation systems. The results were shown in Figure 8, in which the three switch processes could be efficiently performed by control of the cations.

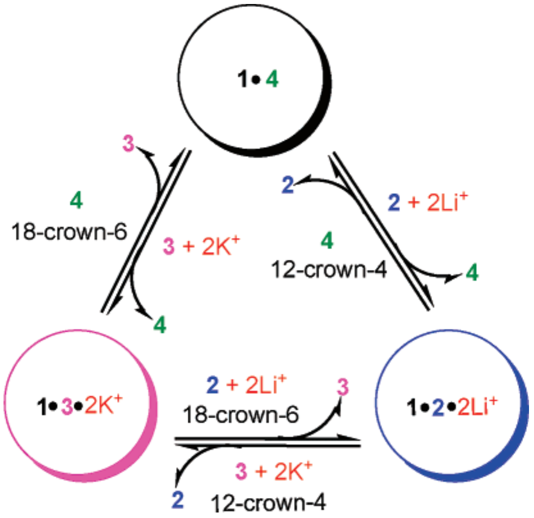

FIGURE 8. Scheme representation of switch processes between the host **1** and guests **2**−**4** controlled by adding and removing cations.

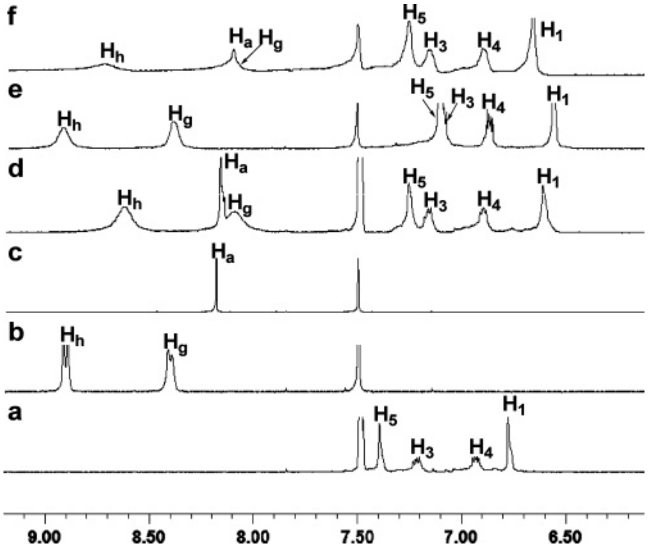

FIGURE 9. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN:CDCl_3$ = 1:1, 295 K) of (a) **1**, (b) **4**, (c) **2**, (d) **1** and 1.0 equiv of **4** and **2**, $[\mathbf{1}]_0$ = 3 mM, (e) the mixture obtained after adding LiBr (6 equiv) to the solution from d, and (f) the mixture obtained after adding 12-crown-4 (6 equiv) to the solution from e.

As shown in Figure 9d, the ^{1}H NMR spectrum of a 1:1:1 mixture of **1**, **2**, and **4** displayed the characteristic proton signal patterns of the complex **1·4** and guest **2**. When 6 equiv of LiBr was added into the solution, proton H_g and H_h signals of the guest **4** shifted downfield almost to the original positions (Figure 9e), while the proton H_a signal broadened and disappeared[20] and the proton signals of the host shifted to upfield. These

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[18] The complexation between the host and the guest was determined not to be concentration dependent, indicating that the complex is essentially ion paired.[7c]

[19] For the complexation of 18-crwon-6 with K^+ and 12-crown-4 with Li^+, see: (a) Inoue, Y.; Liu, Y.; Tong, L. H.; Ouchi, M.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1947−1950. (b) Danil de Namor, A. F.; Ng, J. C. Y.; Tanco, M. A. L.; Saloman, M. J. *J. Phys. Chem.* **1996**, *100*, 14485−14491.

[20] The signal of proton H_a was supposed to be buried in the residue signal of chloroform.

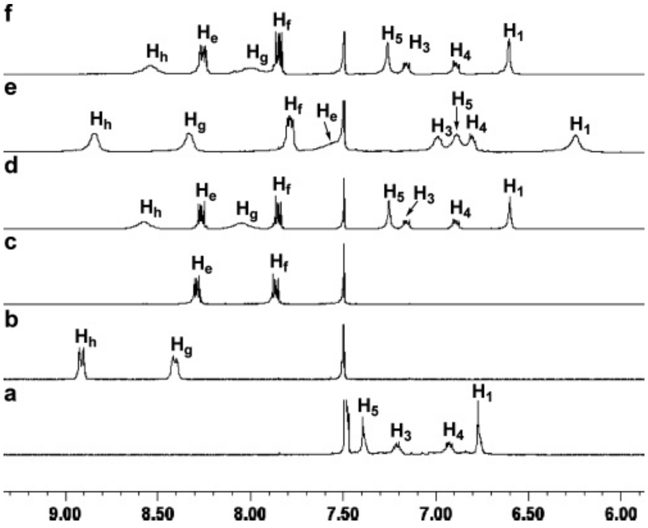

FIGURE 10. Partial ^{1}H NMR spectra (300 MHz, CD_3CN:$CDCl_3$ = 1:1, 295 K) of (a) **1**, (b) **4**, (c) **3**, (d) **1** and 1.0 equiv of **4** and **3**, $[\mathbf{1}]_0$ = 3 mM, (e) the mixture obtained after adding KPF_6 (4 equiv) to the solution from d, and (f) the mixture obtained after adding 18-crown-6 (6 equiv) to the solution from e.

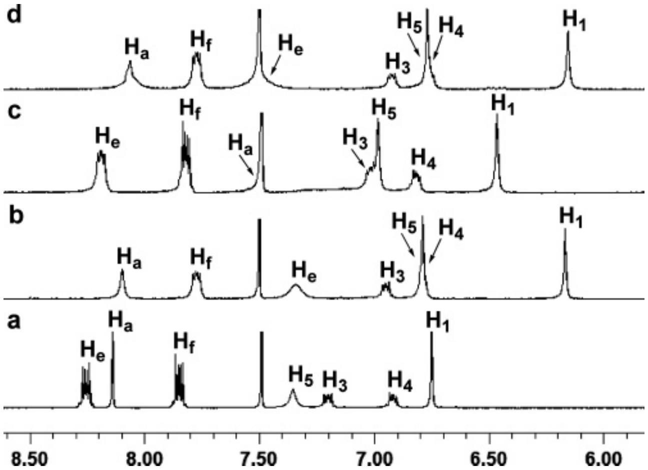

FIGURE 11. Partial ^{1}H NMR spectra (300 MHz, CD_3CN:$CDCl_3$ = 1:1, 295 K) of (a) **1** and 1.0 equiv of **2** and **3**, $[\mathbf{1}]_0$ = 3 mM, (b) the mixture obtained after adding KPF_6 (6 equiv) to the solution from a, (c) the mixture obtained after adding 18-crown-6 (8 equiv) and LiBr (6 equiv) to the solution from b, and (d) the mixture obtained after adding 12-crown-4 (8 equiv) and KPF_6 (6 equiv) to the solution from c.

observations indicated that the complex **1·4** was decomposed while the complex **1·2**·2Li$^+$ was formed. When 12-crown-4 was added into the above system, it was found that the complex **1·2**·2Li$^+$ was dissociated while the complex **1·4** was formed again (Figure 9f).

Similarly, the ^{1}H NMR spectrum of a 1:1:1 mixture of **1**, **3**, and **4** displayed the characteristic shifts of the complex **1·4** and guest **3** (Figure 10d). When 4 equiv of KPF_6 was added to the solution, it was found that proton H_g and H_h signals of **4** shifted downfield to the original positions (Figure 10e). Meanwhile, the proton H_e signal broadened and shifted upfield, and the proton signals of the host shifted to upfield. These observations suggested that the complex **1·3**·2K$^+$ was formed. The subsequent addition of 18-crown-6 could further recover the complex **1·4** again (Figure 10f).

Finally, the switch process between two neutral guests could also be performed. In the ^{1}H NMR spectrum of a 1:1:1 mixture of **1**, **2**, and **3**, no changes of the corresponding signals were observed according to the free species, which suggested that insufficient bonding occurred (Figure 11a). When 6 equiv of KPF_6 was added into the solution, the proton H_e and H_f signals of guest **3** and the proton signals of the host shifted upfield (Figure 11b), which indicated the formation of the complex **1·3**·2K$^+$. When 18-crown-6 and LiBr were added to the above system, the ^{1}H NMR spectrum (Figure 11c) displayed the characteristic signal pattern for the lithium-templated complex. This observation suggested that the potassium ions were peeled off while the complex **1·2**·2Li$^+$ was formed. Furthermore, the addition of 12-crown-4 and KPF_6 could result in dissociation of the complex **1·2**·2Li$^+$ and formation of the complex **1·3**·2K$^+$ again (Figure 11d).

Conclusion

In summary, we have synthesized a novel triptycene-based cylindrical macrotricyclic host and demonstrated that it could not only form a stable pseudorotaxane-type complex with the paraquat derivative, but also show strong and selective templated complexation with pyromellitic diimide and anthraquinone in the presence of lithium or potassium ions, respectively. Consequently, two novel cascade complexes were formed in solution and in the solid state. Moreover, it was also found that three switchable processes between the host and the guests could be efficiently performed by control of lithium or potassium ions. Such multiswitchable systems will be useful in the development of functional supramolecular systems,[21] which are now in progress.

Experimental Section

Synthesis of Cylindrical Macrotricyclic Host 1. A suspension of Cs_2CO_3 (1.75 g, 5.37 mmol) in anhydrous DMF (70 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 110 °C. To the mixture was added dropwise a solution of **5** (0.18 g, 0.67 mmol) and the tetratosylate **6** (1.00 g, 0.67 mmol) in anhydrous DMF (70 mL) over 30 h. The reaction mixture was stirred at 110 °C for another 2 d. After cooling to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was concentrated under reduced pressure to give reddish brown oil, which was redissolved in CH_2Cl_2 (50 mL) and washed with H_2O. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 30/1 CH_2Cl_2/CH_3OH) to obtain 0.17 g (24%) of **1** as a light yellow solid. Mp 192−193 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 6H), 2.82 (s, 6H), 3.65−3.91 (m, 32H), 4.00−4.02 (m, 8H), 4.25−4.30 (m, 4H), 4.48−4.55 (m, 4H), 6.74 (s, 4H), 6.90−6.96 (m, 2H), 7.17−7.22 (m, 2H), 7.39 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 14.7, 47.7, 69.2, 69.7, 69.9, 70.1, 70.9, 71.2, 104.4, 109.5, 119.9, 123.7, 124.5, 125.8, 142.1, 145.9, 147.9, 148.8. MALDI-TOF MS *m/z* 1072.7 $[M]^+$, 1095.6 $[M + Na]^+$. Anal. Calcd for $C_{62}H_{72}O_{16}\cdot 0.5CH_2Cl_2$: C, 67.28; H, 6.59. Found: C, 67.26; H, 6.76.

Synthesis of Pyromellitic Diimide 2. 1-Propylamine (1.18 g, 20 mmol) and pyromellitic dianhydride (2.18 g, 10 mmol) were dissolved in DMF (40 mL), then the mixture was stirred at 110 °C

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[21] (a) Badji, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845−1849. (b) Jeon, W. S.; Ziganshina, A. Y.; Lee, J. W.; Ko, Y. H.; Kang, J-K.; Lee, C.; Kim, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 4097−4100. (c) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72−191 and references cited therein.

overnight. After cooling to ambient temperature, the mixture was filtered and washed with methanol and a white solid (1.76 g, 59%) was obtained. Mp 202−203 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96−1.00 (t, $J = 7$ Hz, 6H), 1.72−1.79 (m, 4H), 3.71−3.76 (t, $J = 7$ Hz, 4H), 8.29 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3, 21.8, 40.3, 118.1, 137.2, 166.3. ESI MS *m/z* 300.06 $[M]^+$. Anal. Calcd for $C_{16}H_{16}O_4N_2$: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.06; H, 5.39; N, 9.50.

Complexation Studies by Proton NMR. A 1:1 $CDCl_3/CD_3CN$ solution was chosen as the NMR solvent to dissolve the host and guests. In the NMR measurements, the CD_3CN was used as the lock, while the TMS was employed as the internal standard. Chemical shifts were reported in parts per million (ppm). ^{1}H NMR characterization was done on solutions with a constant $[\mathbf{1}]_0$ and varied $[\mathbf{2}]_0$, $[\mathbf{3}]_0$, or $[\mathbf{4}]_0$. All solutions were prepared as follows. Precisely weighted amounts of dried host and guests were added into separate screw cap vials. The NMR solvents were added with to-deliver volumetric pipets. Then specific volumes of each fresh solution were mixed to yield the desired concentration. Δ is the observed chemical shift change relative to uncomplexed species, and Δ_0 is the difference between the uncomplexed and fully complexed species, and is determined by extrapolation of a plot of Δ vs $1/[\text{guest}]_0$ in the high initial concentration range of guest. The complex fraction (*p*) value was calculated from $p = \Delta/\Delta_0$, and [guest] values were calculated form $[\text{guest}]_0 - p[\mathbf{1}]_0$. A plot of $p/[\text{guest}]$ vs p was used to determine the association constant K_a, which is the average value of the slope and the intercept.

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Supporting Information Available: Experimental procedures and charaterization for the complexes and determination of the association constants for the complexes, as well as X-ray crystallographic files (CIF) for the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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