JOC The Journal of Organic Chemistry

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Complexation of Triptycene-Derived Macrotricyclic Polyether with Paraquat Derivatives, Diquat, and a 2,7-Diazapyrenium Salt: Guest-Induced Conformational Changes of the Host

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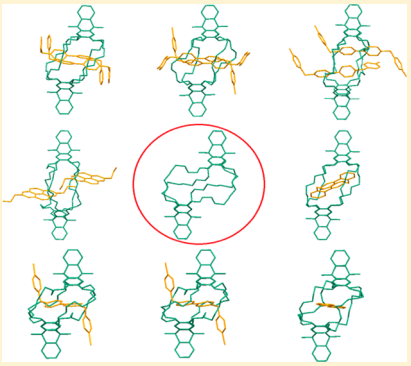
Supporting Information

ABSTRACT: Complexation between a triptycene-derived macrotricyclic polyether containing two dibenzo-[30]-crown-10 cavities and different functionalized paraquat derivatives, diquat, and a 2,7-diazapyrenium salt in both solution and solid state was investigated in detail. It was found that depending on the guests with different terminal functional groups and structures, the macrotricyclic polyether could form 1:1 or 1:2 complexes with the guests in different complexation modes in solution and also in the solid state. Especially, the conformation of the macrotricyclic polyether was efficiently adjusted by the encapsulated guests, which was to some extent similar to substrate-induced fit of enzymes. Moreover, the binding and releasing of the guests in the complexes could be controlled by potassium ions.



INTRODUCTION

Development of novel macrocyclic hosts with the capability of binding selected substrates in specific complexation modes is always a very important and attractive topic in host−guest chemistry.[1] Consequently, various macrocyclic hosts including crown ethers,[2] cryptands,[3] calix[n]arenes,[4] cucurbit[*n*]urils,[5] and other macrocycles[6] have been designed and synthesized during the past decades. These macrocyclic hosts have shown complexation with different cations, anions, and neutral organic molecules, which thus resulted in a variety of new supramolecular systems with specific structures and properties. In addition, it was known that paraquat derivatives[7] have become some of the most common guests and have also been utilized for construction of different kinds of interlocked assemblies, such as pseudorotaxanes, rotaxanes, and catenanes.

In biological systems, it is general that a substrate can induce the conformational change of a receptor, like an enzyme, to achieve the most efficient interaction between the substrate and the receptor. This process called induced fit was put forward by Daniel Koshland in 1958.[8] However, in the case of synthetic macrocycles, few examples of guest-induced conformational changes of the hosts have been reported, because most of the known macrocyclic hosts are either too rigid or show no complexation behaviors with different guests.[9]

Recently, we[10] reported a novel macrotricyclic polyether **1** that was composed of two triptycene moieties with rigid structure and four flexible crown ether chains, which results in two dibenzo-[30]-crown-10 cavities and one large central cavity (Figure 1).

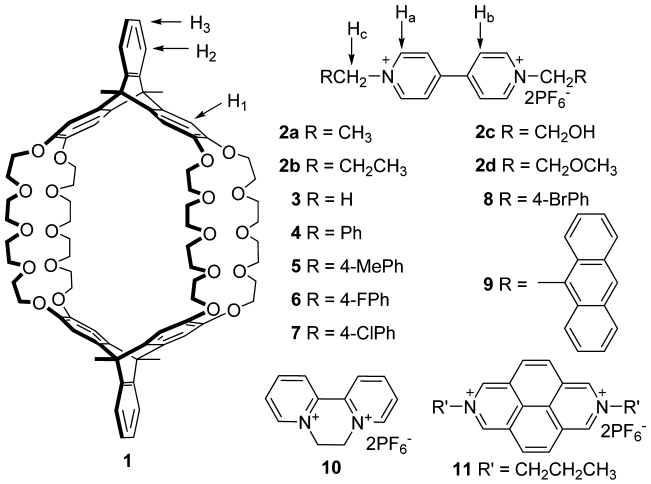


Figure 1. Chemical structures and proton designations of host **1** and guests **2**−**11**.

These structural features could show wide complexation abilities toward different kinds of guests, and the conformation of the macrocycle could easily be adjusted by the different encapsulated guests as well. In the previous report, we found that the macrotricyclic host forms stable 1:2 complexes with paraquat

Received: January 23, 2013
Published: February 26, 2013

   dx.doi.org/10.1021/jo400148b | *J. Org. Chem.* 2013, 78, 3235−3242

derivatives **2a−d** with different terminal functional groups, in which the host takes a rectangle-like structure, and two guests are situated at each short side of the rectangle, respectively.[10b] In this paper, we report complexation between the macrotricyclic polyether and different functionalized paraquat derivatives **3−9**, diquat **10**, and a 2,7-diazapyrenium salt **11** (Figure 1) in both solution and solid state. It was found that, depending on the guests with different terminal functional groups and structures, the macrotricyclic polyether can form 1:1 or 1:2 complexes in different complexation modes. It was also noteworthy that host **1** and guest **11** form a ladder-like supramolecular polymer in the solid state. Notably, the conformation of the macrotricyclic polyether can also be efficiently adjusted by the encapsulated guests, which was to some extent similar to the substrate-induced fit of enzymes. Moreover, the binding and releasing of the guests in the complexes can further be controlled by potassium ions. The specific complexation of the macrotricyclic polyether with extensive organic guests in different modes and the guest-induced conformational changes of the macrocyclic host could find wide applications in supramolecular chemistry.

RESULTS AND DISCUSSION

Complexation between Macrotricyclic Host 1 and Guests 3−11 in Solution. First, complexation between host **1** and the guests **3−11** was studied in solution by the ^{1}H NMR spectroscopic method. Consequently, when we mixed the host **1** (3.0 mM) and 1.0 equiv of **3** in 1:1 (v/v) $CD_3CN/CDCl_3$, a deep yellow 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.[11] As shown in Figure 2, the ^{1}H NMR spectrum of the mixture of host **1** and

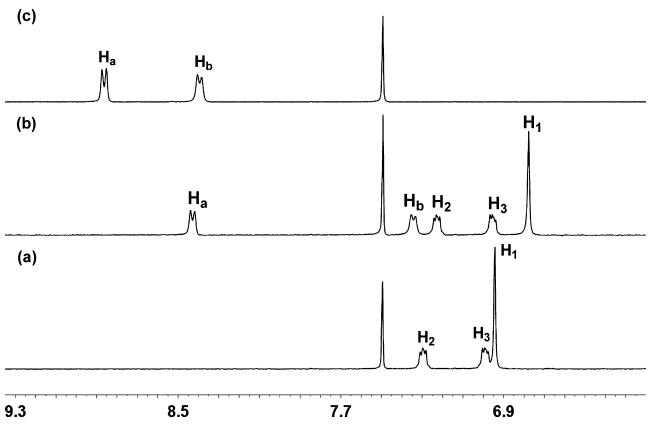


Figure 2. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of (a) free **1**, (b) **1** and 1.0 equiv of **3**, (c) free **3**. $[\mathbf{1}]_0$ = 3.0 mM.

1.0 equiv of guest **3** exhibited a well-defined set of signals, which are different from those for both **1** and **3**. The H_1 proton signal of the benzene ring in **1** showed a upfield shift ($\Delta\delta$ = 0.13 ppm for H_1), which might be due to the $\pi-\pi$ interaction between the electron-rich triptycene moiety and the electron-poor bipyridine moieties. Similarly, the protons H_a and H_b also shifted upfield, which was attributed to their positions in the shielding region of the aromatic rings of **1**. These observations suggested that a stable complex between host **1** and guest **3** might be formed in solution, and the corresponding complexation is a fast process. The ^{1}H NMR spectroscopic titrations further afforded a quantitative estimate for the complexation between host **1** and guest **3** by monitoring the changes of the chemical shift of the proton H_1 of **3**. The results showed that a 1:1 complex between **1** and **3** was formed by a mole ratio plot. Accordingly, the apparent association constant $K_{a,exp}$ was calculated to be 5.3(±0.1) × 10^3 M^{-1} by a Scatchard plot.[11,12] Moreover, the 2D NMR spectral technique was used to investigate the nonconvalent interactions between the two components. The results showed that cross-peaks between proton H_a in the bipyridinium ring of **3** and the protons in the crown ether units of **1** were found, which suggested that the guest threaded the central cavity of host **1** to form a 1:1 complex. Moreover, proton H_c of **3** also exhibited a cross-peaks signal with the protons in crown ether units of **1**. These results implied that the methyl group of **3** was close to the crown ether units of **1**, which also proved the formation of the complex.

Similarly, we found that the complexation between host **1** and benzyl substituted paraquat salt **4** was also a fast exchange process (Figure 3), but the stoichiometry of the complex was

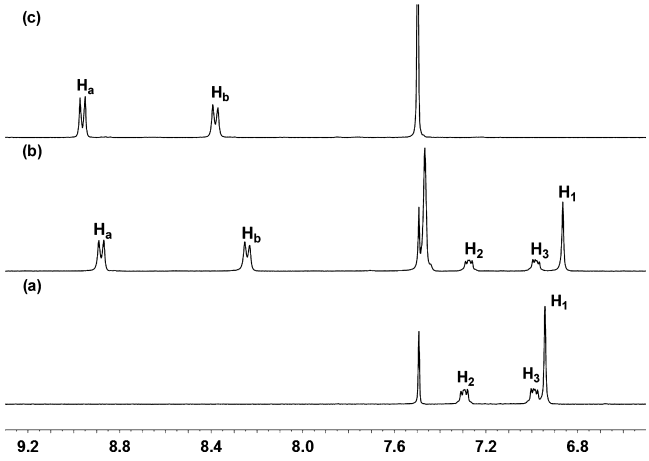


Figure 3. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of (a) free **1**, (b) **1** and 1.0 equiv of **4**, (c) free **4**. $[\mathbf{1}]_0$ = 3.0 mM.

determined to be 1:2 by a mole ratio plot, and the average association constant K_a for the complex was calculated to be 3.1(±0.01) × 10^2 M^{-1} by the Scatchard plot. A 2D ROESY experiment[11] of complex **1**·$\mathbf{4}_2$ was also carried out to investigate the complexation between the host and the guest. Consequently, cross-peaks between protons H_a and H_b in the bipyridinium ring of **4** and the protons in crown ether units of host **1** were observed, which suggested that two of the guest molecules threaded the central cavity. This result was different from that of the 1:1 complex between host **1** and guest **3**, which might be attributed to the variable structure of the flexible macrocyclic host **1**.

Moreover, we also tested the complexation between host **1** and other guests with different functional groups and structures in solution by NMR spectroscopy.[11] The results showed that under the tested conditions, the guests **7−9** and **11** threaded the central cavity of host **1** to form 1:1 complexes. Meanwhile, the guests **5**, **6**, and **10** formed 1:2 complexes with host **1** in a complexation mode similar to that between host **1** and guest **4**. Moreover, the association constants for the complexes were all calculated by Scatchard plots, and the results are summarized in Table 1. These results indicate that, depending on the guests, the macrocyclic host forms 1:1 or 1:2 stable complexes with not only paraquat derivatives with different functional groups but also diquat and 2,7-diazapyrenium salt in the tested solution conditions.

ESI-MS Studies on Formation of the Complexes between Host 1 and Guests 3−11. Electrospray ionization (ESI) mass spectrometry was also used to characterize the

dx.doi.org/10.1021/jo400148b | J. Org. Chem. 2013, 78, 3235−3242

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

complexes	stoichiometry (H/G)	K_a [M^{-1}][a]
1·3	1:1	$5.3(\pm0.1) \times 10^3$
1·4$_2$	1:2	$3.1(\pm0.01) \times 10^2$
1·5$_2$	1:2	$3.1(\pm0.01) \times 10^2$
1·6$_2$	1:2	$3.8(\pm0.01) \times 10^2$
1·7	1:1	$4.3(\pm0.07) \times 10^2$
1·8	1:1	$7.4(\pm0.1) \times 10^2$
1·9	1:1	$5.6(\pm0.1) \times 10^2$
1·10$_2$	1:2	$2.6(\pm0.01) \times 10^3$
1·11	1:1	$9.0(\pm0.1) \times 10^2$

[a]From the ^{1}H NMR titration experiments in $CD_3CN/CDCl_3$ (1:1, v/v). The K_a values of **1·4$_2$**, **1·5$_2$**, **1·6$_2$**, and **1·10$_2$** are average association constants.

complexes between host **1** and the guests **3**−**11**.[11] Consequently, the strongest peak at m/z 756.3 for $[\mathbf{1}\cdot\mathbf{3}\text{-}2PF_6]^{2+}$ and 1658.4 for $[\mathbf{1}\cdot\mathbf{3}\text{-}PF_6]^{+}$ was found by using a solution of **1** and **3** in 1:1 (v/v) chloroform and acetonitrile, which supported the formation of a 1:1 stable complex. Similarly, formation of the complexes between host **1** and the guests **4**−**11** were also supported by the ESI mass spectra, in which the strong peaks at m/z 1147.0, 511.8, 1175.2, 519.7, 1182.8, 866.4, 911.7, 932.6, 992.8, 808.3, and 1762.6 for $[\mathbf{1}\cdot\mathbf{4}_2\text{-}2PF_6]^{2+}$, $[\mathbf{1}\cdot\mathbf{5}_2\text{-}4PF_6]^{4+}$, $[\mathbf{1}\cdot\mathbf{5}_2\text{-}2PF_6]^{2+}$, $[\mathbf{1}\cdot\mathbf{6}_2\text{-}4PF_6]^{4+}$, $[\mathbf{1}\cdot\mathbf{6}_2\text{-}2PF_6]^{2+}$, $[\mathbf{1}\cdot\mathbf{7}\text{-}2PF_6]^{2+}$, $[\mathbf{1}\cdot\mathbf{8}\text{-}2PF_6]^{2+}$, $[\mathbf{1}\cdot\mathbf{9}\text{-}2PF_6]^{2+}$, $[\mathbf{1}\cdot\mathbf{10}_2\text{-}2PF_6]^{2+}$, $[\mathbf{1}\cdot\mathbf{11}\text{-}2PF_6]^{2+}$, and $[\mathbf{1}\cdot\mathbf{11}\text{-}PF_6]^{+}$, respectively, were all observed.[11]

Complexation between Macrotricyclic Host 1 and Guests 3−11 in the Solid State. The crystal structures of the complexes not only provided direct evidence for formation of the complexes but also gave insight into their complexation modes. Consequently, a series of single crystals of the different complexes suitable for X-ray diffraction analysis were obtained.

First, we obtained a single crystal suitable for X-ray diffraction analysis by vapor diffusion of diisopropyl ether into a solution of macrocycle **1** in CH_3CN and $CHCl_3$ (1:1, v/v).[11] As shown in Figure 4, the crystal structure showed that two rigid triptycene

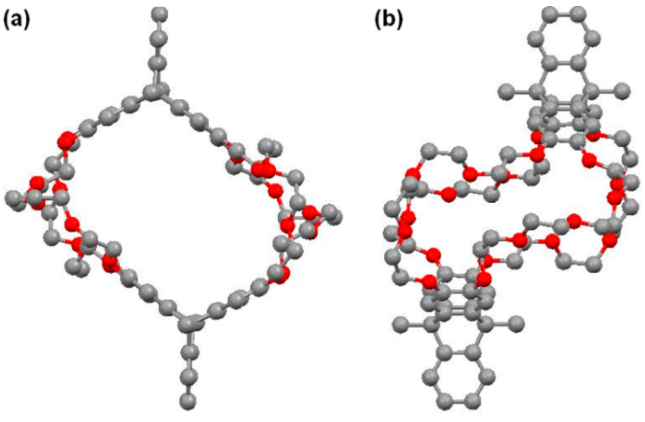


Figure 4. Side view (a) and top view (b) of the crystal structure of **1**. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

subunits and four flexible crown ether groups formed a macrocyclic molecule with a large central cavity of about 10.89 × 8.23 Å^2. One triptycene subunit was far away from the other so that a rectangle-like macrocycle formed (Figure 4a). Moreover, it was also found that molecule **1** self-assembled into a linear supramolecular array, which further resulted in a 2D wave-like structure and 3D microporous network architecture.[11]

Similarly, we obtained single crystals suitable for X-ray diffraction analysis from the $CH_3CN/CHCl_3$ mixture solution of **1** and **3**. As shown in Figure 5, the guest **3** is encapsulated in

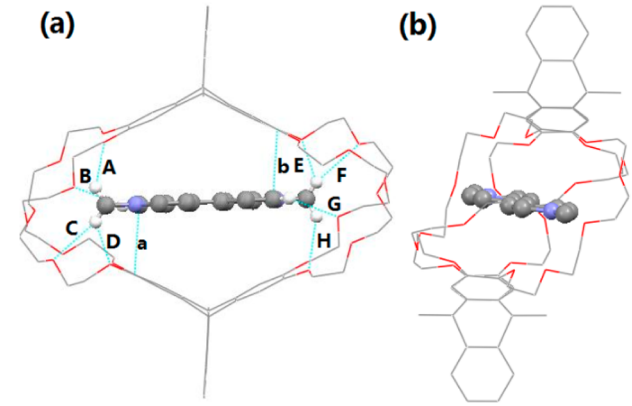


Figure 5. Top view (a) and side view (b) of the crystal structure of complex **1·3**. Blue lines denote the noncovalent interactions between host **1** and guest **3**. PF_6^- counterions and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

the center of the macrotricyclic host, and the two pyridinium rings of **3** are nearly coplanar. Moreover, the two *N*-methyl groups in **3** were positioned in the two crown ether cavities, which results in 1:1 complex **1·3** with a pseudorotaxane-like structure. There existed multiple $\pi-\pi$ stacking interactions between the bipyridinium ring and the aromatic rings of host **1** with distances of 3.28 (a) and 3.28 Å (b), respectively. Moreover, C−H···O hydrogen bonds (2.69 for A, 2.51 for B, 2.61 for C, 2.62 for D, 2.62 for E, 2.61 for F, 2.51 for G, and 2.69 Å for H, respectively) between the protons of methyl group in **2** and ether oxygen atoms of the host were also observed. These multiple intermolecular interactions might play an important role in the formation of complex **1·3**. In addition, a cross-peak signal between the methyl proton H_c of **3** and the protons in crown ether units of **1** in the 2D NMR spectrum of the complex was observed as well, suggesting that complex **1·3** adopted the same complexation mode in solution as that in the solid state.

Paraquat derivatives **7** and **8** containing 4-chlorobenzyl and 4-bromobenzyl groups formed 1:1 complexes **1·7** and **1·8** with host **1**, respectively, but showed different complexation modes compared with with that of complex **1·3**. As shown in Figure 6, the guest **7** or **8** threaded symmetrically the central cavity of the host **1**, and the two substituted benzyl groups in **7** or **8** were located outside the cavity, which might be due to the large chlorine or bromine terminal groups and the need of the host to be reshaped to fit the guests. There existed multiple C−H···O hydrogen bonding interactions between the protons of the bipyridinium rings of the guests and ether oxygen atoms of the host with the distances of 2.55 (A), 2.60 (B), 2.42 (C), 2.22 (D), 2.08 (E), 2.65 (F), and 2.35 Å (G) for complex **1·7**, and 2.26 (H), 2.55 (I), 2.63 (J), 2.63 (K), 2.55 (L), and 2.26 Å (M) for **1·8**, respectively. There also existed $\pi-\pi$ stacking interactions between the pyridinium ring of the guests and the aromatic rings of host **1** with the distances of 3.40 for (a), 2.76 for (b), 3.33 for (c), 3.33 for (d), 3.35 for (e), 3.33 for (f), 3.33 Å for (g) for **1·7**, and 3.38 (h), 3.36 (i), 3.38 (j), 3.38 (k), 3.36 (l), and 3.38 Å (m) for **1·8**, respectively. The multiple intermolecular interactions resulted in the stable complexes **1·7** and **1·8**.

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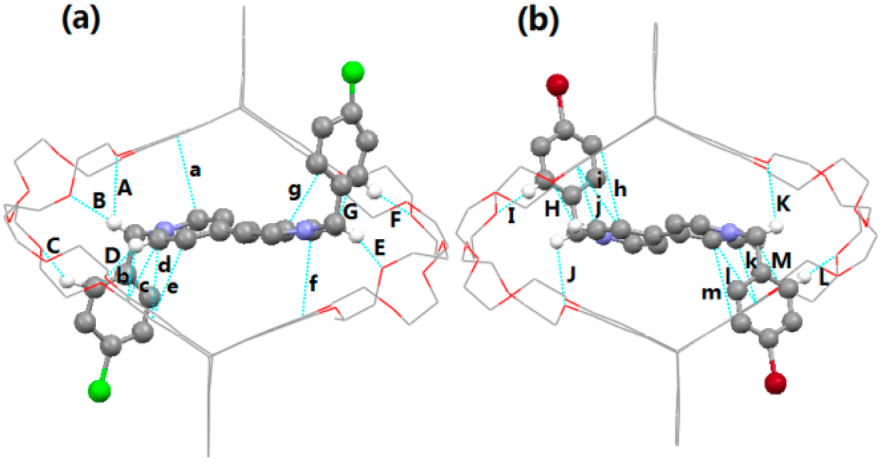

Figure 6. Top views of the crystal structures of complexes **1**·**7** (a) and **1**·**8** (b). Blue lines denote the noncovalent interactions between the host and the guests. PF_6^- counterions and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

Different from those 1:1 complexes described above, host **1** forms 1:2 complexes with a paraquat derivative **6** containing a 4-fluorobenzyl group. As shown in Figure 7b, two guests **6**

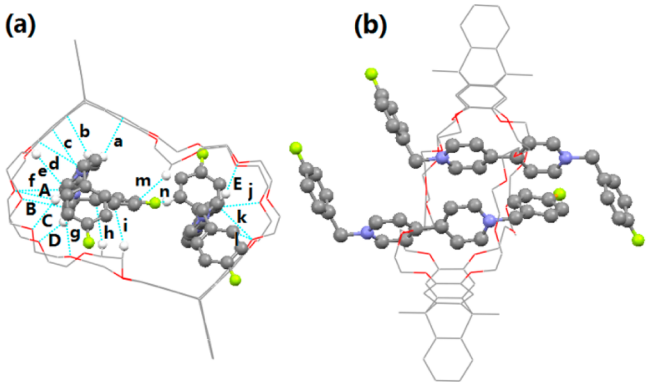

Figure 7. Top view (a) and side view (b) of the complex **1**·$\mathbf{6}_2$. Blue lines denote the noncovalent interactions between the host and the guests. Solvent molecules, PF_6^- counterions and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

threaded the central cavity of the host **1** to form 1:2 complex **1**·$\mathbf{6}_2$. The two 4-fluorobenzyl groups in **6** were located outside the cavity and nearly orthogonal to the pyridinium rings, which resulted in a "Z"-like structure of the guest. Formation of 1:2 complex **1**·$\mathbf{6}_2$ in the solid state was also consistent with the result in solution. As shown in Figure 7a, it was found that the guests were distorted by the dihedral angles between the pyridinium rings of 27.14° and 10.33°, respectively. There existed multiple C−H···O hydrogen bonding interactions between the protons of the bipyridinium ring and ether oxygen atoms of the host with distances of 2.61 for A, 2.55 for B, 2.43 for C, 2.64 for D, and 2.35 Å for E, respectively. Moreover, multiple $\pi-\pi$ stacking interactions between the pyridinium rings of the guest and the aromatic rings of host **1** with distances of 2.85 (a), 2.87 (b), 3.31 (c), 3.27 (d), 2.86 (e), 3.19 (f), 3.21 (g), 2.87 (h), 2.82 (i), 3.19 (j), 3.17 (k), 3.01 (l), and 2.72 Å (m), respectively, were also observed. In addition, C−H···F hydrogen bonding between the two adjacent guests with a distance of 2.49 Å (e) was found. It was worthy of note that formation of complex **1**·$\mathbf{6}_2$ was different from the 1:1 complexes between host **1** and guests **7** and **8**, which might be because the atomic radius of fluorine is smaller than those of chlorine and bromine, and two molecules of guest **6** might not exclude each other in one cavity of the host. Similarly, host **1** also forms 1:2 complexes not only with paraquat derivatives **4** and **5** but also with diquat **10** in the solid state, and complexation modes similar to that of complex **1**·$\mathbf{6}_2$ were found.[11]

With guest **11**, the complexation mode with host **1** was different from those of the above-described complexes. As shown in Figure 8, one guest **11** was located in the central cavities of two

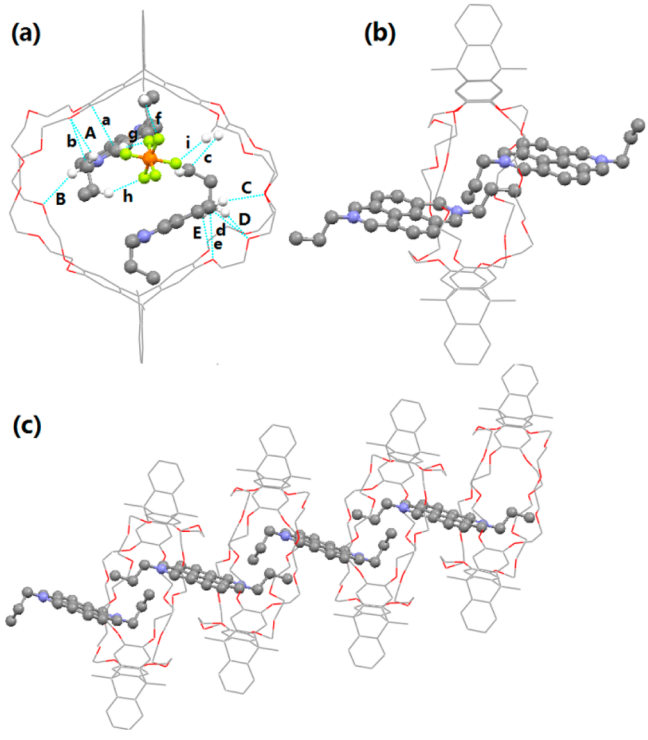

Figure 8. Top view (a) and side view (b) of the crystal structure of complex **1**·**11**. Blue lines denote the noncovalent interactions. (c) View of the ladder-like supramolecular poly[3]pseudorotaxane $(\mathbf{1}\cdot\mathbf{11})_n$. PF_6^- counterions, and hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

adjacent macrocyclic molecules, while each host **1** included parts of two guest molecules. This alternate complexation results in a ladder-like supramolecular poly[3]pseudorotaxane $(\mathbf{1}\cdot\mathbf{11})_n$ in

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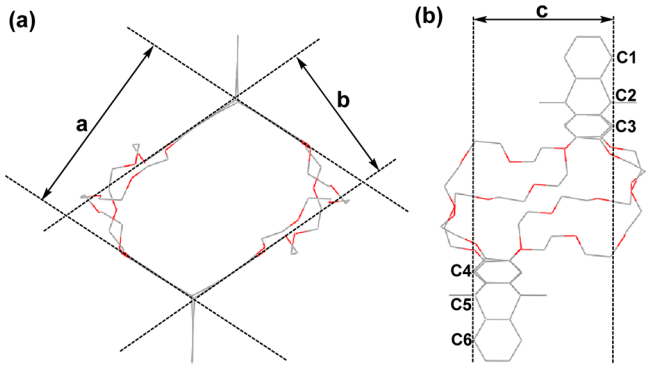

Figure 9. Side view (a) and top view (b) of the crystal structure of host **1**: **a**, the distance between the planes of two opposite benzene rings in triptycene moieties; **b**, the distance between the planes of other two opposite benzene rings in triptycene moieties; **c**v the distance between the plane composed by C1, C2, C3 in one triptycene moiety and the plane composed by C4, C5, C6 in other triptycene moiety. Solvent molecules and hydrogen atoms were omitted for clarity.

the solid state[3e] (Figure 8c), which might be also attributed to the variable and flexible structure of macrocyclic host **1**. There existed C−H···O hydrogen bonding interactions between the aromatic and alkyl protons of the guest and oxygen atoms of the crown ethers with the distances of 2.69 (A), 2.60 (B), 2.57 (C), 2.65 (D), and 2.63 Å (E), respectively. Moreover, there also existed the multiple $\pi-\pi$ interactions between the aromatic rings of host **1** and guest **11** with the distances of 3.29 (a), 3.20 (b), 2.74 (c), 3.18 (d), and 3.19 Å (e), respectively. In addition, multiple C−H···F hydrogen bonding interactions between hexafluorophosphate groups and both the host and the guest **11** with the distances of 2.54 (f), 2.51 (g), 2.64 (h) and 2.38 Å (i), respectively, were found. These multiple intermolecular interactions played an important role in formation of supramolecular polymer $(\mathbf{1{\cdot}11})_n$.

Table 2. Summary of Distances for a, b and c of Host 1 and Complexes in the Absence of Guest(s)

host or complex	a	b	c
1	10.89	8.23	8.04
$\mathbf{1{\cdot}2b_2}$	13.85	9.91	3.04
$\mathbf{1{\cdot}2d_2}$	13.70	8.47	3.28
1·3	8.87	8.71	6.08
$\mathbf{1{\cdot}4_2}$	11.25	9.75	5.93
$\mathbf{1{\cdot}5_2}$	11.00	10.09	5.12
$\mathbf{1{\cdot}6_2}$	13.92	9.34	4.44
1·7	8.74	8.11	6.15
1·8	8.72	8.17	6.02
$\mathbf{1{\cdot}10_2}$	10.83	10.72	5.61
1·11	12.32	11.53	3.25

Conformational Changes of the Macrotricyclic Host in the Complexes. Depending on the guests with different terminal groups and structures, host **1** forms different kinds of complexes in different modes in the solid state. Interestingly, it was found that the conformations of macrocyclic host **1** in those complexes was efficiently adjusted by the encapsulated guests, which were to some extent similar to the property of substrate-induced fit of enzymes. To investigate the conformational changes of macrotricyclic host **1** after its complexation with a guest, the distances of **a**, **b**, and **c** were defined (Figure 9), and the distances for **a**, **b** and **c** of host **1** itself and the complexes in the absence of guest(s) are summarized in Table 2.

First, we found that the crystal structure of macrocycle **1** showed that it adopts a rectangle-like conformation by top view and an "N-like" conformation by side view, which results in a central cavity 10.89 × 8.23 Å^2 (Figure 9). In the 1:2 complexes

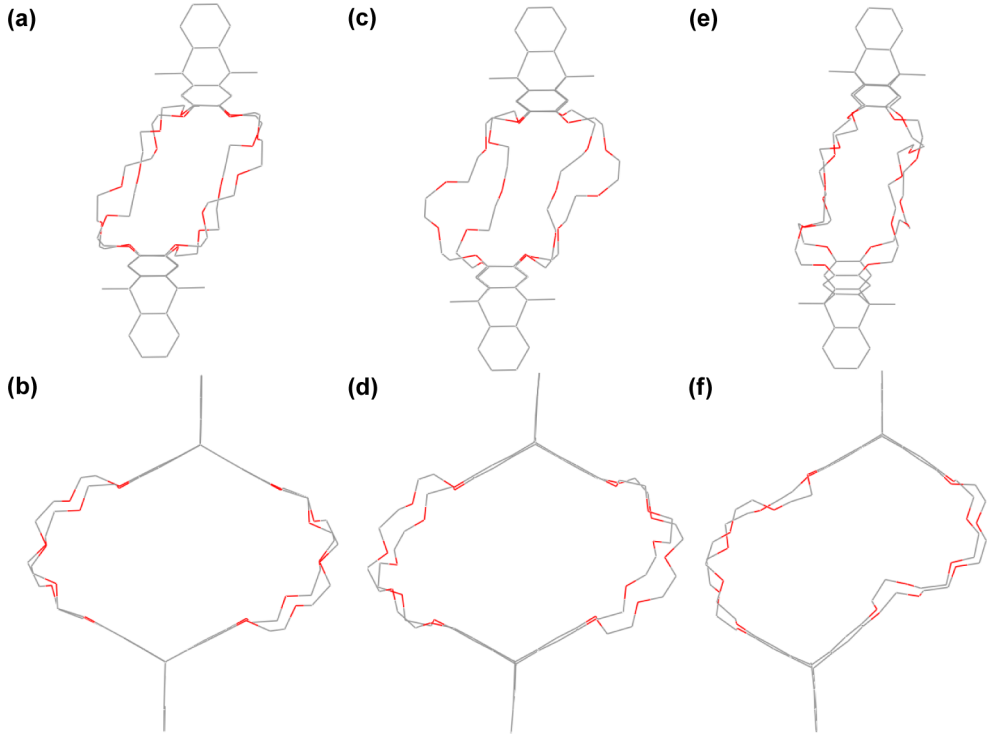

Figure 10. Crystal structures the complexes in the absence of guest(s). Side view (a) and top view (b) of $\mathbf{1{\cdot}4_2}$. Side view (c) and top view (d) of $\mathbf{1{\cdot}5_2}$. Side view (e) and top view (f) of $\mathbf{1{\cdot}6_2}$. Hydrogen atoms were omitted for clarity.

dx.doi.org/10.1021/jo400148b | J. Org. Chem. 2013, 78, 3235−3242

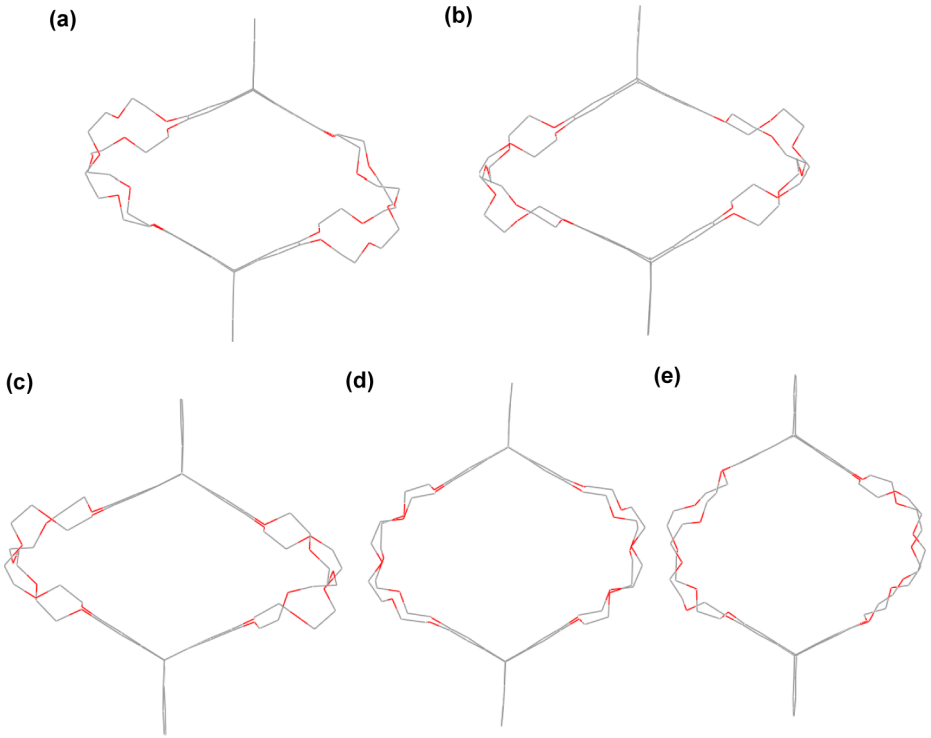

Figure 11. Top views of (a) **1**·**3**, (b) **1**·**7**, (c) **1**·**8**, (d) **1**·**10**$_2$, and (e) **1**·**11**. Solvent molecules and hydrogen atoms were omitted for clarity.

between **1** and paraquat derivatives **2b** and **2d** containing alkyl chains we reported previously,[9] the macrocyclic host also takes a rectangle-like structure by top view but an "I-like" conformation by side view,[11] which are obviously different from that of macrocyclic host **1** itself, and the distances for **c** of complexes **1**·**2b**$_2$ and **1**·**2d**$_2$ were 3.04 and 3.28 Å, respectively, which were also markedly less that of macrocyclic host **1** (8.04 Å). These results might be ascribed to the encapsulation of two guests inside the cavity of the host, which resulted in two triptycene moieties located in the same plane and enlarged central cavities of the host (13.85 × 9.91 Å^2 in **1**·**2b**$_2$ and 13.70 × 8.47 Å^2 in **1**·**2d**$_2$).

Compared with complexes **1**·**2b**$_2$ and **1**·**2d**$_2$, some changes for the conformations of host **1** in 1:2 complexes **1**·**4**$_2$, **1**·**5**$_2$, and **1**·**6**$_2$ were observed. As shown in Figure 10, the two triptycene moieties located nearly in the same plane, and the distances for **c** were about 5.93, 5.12, and 4.40 Å, respectively, which were a little larger than those of complexes **1**·**2b**$_2$ and **1**·**2d**$_2$. Moreover, the central cavity of the host in complexes **1**·**4**$_2$, **1**·**5**$_2$, and **1**·**6**$_2$ increased compared with host **1** itself but were smaller than those of complexes **1**·**2b**$_2$ and **1**·**2d**$_2$, which might be due to the existence of one PF_6^- counterion between the two guests in **1**·**2b**$_2$ and **1**·**2d**$_2$. In addition, the macrocyclic hosts in complexes **1**·**4**$_2$, **1**·**5**$_2$, and **1**·**6**$_2$ all took rectangle-like structures by top views as well, but the distances **a** were shorter than those of **1**·**2b**$_2$ and **1**·**2d**$_2$, while the distances **b** were longer than those of **1**·**2b**$_2$ and **1**·**2d**$_2$.

Furthermore, it was found that macrocyclic host **1** in 1:1 complexes **1**·**3**, **1**·**7**, and **1**·**8** took on "rhombus" conformations by top view (Figure 11a, b, and c), which were very different from the rectangle-like macrocyclic molecule **1** in the 1:2 complexes described above. The distances for **a** were almost equal to those for **b**, and the distances for **c** were about 6.08, 6.15, and 6.02 Å, respectively, which were all smaller than that of macrocyclic host **1** itself. For the complexes formed by host **1** and guests **10** and **11**, macrocyclic host **1** was changed from a rectangle-like conformation into a square-like one by top view (Figure 11d and e), which might be attributed to the encapsulation of two big guests into the cavity of host **1** at the same time.

Potassium-Ion-Controlled Binding and Release of the Guests in the Complexes. It was known that host **1** containing two DB30C10 moieties could bind potassium ions to form the stable complex and thus result in the decomplexation of the complexes between **1** and the cationic guests for the electrostatic repellent interactions,[3i,13] which made us further investigate the potassium ion-controlled release and binding process of the guest molecule in the host–guest complexes by a series of ^{1}H NMR experiments. As shown in Figure 12c, when 4.0 equiv of KPF_6 was added into solution of a complex **1**·**3**, the proton

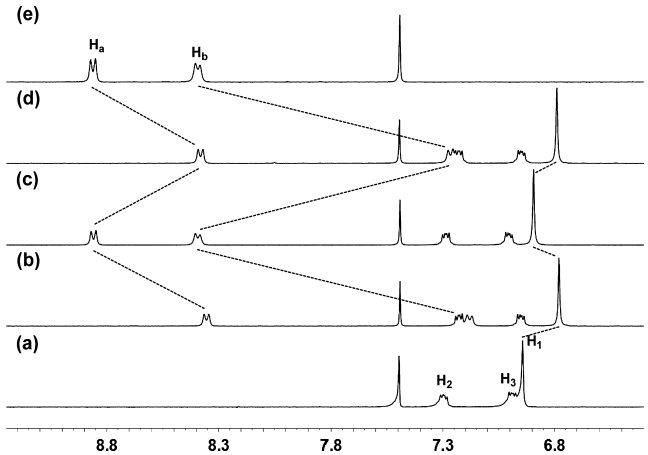

Figure 12. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, v/v, 298 K) of (a) free guest **3**, (b) **1** and 1.0 equiv of **3**, (c) the solution of panel b with 4.0 equiv of KPF_6 added, and (d) the solution of panel c with 6.0 equiv of 18-crown-6 added. $[\mathbf{1}]_0$ = 3.0 mM.

dx.doi.org/10.1021/jo400148b | J. Org. Chem. 2013, 78, 3235–3242

signals of the complex disappeared, while the proton signals of the decomplexated species were observed. However, when 6.0 equiv of 18-crown-6 ether was added into the above system, the proton signals of complex **1·3** were recovered (Figure 12d). Thus, the ion-controlled binding and release of guest **3** in the complex could be easily performed by adding and removing the potassium ions. Similarly, K^+ ion-controlled binding and releasing of guests **6** and **11** in complexes **1·6**$_2$ and **1·11** were also found.[11]

CONCLUSION

In summary, we proved that the triptycene-derived macrotricyclic polyether containing two dibenzo-[30]-crown-10 cavities forms stable complexes with different functionalized paraquat derivatives, diquat, and a 2,7-diazapyrenium salt. Especially, it was found that depending on the guests with different terminal groups and structures, the macrotricyclic polyether forms 1:1, 1:2, or supramolecular poly[3]pseudorotaxane-type complexes in different complexation modes in both solution and solid state. Notably, the conformation of the macrotricyclic polyether in the complexes was efficiently adjusted by the encapsulated guests, which was to some extent similar to the substrate-induced fit of enzymes. Moreover, the binding and releasing of the guests in the complexes could also be controlled by the removing and adding of potassium ions. The specific complexation of this macrotricyclic host with extensive organic guests and the interesting guest-induced conformational changes of the macrocyclic host may provide us the opportunity for further design and construction of new assemblies and functional materials with specific structures and properties, which are now underway.

EXPERIMENTAL SECTION

The guests **3**−**7**, **9**, **10**[13b,14] were prepared according to the published procedures.

Compound 8. A mixture of 4,4′-bipyridine (0.78 g, 5.0 mmol) and 1-bromo-4- (bromomethyl)benzene (3.75 g, 15.0 mmol) in CH_3CN (150 mL) was refluxed for 48 h. The resulting mixture was concentrated under reduced pressure, and a yellow oil was obtained, which was dissolved in acetone and treated with NH_4PF_6. The solution was stirred at ambient temperature until clear. Then acetone was removed, and the solid precipitate was collected by filtration, washed with water, and dried under vacuum to yield compound **8** (1.59 g, 41%) as a white solid. Mp: 268−270 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 5.79 (s, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.67 (d, J = 8.4 Hz, 4H), 8.37 (d, J = 6.6 Hz, 4H), 8.96 (d, J = 6.6 Hz, 4H). ^{13}C NMR (75 MHz, CD_3CN): δ 63.6, 123.6, 127.2, 131.1, 131.5, 132.3, 145.4, 150.1. HR ESI-MS: m/z calcd for $[M - PF_6^-]^+$ $C_{24}H_{20}Br_2F_6N_2P$, 638.9635, found 638.9604.

2,7-Dipropyl-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]-phenanthroline 12. A mixture of $LiAlH_4$ (0.87 g, 20 mmol), $AlCl_3$ (1.0 g, 7.5 mmol), and 2,7-dipropylbenzo [*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (1g, 3 mmol) in THF (100 mL) was stirred for 1 h at room temperature and then refluxed for 2 h. After cooling to ambient temperature, the mixture was poured into 200 mL of water and filtered. The filtrate was concentrated under reduced pressure. The organic layer was dried over anhydrous sodium sulfate. After the solvent was removed under reduced pressure, 2,7-dipropyl-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthroline **12** (0.7 g, 83%) was obtained as a pale yellow solid. Mp: 151−153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, J = 7.5 Hz, 6H), 1.65 (m, 4H), 2.56 (t, J = 7.5 Hz, 4H), 3.94 (s, 8H), 7.12 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.3, 17.9, 53.9, 56.6, 118.9, 125.0, 128.8. EI-MS: m/z 293 $[M]^+$. Anal. Calcd for $C_{20}H_{26}N_2{\cdot}0.5H_2O$: C 79.16, H 8.97, N 9.23. Found: C 79.21, H 8.82, N 9.08.

Compound 11. A mixture of 2,7-dipropyl-1,2,3,6,7,8-hexahydrobenzo-[*lmn*][3,8]phenanthroline (0.16 g, 0.5 mmol) and DDQ (0.64 g, 2.8 mmol) in CH_3CN (37 mL) was stirred at 40 °C for 48 h. To the mixture was dropwise added HCl, and the solid was filtered and washed with CH_3CN. The crude product was dissolved in acetone and treated with NH_4PF_6, and the solution was stirred at ambient temperature until clear. After the solvent was removed, the solid precipitate was collected by filtration, washed with water, and dried under vacuum to give compound **11** (0.19 g, 64%) as a brown solid. Mp: 286−288 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 1.08 (t, J = 7.5 Hz, 6H), 2.39 (m, 4H), 5.05 (t, J = 7.5 Hz, 4H), 8.84 (s, 4H), 9.92 (s, 4H). ^{13}C NMR (75 MHz, CD_3CN): δ 9.5, 24.7, 65.0, 126.6, 129.5, 129.8, 141.1. ESI-MS: m/z 603.7 $[M + Na]^+$. Anal. Calcd for $C_{20}H_{22}F_{12}N_2P_2{\cdot}0.5CH_3CN{\cdot}0.6NH_4PF_6$: C 36.10, H 3.74, N 6.21. Found: C 36.18, H 3.82, N 6.32.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for new compounds. ^{1}H−^{1}H COSY spectra and ROESY spectra for the complexes. Determination of the association constants. ESI-MS for the complexes. X-ray crystallographic files (CIF) for the complex **1·4**$_2$, **1·5**$_2$, and **1·10**$_2$. 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.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (91127009, 20972162) and the National Basic Research Program (2011CB932501) for financial support.

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