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Complexation of Triptycene-Derived Macrotricyclic Host with Bisparaquat Derivative and Self-Folding Guest: A Switchable Process Controlled by K^+ Ions

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Triptycene-derived cylindrical macrotricyclic host with two dibenzo-30-crown-10 cavities could form stable 1∶1 complexes with not only polyether linked bisparaquat derivative but also a self-folding A-D-A guest in solution and/or solid state. Moreover, it was found that switchable processes between the host and both the bisparaquat derivative and the self-folding guest could be further controlled by potassium ions.

Keywords complexation, macrotricyclic host, paraquat, triptycene, switchable

Introduction

In host-guest chemistry, it is always attractive and challenging for a synthetic macrocyclic host with the capability of binding different kinds of organic guests in different complexation modes,[1,2] because such a synthetic host could provide a lot of opportunities in molecular recognition and self-assembly. Moreover, a macrocyclic host, which can encapsulate two or more same[3] or different[4] guests inside its cavity, is also powerful in developing various supramolecular systems with specific structures and properties.

In previous work, we reported a novel triptycene-derived macrotricyclic host **1**[5] with two dibenzo-30-crown-10 cavities and one central cavity, and found that it could form 1∶2 stable complexes with two same molecules of paraquat derivatives, such as **2**.[6] As a continuing work, we herein report the complexation of the host **1** with guest **3** (Figure 1) in which two paraquat subunits were linked by a flexible polyether chain, and a self-folding A-D-A guest **4** which contains two paraquat subunits and a naphthalene group. It was unexpectedly found that host **1** and guest **3** could form a 1∶1 complex **1·3** in both solution and solid state, in which the guest adopts an '*S*' conformation. Moreover, self-folding guest **4** could also be included in the cavity of host **1** to form a stable 1∶1 complex **1·4**, and a potassium ion controlled switchable process in the complex was achieved as well. Although foldamers have attracted much attention in the past two decades,[7] to our knowledge, few examples on self-folding molecules or foldamers used as guests in host-guest systems were reported.[8] This new host-guest complexation could find potential applications in molecular assembly and molecular machines.

Experimental

Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a DMX300 NMR. Tetramethylsilane (TMS) was used as an internal standard, with chemical shifts expressed in parts per million (ppm) downfield from the standard. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. ESI mass spectra were obtained on a Finnigan Surveyor MSQ Plus mass spectrometer. Elementary analyses were performed in the Analytic Laboratory of this Institute. Flash column chromatography was carried out with silica gel (100—200 mesh). Other reagents and solvents were purchased from common commercial sources, and were used as received or purified by distillation from appropriate drying agents.

Compounds 4,[8] 5[9] and 6[3j] were prepared according to the published procedures

Synthesis of compound 3 A mixture of compound **5** (0.377 g, 0.75 mmol) and 1-(2-methoxyethyl)-4,4'-bipyridine hexafluorophosphate **6** (0.54 g, 1.5 mmol) in CH_3CN (30 mL) was refluxed for 72 h. The resulting mixture was concentrated under reduced pressure, and yellow oil was obtained, which was dissolved in acetone

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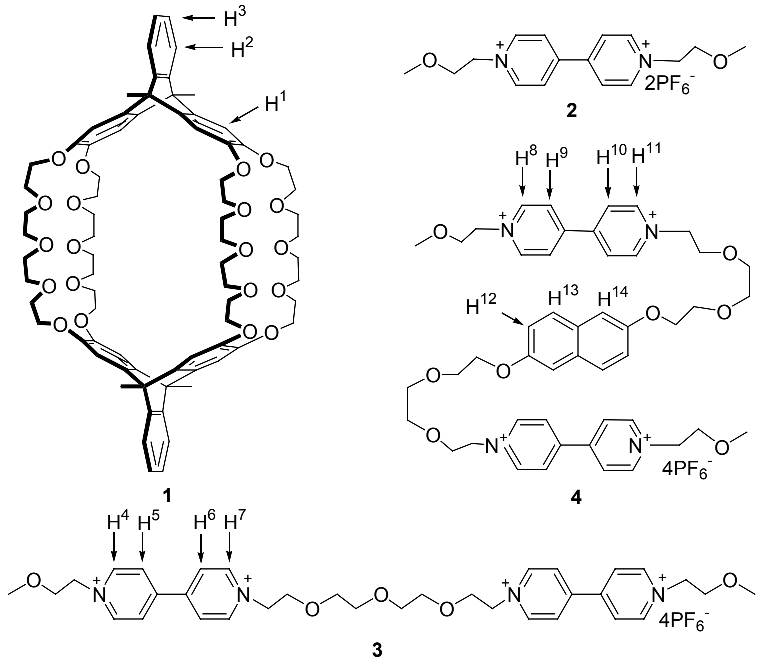


Figure 1 Structures and proton designations of host **1**, and guests **2**—**4**.

and then treated with NH_4PF_6. After the solution was stirred at ambient temperature until clear, the solvent was removed, and the solid precipitate was collected by filtration, washed with water, and then dried under vacuum to yield 0.76 g (87%) of compound **3** as a pale yellow solid. M.p.: 183—185 ℃. ^{1}H NMR (300 MHz, CD_3COCD_3-d_6) δ: 3.37 (s, 6H), 3.58 (dd, J=5.6, 3.3 Hz, 4H), 3.69 (dd, J=5.6, 3.3 Hz, 4H), 4.00—4.10 (m, 4H), 4.10—4.20 (m, 4H), 5.03—5.20 (m, 4H), 8.79 (d, J=5.7 Hz, 8H), 9.34 (d, J=5.6 Hz, 8H). ^{13}C NMR (75 MHz, CD_3COCD_3-d_6) δ: 59.1, 62.7, 69.8, 70.9, 71.0, 71.2, 127.7, 127.8, 147.4, 151.2. ESI-MS *m/z*: 440.7 $[M-2PF_6^-]^{2+}$, 245.9 $[M-3PF_6^-]^{3+}$, 148.0 $[M-4PF_6^-]^{4+}$. Anal. calcd for $C_{34}H_{46}F_{24}N_4O_5P_4 \cdot H_2O$: C 34.36, H 4.07, N 4.71; found C 34.03, H 3.90, N 4.87.

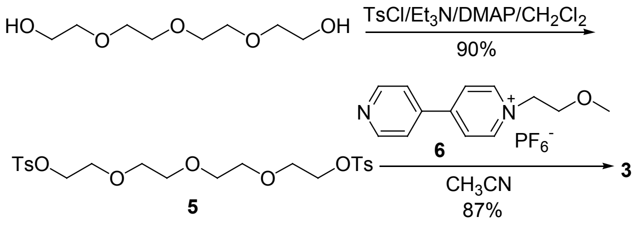
Crystal data for complex 1·3 CCDC 932062, $C_{114}H_{114}F_{24}N_6O_{25}P_4$, M_w=2578.23, crystal size 0.20×0.15×0.1 mm^3, monoclinic, space group $P2(1)/n$, a=16.591(3) Å, b=20.184(4) Å, c=19.083(4) Å, α=90°, β=94.52(3)°, γ=90°, V=6370(2) Å^3, Z=2, D_c=1.344 Mg/m^3, T=173(2) K, μ=0.163 mm^{-1}, 11449 reflections measured, 11146 unique (R_{int}=0.1844), final R indices [$I>2\sigma(I)$]: R_1=0.1934, wR_2=0.4488, R indices (all data): R_1=0.2561, wR_2=0.4853.

Results and Discussion

Synthesis of guest 3

Synthesis of guest **3** was outlined in Scheme 1. Starting from the tetraethylene glycol, the bisparaquat derivative **3** linked by a polyether chain was conveniently synthesized in two steps. First, reaction of the tetraethylene glycol and tosyl chloride in the presence of Et_3N and DMAP gave compound **5**, which was then reacted with 1-(2-methoxyethyl)-4-(pyridin-4-yl)pyridinium **6** to afford compound **3** in 87% yield. Compound **3** was characterized by ^{1}H NMR, ^{13}C NMR, MS spectrum, and elemental analysis.

Scheme 1 Synthesis of guest **3**



Complexation between triptycene-derived macrotricyclic host and guest 3

With the guests in hand, the complexation between host **1** and guest **3** in solution was then investigated. As shown in Figure 2, the ^{1}H NMR spectrum of a 1 ∶ 1 mixture of **1** and **3** in $CD_3CN/CDCl_3$ (1 ∶ 1, V ∶ V) exhibited great difference from those for **1** and **3**. The H^1 proton signal of the benzene ring in **1** showed an obvious upfield shift, which might be attributed to the π-π interaction between the electron-rich triptycene moiety and the electron-poor paraquat moieties. Similarly, the protons H^4, H^5, H^6 and H^7 also shifted upfield due to their positions in the shield region of the aromatic rings of host **1**. These observations indicated that host **1** and guest **3** formed a stable complex, and both of the paraquat rings in **3** were included in the cavity of **1**. Furthermore, a quantitative estimate between **1** and **3** was determined by the ^{1}H NMR spectroscopic titrations. Consequently, a 1 ∶ 1 complex **1·3** was formed by

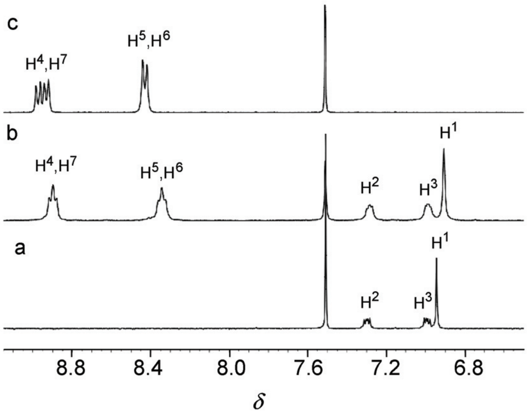


Figure 2 Partial ^1H NMR spectra (300 MHz, 298 K, CD_3CN : $CDCl_3$=1 : 1, *V* : *V*) of (a) free **1**, (b) **1** and 1.0 equiv. of **3**, (c) free **3**. $[\mathbf{1}]_0$=3.0 mmol/L.

monitoring the changes of the chemical shift of proton H^1. Accordingly, the average association constant K_{av} for the 1 : 1 complex **1·3** was calculated to be 1.39 $(\pm 0.04)\times 10^3$ $L\bullet mol^{-1}$.[10,11]

Formation of complex **1·3** was also supported by the electrospray ionization mass spectrum (ESI-MS).[10] As a result, the strong peaks at *m/z* 1103.6, 687.4, 479.6 for $[\mathbf{1}\cdot\mathbf{3}-2PF_6^-]^{2+}$, $[\mathbf{1}\cdot\mathbf{3}-3PF_6^-]^{3+}$, $[\mathbf{1}\cdot\mathbf{3}-4PF_6^-]^{4+}$, respectively, were observed, which was consistent with formation of complex **1·3**.

Fortunately, we obtained the single crystal of complex **1·3**, and its X-ray crystal structure provided further evidence for formation of complex **1·3**. As shown in Figure 3, guest **3** was included in the central cavity of host **1** to form a 1 : 1 complex, which is consistent with that in solution. In complex **1·3**, host **1** adopts a symmetrical conformation, while the guest molecule existed as an *S*-type structure with two paraquat moieties situated at the sides of the crown ether moieties of the host, respectively. The complex was stabilized by multiple non-covalent interactions, including the multiple C—H···π interactions between the protons of ether chain of **3** and the aromatic rings of the triptycene skeleton of **1** with the distances of 2.88 (a), and 2.76 Å (d); multiple C—H···O hydrogen bonding interactions between the protons of the guest and the polyether oxygen atoms of the DB30C10 moiety with the distances of 2.55 (c), 2.42 (d), 2.63 (e), 2.45 (f), 2.26 (g), 2.50 (h), 2.64 (i), and 2.62 Å (j), respectively. These multiple intermolecular interactions might play an important role in formation of complex **1·3**.

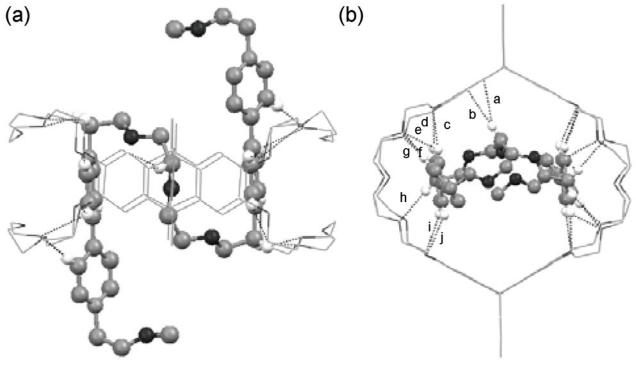


Figure 3 Side view (a) and top view (b) of the crystal structure of complex **1·3**. Dotted lines denote the non-covalent interactions. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the non-covalent interactions are omitted for clarity.

Complexation between triptycene-derived macrotricyclic host and self-folding A-D-A guest 4

Formation of complex **1·3** stimulated us to further design and synthesize guest **4** containing two paraquat subunits and a naphthalene group, and investigated the complexation between host **1** and guest **4**. Similar to that of **1** and **3**, the ^1H NMR spectral experiments (Figure 4) showed that a stable 1 : 1 complex between host **1** and guest **4** in solution was formed, and the complexation between **1** and **4** was also a fast exchange process. Correspondingly, the H^1 proton signal of the benzene ring in **1** showed an upfield shift, while the H^8, H^9, H^{10} and H^{11} proton signals of the bipyridinium, and the H^{12}, H^{13} and H^{14} proton signals of the naphthalene group in guest **4** all shifted upfield as well, which were attributed to their positions in the shield region of the aromatic rings of host **1**. Moreover, the association constant for **1·4** was calculated to be $1.00(\pm 0.03)\times 10^3$ $L\bullet mol^{-1}$.[10] The 2D ROESY spectral experiment of complex **1·4** was further carried out to investigate the interactions between the two components. The results[10] showed that the NOE effects between protons H^8, H^{11} of the guest and the crown protons of the host were observed, respectively, which suggested that self-folding A-D-A guest **4** could be included in the cavity host **1**, and the bipyridinium ring of **4** might be more closed to the crown ether units of **1**.

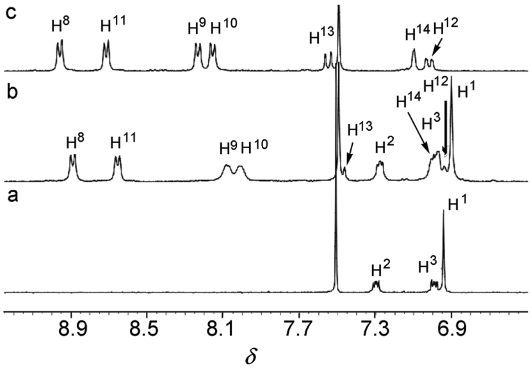


Figure 4 Partial ^1H NMR spectra (300 MHz, 298 K, CD_3CN : $CDCl_3$=1 : 1, *V* : *V*) of (a) free **1**, (b) **1** and 1.0 equiv. of **4**, (c) free **4**. $[\mathbf{1}]_0$=3.0 mmol/L.

The ESI-MS of complex **1·4**[10] showed the strong peaks at *m/z* 536.82 and 763.93 for $[\mathbf{1}\cdot\mathbf{4}-4PF_6^-]^{4+}$ and $[\mathbf{1}\cdot\mathbf{4}-3PF_6^-]^{3+}$, respectively, which provided another evidence for formation of the complex.

In addition, we also tried to obtain the single crystal of complex **1·4** suitable for X-ray diffraction analysis for several times, but they were all unsuccessful. Instead, we obtained the crystal structure of guest **4**,[8] which showed that it adopts an *S*-type self-folding structure stabilized by a couple of C—H···F interactions between the methylene protons of the linked ether chain and the fluorine atoms, and also the anion-π interactions between PF_6^- and two bipyridinium rings of **4**. This specific self-folding structure benefited it to be included by host **1** with a large central cavity.

K^+ ion-controlled binding and release of the guest in the complex

Moreover, we also investigated the potassium ions controlled switchable process between the host and the self-folding guest by a series of ^1H NMR experiments (Figure 5). Consequently, it was found that the ^1H NMR spectrum of a 1∶1 mixture of **1** and guest **4** showed formation of complex **1·4**. When six equivalents of KPF_6 was added to the above solution, the proton signals of the complex totally disappeared, while the proton signals of guest **4** and the aromatic proton signals of the host all shifted downfield almost to the original positions (Figure 5c). These indicated that complexation between the crown ethers and the potassium ions occurred, which resulted in the release of the cationic organic guest **4** from the cavity of the host. When 8 equivalents of 18-crown-6 was then added to the above system, it was found that the proton signals of complex **1·4** recovered (Figure 5d), suggesting complex **1·4** formed again. Thus, the release and binding process of the self-folding A-D-A guest **4** in the complex could be easily controllable switched by addition and removal of the potassium ions. Similarly, K^+ ion-controlled binding and release of guest **3** in complex **1·3** was also found.[10]

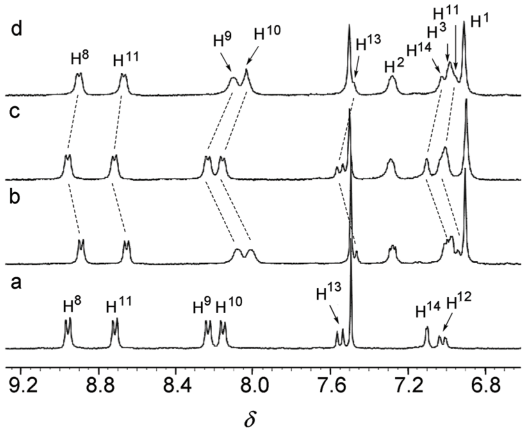


Figure 5 Partial ^1H NMR spectra (300 MHz, CD_3CN∶$CDCl_3$ = 1∶1, 298 K) of (a) free guest **4**, (b) host **1** and 1.0 equiv. of **4**, (c) the mixture obtained after adding 6.0 equiv. of KPF_6 to the solution of a, (d) the mixture obtained after adding 8.0 equiv. of 18-crown-6 to the solution of b. $[\mathbf{1}]_0$ = 3.0 mmol/L.

Conclusions

In conclusion, we have proved that triptycene-derived macrotricyclic host **1** with two dibenzo-30-crown-10 cavities could form stable 1∶1 complexes with not only the bisparaquat derivative **3** linked by a polyether chain in both solution and solid state, but also a self-folding A-D-A guest **4**. Moreover, potassium ion controlled switchable processes between the host and both bisparaquat derivative **3** and the self-folding guest were also achieved. Based on these developed host-guest systems, our further studies will focus on the applications of the novel synthetic host in molecular assembly and molecular machines, which are now in progress.

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