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Formation of 1:2 Host−Guest Complexes Based on Triptycene-Derived Macrotricycle and Paraquat Derivatives: Anion−π Interactions between PF_6^- and Bipyridinium Rings in the Solid State

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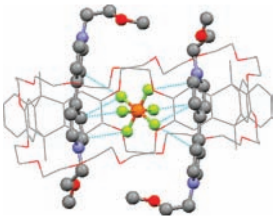
ABSTRACT



A triptycene-derived macrotricyclic host containing two dibenzo-[30]-crown-10 moieties forms stable 1:2 host−guest complexes with paraquat derivatives in both solution and the solid state, in which anion−π interactions between PF_6^- and the bipyridinium rings play an important role. Moreover, it was found that binding and release of the guest molecules in the complexes could be easily controlled by the addition and removal of potassium ions.

The inclusion of two or more guest molecules in the cavity of a host is not only a common issue in biological systems but also an important and challenging goal of supramolecular chemistry.[1] Stable ternary host−guest complexes in which a host includes two different guest organic molecules are usually formed by the effective charge transfer, electrostatic, or hydrogen bonding interactions between the two guests.[2] Compared with ternary complexes, inclusion of two identical organic guests in the cavity of a host is relatively difficult due to the lack of effective attractive interactions between the guests.[3]

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Interactions between anions and various π-electron deficient (π-acidic) arenes have attracted increasing interest both theoretically[4] and experimentally[5] in recent years, owing to the important roles of anions in multidisciplinary areas of research.[6] Moreover, Frontera et al.[7] also proved that anion$-\pi$ interactions played a crucial role in a biological system. Since the first crystallographic example of anion$-\pi$ interactions was reported in 2004,[8] more and more experimental evidence on anion$-\pi$ interactions in crystals and/or in solution has been reported. However, anion$-\pi$ interactions were mostly observed with neutral electron-deficient aromatic rings, such as perfluoroarenes and triazines, and halide ions. Examples of the recognition of other anions based on anion$-\pi$ interactions are rare,[5e] whereas reports on anion$-\pi$ interactions based on charged electron-deficient aromatic rings are also limited.[5g]

Recently, we[9] synthesized a novel triptycene-derived macrotricyclic host **1** containing two dibenzo-30-crown-10 (DB30C10) moieties and found that it forms a 1:2 complex with (9-anthracylmethyl)benzylammonium salt, in which the 9-anthracyl groups were selectively positioned inside the cavity of the host.[10] Herein we report the complexation of **1** with paraquat derivatives **3a**$-$**d** (Figure 1). It was found that **1** forms stable 1:2 complexes with **3** in both solution and the solid state, which is completely different from those of host **2** with two dibenzo-24-crown-8 moieties.[11] Interestingly, we also found that anion$-\pi$ interactions between PF_6^- and the bipyridinium rings of the guest play an important role in the formation of the complexes, which, to our knowledge, has not been reported in similar host$-$guest complexes.

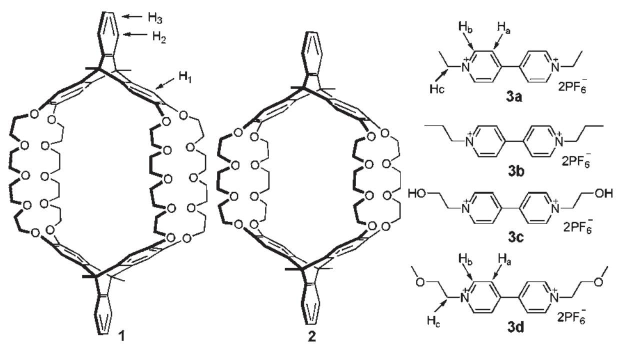

Figure 1. Structures and proton designations of hosts **1**$-$**2** and guests **3a**$-$**d**.

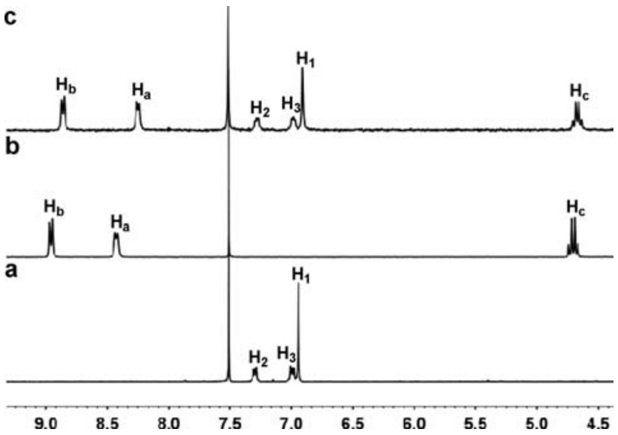

Figure 2. Partial ^1H NMR spectra ($CD_3CN/CDCl_3$ = 1, 300 MHz, 298 K) of (a) free **1**, (b) free **3a**, and (c) **1** and 2.0 equiv of **3a**. $[\mathbf{1}]_0$ = 3.0 mM.

First, we tested the complexation between triptycene-derived host **1** and guests **3a**$-$**d**[10] in solution. As a result, when **1** (3.0 mM) and **3** (6.0 mM) were mixed in CH_3CN and $CHCl_3$ (1:1, v/v), an orange solution was immediately obtained due to the charge transfer interaction between the electron-rich aromatic rings of host **1** and the electron-poor pyridinium rings of the guests. As shown in Figure 2, the ^1H NMR spectrum of a 1:2 solution of host **1** and guest **3a** in 1:1 (v/v) chloroform/acetonitrile exhibited only one set of peaks, which indicated fast-exchange complexation between the host and the guest. The H_a and H_b proton signals of the pyridinium ring and the H_c proton signal of **3a** showed a significant upfield shift ($\Delta\delta$ 0.18 ppm for H_a, 0.10 for H_b, and 0.03 for H_c), which might be due to the strong shielding effect of the aromatic rings in **1**. Similarly, the signals of protons H_1, H_2, and H_3 also shifted upfield,

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(14) Crystal data for $\mathbf{1}\cdot\mathbf{3d}_2\cdot2CH_3CN$: $C_{112}H_{142}F_{24}N_6O_{24}P_4$, M_w = 2536.20, crystal size 0.53 × 0.31 × 0.11 mm^3, triclinic, space group $P\bar{1}$, a = 13.254(3) Å, b = 14.157(3) Å, c = 17.402(4) Å, α = 75.74(3)°, β = 89.09(3)°, γ = 68.84(3)°, U = 2941.7(10) Å^3, Z = 1, D_c = 1.432 Mg/m^3, T = 173(2) K, μ = 0.175 mm^{-1}, 24 324 reflections measured, 11 898 unique (R_{int} = 0.0689), final R indices [$I > 2\sigma(I)$]: R_1 = 0.0773, wR_2 = 0.1974, R indices (all data): R_1 = 0.0946, wR_2 = 0.2112.

which is attributed to their positions in the shielding region of the pyridinium rings of **3a**. These observations suggested that a stable complex between **1** and **3a** was formed. Furthermore, ^{1}H NMR spectroscopic titrations afforded a quantitative estimate between **1** and **3a** by monitoring the changes of the chemical shift of proton H_1. A mole ratio plot showed that a 1:2 complex of $\mathbf{1{\bullet}3a_2}$ was formed,[12] which is different from a 1:1 complex between host **2** and the same guest.[11] Accordingly, the average association constant K_{av} for $\mathbf{1{\bullet}3a_2}$ was calculated to be 10.0 (±0.2) × 10^2 M^{-1}.[13] Similar to the case of **3a**, host **1** also forms 1:2 complexes with paraquat derivatives **3b**–**d**, and the average association constants K_{av} for $\mathbf{1{\bullet}3b_2}$, $\mathbf{1{\bullet}3c_2}$, and $\mathbf{1{\bullet}3d_2}$ were calculated to be 4.8 (±0.1) × 10^2, 12.8 (±0.3) × 10^2, and 6.8 (±0.1) × 10^2 M^{-1}, respectively.[13]

The electrospray ionization mass spectra (ESI-MS) provided more evidence for the formation of the 1:2 host–guest complexes. Thus, the strongest peak at *m*/*z* 1022.51 for $[\mathbf{1{\bullet}3a_2}\text{-}2PF_6^-]^{2+}$ was found by using a solution of **1** and **3a** in 1:1 chloroform and acetonitrile (Figure 3). Similarly, the peak at *m*/*z* 1050.54 for $[\mathbf{1{\bullet}3b_2}\text{-}2PF_6^-]^{2+}$, the peak at *m*/*z* 1054.40 for $[\mathbf{1{\bullet}3c_2}\text{-}2PF_6^-]^{2+}$, and the peak at *m*/*z* 1082.54 for $[\mathbf{1{\bullet}3d_2}\text{-}2PF_6^-]^{2+}$ were also observed under the same conditions.[13]

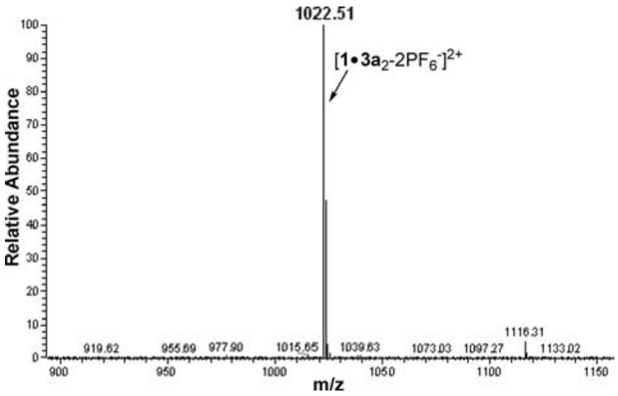

Figure 3. ESI-MS spectrum of 1:2 complex $\mathbf{1\cdot 3a_2}$.

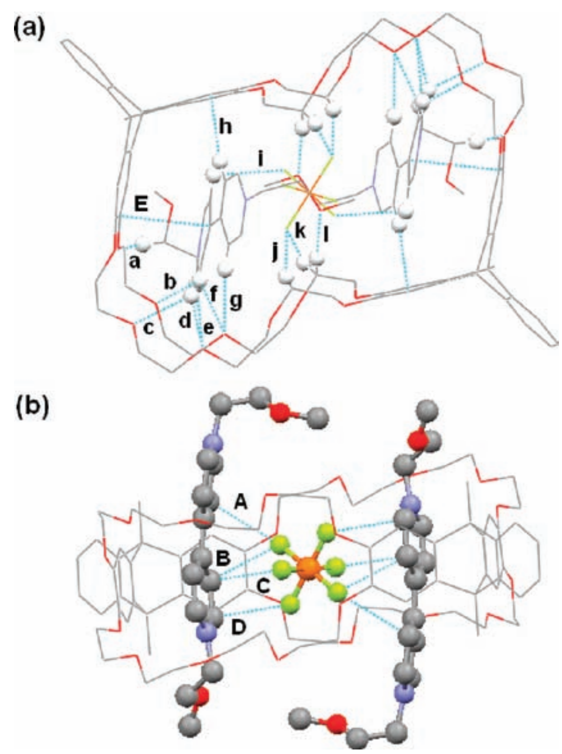

Figure 4. View of the crystal structure of $\mathbf{1{\bullet}3d_2}$. Dashed lines denote the noncovalent interactions between the two components. C–H···O hydrogen bond distances (Å): a = 2.56, b = 2.53, c = 2.43, d = 2.38, e = 2.63, f = 2.70, g = 2.36, l = 2.64. C–H···F hydrogen bond distances (Å): i = 2.63, j = 2.52, k = 2.54. Solvent molecules, PF_6^- ions, and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

Further support for the formation of complex $\mathbf{1{\bullet}3d_2}$ came from its X-ray crystal structure.[14] A single crystal of $\mathbf{1\cdot 3d_2}$ suitable for X-ray diffraction analysis was obtained by vapor diffusion of diisopropyl ether into a solution of **1** and **3d** in 1:1 (v/v) $CHCl_3/CH_3CN$. As shown in Figure 4, host **1** and guest **3d** formed a 1:2 complex in the solid state, which is consistent with that in solution. In complex $\mathbf{1{\bullet}3d_2}$, the macrotricyclic host adopts a rectangular parallelepiped conformation, and two guests of **3d** thread the central cavity of the host. Interestingly, it was found that one PF_6^- ion is situated between the two bipyridinium rings and connected them through not only multiple C–H···F hydrogen bonding but also anion–π interactions with distances of 3.12 (A), 2.99 (B), 2.99 (C), and 2.99 Å (D), respectively (Figure 4b). The complex was also stabilized by the multiple C–H···O hydrogen bonding interactions between the aromatic protons of the bipyridinium rings and the polyether oxygen atoms of the DB30C10 moiety, and between the protons in the DB30C10 moiety and the oxygen atoms of the side chain of the guest. Moreover, C–H···π interaction between proton H_a in the pyridinium ring and the benzene ring of the triptycene moiety with a distance (Å) of 2.70 (h) and a π–π interaction between a benzene ring of the triptycene moiety and a paraquat ring of the guest with a distance of 3.34 Å (E) were also observed. Interestingly, it was further found that the macrocyclic molecule **1** packs in a tubular channel, which extends in the crystallographic *b* direction with the paraquat rings threaded inside the central rings.[13] We also obtained a yellow single crystal of complex $\mathbf{1\cdot 3b_2}$ suitable for X-ray diffraction analysis by vapor diffusion of diisopropyl ether into a solution of **1** and **3b** in 1:1 (v/v) $CHCl_3/CH_3CN$.[13] Because of the lack of heavy atoms in the complex and the presence of disordered PF_6^- and solvent molecules, the quality of the X-ray diffraction data was very low. However, the overall geometry of the complex was clearly established as being similar to that of

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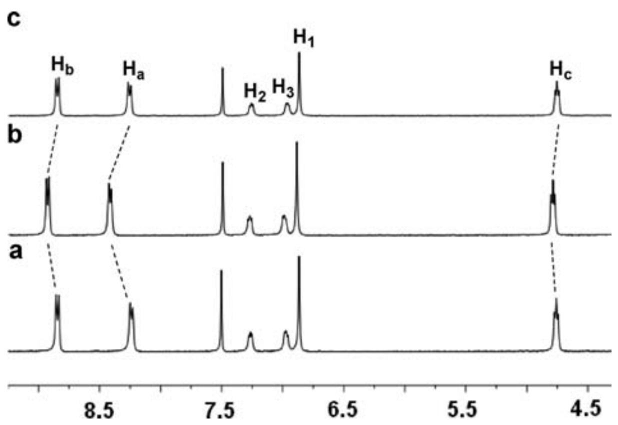

Figure 5. Partial ^{1}H NMR spectra ($CDCl_3/CD_3CN$ = 1:1, 300 MHz, 298 K) of (a) host **1** and 2.0 equiv of **3d**, (b) the mixture obtained after adding 6.0 equiv of KPF_6 to the solution of a, and (c) the mixture obtained after adding 8.0 equiv of 18-crown-6 to the solution of b. $[\mathbf{1}]_0$ = 3.0 mM.

$\mathbf{1{\bullet}3d_2}$. Complex $\mathbf{1{\bullet}3b_2}$ also showed 1:2 host–guest complexation in the solid state, and multiple noncovalent interactions including anion–π interactions between PF_6^- and two bipyridinium rings of the guest play an important role in the formation of the stable complex.

Because host **1** containing two DB30C10 moieties forms a 1:2 complex with potassium ions,[13] the consequent complexation of the cations would introduce extra electrostatic repellent force to the cationic organic guest molecules and dissociate the previously formed host–guest complex. Moreover, 18-crown-6 is known to be a very strong sequestering agent for potassium ions.[15] These results encouraged us to further investigate the potassium ion-controlled binding and release of the guest molecules in complex $\mathbf{1}\cdot\mathbf{3}_2$. Consequently, a series of ^{1}H NMR experiments were carried out. As shown in Figure 5a, the ^{1}H NMR spectrum of a 1:2 mixture of **1** and guest **3d** showed formation of complex $\mathbf{1}\cdot\mathbf{3d}_2$. When excess KPF_6 was added to the above solution, we found that the proton signals of the complex totally disappeared, while the proton signals of guest **3d** shifted downfield almost to the original positions. Moreover, the aromatic proton signals of the host molecule shifted nearly to the original positions, while the peak shape of the crown ether region had a big change. These observations indicated that the potassium ion bonded to the crown ether moiety, which resulted in the release of the guest **3d** from the cavity of the host molecule. When excess 18-crown-6 was added to the above system, it was further found that the proton signals of complex $\mathbf{1}\cdot\mathbf{3d}_2$ recovered (Figure 5c), which suggested that complex $\mathbf{1}\cdot\mathbf{3d}_2$ formed again. Thus, the ion-controlled binding and release of guest **3d** could be easily performed by addition and removal of the potassium ions.

In conclusion, we have demonstrated that the triptycene-derived macrotricyclic host containing two dibenzo-[30]-crown-10 moieties forms 1:2 complexes with paraquat derivatives in solution and in the solid state. Multiple noncovalent interactions, especially, anion–π interactions between PF_6^- and the bipyridinium rings played an important role in the formation of the stable complexes. Moreover, we found that binding and release of the guest molecules in the complexes could be easily controlled by the addition and removal of potassium ions. The results presented here will provide us the opportunity to further develop new supramolecular assemblies with specific structures and properties, which are now underway in our laboratory.

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Supporting Information Available. The comparison of ^{1}H NMR spectra between **1** and **3b**–**d**. ^{1}H–^{1}H COSY, ^{1}H–^{1}H ROESY, ESI-MS spectra of complexes $\mathbf{1}\cdot(\mathbf{3a}\text{–}\mathbf{d})_2$. Determination of the average association constants for the complexes. X-ray crystallographic files (CIF) for the complexes $\mathbf{1}\cdot\mathbf{3b}_2$ and $\mathbf{1}\cdot\mathbf{3d}_2$. This material is available free of charge via the Internet at http://pubs.acs.org.