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Formation of Ternary Complexes between a Macrotricyclic Host and Hetero-Guest Pairs: An Acid–Base Controlled Selective Complexation Process

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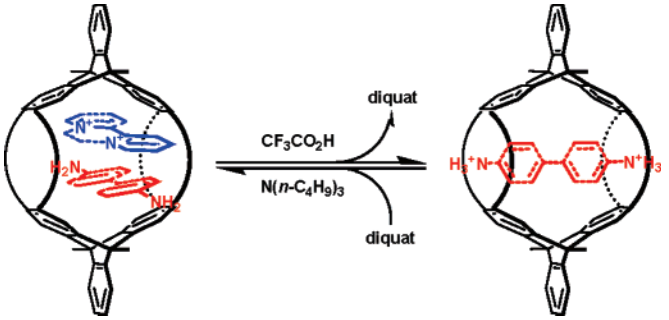
ABSTRACT



A triptycene-based cylindrical macrotricyclic host can include diquat and electron-rich aromatics simultaneously to form stable ternary complexes, which is stabilized not only by a charge-transfer (CT) interaction between electron-rich and electron-deficient guests but also by the face to face π-stacking interactions between the host and the guests. Moreover, a selective complexation process between a ternary complex containing benzidine and a binary complex can be effectively controlled by the use of acid and base.

The inclusion of two or more guest molecules in a host[1] has attracted increasing interest because it offers unique opportunities to study bimolecular reactions[2] and molecular recognition[3] in microenvironments. In 2001, Kim et al.[4] reported the first stable ternary complex formation in CB[8], which is driven and stabilized by a charge-transfer (CT) interaction between electron-rich and electron-deficient guests. This unique ability of CB[8] has been utilized to not only construct various supramolecular assemblies with specific structures and properties,[5,6] but also design and synthesize the redox-driven molecular machines.[7] However, the ternary complexes formed by the CB[8]-stabilized CT

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interactions were achieved in water, and their practical applications are limited due to the poor solubility of the host in common solvents. Moreover, the number of recognition motifs that has been exploited to form stable CT ternary complexes also remains limited.[8]

Cylindrical macrotricyclic hosts[9] consisting of one central cavity and two lateral circular cavities have new topological features with respect to the mono- and bicyclic hosts. Recently, we reported a novel triptycene-based cylindrical macrotricyclic host **1**[10] and proved it could form a 1:1 stable complex with diquat **2**.[10c] The single-crystal structure of the complex **1·2** revealed that the diquat molecule could thread from the central cavity of **1** and occupy half of its cavity, which means that there is free volume available for another guest. This prompted us to study the inclusion of two different guests within the cavity of **1** (Figure 1). Here we report the formation of stable ternary complexes between the host **1** and hetero-guest pairs in solution and in the solid state, which is stabilized not only by a CT interaction between electron-rich and electron-deficient guests but also by the face to face π-stacking interactions between the host and the guests. Moreover, we also find that a selective complexation process between a ternary complex containing benzidine and a binary complex can be effectively controlled by the use of acid and base

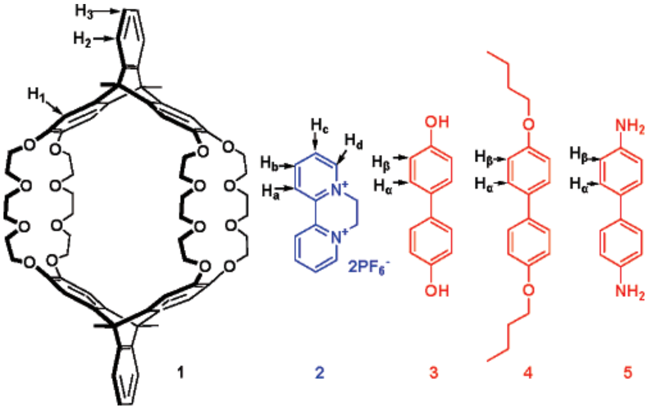

Figure 1. Structures and proton designations of the host **1** and guests **2**−**5**.

We first investigated the complexation between host **1** and biphenyl-4,4′-diol **3** in solution and found that the mixture of **1** and **3** (each 2 mM concentration) in 1:1 chloroform/acetonitrile solution at room temperature showed little change[11] both in color and in the ^{1}H NMR spectra according to the free species, which indicates that the electron-rich guest molecule cannot bind itself in the cylindrical macrotricyclic host. Moreover, it was also found that the ^{1}H NMR spectrum of the 1:1 mixture of **2** and **3** was essentially the sum of the two components, which implied that almost no interactions between the two guests existed. However, instantaneous formation of the ternary complex containing a hetero-guest pair was observed upon the addition of biphenyl-4,4′-diol **3** to the 1:1 complex of **1** and diquat. The color of the mixture immediately changed from light orange to purple (Figure 2) with a charge-transfer absorption band at 515 nm.[11] In the ^{1}H NMR spectrum of the mixture (Figure 3), only one set of peaks was found, which indicated the fast-exchange complexation between the host and the guests. As shown in Figure 3c, the H$_\alpha$ and H$_\beta$ proton signals of guest **3** and the

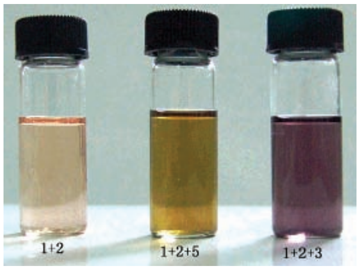

Figure 2. Observed color change of the indicating species (3 mM) in 1:1 CHCl$_3$/CH$_3$CN solution.

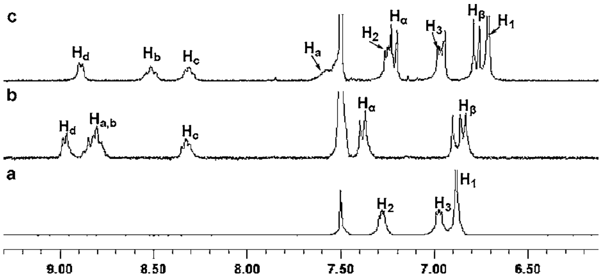

Figure 3. Partial ^{1}H NMR spectra (300 MHz, CD$_3$CN/CDCl$_3$ = 1:1, 295 K) of (a) **1**; (b) **2** and 1.0 equiv of **3**; (c) **1** and 1.0 equiv of **2** and **3**, [**1**]$_0$ = 2 mM.

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(11) See Supporting Information.

H_1 proton signal of **1** shifted to upfield, which might be due to the strong shielding effect of the aromatic rings. These observations suggested that a new ternary complex **1·2·3** was formed in the 1:1 chloroform/acetonitrile solution.

Similarly, cylindrical macrotricyclic host **1** could also form stable ternary complexes with guests **4** and **5** in the presence of guest **2**, which has been confirmed by ^1H NMR spectral studies of the mixtures.[11] There was little color change of complex **1·2·4** according to complex **1·2**; however, the complex **1·2·5** gave a yellow solution immediately due to the CT interaction between the electron-rich aromatic rings of benzidine and electron-poor pyridinium rings.

The electrospray ionization mass spectra (ESI MS) provided more evidence for formation of the 1:1:1 stable ternary complex.[11] Consequently, the peak at *m*/*z* 759.67 for [**1·2·3**$-2PF_6]^{2+}$ was found by using the solution of the 1:1:1 mixture of the three components. Similarly, the peaks at *m*/*z* 815.86 for [**1·2·4**$-2PF_6]^{2+}$ and at *m*/*z* 758.69 for [**1·2·5**$-2PF_6]^{2+}$ were also observed at the same conditions.

Single crystals of these ternary complexes were grown by vapor diffusion of isopropyl ether into a mixture of the three relevant components in a 1:1 $CHCl_3/CH_3CN$ solution. Attempts to determine their structures by X-ray crystallography were hampered by severe disorder in the guest molecules that arises from the high symmetry of their space groups. However, we checked many single crystals, collected diffraction data on more than five occasions, and finally solved the structure of the complex **1·2·3**.[12] As shown in Figure 4,[13] the hetero-guest pair was included inside the cavity of the cylindrical macrotricyclic host. Both the diquat and the biphenyl-4,4′-diol molecule thread the cavity from the central ring of the host. The bipyridinium ring, the biphenyl ring, and two aromatic rings of triptycene are almost parallel, with a mean separation of 3.8 Å for AB, 3.8 Å for BC, and 3.6 Å for CD, which are consistent with the strong face to face π-stacking interactions and the charge-transfer interaction observed by spectroscopy.

Since benzidine contains amine groups and can be protonated to result in formation of cationic diammonium ions, we speculated that the biphenyl-4,4′-diaminium salt could thread from the two lateral dibenzo[24]-crown-8 cavities of cylindrical macrotricylcic host **1** to form a stable 1:1 complex.[14] Consequently, the diquat cation would be extruded and the ternary complex would be decomposed. So we have done a series of ^1H NMR experiments to demonstrate this speculation. As shown in Figure 5c, the H_α and H_β proton signals of guest **5** and the H_1 proton signal of **1** showed a significant upfield shift, which was consistent with formation of the ternary complex **1·2·5**. When 1 μL of trifluoroacetic was added to the above solution, it was found that the proton signals of the guest **2** shifted downfield almost to the original positions; however, the proton signal of the NH_3^+ group appeared at 8.5 ppm, and the aromatic proton signals of biphenyl-4,4′-diaminium salt showed a typical feature of complexation with host **1** (Figure 5d).[15] Moreover, it was found that the aromatic proton signals of the host molecule had a bigger upfield shift, while the peak shape of

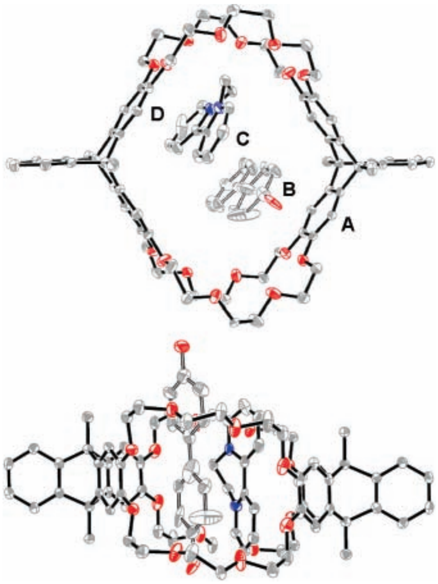

Figure 4. Top view (top) and side view (bottom) of the crystal structure of the complex **1·2·3**. Color code: oxygen, red; nitrogen, blue; carbon, gray. Two PF_6^- counterions, solvent molecules, and hydrogen atoms are omitted for clarity.

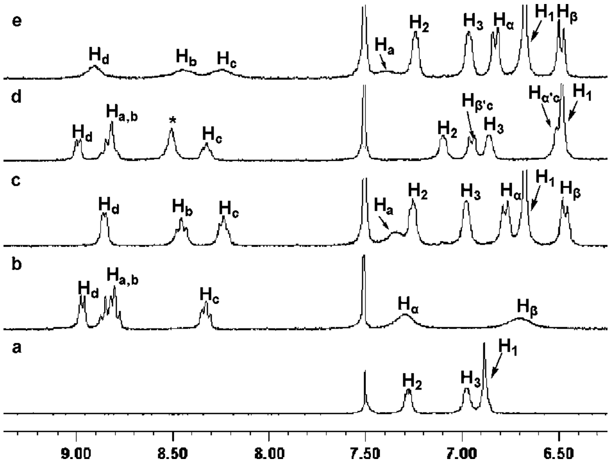

Figure 5. Partial ^1H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 295 K) of (a) **1**; (b) **2** and 1.0 equiv of **5**; (c) **1** and 1.0 equiv of **2** and **5**; (d) the mixture obtained after adding 1 μL of trifluoroacetic to the solution in part c; (e) the mixture obtained after adding 4 μL of tributyl amine to the solution in part d. $[\mathbf{1}]_0$ = 2 mM; "*" in part d represents the protons of $-NH_3^+$ groups; $H_{\alpha'c}$ and $H_{\beta'c}$ in part d represent the complexed aromatic protons of biphenyl-4,4′-diaminium salt.

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(12) Crystal data for the complex **1·2·3**: $C_{47.33}H_{51.97}F_{7.20}N_{2.20}O_{9.19}P_{1.20}$, *M* = 972.70, monoclinic, space group *P*2(1)/*n*, $a = 12.706$ (3) Å, $b = 20.186$ (4) Å, $c = 19.259$ (4) Å, $\beta = 105.74$ (3)°, $V = 4754.5$ (16) Å^3, $Z = 4$, $T = 113(2)$ K, CCD area detector, 35 290 reflections measured, 8354 independent, 6938 used, number of parameters 857, $R_{int} = 0.0469$ $R_1 = 0.1278$ ($I > 2\sigma(I)$), w$R_2 = 0.3975$ for all data.

(13) The crystal structure was drawn by XP in the SHELXTL97 program.

(14) The three acidic hydrogens attached to nitrogen could form a hydrogen bond with oxygens of the lateral crown ether, which would make the guest molecule point to the two lateral cavities of the host **1**.[10b]

the crown ether region became simple, which implied each NH_3^+ group bound to either of the lateral rings. These observations indicated that the protonated benzidine threaded the cavity of host **1** from the lateral rings, which resulted in the release of diquat from the cavity of the host molecule. When 4 μL of tributyl amine was added into the above system, it was further found that the proton signals of ternary complex **1·2·5** recovered, which suggested that the hetero-guest pair threaded the cavity of host **1** from the central ring again. Thus, addition of acid and base could effectively control the selective threading of the hetero-guest pair and protonated benzidine from a different direction than the cylindrical macrotricyclic host, which would represent a new type of molecular machinery.

In summary, we have demonstrated that the triptycene-based cylindrical macrotricyclic host could encapsulate a hetero-guest pair of the diquat and electron-rich aromatics simultaneously to form 1:1:1 stable ternary complexes, which were stabilized not only by the charge-transfer interactions between the electron-deficient and electron-rich guests but also by the face to face π-stacking interactions between the host and the guests. Moreover, we have also found that a selective complexation process between a ternary complex containing benzidine and a binary complex could be effectively controlled by the use of acid and base. We believe that the work described here will provide us new opportunities for creating elaborated supramolecular assemblies, which are now in process.

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Supporting Information Available: Comparison of ^{1}H NMR spectra of the host and the guests and their mixtures; UV−vis spectra of the host and the guests and their mixtures; ESI-MS spectra for the complexes; X-ray crystallographic file (CIF) for complex **1·2·3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Two sets of peaks were found in the ^{1}H NMR spectrum of the mixture of protonated **5** and **1**, which indicated that the slow-exchange complexation between the host and the guest occurred on the NMR time scale.[11]