# Novel Anthracene-Based Cylindrical Macrotricyclic Polyether: Powerful Host for Bispyridinium Dications
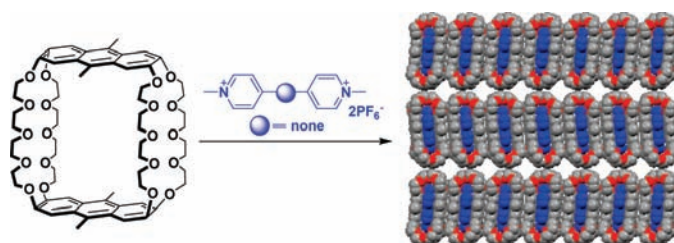
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**ABSTRACT**



A novel anthracene-based cylindrical macrotricyclic polyether containing two dibenzo-30-crown-10 cavities has been synthesized and shown to be a powerful host to form 1:1 stable complexes with the rodlike bispyridinium dications ($K_a > 10^5$ M$^{-1}$). Moreover, it was found that the complexes could all self-assemble into linear supramolecular arrays and further 2D mosaic-like architectures in the solid state.

Since Pedersen[1] first reported the synthesis and cation complexation properties of the crown ethers, host–guest chemistry[2] has attracted great interest during the past 40 years. One particular interest in this regard came from the paraquat derivatives (*N,N*′-dialkyl-4,4′-bipyridinium salts) that have been widely used as guests to construct numerous complexes with large crown ethers, such as bis(*m*-phenylene)-32-crown-10 derivatives,[3] and bis(*p*-phenylene)-34-

crown-10 derivatives.[4] Comparably, host–guest systems based on the recognition motif of dibenzo-30-crown-10 derivatives to paraquat derivatives have still been scarcely investigated.[5]

Cylindrical macrotricyclic polyethers[6] consist of one central cavity and two lateral circular cavities, which have new topological features with respect to the macromono- and

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macrobicyclic ligands. The first cylindrical host for paraquat derivatives was reported by Gibson's group[7] in 2005. Recently, we[8] have synthesized a novel triptycene-based cylindrical macrotricyclic polyether containing two dibenzo-24-crown-8 cavities and found that it could also be a highly efficient host for complexation with different functional paraquat derivatives in different modes. Herein, we report synthesis of a novel cylindrical macrotricyclic host containing two anthracene units as skeleton and two dibenzo-30-crown-10 cavities **1** (Figure 1), which shows to be a powerful host
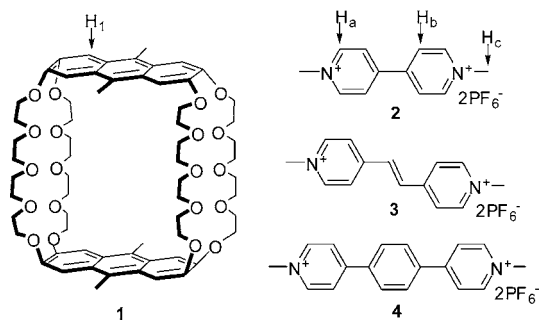


**Figure 1.** Structure and proton designations of the host **1** and guests **2**−**4**.

for the formation of 1:1 stable complexes with different sizes of rodlike bispyridinium dications. Interestingly, it is also found that the complexes can all self-assemble into linear supramolecular arrays, and further 2D mosaic-like architectures in the solid state due to the planar skeleton and high symmetry of the host in the complexes.

Synthesis of host **1** is depicted in Scheme 1. Reaction of 9,10-dimethyl-2,3,6,7-tetrahydroxyanthracene **5** with com-

**Scheme 1.** Synthesis of Host **1**
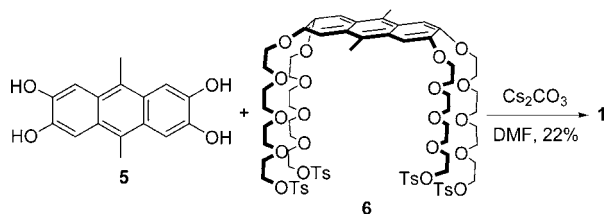


pound **6** under high dilution conditions in the presence of cesium carbonate gave **1** in 22% yield. Host **1** was characterized by $^1$H and $^{13}$C NMR spectrometry, mass spectrometry, and elemental analysis.[9]

We first investigated the complexation between host **1** and guest **2** in solution. Consequently, when **1** and **2** (4 mM each)

were mixed in a 1:1 chloroform/acetonitrile solution, a bright red solution formed immediately due to the charge-transfer interaction between the electron-rich aromatic rings of host **1** and the electron-poor pyridinium rings of guest **2**. Complex studies of host **1** with the bispyridinium dications were further carried out in a 1:1 CDCl$_3$/CD$_3$CN solution by $^1$H NMR spectroscopy. As shown in Figure 2, when 1.0 equiv
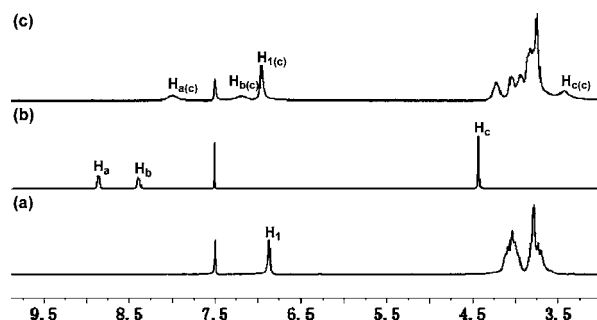


**Figure 2.** Partial $^1$H NMR spectra (300 MHz, CD$_3$CN/CDCl$_3$ = 1:1, 295 K) of (a) free host **1**, (b) free guest **2**, and (c) **1** and 1.0 equiv of **2**. [**1**]$_0$ = 4.0 mM.

of guest **2** was added to a solution of host **1**, only one set of resonances for complex **1·2** was observed. If either the host or the guest was in excess, the spectrum showed one set of resonances for host **1** or guest **2** besides those for the complex.[9] These observations suggested that host **1** and guest **2** formed a 1:1 stable complex **1·2**, and the rates of the complexation and decomplexation were both slow. Moreover, we found that the protons H$_a$ and H$_b$ of guest **2** shifted significantly upfield, which was attributed to the strong shielding effect of the aromatic rings of **1**. Meanwhile, the methyl proton of guest **2** also showed considerable upfield shift ($\Delta\delta$ = 1.0 ppm). These results are contrary to those of guest **2** in its complexation with the triptycene-based analogue,[8a] which could be explained by the extension of the aromatic skeleton of **1** placing the methyl protons of **2** in the strong shielding region of the aromatic rings of the host. A similar effect also resulted in the downfield shift of proton H$_1$ of host **1**. With diquat as the reference guest, the association constant ($K_{a1·2}$)[9] for the 1:1 complex **1·2** was determined by a competitive method[10] to be 3.1 × 10$^5$ M$^{-1}$.

Similar to the case of **1·2**, complexes **1·3** and **1·4** also showed typical charge transfer features with the mixed solutions of bright red and yellow color, respectively. Owing to the strong shielding effect of the aromatic rings of **1**, significant upfield shifts of the aromatic protons for both **1·3** and **1·4** were observed. However, the N-methyl protons of guests **3** and **4** shifted downfield, and proton H$_1$ of host **1** shifted to the upfield, which are similar to the cases of the triptycene-based analogue[8a] but contrary to those of complex

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**1·2**. These results could be attributed to the extension of the guests which place the *N*-methyl protons in different chemical environments compared with the complex **1·2**. Moreover, it was found that the complexes **1·3** and **1·4** also showed slow rates of the complexation and decomplexation at room temperature. Consequently, the association constants for the 1:1 complexes **1·3** and **1·4** at $K_{a1·3} = 1.4 \times 10^6$ and $K_{a·4} = 2.1 \times 10^6$ M$^{-1}$, respectively, were obtained by the competitive method.[9]

The electrospray ionization mass spectra (ESIMS) provided more evidence for formation of the stable 1:1 complexes **1·2**, **1·3**, and **1·4**.[9] Consequently, the strongest (base) peaks at *m/z* 679.7 for [**1·2**-2PF$_6^-$]$^{2+}$, 692.7 for [**1·3**-2PF$_6^-$]$^{2+}$, and 717.9 for [**1·4**-2PF$_6^-$]$^{2+}$, respectively, were observed.

Formation of the 1:1 complex between **1** and **2** was further confirmed by its X-ray crystal structure.[11] As shown in Figure 3a, it was found that the guest **2** was included in the central
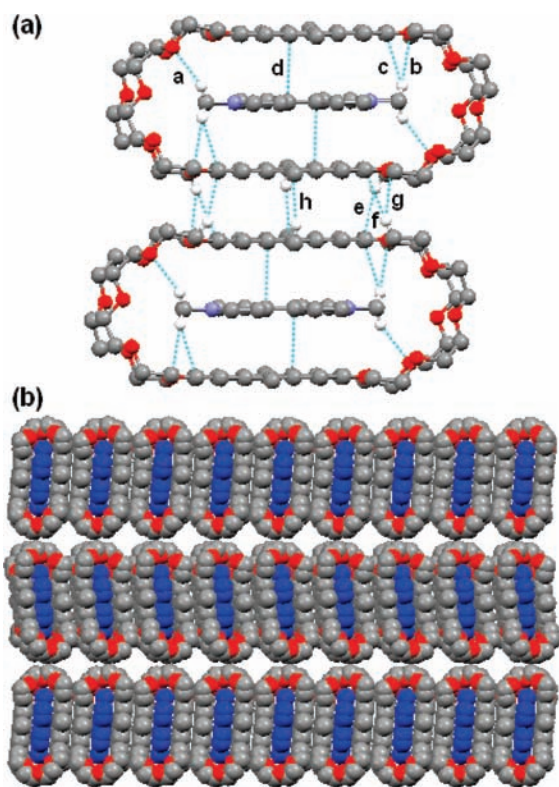


**Figure 3.** (a) Crystal structure of **1·2**; the blue lines denote the nocovalent interactions. (b) 2D mosaic-like sheet; the guests are shown in blue. Solvent molecules, PF$_6^-$ counterions, and hydrogen atoms not involved in the interactions were omitted for clarity.

cavity of host **1** and the two *N*-methyl groups pointed to the two dibenzo-30-crown-10 cavities, respectively. Moreover,

the two pyridinium rings were well coplanar and parallel with the anthracene rings of **1**. These structural features of complex **1·2** were quite different from those of the paraquat-based complexes reported previously. We further found that there existed not only two pairs of C–H···O hydrogen bonds between the protons of *N*-methyl groups and the ether oxygen atoms with the distances of 2.58 (a) and 2.64 Å (b), respectively, but also a pair of face–face π-stacking interactions between the pyridinium rings of the guest and the aromatic rings of the host ($d_{\pi-\pi} = 3.37$ Å for d). Moreover, a pair of C–H···π interactions between the protons of *N*-methyl groups and the aromatic rings of the host with the distance of 2.80 Å (c) were also observed. These multiple noncovalent interactions played an important role in formation of the stable complex, which is consistent with the result in solution. Due to the planar skeleton and high symmetry of the host in the complex, it was also found that by virtue of three pairs of C–H···π interactions between the methylene and methyl protons of host **1** and the adjacent anthracene ring ($d_{C-H\cdots\pi} = 2.62$ for e, 2.75 for f, and 2.74 Å for h), and a pair of C–H···O hydrogen bond between the methylene proton and the ether oxygen atom of the host with the distance of 2.65 Å (g), the complex **1·2** could self-assemble into a linear supramolecular array, which further formed a 2D mosaic-like architecture[12] (Figure 3b) by virtue of the noncovalent interactions between the macrocycle and the solvent molecule and PF$_6^-$ counterions.[9]

We also obtained single crystals of complexes **1·3**[13] and **1·4**[14] by diffusion of isopropyl ether into an equimolar mixture of the host and the guest in CH$_3$CN/CHCl$_3$ (1:1, v/v) solution. The crystal structures showed that the rodlike guests **3** and **4** with considerable length (ca. 12.7 Å for **3** and 15.0 Å for **4**) could also be completely included inside the cavity of the host to form 1:1 complexes in the similar complexation mode to the complex **1·2**. As shown in Figure 4a,b, there existed multiple C–H···O hydrogen bonding (a = 2.70, b = 2.66, c = 2.66, d = 2.44, e = 2.45, and f = 2.62 Å) between the *N*-methyl protons and the aromatic proton of guest **3** and the ether oxygen atoms of the host and also face–face π-stacking interactions between the pyridinium rings of the guest and the aromatic rings of the host with distances of 3.28 (g), 3.35 (h), 3.39 (i), and 3.34 Å (j), respectively. Moreover, it was found that complex **1·3** could also stack into a linear supramolecular array by C–H···O hydrogen bonding (2.65 for A, and 2.60 Å for B), and C–H···π interactions (2.78 for C, 2.62 for D, and 2.77 Å for E) between the two adjacent macrocycles, which

(11) Crystal data for **1·2·**3CH$_3$CN·2H$_2$O: C$_{82}$H$_{111}$F$_{12}$N$_5$O$_{22}$P$_2$; $M_r$ = 1808.70; monoclinic, *C2/c*; $a$ = 28.597(6) Å, $b$ = 10.465(2) Å, $c$ = 29.068(6) Å; $\beta$ = 95.36(3)°; $V$ = 8661(3) Å$^3$; $Z$ = 4; $d$ = 1.387 g cm$^{-3}$; $T$ = 173(2) K; $R_1$ = 0.0718, w$R_2$ = 0.1662 (all data); $R_1$ = 0.0650, w$R_2$ = 0.1599 [$I > 2\sigma(I)$].

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(13) Crystal data for **1·3·**3CH$_3$CN·CHCl$_3$·H$_2$O: C$_{85}$H$_{112}$F$_{12}$N$_5$O$_{21}$P$_2$; $M_r$ = 1936.09; triclinic, *P1*; $a$ = 10.5785(15) Å, $b$ = 12.5308(17) Å, $c$ = 20.433(4) Å; $\alpha$ = 97.683(11)°, $\beta$ = 97.630(11)°, $\gamma$ = 111.007(7)°; $V$ = 2457.5(6) Å$^3$; $Z$ = 1; $d$ = 1.308 g cm$^{-3}$; $T$ = 173(2) K; $R_1$ = 0.1061, w$R_2$ = 0.2293 (all data); $R_1$ = 0.0885, w$R_2$ = 0.2157 [$I > 2\sigma(I)$].

(14) Crystal data for **1·4·**2CH$_3$CN: C$_{86}$H$_{108}$F$_{12}$N$_4$O$_{20}$P$_2$; $M_r$ = 1807.70; triclinic, *P-1*; $a$ = 11.732(2) Å, $b$ = 12.020(2) Å, $c$ = 18.224(3) Å; $\alpha$ = 79.289(5)°, $\beta$ = 85.127(6)°, $\gamma$ = 88.981(6); $V$ = 2516.1(8) Å$^3$; $Z$ = 1; $d$ = 1.193 g cm$^{-3}$; $T$ = 173(2) K; $R_1$ = 0.0992, w$R_2$ = 0.2207 (all data); $R_1$ = 0.0754, w$R_2$ = 0.2040 [$I > 2\sigma(I)$].
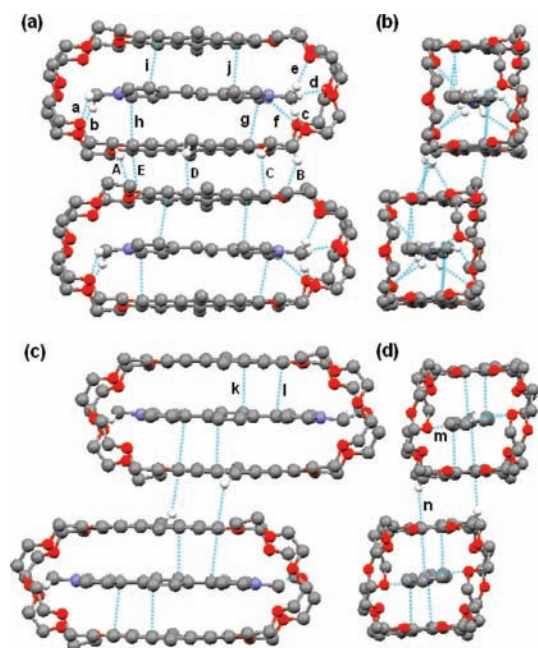
**Figure 4.** Top (a) and side (b) view of the crystal structure of **1·3**. Top (c) and side (d) view of the crystal structure of **1·4**. The blue lines denote the noncovalent interactions. Solvents, $PF_6^-$ counterions, and hydrogen atoms not involved in the interactions were omitted for clarity.

further self-assembled into a 2D mosaic-like sheet.[9] In the case of complex **1·4**, besides the C−H···O hydrogen bonding between the *N*-methyl proton of guest **4** and the ether oxygen atom of the host with the distance of 2.61 Å (m), two pairs of face-to-face $\pi$-stacking interactions between the aromatic rings of guest **4** and the host with the distances of 3.34 (k),

and 3.39 Å (l), respectively, were also observed (Figure 4c,d). These multiple noncovalent interactions play a very important role in formation of the stable complexes. Similarly, the complex **1·4** could also stack into a linear supramolecular array, and further a 2D mosaic-like sheet.[9] Moreover, it was further found that because of same orientation of the complexed molecules, complex **1·4** could stack more intensively than that of **1·2**.

In summary, we have synthesized a novel anthracene-based cylindrical macrotricyclic polyether containing two dibenzo-30-crown-10 cavities, which showed to be a powerful host for complexation with different sizes of the rodlike bispyridinium dications. Moreover, it was also found that the complexes could all self-assemble into linear supramolecular arrays, and further mosaic-like sheets in the solid state. This new kind of donor−acceptor system could provide useful building blocks for the construction of supramolecular assemblies with specific structures and properties,[15] which are in progress in our laboratory.

**Supporting Information Available:** Experimental procedures and characterization data for new compounds. Characterization data for the complexes **1·2**, **1·3**, and **1·4**. The X-ray crystallographic files (CIF) for complexes **1·2**, **1·3**, and **1·4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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