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Self-Assembly of Triptycene-Based Cylindrical Macrotricyclic Host with Dibenzylammonium Ions: Construction of Dendritic [3]Pseudorotaxanes

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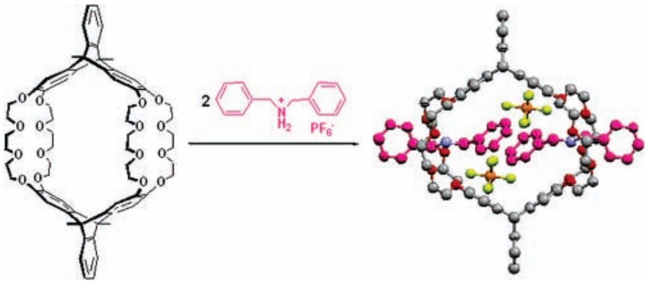
ABSTRACT



It was found that a cylindrical macrotricyclic host containing two dibenzo[24]crown-8 cavities could self-assemble with two dibenzylammonium salts to form a stable 1:2 complex in solution and in the solid state, in which multiple hydrogen-bonding and π–π stacking interactions between the host and the guest played an important role. Furthermore, a series of dendritic pseudorotaxanes were constructed and structurally studied.

Dendrimers[1] are interesting nanoscale compounds that have found many potential applications in materials science as well as in macro- and supramolecular chemistry.[2] In recent years, self-assembled dendrimers,[3] in particular, mechanically interlocked dendrimers,[4] have attracted much interest as they offered reversible, structural control and relatively large three-dimensional architectures starting from dendritic building blocks within the nanometer range.

Recently, we reported[5] a novel triptycene-based[6] cylindrical macrotricyclic polyether,[7] which proved to be a highly efficient host for the complexation with paraquat derivatives. Because of the host containing two dibenzo-24-crown-8 (DB24C8) moieties, we deduced that it could form a 1:2

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(2) For some recent examples, see: (a) Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 1604−1605. (b) Tang, W. J.; Yang, N. F.; Yi, B.; Deng, G. J.; Huang, Y. Y.; Fan, Q. H. *Chem. Commun.* **2004**, 1378−1379. (c) Nakajima, R.; Tsuruta, M.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2004**, *126*, 1630−1631. (d) Chen, H.-T.; Neerman, M. F.; Parrish, A. R.; Simanek, E. E. *J. Am. Chem. Soc.* **2004**, *126*, 10044−10048. (e) Huang, J.-F.; Luo, H.; Liang, C.; Sun, I.-W.; Baker, G. A.; Dai, S. *J. Am. Chem. Soc.* **2005**, *127*, 12784−12785.

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complex with two dialkylammonium salts.[8] Herein, we report the formation of the stable complex $\mathbf{1}\cdot\mathbf{2}_2$ between the host **1** (Figure 1) and two dibenzylammonium salts **2** in solution and in the solid state and the construction of a series of consequent dendritic [3]pseudorotaxanes.

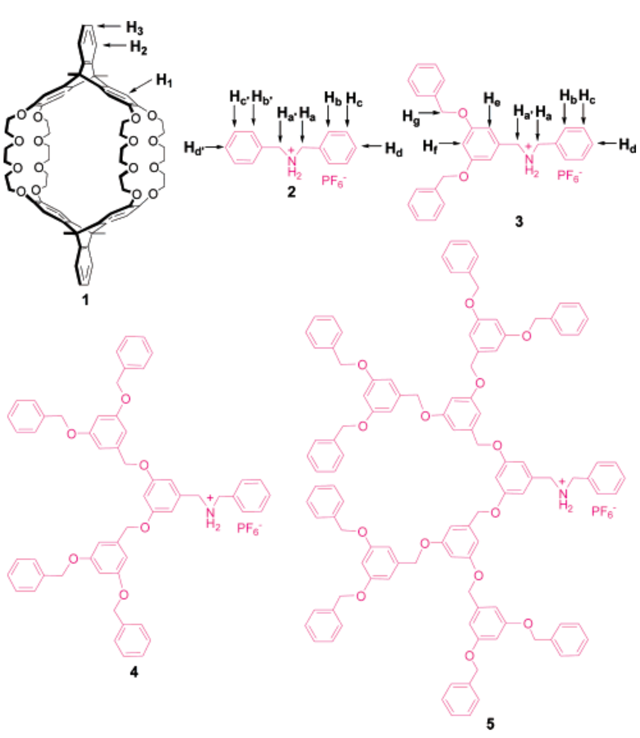

Figure 1. Structures and proton designations of the host **1** and guests **2**−**5**.

Initially, we investigated the formation of the complex between **1** and **2** in solution. As shown in Figure 2b, the ^{1}H NMR spectrum of a 1:2 mixture of **1** and **2**, recorded in $CDCl_3/CD_3CN$ (10:1), showed a dispersed array of well-defined resonances and a great difference from those for host **1** (Figure 2a) and guest **2** (Figure 2c). The resonances of the complex were assigned by its ^{1}H−^{1}H COSY and NOESY 2D NMR spectra.[9] It was noted that the signals of the benzyl protons of **2** located outside the cavity of **1** shifted downfield, whereas those of the benzyl protons inside the cavity shifted upfield. Particularly, striking upfield shifts ($\Delta\delta = -1.39 \sim -1.82$ ppm) for the inner phenyl proton ($H_b \sim H_d$) signals were observed, which might be due to the strong shielding effect of the macrocycle. The signal of the outer benzylic methylene proton $H_{a'}$ adjacent to the NH_2^+ center exhibited a large downfield shift ($\Delta\delta = 0.58$ ppm), which was attributed to the hydrogen-bond interactions and the deshielding effect of the aromatic rings in **1**. Moreover, an upfield shift for aromatic proton H_1 ($\Delta\delta = -0.14$ ppm) of **1** and significant changes in the chemical shifts of the protons in crown ether units were also observed. These observations suggested that a novel triptycene-based complex $\mathbf{1}\cdot\mathbf{2}_2$ was formed. Because the host−guest exchange is slow on the ^{1}H NMR time scale at room temperature, the association constants K_1 and K_2 for the first and second binding events were calculated to be 1.2×10^4 ($\Delta G = -23$ kJ/mol) and 2.4×10^3 M^{-1} ($\Delta G = -19$ kJ/mol), respectively.[10]

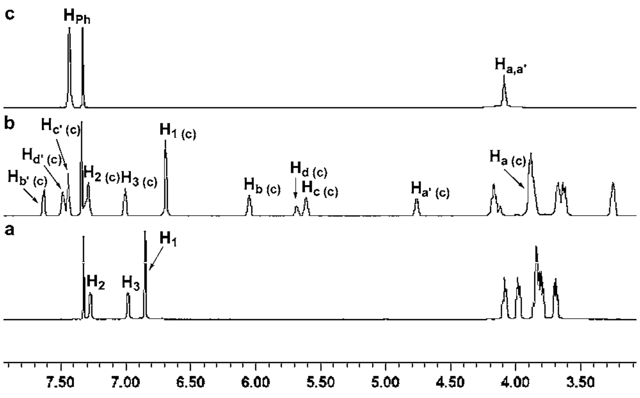

Figure 2. Partial ^{1}H NMR spectra ($CDCl_3/CD_3CN$ = 10:1, 600 MHz, 295 K) of (a) free host **1**, (b) **1** and 2.0 equiv of **2**, and (c) free guest **2**. $[\mathbf{1}]_0$ = 5 mM.

The electrospray ionization mass spectrum of a solution of **1** and **2** also confirmed their strong complexation. Consequently, the strong peak was found at *m*/*z* 772.8, due to $[\mathbf{1}\cdot\mathbf{2}_2-2PF_6^-]^{2+}$. Moreover, it was found that the complex $\mathbf{1}\cdot\mathbf{2}_2$ was partly decomposed in $CDCl_3/CD_3CN$ (10:1) at 323 K and completely decomposed in DMSO-d_6.[9]

Further support for the formation of the complex $\mathbf{1}\cdot\mathbf{2}_2$ came from its X-ray analysis.[11] As shown in Figure 3, two dibenzylammonium ions were threaded symmetrically through the center of the DB24C8 cavities of the host **1**, which resulted in a "gull-wing" conformation. In the complex, the planes of two phenyl rings in **2** were inclined by 63° and 55° to the $C-CH_2-NH_2^+-CH_2-C$ backbone. Multiple hydrogen-bonding interactions existed between the polyether oxygen atoms and NH_2^+ hydrogen atoms and the benzylic methylene hydrogen atoms located both inside and outside the cavity. A C−H···π interaction ($d_{H\cdots\pi} = 2.86$ Å) between the guest and the host also existed. Moreover, there were additional face−face π−π stacking interactions not only between the inner phenyl ring of the guest and one of the aromatic rings of the host with the centroid−centroid distance of 4.20 Å and a dihedral angle of 23° but also between the

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(8) Stoddart et al. reported that DB24C8 could be threaded by a secondary dialkylammonium ion to form [2]pseudorotaxane. Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philip, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 1869−1871.

(9) See Supporting Information.

(10) An ion pairing effect was considered.[9] Elizarov, A. M.; Chiu, S.-H.; Glink, P. T.; Stoddart, J. F. *Org. Lett.* **2002**, *4*, 679−682.

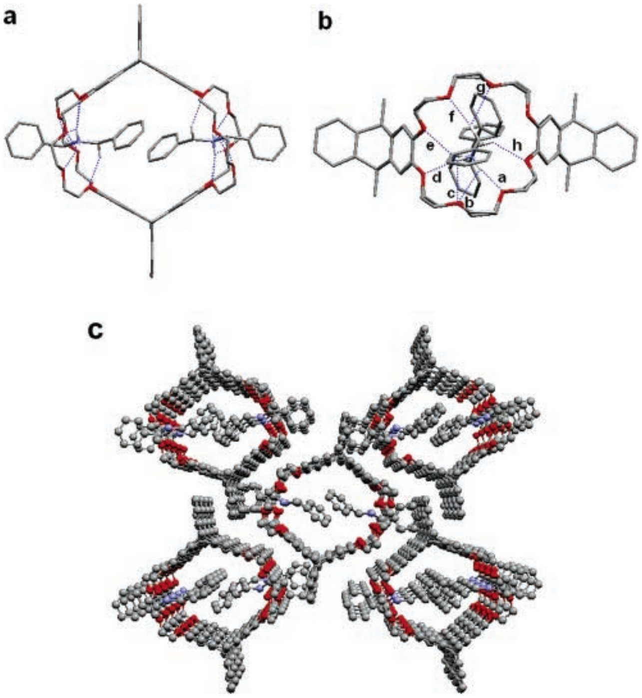
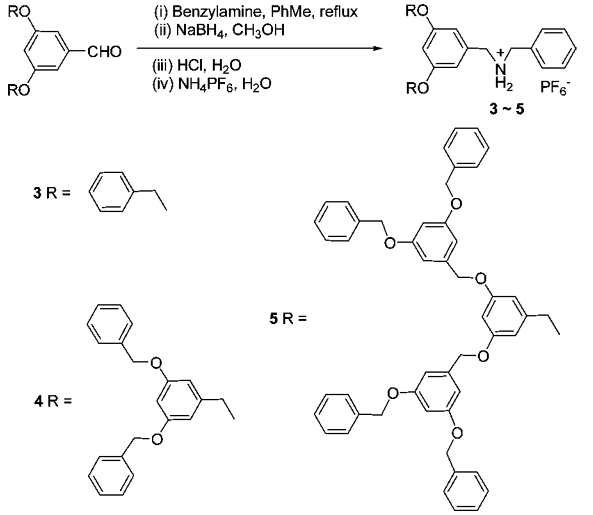


Figure 3. Top view (a) and side view (b) of the crystal structure of the complex $\mathbf{1}\cdot\mathbf{2}_2$. (c) Crystal packing of the complex $\mathbf{1}\cdot\mathbf{2}_2$ viewed along the *a*-axis. Solvent molecules, PF_6^- counterions, and hydrogen atoms not involved in the hydrogen-bonding interactions are omitted for clarity. Hydrogen-bond distances (Å): a = 2.135, b = 2.566, c = 2.688, d = 2.232, e = 2.649 for N−H···O; f = 2.221, g = 2.717, h = 2.504 for C−H···O.

inner phenyl rings of the two guests with the centroid−centroid distance of 4.45 Å and a dihedral angle of 0°. It was further found that the anions in the crystal were adjacent to two sides of the complex and connected to the ammonium ions and the host by hydrogen bonds.[9] These multiple noncovalent interactions resulted in the stable complex $\mathbf{1}\cdot\mathbf{2}_2$, which was consistent with that one in solution. Interestingly, it was also found that the macrocyclic components could pack into tubular channels with the wall containing four aromatic rings,[12] which extended in the crystallographic *a* direction with the ammonium ions threaded inside (Figure 3c).

The formation of the stable complex $\mathbf{1}\cdot\mathbf{2}_2$ encouraged us to design and construct dendritic [3]pseudorotaxanes. Consequently, a series of the dendritic ammonium salts **3**−**5** were prepared in 66−94% overall yield by the reactions of the corresponding dendritic aldehyde[13] and benzylamine and then by reduction with $NaBH_4$, protonation of the resulting amine, and counterion exchange with NH_4PF_6 (Scheme 1).

Scheme 1. Synthesis of the Dendritic Ammonium Salts **3**−**5**



The first evidence for the formation of the dendritic complexes in solution came from ^1H NMR spectrometry. When a solution of **1** in $CDCl_3/CD_3CN$ (10:1) was mixed with 2 equiv of **3**, its ^1H NMR spectrum[14] displayed signal changes similar to those of the complex $\mathbf{1}\cdot\mathbf{2}_2$ (Figure 4b).

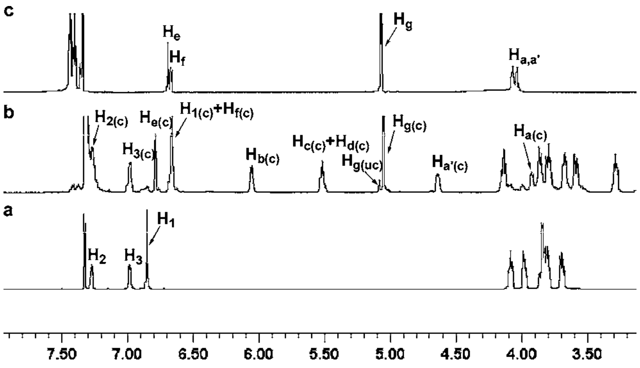


Figure 4. Partial ^1H NMR spectra ($CDCl_3/CD_3CN$ = 10:1, 600 MHz, 295 K) of (a) free host **1**, (b) **1** and 2.0 equiv of **3**, and (c) free guest **3**. $[\mathbf{1}]_0$ = 5 mM.

Consequently, large upfield shifts for the inner phenyl protons and downfield shifts for the benzylic methylene protons $H_{a'}$ were observed. Moreover, significant chemical shifts for the signals of proton H_1 and protons of crown rings of the host were also observed. These observations suggested that a new dendritic [3]pseudorotaxane $\mathbf{1}\cdot\mathbf{3}_2$ was formed. Similarly, the dendritic complex $\mathbf{1}\cdot\mathbf{4}_2$ could also be formed, which was proved by the ^1H NMR experiments in $CDCl_3/CD_3CN$ (10:1).[9] However, it was noted that proton signals of an uncomplexed host and guest in the complexes $\mathbf{1}\cdot\mathbf{3}_2$ and $\mathbf{1}\cdot\mathbf{4}_2$ were obviously observed, which is different from

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(11) Crystal data for $\mathbf{1}\cdot\mathbf{2}_2\cdot\mathbf{2CH_3CN}$: $C_{100}H_{114}F_{12}N_4O_{16}P_2$; M_r = 1917.9; monoclinic; space group *P*2(1)/*n*; a = 12.3934(15) Å, b = 22.795(3) Å, c = 17.545(2) Å; β = 102.413(2); V = 4840.5(10) Å^3; Z = 2; T = 294(2) K, R_1 = 0.1895, wR_2 = 0.3246 (all data); R_1 = 0.0905, wR_2 = 0.2420 ($I > 2\sigma(I)$).

(12) Hu, Z. Q.; Chen, C. F. *Chem. Commun.* **2005**, 2445−2447.

(13) Gibtner, T.; Hampel, F. K.; Gisselbrecht, J.-P.; Hirsch, A. *Chem.*−*Eur. J.* **2002**, *8*, 408−432.

(14) The resonances of the complex $\mathbf{1}\cdot\mathbf{4}_2$ were assigned by its $^1H-^1H$ COSY and NOESY 2D NMR spectra.[9]

those in the complex **1·2$_2$**. The results indicated that the association would become more and more difficult with the increase of the generation. Consequently, little formation of the dendritic complex **1·5$_2$** was found because of the large bulk of the guest.

Mass spectrometry[4b,c] was further utilized for testing the formation of the dendritic complexes between **1** and guests **3** and **4** by both the electrospray ionization (ESI) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) techniques. Because of its high mass, the third-generation dendritic complex was only characterized by MALDI-TOF MS. The results are summarized in Table 1, which shows that the wholly complexed dendritic [3]-pseudorotaxanes were detected not only for **1·3$_2$** and **1·4$_2$** but also for **1·5$_2$**. Moreover, it was found that the dendritic complexes gave rise to the peaks at 1558.4 for **[1·3-PF$_6^-$]$^+$**, 1983.4 for **[1·4-PF$_6^-$]$^+$**, and 2831.3 for **[1·5-PF$_6^-$]$^+$**, which indicated that a singly threaded dendritic pseudorotaxane might also exist.

Table 1. Molecular Formulas and MS Mass/Charge Ratios of Supramolecular Structures

structure	molecular formula	ESI MS (*m/z*)	MALDI-TOF MS (*m/z*)
[1·3$_2$−PF$_6^-$]$^+$	$C_{124}H_{132}F_6N_2O_{20}P^+$		2113.5
[1·3$_2$−2PF$_6^-$]$^{2+}$	$C_{124}H_{132}N_2O_{20}{}^{2+}$	984.4	
[1·3−PF$_6^-$]$^+$	$C_{96}H_{104}NO_{18}{}^+$		1558.4
[1·4$_2$−PF$_6^-$]$^+$	$C_{180}H_{180}F_6N_2O_{28}P^+$		2962.1
[1·4$_2$−2PF$_6^-$]$^{2+}$	$C_{180}H_{180}N_2O_{28}{}^{2+}$	1408.7	2817.4
[1·4−PF$_6^-$]$^+$	$C_{124}H_{128}NO_{22}{}^+$		1983.4
[1·5$_2$−PF$_6^-$]$^+$	$C_{292}H_{276}F_6N_2O_{44}P^+$		4658.8
[1·5−PF$_6^-$]$^+$	$C_{180}H_{176}NO_{30}{}^+$		2831.3

In summary, we have demonstrated that the cylindrical macrotricyclic polyether could form a 1:2 stable complex with two dibenzylammonium salts in solution and in the solid state, which resulted in the construction of a series of novel dendritic [3]pseudorotaxanes. If bisammonium salts were used, supramolecular polymers[15] or necklaces[16] could be constructed. More applications of the cylindrical macrotricyclic polyether in supramolecular chemistry are now in progress.

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Supporting Information Available: Experimental procedures and characterization for the guests and the complexes. The crystal structure for **1·2$_2$** and its CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] (a) Ciferri, A., Ed. *Supramolecular Polymers*; Marcel Dekker: New York, 2000. (b) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4098.

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