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Extended and Contorted Conformations of Alkanediammonium Ions in Symmetrical α,α′,δ,δ′-Tetramethylcucurbit[6]uril Cavity

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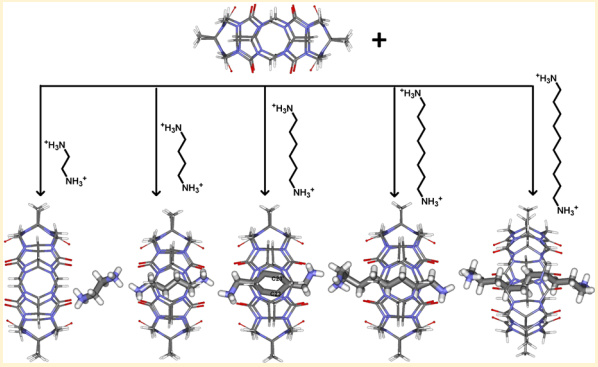
Supporting Information

ABSTRACT: Binding interactions between symmetrical α,α′,δ,δ′-tetramethylcucurbit[6]uril (TMeQ[6]) and a series of alkyldiammonium ions in aqueous solution and in the solid state were investigated by ^{1}H NMR spectroscopy, MALDI-TOF mass spectrometry, X-ray crystallography, and isothermal titration calorimetry (ITC). Their ^{1}H NMR spectra reveal that the actual binding behaviors vary depending upon the alkyl chain length. Their single-crystal X-ray diffraction analyses indicate the guest 1,2-ethanediammonium is located outside of the TMeQ[6] portal, while the other four alkyldiammonium guests can be accommodated in the TMeQ[6] cavity, forming 1:1 inclusion complexes. Most importantly, the long-chain alkyldiammoniums (1,8-octanediammonium and 1,10-decanediammonium) take a contorted conformation when bound within the TMeQ[6] cavity. Additionally, ITC experiments show that the complexation of the alkyldiammonium guests with TMeQ[6] is mainly enthalpy driven, which benefits from ion−dipole interactions.



INTRODUCTION

Molecular conformations and reactivity in small spaces of cavitands or capsules behave quite differently than those in dilute solution, which have attracted considerable interest in the areas of host−guest chemistry in the past decade.[1] There are many reasons for this scientific interest. First, this study can lead to an understanding of synthetic medicine activities in small spaces of proteins and nucleic acids, which is of fundamental importance for life. Second, molecular behavior in small spaces provides unique opportunities to study fascinating conformations, such as helices and stereoisomerism. Furthermore, the cavitand microenvironments offer new perspectives to unusual reactions. In a series of elegant papers, Rebek, Jr., et al. have reported the preparation of numerous cylindrical capsules in which multifarious alkanes display special conformations and reactivities.[2]

Cucurbit[n = 5−8, 10, 14]urils[3,4] (Q[n]), a unique class of macrocyclic cavitands consisting of methylene-bridged glycoluril units, have a hydrophobic cavity and two identical carbonyl-laced portals. Naturally, molecular conformations in the hydrophobic cavity of Q[n]s attract much attentions. Several examples where alkyl chains adopt contorted conformations when bound within the cavity of Q[8] have been reported by Kim and other groups in the past few years.[5−7] Although the interactions of Q[6] with various alkyldiammonium were investigated,[8,9] possibly due to too little Q[6] cavity, no examples of alkyl chains adopting contorted conformations in the Q[6] cavity have been reported. Recently, we prepared and characterized a novel type of chiral helical polyrotaxanes in which the long alkyl chain adopts different chiral conformations when bound within the ellipsoidal cavity of symmetrical α,α′,δ,δ′-tetramethylcucurbit[6]uril (a derivative of Q[6], hereafter abbreviated as TMeQ[6]).[10] These results prompted us to wonder how long alkyl chains could be encapsulated into the TMeQ[6] cavity and compressed into contorted conformations. In order to address this question, we carried out a systematic investigation with a series of alkyldiammonium ions (1,2-ethanediammonium (**1**), 1,4-butanediammonium (**2**), 1,6-hexanediammonium (**3**), 1,8-octanediammonium (**4**), and 1,10-decanediammonium (**5**)) of increasing alkyl chain (Figure 1) by using ^{1}H NMR spectroscopy, MALDI-TOF mass spectrometry, X-ray crystallography, and isothermal titration calorimetry (ITC). Herein,

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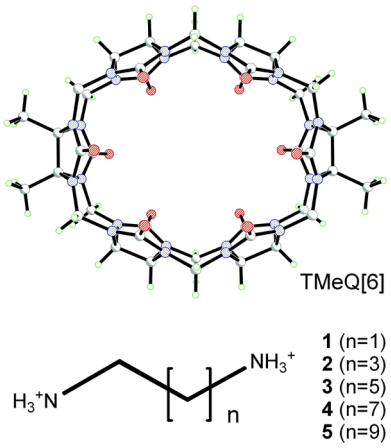

Figure 1. Host and guests used in this study.

we report the unusual binding behaviors of five alkyldiammonium guests with a TMeQ[6] host in aqueous solution and in the solid state.

RESULTS AND DISCUSSION

Binding Behaviors in Aqueous Solution. The binding behaviors of the TMeQ[6] host with the alkyldiammonium guests in aqueous solution can be conveniently monitored by NMR spectroscopic methods. In the following, we describe the ^{1}H NMR spectroscopy of each alkyldiammonium guest when bound with the TMeQ[6] host and discuss their binding behaviors in detail.

As shown in Figure 2, upon the addition of more and more TMeQ[6] host, the resonances for the α of the guest **1** shifted

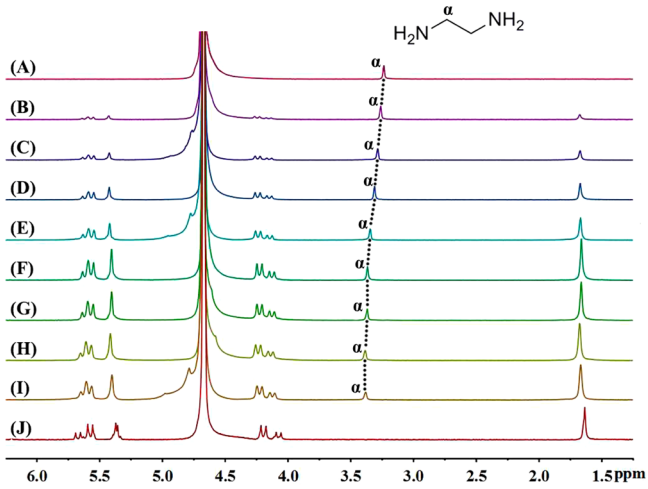

Figure 2. ^{1}H NMR spectra (400 MHz, D_2O) of guest **1** in the absence (A) and in the presence of increasing equivalents of TMeQ[6] (B–I).

downfield gradually. This observation suggests that the guest **1** were located out side of the portal of TMeQ[6],[11] as the downfield shift of the resonances may be attributed to the deshielding effect of the carbonyl-rimmed portal of TMeQ[6]. Obviously, the guest **1** cannot encapsulated into the cavity of TMeQ[6] to form inclusion complex.

Figure 3a shows the ^{1}H NMR spectra of guest **2** in the absence and presence of 1.02 equiv of TMeQ[6] in neutral D_2O solution. The resonances for the α and β protons of the guest **2** shifted upfield by 0.78 and 1.21 ppm, respectively, from those of the free guest **2**. Such a large upfield shift (0.78 and 1.21) indicates that the guest **2** is buried deeply inside the TMeQ[6] cavity, leading to the formation of a stable 1:1 inclusion complex **2**·TMeQ[6].

As can be seen in Figure 3b, in the presence of 1.0 equiv of TMeQ[6], the resonances for β and γ protons of the guest **3** shifted upfield by 1.07 and 0.90 ppm, respectively, indicative of their positioning within the cavity of TMeQ[6]. In contrast, the resonances of α proton exhibit no any changes, indicating the carbon atoms is situated at the center of the TMeQ[6] portal. Evidently, guest **3** forms a stable 1:1 inclusion complex with TMeQ[6] host too.

The binding behavior of TMeQ[6] with guest **4** is shown in Figure 3c, which clearly departs from those observed with guests **2** and **3**. After the addition of 1.01 equiv of TMeQ[6], the β, γ, and δ protons on the alkyl chains are shifted upfield by 0.30, 0.65, and 0.88 ppm, respectively, while the α proton are shifted downfield by 0.08 ppm. This phenomena can only be rationalized by the fomation of a 1:1 inclusion complex **4**·TMeQ[6], in which only part of the chain was buried into the cavity of TMeQ[6] while the α carbon atoms were located outside the portal of the TMeQ[6].

At first glance, the alkyl chain of guest **5** is too long and the TMeQ[6] cavity is not large enough to encapsulate the whole alkyl chain even in a contorted conformation. In the presence of 1.0 equiv of TMeQ[6], however, all the protons of the long alkyl chain experience a considerable upfield shift, indicating the long alkyl chains were encapsulated into the TMeQ[6] cavity (Figure 3d). It is reasonable to presume that the TMeQ[6] "wheel" thread on the guest **5** "axle" and the TMeQ[6] can move back and forth along the long alkyl chain of the guest **5**. Ion–dipole interactions between positively charged nitrogen atoms of the guest **5** and the carbonyl oxygen atoms of the TMeQ[6] host prevent the TMeQ[6] "wheel" dissociated from the guest **5** "axle". This motion is relatively fast on the NMR time scale as only one set of guest signals was observed. In other words, the TMeQ[6] forms a special 1:1 inclusion complex, [2]pseudorotaxane, with the guest **5**.

Further evidence for the formation of the 1:1 inclusion complexes of TMeQ[6] and guests **2**–**5** was provided by the MALDI-TOF mass spectrometry experiments. In their MALDI-TOF MS spectra (Figure S1, Supporting Information), four major signals at m/z = 1141.96, 1169.82, 1197.50, 1225.34, corresponding to **2**·TMeQ[6] (caculated 1141.08), **3**·TMeQ-[6] (caculated 1169.13), **4**·TMeQ[6] (caculated 1197.19), and **5**·TMeQ[6] (caculated 1225.24), respectively, were observed.

It is evident that the major driving force for above-mentioned binding behavior in aqueous solution appears to be the ion–dipole interactions between the positive charge of the guest and the portal oxygen atoms of TMeQ[6]. However, the actual binding behaviors vary depending upon the alkyl chain length because the hydrophobic interaction between the alkyl chains of the guest and the inner cavity of TMeQ[6] must be taken into account. In the case of guest **1**, no encapsulation occurs because the TMeQ[6] cavity is too large to accept one guest molecule alone but too small to accommodate two guest molecules. For the guests **2** and **3**, both guest molecules are favorably encapsulated into the TMeQ[6] cavity in their extended conformation. For the guest **4**, encapsulation of the alkyl chain by TMeQ[6] is less favorable, and part of the alkyl chain is located outside of the TMeQ[6] cavity. As for guest **5**, the macrocycle thread on the alkyl chain to form a [2]pseudorotaxane, with the "wheel" moving fast on the "axle".

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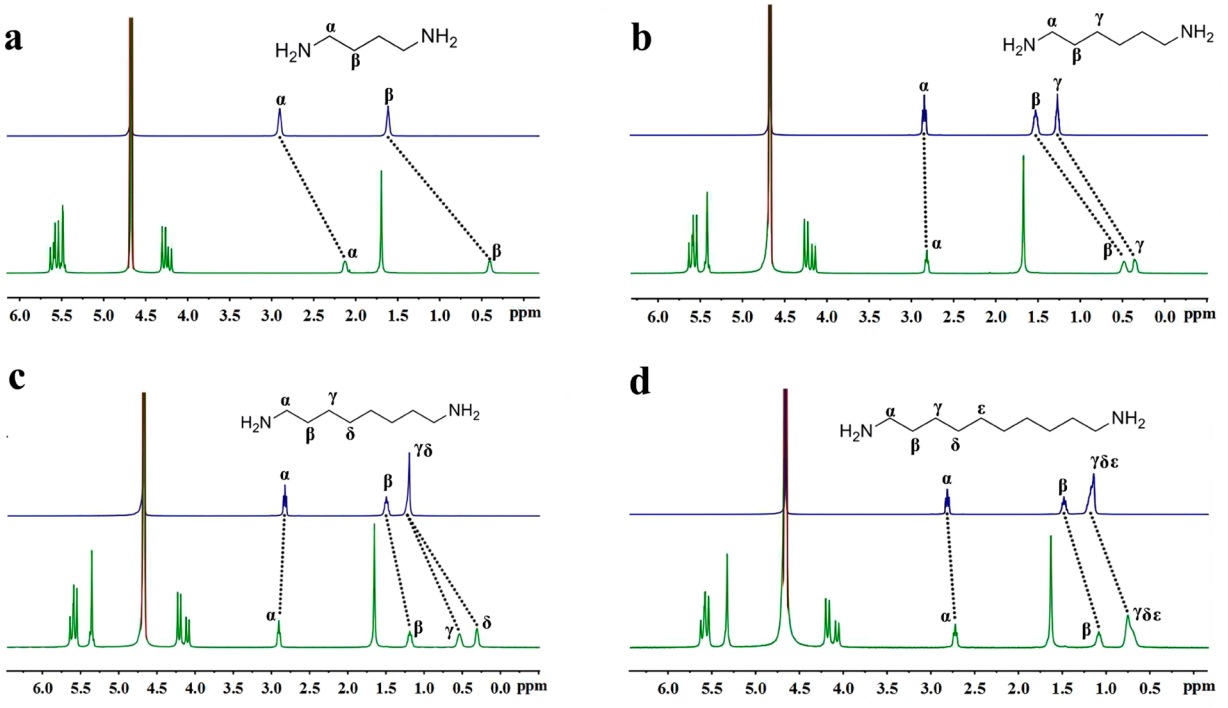

Figure 3. ^{1}H NMR spectra (400 MHz, D_2O) of guest **2**–**5** (a–d) in the absence (up) and in the presence of 1.1 equiv of TMeQ[6] (down).

Structural Analysis. We fortunately obtained all single crystals of TMeQ[6] with these five guests by slow vapor evaporation of aqueous solution containing TMeQ[6] and the corresponding alkyldiammonium ions. Thus, the binding behaviors of TMeQ[6] with these five guests in the solid state can be clearly examined by single-crystal X-ray crystallography.

A brief description of the structures of compounds **1**–**3** is in order. As predicted on the basis of the ^{1}H NMR studies, guest **1** is located outside of the TMeQ[6] portal (Figure 4) instead of

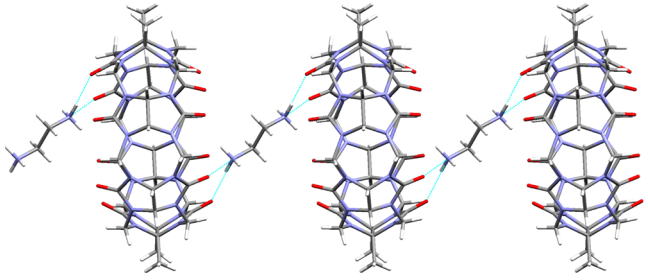

Figure 4. Stick representation showing guest **1** connected to TMeQ[6] molecules through hydrogen bonds, forming a 1D supramolecular strucure. Solvate water molecules and chloride anions are omitted for clarity. O = red, C = gray, N = light blue.

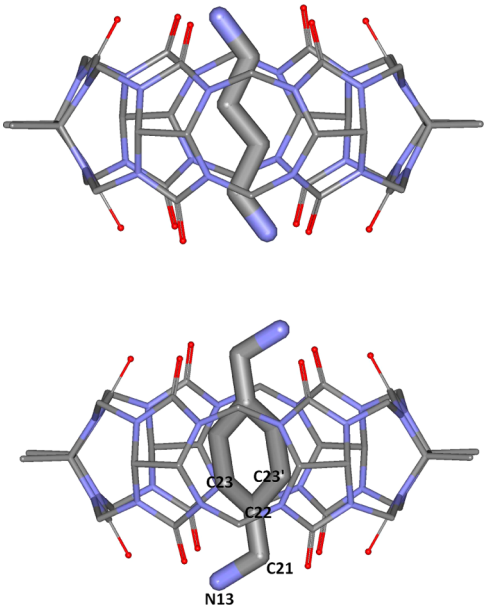

Figure 5. Stick representation of compounds **2** (up) and **3** (down). Solvate water molecules and nitrate anions are omitted for clarity. O = red, C = gray, N = light blue.

encapsulated into the TMeQ[6] cavity. Interestingly, each guest molecule connects to two TMeQ[6] molecules through hydrogen bonds, generating a 1D supramolecular assembly. The perspective view of compounds **2** and **3** is shown in Figure 5. In the crystal structures of compound **2**, guest **2** buried deeply inside the TMeQ[6] cavity adopts an extended conformation, forming a stable 1:1 inclusion complex, which is in agreement with their ^{1}H NMR spectroscopic data. In the case of compound **3**, the guest **3** is encapsulated in the TMeQ[6] cavity, in which one carbon atom (C23) is disordered over two sides.

Compounds **4** and **5** crystallized in the same space group $P\bar{1}$. The asymmetric unit of both compounds consists of one TMeQ[6] host, one alkyldiammonium guest, and two nitrate ions to balance the charge. The X-ray crystal structure of compound **4** reveals a unique inclusion complex in which the guest **4** exhibits a back-folded geometry. As seen in Figure 6, five carbon atoms (C14, C15, C16, C17, and C18) of the guest **4** are located inside the cavity of the TMeQ[6] host while the

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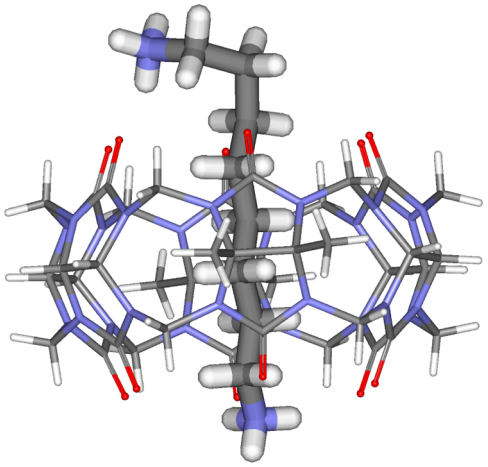

Figure 6. Stick representation of compound **4** showing a back-folded geometry of the guest **4**. Solvate water molecules and nitrate anions are omitted for clarity. O = red, C = gray, N = light blue.

other three carbon atoms (C19, C20, and C21) remain outside of the portal, which is distinctly different from what we have observed in the aqueous solution. It is interesting to note that N(25) and N(26) are displaced from the six-oxygen plane of the portal by 0.706(2) and 2.377(7) Å, respectively. As a result, strong hydrogen bonds between the ammonium groups of the guest **4** and the oxygen atoms of TMeQ[6] are formed, which is the main reason why the guest **4** exhibits a back-folded geometry. This phenomena is agree with what Isaacs et al. have observed with the *ns*-CB[6] and 1,12-dodecane diammonium.[6]

X-ray structural analysis reveals that the guest **5** takes a contorted conformation instead of extended conformation when bound within the TMeQ[6] cavity. As depicted in Figure 7, six carbon atoms (C21, C22, C23, C21A, C22A, and C23A) of the guest **5** are squeezed into the small TMeQ[6] cavity. The alky chain of guest **5** takes the *−sc,−ap,−ap,−sc,−ap,−sc,−ap,−ap,−sc* conformation with torsion angles of −68.5, −175.3, −174.3, −65.33, 180, 65.33, 174.32, 175.34, and 68.5, respectively. As a result, both terminal ammonium groups

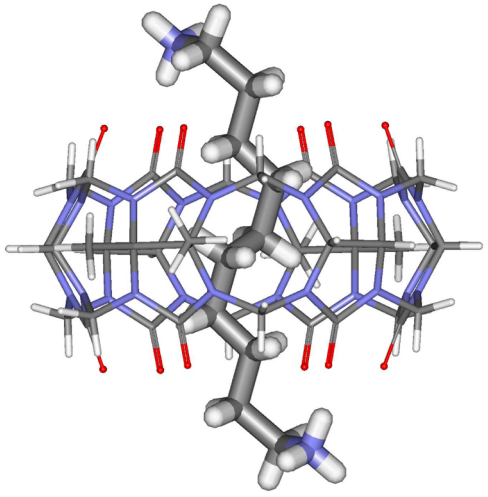

Figure 7. Stick representation of compound **5** showing the guest **5** takes a contorted conformation when bound within the TMeQ[6] cavity. Solvate water molecules and nitrate anions are omitted for clarity. O = red, C = gray, N = light blue. Symmetry codes: A $-x+1$, $-y+1$, $-z+1$.

bent toward the TMeQ[6] portal to form strong hydrogen bonds: N(13)···O(6) 2.885(10) Å and N(13)···O(4) 2.969(10) Å. Apparently, the assembly of the inclusion complex **5**·TMeQ[6] is mainly contributed to strong hydrogen bonds and hydrophobic effect. Furthermore, a significant deformation of the TMeQ[6] host was also observed both in compounds **4** and **5**, which provides a better shape complementarity and facilitates the TMeQ[6] cavity to accommodate the alkyl chain of the guests.

Description of ITC. Isothermal titration calorimetry (ITC) experiments (Figure S2, Supporting Information) were conducted at room temperature to quantify the enthalpic and entropic contribution to the binding interactions of the TMeQ[6] host and the alkyldiammonium guests. The result is shown in Table 1, indicating the complexation of guest **1** with

Table 1. Binding Constants (K) and the Relevant Thermodynamic Parameters for the Complexation of the Alkyldiammonium Guests with TMeQ[6]

experiment	K (M^{-1})	$\Delta H°$ (kJ·mol^{-1})	$T\Delta S°$ (kJ·mol^{-1})
1·TMeQ[6]	8.49(±0.86) × 10^4	−14.52 ± 0.45	13.61
2·TMeQ[6]	5.13(±0.80) × 10^6	−41.74 ± 0.41	−3.43
3·TMeQ[6]	4.09(±0.94) × 10^7	−46.70 ± 0.29	−3.25
4·TMeQ[6]	1.17(±0.57) × 10^7	−36.63 ± 0.33	3.71
5·TMeQ[6]	1.48(±0.34) × 10^6	−29.06 ± 0.56	6.16

TMeQ[6] is driven by both enthalpy and entropy ($\Delta H°$ = −14.52 kJ·mol^{-1}, $T\Delta S°$ = 13.61 kJ·mol^{-1}), while the formation of the inclusion complexes **2**·TMeQ[6] and **3**·TMeQ[6] is almost exclusively enthalpy driven ($\Delta H°$ = −41.74 kJ·mol^{-1}, $T\Delta S°$ = −3.43 kJ·mol^{-1} for inclusion complex **2**·TMeQ[6]; $\Delta H°$ = −46.70 kJ·mol^{-1}, $T\Delta S°$ = −3.25 kJ·mol^{-1} for inclusion complex **3**·TMeQ[6]). In the case of inclusion complexes **4**·TMeQ[6] and **5**·TMeQ[6], the complexation of TMeQ[6] with guests **4** and **5** is driven mostly by enthalpy and to some extent by entropy as well ($\Delta H°$ = −36.63 kJ mol^{-1}, $T\Delta S°$ = 3.71 kJ·mol^{-1} for inclusion complex **4**·TMeQ[6]; $\Delta H°$ = −29.06 kJ·mol^{-1}, $T\Delta S°$ = 6.16 kJ·mol^{-1} for inclusion complex **5**·TMeQ[6]). For these five inclusion complexes, the high enthalpy gain may be attributed to the strong ion−dipole interactions between the ammonium groups and the carbonyl groups of the host portal. The $\Delta H°$ trend ($\Delta H°_{\mathbf{1}\cdot\mathrm{TMeQ[6]}} > \Delta H°_{\mathbf{5}\cdot\mathrm{TMeQ[6]}} > \Delta H°_{\mathbf{4}\cdot\mathrm{TMeQ[6]}} > \Delta H°_{\mathbf{2}\cdot\mathrm{TMeQ[6]}} > \Delta H°_{\mathbf{3}\cdot\mathrm{TMeQ[6]}}$) is in accord with the efficiency of the ion−dipole interactions. Evidently, the complexation of the alkyldiammonium guests with TMeQ[6] is mainly enthalpy driven.

■ CONCLUSION

In summary, we have investigated the binding interactions between TMeQ[6] and a series of alkyldiammonium ions both in the aqueous solution and in the solid state by using NMR spectroscopy, MALDI-TOF mass spectrometry, X-ray crystallography, and ITC. We discovered that these alkyldiammonium guests form stable 1:1 inclusion complexes with the TMeQ[6] host not only in the aqueous solution but also in the solid state except for the 1,2-ethane diammonium guest. Most importantly, conformational changes for both guests and hosts are observed when the alkyl chain's length (in its extended conformation) exceeds the dimensions of the TMeQ[6] cavity. These results provide an insight into designing and constructing novel molecular machines and switches in small spaces of cavitands or capsules.

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EXPERIMENTAL SECTION

Materials and Methods. 1,4-Butanediammonium was purchased and used as supplied without further purification. 1,2-Ethanediammonium, 1,6-hexanediammonium, 1,8-octanediammonium, and 1,10-decanediammonium were prepared by protonation of the corresponding amines. TMeQ[6] was prepared according to a literature method.[12] All NMR data were recorded in D_2O. MALDI-TOF mass spectra were taken on an ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix.

Single-Crystal X-ray Crystallography. Single crystals of compounds **1**−**5** were grown from water by vapor diffusion. Diffraction data for these five compounds were collected at 293 K with a CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by using the multiscan program SADABS. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages, respectively. For compound **1**, the SQUEEZE process in PLATON program was applied to remove the nitrate anion because it could not be satisfactorily modeled.[13] CCDC 1026711−1026715 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of Compounds 1−5. *TMeQ[6]·1 (**1**).* To a solution of **1** (6.7 mg, 0.050 mmol) in HNO_3 (1 M, 10 mL) was added TMeQ[6] (6.2 mg, 0.005 mmol). The resulting reaction mixture was stirred for 5 min at 50 °C and filtered. Slow solvent evaporation of the filtrate in air over a period of about 3 weeks provided rhombic colorless crystals of TMeQ[6]•**1** with a yield of 1.2 mg (20%). Anal. Calcd for $C_{42}H_{78}N_{26}O_{30}$ (**1**): C, 35.34; H, 5.51; N, 25.52. Found: C, 35.42; H, 5.62; N, 25.47.

*TMeQ[6]·2 (**2**), TMeQ[6]·3 (**3**), TMeQ[6]·4 (**4**), and TMeQ[6]·5 (**5**).* All these compounds were obtained following the method described above for compound **1**. The yields based on TMeQ[6] for these compounds are in the range 20−25%. Anal. Calcd for $(C_{40}H_{44}N_{24}O_{12})\cdot(C_4N_2H_{14})\cdot 2NO_3\cdot 8H_2O$ (**2**): C, 37.45; H, 5.29; N, 27.79. Found: C, 37.46; H, 5.23; N, 27.65. Anal. Calcd for $(C_{40}H_{44}N_{24}O_{12})\cdot(C_6N_2H_{18})\cdot 2NO_3\cdot 10H_2O$ (**3**): C, 37.45; H, 5.60; N, 26.58. Found: C, 37.53; H, 5.63; N, 26.67. Anal. Calcd for $(C_{40}H_{44}N_{24}O_{12})\cdot(C_8N_2H_{22})\cdot 2NO_3\cdot 10H_2O$ (**4**): C, 38.35; H, 5.77; N, 26.09. Found: C, 38.31; H, 5.82; N, 26.18. Anal. Calcd for $(C_{40}H_{44}N_{24}O_{12})\cdot(C_{10}N_2H_{26})\cdot 2NO_3\cdot 8H_2O$ (**5**): C, 40.16; H, 5.80; N, 26.23. Found: C, 40.13; H, 5.70; N, 26.27.

Isothermal Titration Calorimetry Experiments. The association constants and thermodynamic parameters for the inclusion complexation of aliphatic ammonium ions with TMeQ[6] were determined by titration calorimetry with an ITC instrument in 10 mM sodium phosphate buffer (pH = 7.0). An aqueous solution (0.1 mM) of TMeQ[6] was placed in the sample cell (1.3 mL). As a solution (1 mM) of the guests **1**, **2**, **4**, and **5** was added in a series of 25 injections (10 μL), the heat evolved was recorded at T = 298.15 K. As a solution (1 mM) of the guest **3** was added in a series of 50 injections (5 μL), the heat evolved was recorded at T = 298.15 K. The heat of dilution was corrected by injecting the guest solution into deionized water and subtracting these data from those of the host−guest titration. Computer simulations (curve fitting) were performed using the Nano ITC analyze software.

ASSOCIATED CONTENT

Supporting Information

MALDI-TOF mass spectrum of inclusion complexes **2**·TMeQ[6], **3**·TMeQ[6], **4**·TMeQ[6], and **5**·TMeQ[6], ITC profile of TMeQ[6] with guests **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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