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Host-guest complexes of a water soluble cucurbit[6]uril derivative with some dications of 1,ω-alkyldipyridines: ^{1}H NMR and X-ray structures

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Interactions between a symmetrical tetramethyl-substituted cucurbit[6]uril (host: TMeQ[6]) and 1,ω-alkylenedipyridine (ω = 2, 4, 6, 8,10) dicationic guests were investigated using ^{1}H NMR spectroscopy and single crystal X-ray crystallography. In these inclusion complexes, combined cavity and portal binding in TMeQ[6] were observed, and the length of the bridged alkylene was found to play an important role not only in balancing the overall hydrophilic/hydrophobic interaction between the host and the guest, but also in defining the structure of the resulting inclusion complexes. For the guest 1,2-ethylenedipyridine (Edpy), TMeQ[6] includes a positively charged pyridine ring of Edpy to form an unsymmetrical inclusion complex; for the guest 1,4-butylenedipyridine (Bdpy), TMeQ[6] includes a positively charged pyridine ring of Bdpy, but the different competitive interactions in and between the related inclusion complexes could lead to a fast exchange between the hosts and guests. For the guests with longer bridge chains, such as 1,6-hexamethylenedipyridine (Hdpy) or 1,8-octylenedipyridine (Odpy), a stable pseudorotaxane inclusion complex is formed by combining the hydrophobic cavity and the outer portal dipole-ion interactions. However, for 1,10-decatylenedipyridine (Ddpy), the two TMeQ[6] host molecules include the two end pyridine rings of Ddpy and form a dumbbell inclusion complex.

symmetrical tetramethyl-substituted cucurbit[6]uril, 1,ω-alkylenedipyridine (ω = 2, 4, 6, 8, 10) dicationic guests, host-guest complex, ^{1}H NMR spectroscopy, single crystal X-ray crystallography

1 Introduction

A hydrophobic cavity and polar carbonyl groups surrounding the opening portals are common characteristic features for the new macrocyclic receptor family: Cucurbit[n]urils (Q[*n*]s) and their derivatives. Among them, the structure of cucurbit[*n*=6]uril (Q[6]) was first determined and reported by Mock and co-workers in 1981[1]. A series of cucurbituril homologues, cucurbit[*n*=5,7, 8]urils (Q[5], Q[7], Q[8]), were synthesized and reported by Day and Kim et al. in 2000[2,3]. Cucurbit[*n* = 10]uril (Q[10]) including Q[5], reported by Day et al. in 2002, is the largest one in the family[4]. The varying cavity and portal sizes, and particularly the ability to form inclusion or exclusion complexes with organic species or inorganic ions lead to the remarkable molecular recognition properties of Q[*n*]s and make them into building blocks for supramolecular chemistry, thus leading quite a few researchers to focus on this area. The corresponding summaries have been extensively reviewed[5−12].

Recently, a series of Q[*n*] derivatives including fully substituted cyclohexano Q[5] and Q[6][13], diphenyl

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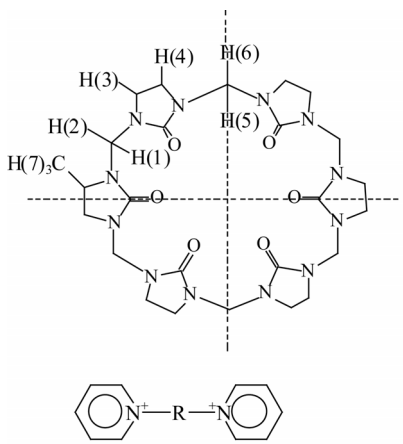
Q[6][14], perhydroxycucurbit[6]uril ($(OH)_{12}$Q[6])[15] and others[16−20] were synthesized and reported to overcome the poor solubility of the general Q[*n*]s in common solvents. More recently, using a dimer of glycoluril synthesized in our laboratories and the diether of alkylglycoluril, we synthesized new symmetrical and unsymmetrical substituted cucurbit[*n*]urils[21]. Some Q[*n*]s showed surprising water solubility, which allowed us to investigate their host-guest chemistry in neutral water[22].

Similar to the well-known receptors or hosts such as crown ethers, cyclodextrins and calix[*n*]arenas, the interaction between the Q[*n*]s and guests can be investigated using various NMR methods, including ^{1}H NMR, ^{13}C NMR, COSY and NOESY techniques, mass spectrometry, X-ray crystallography, electronic absorption spectroscopy, and fluorescence spectroscopy. Generally, these methods give a consistent conclusion or some supporting information for a certain host-guest interaction system. In this work, we report some host-guest interaction systems in which the host is a water-soluble symmetrical substituted cucurbit[6]uril (TMeQ[6])[21] and the guests are dibromine salts of a series of 1,ω-alkyldipyridine, including 1,2-ethylenedipyridine (**Edpy**), 1,4-butylenedipyridine (**Bdpy**), 1,6-hexamethylenedipyridine (**Hdpy**), 1,8-octylenedipyridine (**Odpy**) and 1,10-decatylenedipyridine (**Ddpy**) (Scheme 1).



R = CH_2CH_2, **Edpy**

R = $CH_2CH_2CH_2CH_2$, **Bdpy**

R = $CH_2CH_2CH_2CH_2CH_2CH_2$, **Hdpy**

R = $CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$, **Odpy**

R = CH_2CH_2 $CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$, **Ddpy**

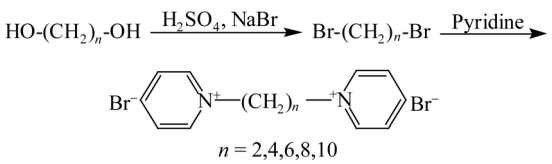
Scheme 1 Structures of the host TMeQ[6] and related 1,ω-alkylenedipyridine dicationic guests.

2 Experimental

Symmetrical substituted cucurbit[6]uril (TMeQ[6]) was prepared and purified according to the method developed in our laboratories[21]. All chemicals were of analytical grade and were used without further purification. ^{1}H NMR spectra were recorded at 293K on a VARIAN INOVA-400 spectrometer, and samples for ^{1}H NMR were prepared in a similar manner using D_2O as the solvent.

The general procedure for the synthesis of 1,ω-alkyldipyridines is as follows (Scheme 2): A mixture of pyridine (2.0 equiv), 1,ω-alkyldibromine (1 equiv) and triethylamine (0.05 equiv) was refluxed for 2 h. The resulting white precipitate was filtered, washed with ether, and air-dried. ^{1}H NMR of **Edpy** (D_2O, 400 MHz), δ: 8.70 (d, J = 6 Hz, 4H), 8.51 (t, J = 7 Hz, 2H), 7.97 (t, J = 7 Hz, 4H), 5.19 (s, 4H), MS *m/z*(%): 52 ($CH_3CH_2 + Na^+$, 50), 79 ($C_5H_5N^+$,100), 106 ($CH_2CH_2C_5H_5N^+$, 38); mp: 309−310℃; yield: 66%. ^{1}H NMR of **Bdpy** (D_2O,400 MHz), δ: 8.742 (d, J = 6 Hz, 4H), 8.44 (t, J = 8 Hz, 2H), 7.96 (t, J = 7 Hz, 4H), 4.57 (s, 4H), 2.014 (s, 4H); MS *m/z*(%): 52 ($CH_3CH_2 + Na^+$, 58), 79 ($C_5H_5N^+$, 100); mp: 248−249℃; yield: 61%. ^{1}H NMR of **Hdpy** (D_2O, 400 MHz), δ: 8.68 (d, J = 8 Hz, 4H), 8.37 (t, J = 8 Hz, 2H), 7.89 (t, J = 7 Hz, 4H), 4.44 (t, J = 8 Hz, 4H), 1.85 (t, J = 7 Hz, 4H), 1.23 (s, 4H); MS *m/z* (%): 121.2 ($M/2^+$, 100), 321.1 ($M + Br^-$, 10), mp: 242−244℃; yield: 56%. ^{1}H NMR of **Odpy** (D_2O, 400 MHz), δ: 8.74 (d, J = 6 Hz, 4H), 8.43 (t, J = 8 Hz, 2H), 7.95 (t, J = 6 Hz, 4H), 4.49 (t, J = 8 Hz, 4H), 1.89 (t, J = 7 Hz, 4H), 1.210 (s, 8H); MS *m/z* (%): 135 ($M/2^+$,100), 349 ($M + Br^-$, 10); mp: 192−193℃; yield: 54%. ^{1}H NMR of **Ddpy** (D_2O, 400 MHz), δ: 8.68 (d, J = 6 Hz, 4H), 8.39 (t, J = 8 Hz,2H), 7.91 (t, J = 7 Hz,4H), 4.45 (t, J = 7 Hz,4H), 1.85 (t, J = 7 Hz,4H), 1.161 (s, 8H), 1.161(s, 4H); MS *m/z* (%): 149.1 ($M/2^+$, 100), 379.1 ($M + Br^-$, 10); mp: 189−192℃; yield: 59%.

Single crystals of TMeQ[6] adduct with dibromine salts of 1,4-butylenedipyridine (**Bdpy**), 1,8-octylenedi-



Scheme 2 Synthesis route of the guests.

pyridine (**Odpy**) and 1,10-decatylene dipyridine (**Ddpy**), respectively were obtained by dissolving TMeQ[6] (0.20 g, 0.19 mmol) in a solution of **Bdpy** or **Hdpy** or **Ddpy** Br_2 (0.075, 0.086, 0.092 g, 0.20 mmol) in water (5 mL). The final solution was mixed thoroughly and allowed to stand at room temperature; crystals formed after several days and were collected.

X-ray crystallography: the crystal data of host-guest complexes of TMeQ[6] with 1,4-butylenedipyridine (**Bdpy**), 1,8-hexamethylenedipyridine (**Odpy**) and 1,10-decatylenedipyridine (**Ddpy**) were collected with a SMART Apex Ⅱ CCD diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å, μ= 0.828 mm^{-1}) in the ω scan mode. Lorentz polarization and absorption corrections were applied. Structural solution and full matrix least squares refinement based on F2 were performed with the SHELXS-97 and SHELXL-97 program packages[23], respectively. All the non-hydrogen atoms were refined anisotropically. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition Nos. CCDC 705451, CCDC 705452 and CCDC 705453. Copies of the data can be obtained free of charge on application to CCDC (12 Union Road, Cambridge CB2 1EZ, UK. Fax, +44 1223/336 033; e-mail, deposit@ccdc.cam.ac.uk).

3 Results and discussion

3.1 The binding interactions between TMeQ[6] and Bdpy

We first discuss the experimental results of the interaction system of TMeQ[6]-1,4-butylenedipyridine (**Bdpy**). The X-ray crystallographic determination for the single crystals reveals that each TMeQ[6] host includes only one pyridine ring of a **Bdpy** guest in its cavity. Another pyridine ring and the butylene of the **Bdpy** guest are located at one portal of the TMeQ[6] to form an asymmetrical host-guest inclusion complex (Figure 1(a) and (b)). The stacking of the inclusion complexes presents a one-dimensional assembled host-guest supramolecular structure (Figure 1(c)). For an isolated host-guest inclusion complex in the crystals, the included pyridine ring moiety is balanced by a hydrophobic cavity interaction that draws the pyridine ring into the cavity and an inter portal dipole-ion interaction that pulls the pyridine ring to a portal of the host TmeQ[6]. The short distances of

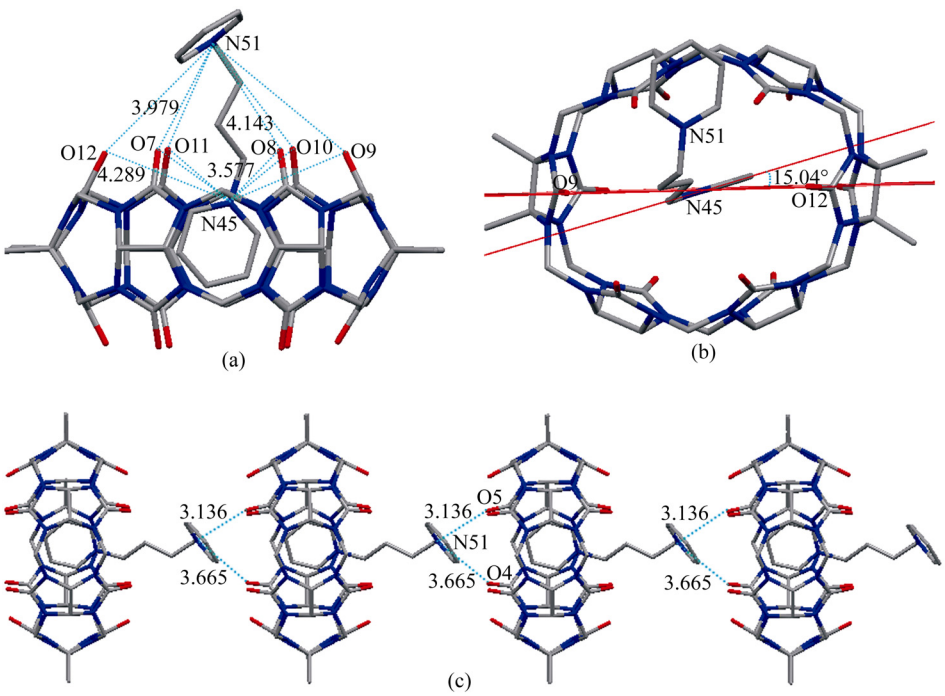


Figure 1 X-ray crystal structure of the TMeQ[6]-**Bdpy** inclusion complex. (a) Side view; (b) top view and (c) one-dimensional assembled host-guest supramolecule structure. All hydrogen atoms are omitted for clarity.

$N45^+$ on the inter pyridine to the carbonyl oxygens O7—O12 of the portal of TMeQ[6] are between 3.577 and 4.289 Å, with an average of 3.917 Å. Moreover, the outer portal dipole-ion interaction pulls the included pyridine ring back to the cavity of the host TMeQ[6], and the short distances of $N51^+$ on the protruded pyridine to the carbonyl oxygens O7 and O8 of the portal of TMeQ[6] are 3.978 and 4.143 Å, respectively (referring to Figure 1(a) and (b)). An additional dipole-ion interaction between the two adjacent host-guest inclusion complexes in the one-dimensional assembled host-guest supramolecular structure pulls the bound **Bdpy** out of the cavity of the TMeQ[6] and decreases the stability of the inclusion complex of TMeQ[6]-**Bdpy** (referring to Figure 1(c)); the shortest distances of $N51^+$ on the outer pyridine of the included **Bdpy** to a portal carbonyl oxygens (O4 and O5) of the next TMeQ[6] are only 3.137 and 3.665 Å, respectively, even shorter than those occurring in the inter portal dipole-ion interaction. Thus, these four main interactions coexist competitively in the formed inclusion complexes, and combined cavity and portal binding interactions in and between TMeQ[6] with a **Bdpy** molecule being observed.

In the solid state, the guest is inserted to the extent that the pyridyl ring sits essentially in line with opposite sets of the portal carbonyl oxygens O9 and O12, but is twisted away from linearity by 15.04°. The several closest contacts are between the $N45^+$ and carbonyl atoms (O7, O8, O10 and O11) of the cucurbituril, with N45⋯O7, N45⋯O8, N45⋯O10 and N45⋯O11 of 4.091, 3.577, 3.916 and 3,467 Å, respectively (Figure 1(a) and (b)).

According to the structure of the TMeQ[6]-**Bdpy** complex determined, the corresponding ^{1}H NMR spectrum of the bound **Bdpy** should show six pyridine ring proton resonances, three resonances of the included pyridine with upfield shift, three resonances of the excluded pyridine with downfield shift, and four methylene proton resonances due to the unsymmetrical TMeQ[6]-**Bdpy** complex, thus, there should be total ten proton resonances of the bound **Bdpy** in the spectrum. Figure 2 shows titration ^{1}H NMR spectra of **Bdpy** with TMeQ[6]. Compared to Figure 2(a) and (b), only the bound (linked by dash lines) **Bdpy** signals are present after addition of 1.0 equiv of TMeQ[6], while the signals of the unbound guest (linked by solid lines) appear when the concentration of **Bdpy** is 2.5 equiv of TMeQ[6] (Figure 2(c)). Three rather than the expected six bound pyridine ring resonances are displaced by upfield shifts of 0.11 (for proton H^1), 0.15 (for proton H^3) and 0.23 (for proton H^2) ppm, respectively, while not two but four methylene resonances are displaced by downfield shifts of 0.37 (for proton H^5) and 0.12 (for proton H^4) ppm compared to the resonances of the free **Bdpy**. The broaden peaks of the bound **Bdpy** indicate that the exchange between including and excluding the guest is moderately fast at the NMR time scale.

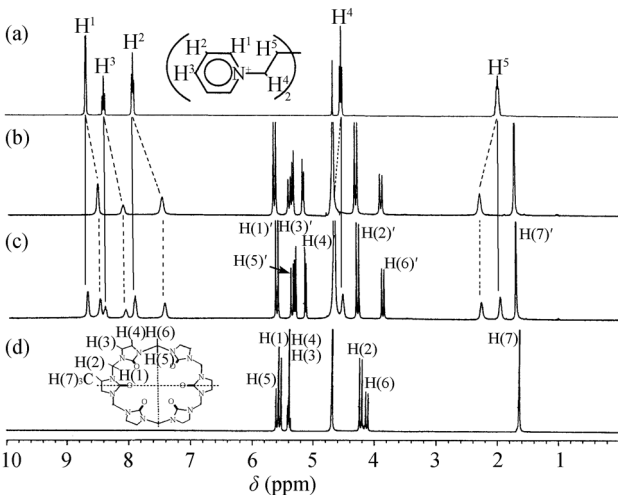


Figure 2 ^{1}H NMR spectra (400 MHz, D_2O) of **Bdpy** in the absence (a), in the presence of 1.0 (b), 2.5 (c) equiv of TmeQ[6], and the neat TMeQ[6] (d).

On the other hand, the resonances of the protons H(1)′, H(2)′ and H(7)′ on the interacting TMeQ[6] experience a downfield shift of 0.13 ppm, while the resonances of the protons H(5)′, H(6)′ and H(4)′ on the interacted TMeQ[6] experience an upfield shift of 0.27 ppm compared to the free TMeQ[6] (Figure 2(c) and (d)). The difference of 0.25—0.41 ppm for the different portal methylene pair protons H(1)/H(2) and H(5)/H(6) suggests that the protons on TMeQ[6] lie in different magnetic environments caused by a preferential orientation of intruding or protruding pyridine of bound Bdpy from the portal of TMeQ[6]. This behavior is consistent with the results from the crystal structural study (referring to Figure 1(a) and (b)). A comparison of the integrals of the protons of the bound **Bdpy** with the protons of TMeQ[6] revealed the complex to be 1:1.

Thus, the ^{1}H NMR information implies that the two pyridine moieties of a **Bdpy** are in the shielding zone in the cavity of TMeQ[6], and the alkyl part of the guest

Bdpy is in the deshielding zone of the portal of TMeQ[6]. In addition, the structure of the inclusion complex is symmetrical, as evidenced by the lack of splitting of the portal methylene proton resonances, and the interaction of the host and guest has a ratio of 1:1. Therefore, the complexation of TMeQ[6] and **Bdpy** could be described by a TMeQ[6] threaded by a **Bdpy** to form a transition state, and the host TMeQ[6] shuttles between the two end pyridyl moieties of the guest. Thus, the NMR spectra show the average of the interaction between the host TMeQ[6] and the guest **Bdpy**. The broadening of the bound **Bdpy** supports this interaction model.

3.2 The binding interactions between TMeQ[6] and Edpy

To understand the arguments about the interaction mode(s) of the TMeQ[6] with **Bdpy**, we introduced some homologues of **Bdpy**, in which the bridged alkylene chain is shorter or longer than the butylenes for further study of this kind of inclusion complexation. Figure 3 shows the titration ^{1}H NMR spectra of **Edpy** recorded in the absence (a) and in the presence of 0.4 (b) and 1.1 (c) equiv of TMeQ[6]. Unlike the case of the bound **Bdpy**, the ^{1}H NMR spectrum of the bound **Edpy** shows six pyridine ring proton resonances, three resonances of the included pyridine ring shift upfield by 0.51 (for proton H^1), 0.55 (for proton H^3) and 0.93 (for proton H^2) ppm, and three resonances of the excluded pyridine ring shift downfield by 0.14 (for proton H^1), 0.08 (for proton H^3) and 0.43 (for proton H^2). Clearly, the two pyridine rings of **Edpy** are in different magnetic environments; one ring is contained within the cavity, and the other is contained within the portal. The significant upfield shifts of the protons on the pyridine ring indicate a deep cavity binding[22].

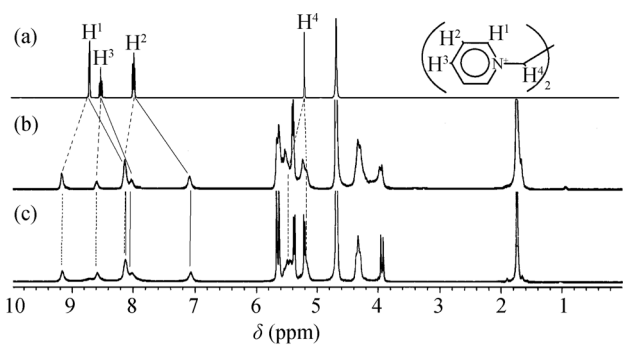


Figure 3 ^{1}H NMR spectra (400 MHz, D_2O) of **Edpy** in the absence (a), in the presence of 0.4 (b), 1.1 (c) equiv of TmeQ[6].

In the inclusion complex of TMeQ[6]-**Edpy**, the included pyridine ring is balanced by not only a competitive of a hydrophobic cavity interaction and the inter portal dipole-ion interaction between the N^+ on the included pyridine ring of the guest and the portal carbonyl of the host, but also an outer portal dipole-ion interaction between the N^+ on the excluded pyridine ring of **Edpy** and the portal of the TMeQ[6], which would further push the included pyridine ring deeply into the cavity of TMeQ[6]. Thus, the split pyridine proton resonances with the significant upfield and downfield shifts can be observed in the corresponding ^{1}H NMR spectra. The broadened peaks of the pyridine proton resonances suggest that the exchange between the included and excluded guests is moderately fast at the NMR time scale. A comparison of the integrals of the protons of the bound **Ebpy** with the protons of TMeQ[6] also revealed the complex to be 1:1.

3.3 The binding interactions between TMeQ[6] and Hdpy or Odpy

Figure 4 shows the titration ^{1}H NMR spectra of **Hdpy** recorded in the absence (a) and in the presence of 1.0 (b) and 2.1 (c) equiv of TMeQ[6]. Only signals corresponding to the bound **Hdpy** are present when the concentration of **Hdpy** is close to that of the host TMeQ[6] (Figure 4(a) and (b)), with the signals of the unbound guest appearing when the concentration of **Hdpy** reaches 2.1 equiv of TMeQ[6] (Figure 4(c)). Two of three methylene proton resonances shift significantly upfield by 0.84 (for H^5 and H^6), suggesting that the center part of the hexamethylene moiety of the bound guest is deep in the shielding zone in the cavity of the host. However, a significant downfield shift for the pyridyl proton H^1 (0.6 ppm) suggests that the two pyridyl rings of the bound guest are in the deshielding zone and protrude in both portals of the host. Obviously the results suggest that the included site for the bound **Hdpy** is the hexamethylene chain, while the two-pyridine ring is located at the portal of TMeQ[6] in the inclusion host-guest complex of TMeQ[6]-**Hdpy**. A similar titration ^{1}H NMR result was obtained for the TMeQ[6]-**Odpy** system (see supplymetary material Figure S1 for electronic version), where the methylene proton resonances close to the center of octylene chain of the bound guest experience upfield shifts of up to ~1.0 ppm, while a downfield shift for the pyridyl proton H^1 is only ~0.3 ppm due to the longer bridge alkyl chain, which leads the two-pyridine

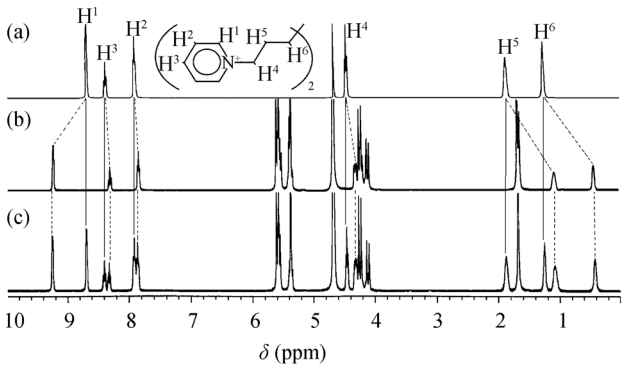


Figure 4 ^{1}H NMR spectra (400 MHz, D_2O) of **Hdpy** in the absence (a), in the presence of 1.0 (b), 2.1 (c) equiv of TMeQ[6].

ring to move farther away from the two portals of the TMeQ[6]. Moreover, the quite sharp resonances of the bound guest indicate that the exchange of the bound and unbound Hdpy is slow at the NMR time scale, and formed inclusion complex has a stable pseudorotaxane structure.

Fortunately, we obtained the corresponding crystal structures of the inclusion complexes of TMeQ[6]-**Hdpy** and TMeQ[6]-**Odpy**. Both showed the alkyl moiety of the guests inserted into the host cavity, and the two end pyridyl moieties protrude from the two portals of the host molecule, such that the pseudorotaxane structures of these two inclusion complexes support in particular ^{1}H NMR spectroscopic study in solution. For example, in the crystal structure of the TMeQ[6]-**Odpy** complex, the main octylene chain of the bound guest is included in the cavity of the host TMeQ[6] in an asymmetrical manner. The quaternized nitrogen $N25^+$ of one end of the bound guest can interact with the portal carbonyl oxygens O1-O6, while the end of the bound guest with the quaternized nitrogen $N26^+$ can interact with the portal carbonyl oxygens O7-O12 through dipole-ion interactions, with N25···O1, N25···O2, N25···O3, N25···O4, N25···O5, N25···O6, and N26···O7, N26···O8, N26···O9, N26···O10, N26···O11, N26···O12 of 3.972, 4.442, 5.318, 5.396, 4.627, 3.903 and 4.056, 3.826, 3.786, 3.998, 3.770, 3.990 Å, respectively (Figure 5(a)). Thus, a combination of a hydrophobic interaction between the cavity of the TMeQ[6] and the octylene moiety of **Odpy** together with the dipole-ion interactions between a polar carbonyl portal group of TMeQ[6] and the two positively charged quaternized nitrogens of **Odpy** was observed in this inclusion complex.

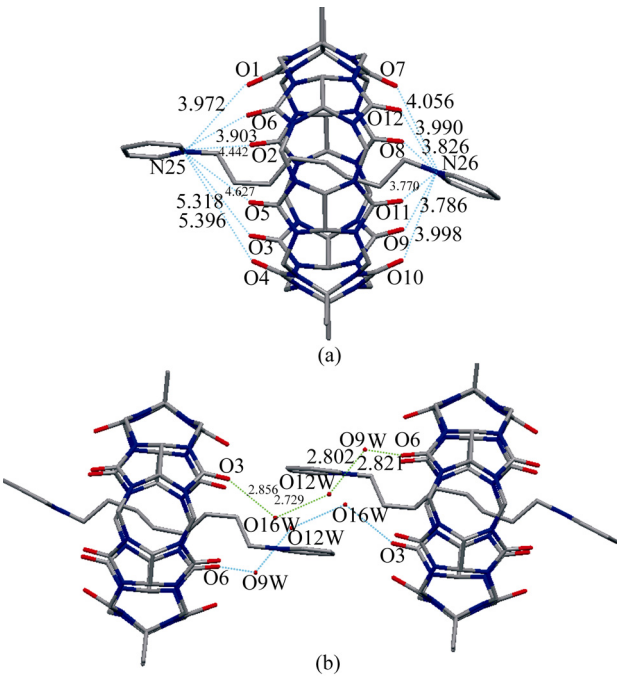


Figure 5 (a) X-ray crystal structure of the pseudorotaxane inclusion complex of TMeQ[6]-**Odpy**; (b) head-to-head combination of a pair of inclusion complexes. All hydrogen atoms are omitted for clarity.

Cucurbit[*n*]urils and their derivatives have been studied extensively as the building blocks for supramolecular chemistry, summarized in an extensive series of reviews[5−12]. Drawing on these investigations to inform the cases in this work, one might expect a one-dimensional supramolecular structure in which the inclusion complexes combine through simple dipole interactions, hydrogen bonds, and π···π stacking in a head-to-tail manner. Indeed, such one-dimensional supramolecular structures were observed in the crystal structures of TMeQ[6]-**Hdpy**. However, the TMeQ[6]-**Odpy** inclusion complexes actually combine in a head-to-head manner in the solid state, with pairs of inclusion complexes forming dimers held together through π···π stacking between the pyridyl rings of **Odpy** and hydrogen binding between the latticed water molecules and the carbonyl oxygens (Figure 5(b)). The distance between the two pyridyl rings is 3.800 Å. The O3···O16W, O16W···O12W, O12W···O9W and O9W···O6 distances are 2.856, 2.729, 2.802 and 2.821 Å, respectively.

3.4 The binding interactions between TMeQ[6] and Ddpy

The ^{1}H NMR spectra of TMeQ[6]-**Ddpy** could not be obtained due to its extremely poor solubility in D_2O;

when the solutions of TMeQ[6] and **Ddpy** were mixed together, the insoluble host-guest inclusion complex precipitated from the solution immediately. However, the crystal structure of TMeQ[6]-**Ddpy** was successfully obtained. In the solid state, the structure of the inclusion complex of TMeQ[6]-**Ddpy** is totally unexpected. Unlike the inclusion complexes of TMeQ[6]-**Hdpy** or TMeQ[6]-**Odpy**, the hosts include the two ends of the pyridyl moieties, other than the decatylene chain of the **Ddpy** guest, which leads to the formation of a dumbbell shape-like host-guest inclusion complex (Figure 6).

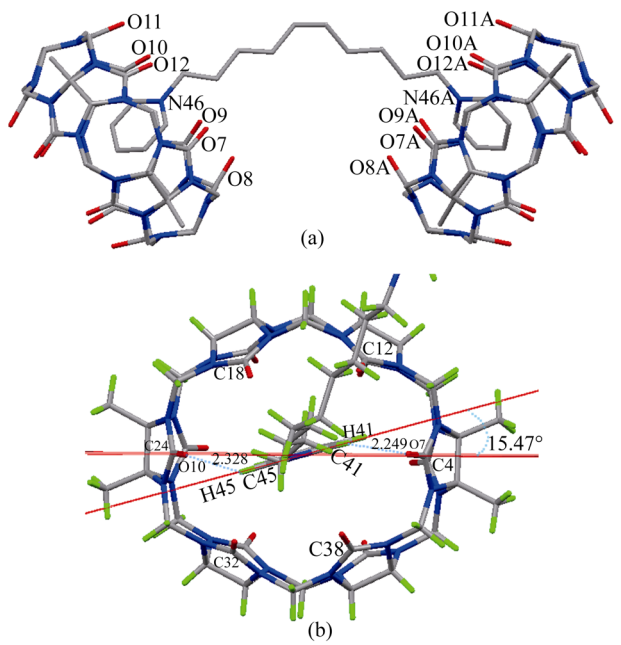


Figure 6 (a) View of the crystal structure of a dumbbell-like inclusion complex TMeQ[6]-**Ddpy**; (b) top view (with the small twist of the guest highlighted by the inserted lines).

In this dumbbell structure of TMeQ[6]-**Ddpy**, the quaternized nitrogens $N46^+$ of the bound guest interacts with the portal carbonyl oxygens O7-O12 that belong to the two dumbbell hosts, with N46⋯O7, N46⋯O8, N46⋯O9, N46⋯O10, N46⋯O11 and N46⋯O12 of 4.073, 3.858, 3.199, 3.721, 3.589 and 3.206 Å, respectively (Figure 6). There are some close contacts between the hydrogen atoms on the pyridyl ring and the carbonyls as well (e.g. C41—H41⋯O7 of 2.249 Å and C45—H45⋯O10 of 2.328 Å). The carbon atoms of the pyridyl ring, such as C41 and C45, lie between 3.235 Å and 3.644 Å from nearest-neighbor atoms in the host ring, such as C4, C12 and so on, with space-filling models showing that the ring fits reasonably tightly in the cavity (Figure 6(b)). Thus, a combination of a hydrophobic interaction between the cavity of the TMeQ[6] and the pyridyl moiety of **Ddpy** together with the dipole-ion interactions between a polar carbonyl portal group of TMeQ[6] and the positively charged pyridyl of **Ddpy** can be observed in this inclusion complex.

4 Conclusions

We presented five host-guest inclusion complexes of TMeQ[6] with five 1,ω-alkylenedipyridine dicationic guests, in which the length of alkylene varies from 2C to 10C. In these inclusion complexes, combined cavity and portal binding in TMeQ[6] have been observed for these alkylenedipyridine dicationic guests, and the length of the bridged alkylene plays an important role not only in balancing the overall hydrophilic/hydrophobic interaction between the host and guest, but also in defining the structure of the resulting inclusion complexes. It is well known that the Qs have a strong tendency to include the hydrophobic organic species, particularly alkyl groups[25,27], phenyl groups[28−30], even free pyridine rings and so on[24,28−30]. For the guests in this work, the typical hydrophobic organic species are the bridged alkylene moieties with different lengths, and the positively charged pyridine ring shows both hydrophobic and hydrophilic properties when the bridged alkylene is shorter. For example, the ethylene, TMeQ[6], has to include a positive charged pyridine ring of **Edpy** for the TMeQ[6]-**Bdpy** system, and TMeQ[6] includes a positive charged pyridine ring of **Bdpy**. However, the different competitive interactions in and between the related inclusion complexes could lead to a fast exchange between the hosts and guests. For the guests with a longer bridge chain such as **Hdpy** or **Odpy**, a stable pseudorotaxane inclusion complex is formed by combining the hydrophobic cavity with the outer portal dipole-ion interactions; however, for the **Ddpy**, the two TMeQ[6] host molecules include the two end pyridine rings of **Ddpy** and form a dumbbell inclusion complex.

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