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Guest releasing from solution to solid-state triggered by cyclomaltohexaose (α-cyclodextrin) aggregation

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ABSTRACT

Supramolecuar aggregations **1** and **2** were prepared by complexing cyclomaltohexaose with two azodipyridine isomers: 4,4′-azodipyridine and 2,2′-azodipyridine, and their binding abilities and assembly behaviors were investigated comprehensively by X-ray crystallography, 2D NMR spectroscopy, and isothermal titration calorimetry. In solution, 1:1 host–guest complexation is generally assumed, whereas in the solid state, a 2:1 stoichiometry is observed. Crystal structures reveal that channel-type aggregation exists in complex **1**, while a layer-type manner is the dominant packing mode in complex **2**. The disparity of nitrogen atom position leads to the different binding modes and further affects the aggregation types in complexes **1** and **2**.

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1. Introduction

Cyclic oligosaccharides with 6, 7, or 8 (α-, β-, γ-) α-glucose units linked by α-(1→4)-glucose bonds,[1] called cyclomaltooligosaccharides (cyclodextrins, CDs), have been extensively investigated in not only molecular recognition but also self-assembly with various well-defined nanoarchitectures.[2,3] Nowadays, research on CDs and derivatives becomes more and more significant benefiting from their benign water solubility, their biological compatibility, and from an economics perspective, their relatively low cost. In addition, their capability of including various molecules in both the solution and the solid state enhances their importance.[4] The cavities of CDs accommodate guest molecules via synergistic contribution of several non-covalent interactions, such as van der Waals, hydrophobic, and hydrogen-bonding interactions. In order to obtain direct evidence for the information of the inclusion complexes,[5] a number of crystallographic complexes of CDs with guests have been reported during the past few decades.[6,7] Many of these studies elucidated the relationship between the structures of the CD complexes and the structures of the guest molecules, and further revealed that the geometrical complementarity and/or size/shape matching between host and guest is certainly one of the most important factors in determining the complex conformation and packing mode.[8] In this context, it seems to be more fascinating to compare the influence of subtle differences between guest molecules over the binding and overall structures of CD complexes, especially in the case of isomeric compounds. Kamitori et al. reported two crystal structures of cyclomaltohexaose (α-cyclodextrin) upon complexation with isomeric phenol derivative, which give different types of aggregations resulting from the disparity in position of bromine substituted to benzene ring.[7] In our previous work,[9,10] we also studied a series of cyclomaltoheptaose (β-cyclodextrin) complex crystals with similar structural guests to explore how and to what extent the slight differences affect the inclusion modes and aggregation structures.[11,12]

In the present study, we investigated the inclusion complexation of cyclomaltohexaose with 4,4′-azodipyridine (4-ADP) and 2,2′-azodipyridine (2-ADP) isomers by NMR spectroscopy, isothermal titration calorimetry (ITC), and X-ray crystallography. Similar binding behavior was detected in solution, whereas appreciable differences were observed in the solid state between the complexes of 4-ADP (**1**) and 2-ADP (**2**). More interestingly, a process of releasing guest molecules was found to be occurring with the aggregation of cyclomaltohexaose units from the solution state to the solid state.

2. Results and discussion

2.1. Binding modes in solution

2D NMR spectroscopy, as an important method for identifying compound structures,[9,13] is frequently used to investigate the inclusion geometry of CDs with guests, where the cross-peak between the protons that are closer than 0.4 nm in space will be observed in NOESY spectrum, and the relative intensities of these

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cross-peaks depend on the spaces between the corresponding protons.[10] In order to get structural information about complexes **1** and **2** in aqueous solution, 2D NMR spectra were, therefore, employed as shown in Figure 1a and b. Clear cross-peaks between H_3 of cyclomaltohexaose and H_a/H_b of the 4-ADP (Peaks A and B, Fig. 1a) as well as H_5 and H_b (Peak B, Fig. 1a) were observed, indicating that 4-ADP is included into the hydrophobic cavity of cyclomaltohexaose. The correlations between H_6 and H_a/H_b (Peak B, Fig. 1a) illustrate that one pyridine ring of 4-ADP locates at the narrow-rim of cyclomaltohexaose. A similar phenomenon was observed in the case of 2-ADP, presenting correlations not only between H_3 of cyclomaltohexaose and H_c/H_d of 2-ADP (Peaks C and D, Fig. 1b) but also between H_5 and H_d (Peak D, Fig. 1b), as well as the correlated signals between H_6 and H_a/H_d (Peaks A and D, Fig. 1b), with the absence of correlation between H_b and cyclomaltohexaose protons. The reasonable binding modes were, therefore, deduced: 4-ADP and 2-ADP penetrate axially into the cavity of cyclomaltohexaose in almost the same manner, in which the azo group is thoroughly immersed, while two pyridine rings point out of both narrow and of wide-rims to some extent (Fig. 1c and d). This is easily acceptable by taking the molecular length of guest and height of host into account, which will be discussed more in detail in the crystal section.

2.2. Complexation stabilities and thermodynamics

To obtain a quantitative insight on the binding stabilities (K_S) and the thermodynamic parameters (ΔH° and ΔS°) of complexes **1** and **2**, ITC has been performed at 25 °C in phosphate buffer solution (pH 7.2), and a typical titration curve of cyclomaltohexaose with 4-ADP is shown in Figure 2. For complex **1**, the titration data could be well fitted using the 'one set of binding sites' model and repeated as a 1:1 complex formation; thereby, higher order complexes did not need to be postulated.[14,15] However, we could not obtain reliable thermodynamic parameters for complex **2**, owing to no significant heat effect[16] upon cyclomaltohexaose complexing with 2-ADP (see Section 4). Two independent measurements were performed for complex **1**, and the data obtained are as follows: $n = 0.9$, $K_S = 272.9\ M^{-1}$ with $\Delta H^\circ = -3.9\ kJ\ mol^{-1}$ and $T\Delta S^\circ = -0.6\ kJ\ mol^{-1}$ for the first time, and $n = 1.0$, $K_S = 279.8\ M^{-1}$ with $\Delta H^\circ = -3.7\ kJ\ mol^{-1}$ and $T\Delta S^\circ = -0.4\ kJ\ mol^{-1}$ for the second time. And then the calculated average data with reasonable errors are as follows: $K_S = 276.4 \pm 3.4\ M^{-1}$ with $\Delta H^\circ = -3.8 \pm 0.1\ kJ\ mol^{-1}$ and $T\Delta S^\circ = -0.5 \pm 0.1\ kJ\ mol^{-1}$. Especially, both titrations show excellent n values, indicating a 1:1 complexation between cyclomaltohexaose and 4-ADP. As can be seen from the thermodynamic parameters, the complexation of cyclomaltohexaose with 4-ADP is driven by a favorable enthalpy change, over-ruling the unfavorable entropy change. Such a favorable enthalpy change may originate from the collective contributions of the hydrophobic interactions, the van der Waals interactions, as well as the release of high-energy water molecules, arising from the inclusion of the guest molecules.[17,18] Further, the observed negative entropy change may be attributed to the conformational freedom limitations of the 4-ADP molecule where the cis- and trans-forms of 4-ADP may co-exist before inclusion into the CD cavity, while only the trans form is preferred in the inclusion complex.

2.3. Crystal structures

In both of the solid-state complexes **1** and **2**, the inclusion structures are in accordance with the binding modes in solution inferred

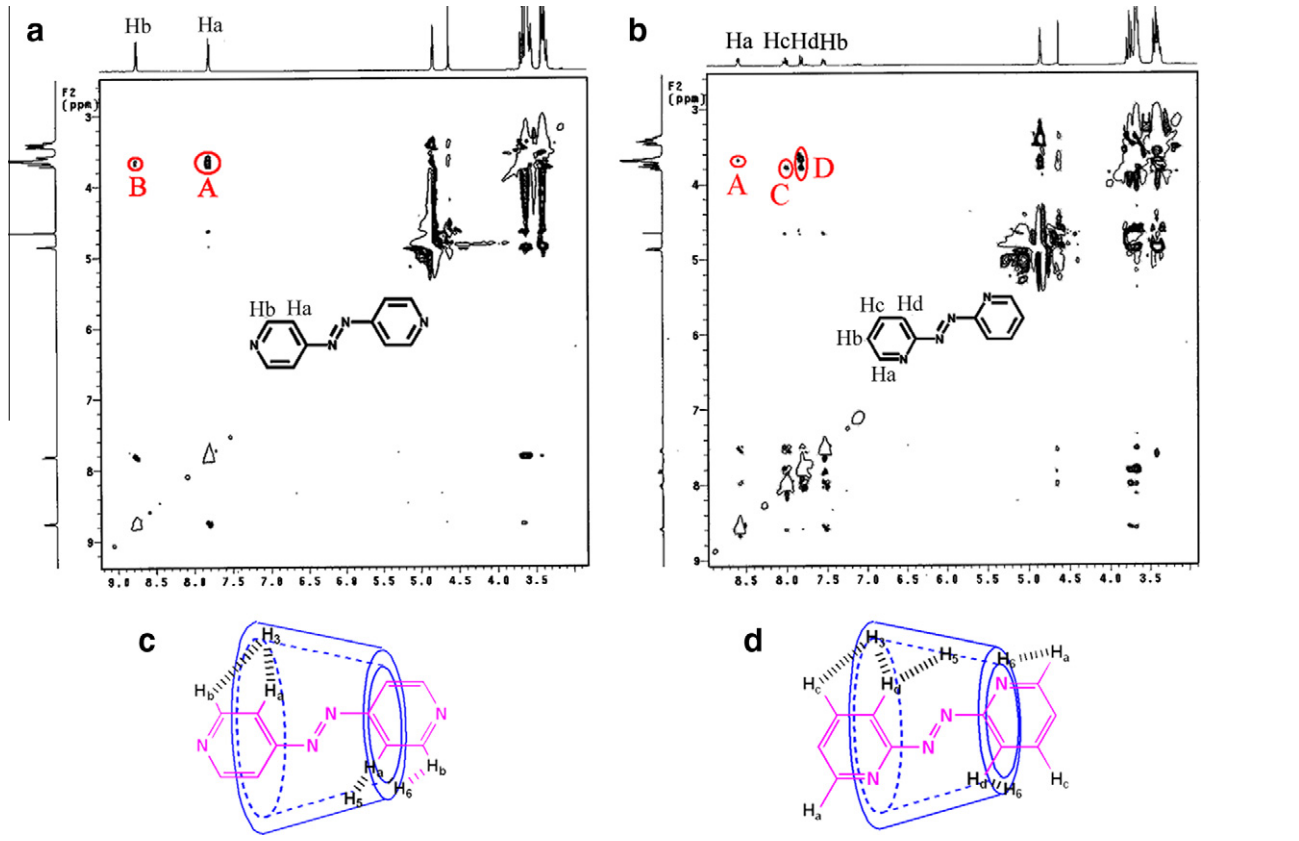


Figure 1. (a) ROESY spectra of complexes **1** and (b) **2** in D_2O (5.0 mM) at 25 °C with mixing time of 250 ms, and (c) the corresponding binding modes of cyclomaltohexaose with 4-ADP and (d) 2-ADP.

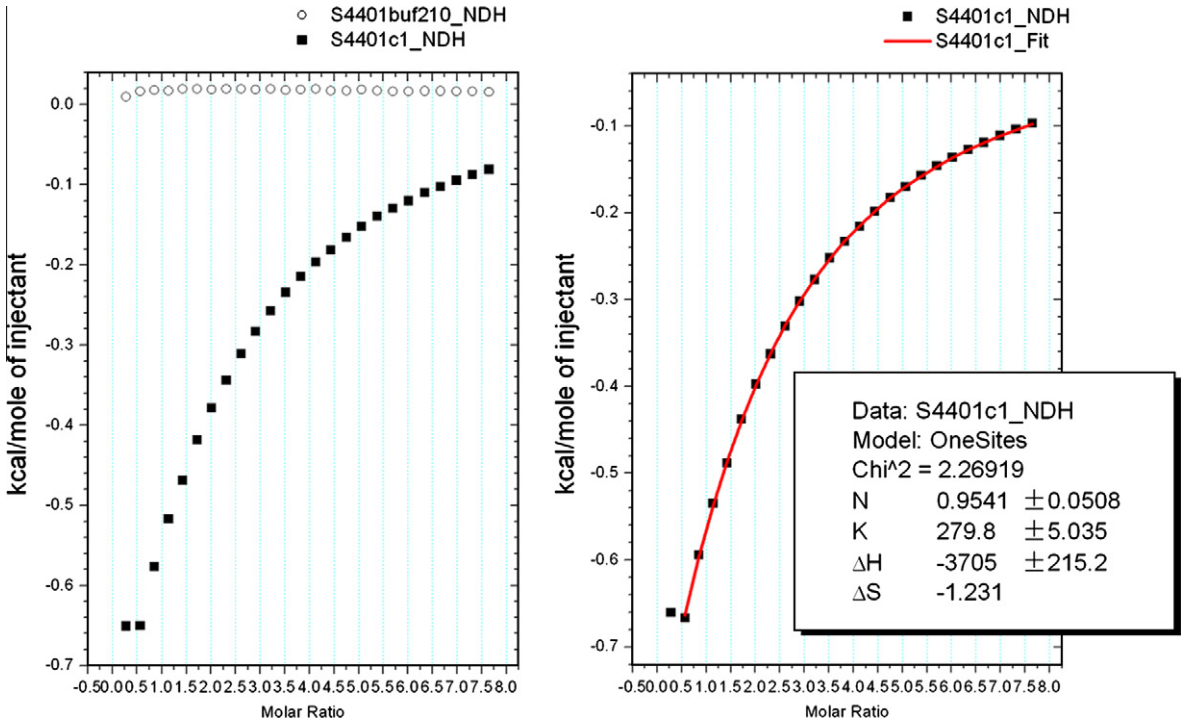


Figure 2. ITC experiment of 4-ADP with cyclomaltohexaose in aqueous solution at 25 °C: (left) heat effects of dilution and of complexation of cyclomaltohexaose with 4-ADP for each injection during titration of micro-calorimetric experiment; (right) 'net' heat effect obtained by subtracting the heat of dilution from the heat of reaction, which was analyzed by computer simulation with the use of the 'one set of binding sites' model.

from the NMR studies (Fig. 3). 4-ADP and 2-ADP penetrate into the cavity of cyclomaltohexaose with almost parallel orientation to the cavity axis, which is somewhat different from those cyclomaltoheptaose cases that have been reported (where guest molecules are 2,2′-/4,4′-dipyridines, 4-hydroxyazobenzene and 4-aminoazobenzene, respectively).[10,11] Cyclomaltohexaose is 33.6% smaller in cavity volume than cyclomaltoheptaose, and therefore, the departure of inclusion orientation from the cavity axis is relatively restrained. We measured the guest lengths and host height as follows: 4-ADP, 9.42 Å; 2-ADP, 10.85 Å; cyclomaltohexaose, ~8 Å.[19] These data reinforced the deduced binding modes determined by NMR spectroscopy. In addition, the distances between the pyridine nitrogen atoms are 9.42 Å in 4-ADP and 5.67 Å in 2-ADP, which illustrates the large disparities of the aforementioned thermodynamic parameters to some extent. It can also be clearly seen that the pyridine nitrogen atoms of 4-ADP are located outside the cavity of cyclomaltohexaose, while the nitrogen atoms of 2-ADP are positioned at the narrow and wide rims, respectively.

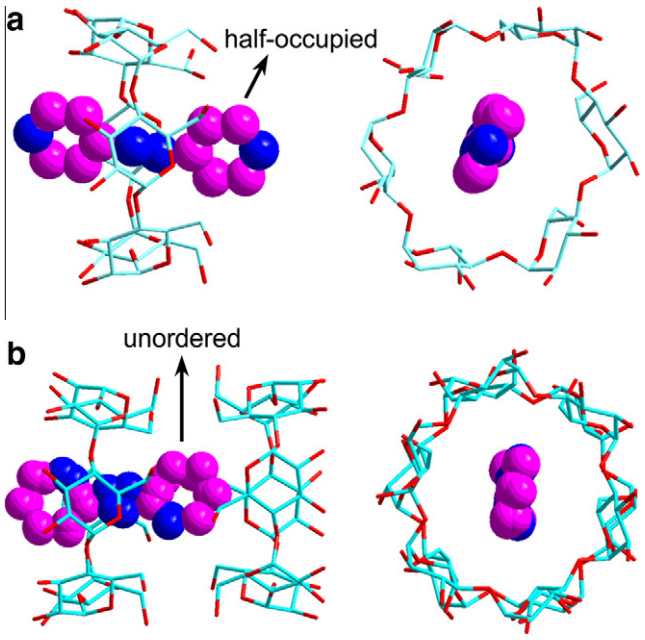
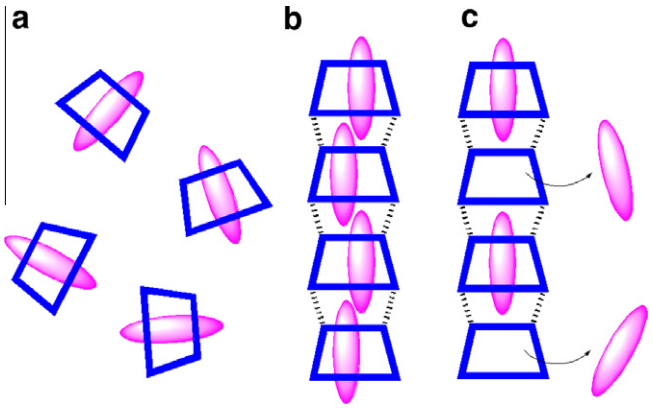


Figure 3. (a) Crystal cells of complexes **1** and (b) **2** showing host and guest molecules, only.

The host–guest molar ratio in the solid state is dramatically different from the binding stoichiometry in solution. In complex **1**, there are 1 cyclomaltohexaose unit and 0.5 4-ADP molecules in the crystal cell and in complex **2**, there are 2 cyclomaltohexaose units and 1 2-ADP molecule. Both solid-state complexes present a 2:1 host–guest ratio. This is an interesting and infrequent phenomenon in CD complexes, where the stoichiometries are generally the same in solution and in the solid state.[5–12] In the present case, the guest-release process from solution to solid state can be well interpreted in view of aggregation of CD, guest lengths, and binding abilities. It is well-known that CD molecules aggregate into channels, layers, or cages through the intermolecular hydrogen bonds donated by narrow-rim and wide-rim hydroxyl groups.[8] However, it seems to be complicated for complexes **1** and **2**, and three theoretical possibilities can be assumed as illustrated in Scheme 1 when taking into account the excessive lengths of the ADP guests. Pattern b can be reasonably eliminated because the cavity of the cyclomaltohexaose unit cannot accommodate two ADP guests simultaneously according to its size (diameters of only 5.3 and 4.7 Å for the wide and narrow rims, respectively). Consequently, a competition between guest inclusion and aggregation of CD themselves emerges in fact (Patterns a and c). As proved by ITC measurements, cyclomaltohexaose offers weak (medium at most) binding affinities to ADP guests, and therefore, the host–guest interactions are overcome by the hydrogen bonds leading



Scheme 1. Three possible patterns in the solid-state complexes of cyclomaltohexaose with ADP guests: (a) inclusion without aggregation, (b) synergic inclusion and aggregation, (c) aggregation with partial release of guest.

to aggregation. Figure 4 shows the multiple hydrogen bonds between CD hosts. The heights of the asymmetrical units of CD aggregations are 7.92 Å in **1** and 7.89 Å in **2**, about 2 Å shorter than the ADP lengths, which further confirms the rationality of Pattern c.

As shown in Scheme 2, cyclomaltohexaose forms a 1:1 complex with 4-ADP in solution, and therein, the aggregation between cyclomaltohexaoses is weak because the intermolecular hydrogen bonds between the narrow/wide-rim hydroxyl groups can hardly form because of the effect of the water medium. That is, the host–guest inclusion affinity is dominant rather than the aggregation affinity of CD themselves in aqueous solution. However, going with the phase transfer from liquid solution to solid state, the aggregation affinity emerges to be the dominant force in conversion. Once CD molecules arrange into channel-type structure, there is not enough space to accommodate all the guest molecules, and then half of the ADP guests are released before crystallization.

For a different construction of the crystal cells of **1** and **2**, we inferred that the termini of 4-ADP are hydrophilic nitrogen atoms, and no other neighboring CD prefers to include the pyridine portion, whereas the termini of 2-ADP are hydrophobic carbon atoms, and the neighboring CD prefers to include the pyridine portion, albeit shallowly (It should be mentioned herein that no specific host–guest interactions, such as non-conventional hydrogen bonds and C–H$\cdots\pi$ interactions, were discussed because the ADP guests are either the half-occupied or unordered in the CD cavity.). As a result, all CD units in **1** are equal in position, forming head-to-tail aggregation with half-occupied 4-ADP guest in each CD cavity. However in **2**, the asymmetrical cell is composed of two head-to-head CD units. The 2-ADP guest mainly resides in one CD cavity, although it is unordered and equally distributed in two positions. The CD dimer mediated by guest molecules further forms the tail-to-tail aggregation through intermolecular hydrogen bonds.

Taking the host molecules into account only for clarifying the aggregation behavior of cyclomaltohexaose in complexes **1** and **2**, cyclomaltohexaose forms channel aggregation in **1** and layer aggregation in **2** (Fig. 4). The channel in **1** extends infinitely along the crystallographic *a* direction, jointed by the multiple hydrogen bonds between 2,3- and 6-hydroxyl groups (O13–H$\cdots$O15, 2.837 Å; O3–H$\cdots$O5, 2.864 Å; O8–H$\cdots$O10, 2.855 Å; O38–H$\cdots$O30, 2.826 Å; O18–H$\cdots$O20, 2.836 Å; O2–H$\cdots$O30, 2.832 Å). Water molecules are filled in the interspaces between channels, forming hydrogen bonds with the sidewalls of cyclomaltohexaoses. There are no hydrogen bonds between cyclomaltohexaoses themselves that link the sidewalls of the channels directly. Only hydrogen bonds between 2,3- and 2,3-hydroxyl groups (O28–H$\cdots$O47, 2.736 Å; O27–H$\cdots$O48, 2.847 Å; O23–H$\cdots$O52, 2.827 Å; O8–H$\cdots$O38, 2.811 Å; O12–H$\cdots$O37, 2.864 Å; O18–H$\cdots$O57, 2.749 Å; O13–H$\cdots$O33, 2.761 Å; O17–H$\cdots$O58, 2.737 Å) were observed in **2**, which then lead to the layer aggregation in the crystallographic $a \times b$ plane together with the hydrogen bonds between 2,3-hydroxyl and 2,3-hydroxyl groups on the sidewall direction (Fig. 4b,

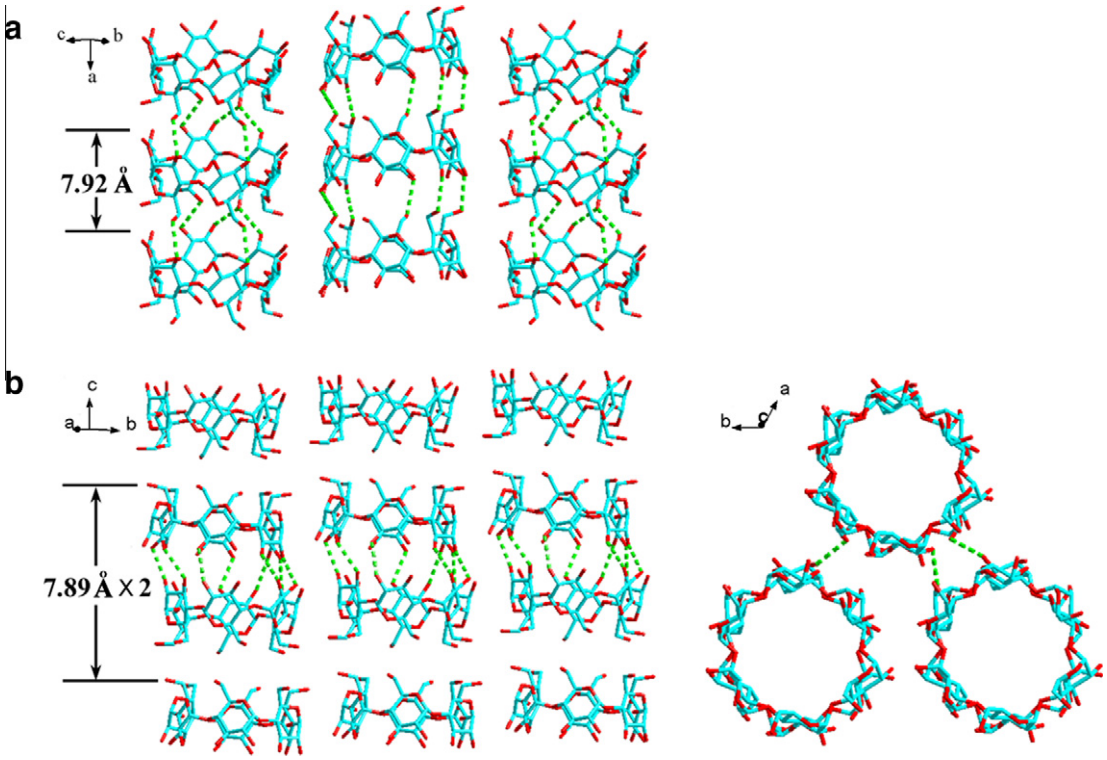
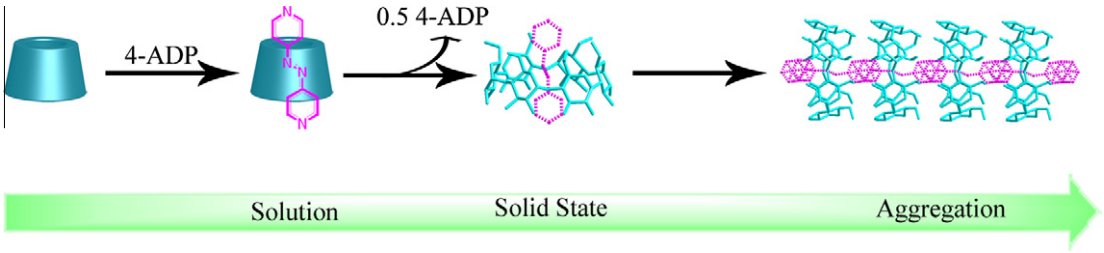


Figure 4. Views showing the aggregation of cyclomaltohexaose via intermolecular hydrogen bonds in complexes (a) **1** and (b) **2**.



Scheme 2. An illustration showing the releasing process of ADP guests from solution to solid state.

right). No hydrogen bond between the 6-hydroxyl and 6-hydroxyl groups forms because the narrow rims of cyclomaltohexaoses are held apart from each other by the 2-ADP guest as a pillar.

3. Conclusions

Two solid-state complexes **1** and **2** were obtained by cyclomaltohexaose complexing with two azodipyridine isomers, 4-ADP and 2-ADP, presenting a host–guest molar ratio of 2:1. However, the binding stoichiometry in solution is determined as 1:1 with a relatively weak binding affinity. We infer that the complexes undergo a release process of half of the guest molecules in going from solution to the solid state, owing to the hydrogen-bonding aggregation of cyclomaltohexaoses themselves. Moreover, complexation of isomeric compounds leads to different aggregation modes: cyclomaltohexaose presents a 1D channel-type complex with a head-to-tail arrangement in **1**, while there is a 2D layer-type arrangement in **2** with a head-to-head orientation. The present results help us to further understand the inclusion and aggregation behavior between the cyclomaltohexaose host and isomeric guests and help us understand to what extent the size/shape matching factor affects the aggregation mode, which is beneficial in the design and construction of diverse supramolecular assemblies based on cyclomaltohexaose.

4. Experimental

4.1. Materials and instruments

4,4′-Azodipyridine and 2,2′-azodipyridine were prepared according to the literature method.[20] Reagent grade cyclomaltohexaose was recrystallized from water twice and dried in vacuo at 95 °C for 24 h prior to use.

^{1}H NMR and 2D ROESY spectra were obtained in D_2O using a Varian Mercury VX300 instrument with a mixing time of 250 ms.

The isothermal titration calorimetry (ITC) experiments were performed by an isothermal titration microcalorimeter at atmospheric pressure and at 25 °C in aqueous phosphate buffer solution (pH 7.2). In each run, a solution of host in a 0.250 mL syringe was sequentially injected with stirring at 300 rpm into a solution of guest in the sample cell (1.4227 mL volume). All thermodynamic parameters reported in this work were obtained by using the 'one set of binding sites' model. Two independent titration experiments were performed to afford self-consistent parameters and to give the averaged values. For complex **1**, the concentrations were used as 40 mM for cyclomaltohexaose and 1 mM for 4-ADP. For complex **2**, we could not obtain reliable thermodynamic parameters although various conditions were conducted. The concentrations selected were as follows: 10 mM for cyclomaltohexaose and 1 mM for 2-ADP; 40 mM for cyclomaltohexaose and 1 mM for 2-ADP; 80 mM for cyclomaltohexaose and 1 mM for 2-ADP; 80 mM for cyclomaltohexaose and 2 mM for 2-ADP; 100 mM for cyclomaltohexaose and 1 mM for 2-ADP.

The X-ray intensity data were collected on a Rigaku MM-007 rotating anode diffractometer equipped with a Saturn CCD Area Detector System using monochromated Mo Kα radiation at $T = 113(2)$ K. Data collection and reduction were performed with the use of the CRYSTALCLEAR[21] program. The structures were solved by using direct methods and refined by employing full-matrix least squares on F^2 (CrystalStructure, SHELXTL-97).[22]

4.2. Preparation of cyclomaltohexaose/4-ADP crystal 1

An aqueous solution of 4-ADP (1 mmol, 2.5 mL) was added dropwise to an aqueous solution of cyclomaltohexaose (1 mmol, 2.5 mL) and stirred at 40 °C for 5 h. The solution was cooled to room temperature, and the precipitate was filtered and redissolved in hot water to make a saturated solution and then cooled to room temperature. After removing the precipitates by filtration, a small amount of water was added to the filtrate. The resultant solution was kept at room temperature for about two weeks. The orange-red crystals formed were collected along with its mother liquor for the X-ray crystallographic analysis. Yield: 43%. ^{1}H NMR (300 MHz, D_2O): δ 8.85 (d, 4H, py-H), 7.89 (d, 4H, py-H), 4.95 (s, 12H, 1-H), 3.83–3.45 (m, 72H) ppm. Crystal data for **1**: $C_{41}H_{76}N_2O_{36}$ $M = 1173.04$, monoclinic, space group $P21$, $a = 7.9194(18)$, $b = 13.581(4)$, $c = 24.843(6)$ Å, $\alpha = 90°$, $\beta = 90.653(14)°$, $\gamma = 90°$, $V = 2671.8(12)$ Å^3, $F(0\,0\,0) = 1248$, $Z = 2$, $D_c = 1.458$ g/cm^{-3}, $\mu = 0.129$ mm^{-1}, approximate crystal dimensions, $0.24 \times 0.22 \times 0.20$ mm^3, θ range = 1.64–26.00°, 18,779 measured reflections, of which 5482 ($R_{int} = 0.0708$) were unique, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0909$, $wR_2 = 0.2480$, R indices (all data): $R_1 = 0.0957$, $wR_2 = 0.2567$, goodness of fit on $F^2 = 1.027$.

4.3. Preparation of cyclomaltohexaose/2-ADP crystal 2

Crystal **2** was prepared by a method similar to that for **1**, using 2-ADP instead of 4-ADP. Yield: 36%. ^{1}H NMR (300 MHz, D_2O): δ 8.66 (d, 2H, py-H), 8.10 (t, 2H, py-H), 7.90 (d, 2H, py-H), 7.63 (t, 2H, py-H), 4.95 (s, 12H, 1-H), 3.85–3.43 (m, 72H) ppm. Crystal data for **2**: $C_{82}H_{149.50}N_4O_{70.75}$ $M = 2323.56$, triclinic, space group $P1$, $a = 13.6989(10)$, $b = 13.9700(10)$, $c = 15.7722(10)$ Å, $\alpha = 93.183(2)°$, $\beta = 91.938(2)°$, $\gamma = 118.718(2)°$, $V = 2636.7(3)$ Å^3, $F(0\,0\,0) = 1236$, $Z = 2$, $D_c = 1.463$ g/cm^{-3}, $\mu = 0.129$ mm^{-1}, approximate crystal dimensions, $0.12 \times 0.10 \times 0.08$ mm^3, θ range = 1.70–27.88°, 24,868 measured reflections, of which 20,083 ($R_{int} = 0.0271$) were unique, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0487$, $wR_2 = 0.1095$, R indices (all data): $R_1 = 0.0568$, $wR_2 = 0.1155$, goodness of fit on $F^2 = 1.026$.

Supplementary data

Complete crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 768430 for **1** and 768431 for **2**). Copies of this information may be obtained free of charge from the Director, Cambridge

Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or via: http://www.ccdc.cam.ac.uk).

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