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# Assembly behavior of inclusion complexes of β-cyclodextrin with 4-hydroxyazobenzene and 4-aminoazobenzene†

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To further reveal the factors governing the supramolecular assembly of β-cyclodextrin (β-CD) inclusion complexes, two aggregates (**1** and **2**) were prepared from the inclusion complexes of β-CD with 4-hydroxyazobenzene and 4-aminoazobenzene, respectively, and their binding behavior were investigated by means of X-ray analysis, UV-vis, NMR, and circular dichroism spectra in both solution and the solid state. The obtained results indicated that the β-CD/4-hydroxyazobenzene complex **1** could form head-to-head dimers (triclinic system, space group *P*1) in the solid state, which were further self-assembled to a linear supramolecular architecture by the intra- and interdimer hydrogen bond interactions as well as the intradimer π–π interactions. However, when the included guest 4-hydroxyazobenzene was switched to a 4-aminoazobenzene, the resultant β-CD/4-aminoazobenzene complex **2** (monoclinic system, space group *P*2(1)) could be self-assembled to a wave-type supramolecular aggregate under similar conditions. Furthermore, the combination of crystallographic and spectral investigations jointly revealed the inclusion complexation geometry of β-CD with 4-hydroxyazobenzene and 4-aminoazobenzene in both solution and the solid state, which demonstrated that the disparity of substituents in the azobenzenes played an important role in the inclusion complexation and molecular assembly, affecting not only the structural features of aggregates but also the binding abilities of azobenzenes with β-CD.

## Introduction

One-dimensional supramolecular aggregates with well-defined structures assembled from cyclodextrin-based building blocks, such as rotaxenes/catenanes,[1–9] molecular shuttles,[10–12] molecular tubes,[13–15] and missing links[16] *etc.*, are currently of much interest in chemistry and materials science. A generally accepted reason for choosing cyclodextrins (CDs), a class of cyclic oligosaccharides with 6–8 D-glucose units linked by α-1,4-glucose bonds, as the starting materials to construct the supramolecular architectures is that the truncated cone-shaped hydrophobic cavities of CDs have a remarkable ability to include various guest molecules either in solution or in the solid state to form the functional host–guest inclusion complexes,[17–24] which can be subsequently used as the building blocks of supramolecular aggregates. Among the various families of organic compounds used as guest molecules, the chromophoric guests, such as anthracenes,[25] pyrenes,[26–28] and azobenzenes,[29–36] are of particular importance because they can exhibit appreciable spectral changes upon inclusion complexation with CDs in solution, and thus can be applied as the versatile spectral probes to investigate host–guest complexation. In the past three decades, a number of crystallographic studies on the host–guest inclusion complexes of CDs with guest molecules have been performed to obtain direct evidence for the formation of the inclusion complexes.[37–47] The obtained results indicate that the crystal structure of these CD complexes is designable by appropriately selecting the type, length, functional substituent group, and heteroatom in the guests. However, comparative studies on the inclusion complexation and assembly behavior of CDs with azo derivatives are still rare, to the best of our knowledge, although azo derivatives are widely focused upon because of their potential to construct photo-driven molecular machines.[12,29] We have recently reported a systematic study on the binding ability and assembly behavior of β-CD with 2,2′-dipyridine and 4,4′-dipyridine in both solution and the solid state,[45c] which indicated that the disparity of nitrogen atom position in dipyridines leads not only to distinct crystal systems and space groups, but also to different binding modes and thermodynamic parameters upon complexation of 2,2′-dipyridine and 4,4′-dipyridine with β-CD in aqueous solution. In the present study, we report the formation of two self-assembled supramolecular aggregates from β-CD/4-hydroxyazobenzene (**1**) and β-CD/4-aminoazobenzene (**2**) complexes by extensive hydrogen bond and π–π interactions. A special interest of these aggregates is their linear or wave-type array achieved by slightly tuning the substituents of the azobenzene derivatives, which will provide an efficient method to control the inclusion and packing mode of supramolecular self-assemblies based on the molecular recognition mechanism. Moreover, the present investigation results will also help us understand not only the simultaneous operation of several noncovalent weak interactions in the construction of ordered supramolecular architectures but also how and to what extent the disparity of substituents affects the inclusion complexation and assembly behavior of azobenzene guests with CDs.

## Experimental

### Materials and instruments

4-Hydroxyazobenzene (4-HAB) and 4-aminoazobenzene (4-AAB) was commercially available and used without further purification. Reagent grade β-CD was recrystallized twice from water and dried *in vacuo* at 95 °C for 24 h prior to use.

The X-ray intensity data were collected on a standard area detector system equipped with a normal-focus molybdenum-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at $T = 293(2)$ K. The structures were solved by using direct method and refined, employing full-matrix least squares on $F^2$ (Siemens, SHELXTL, version 5.04). Because of the occurrence of many disordered

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† Electronic supplementary information (ESI) available: CIF files, ORTEP plots, $^1$H NMR spectra, UV-vis spectra, and curve-fitting analyses. See http://www.rsc.org/suppdata/ob/b4/b415946b/

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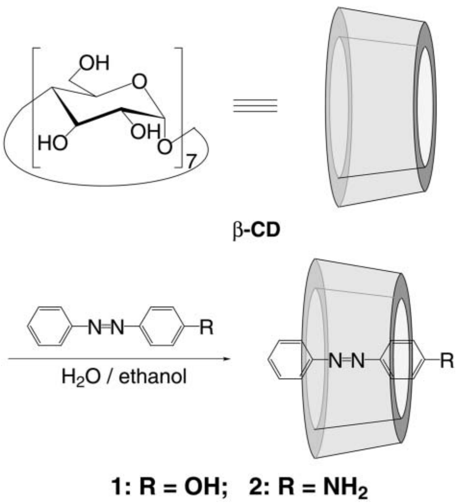
waters in the crystals, we had to use some restraints to make the crystal parameters (such as the parameters of thermal vibration) reasonable during the crystal refinements, and some oxygen atoms in the disordered waters also could not give reasonable O–H bonds. Elemental analysis was performed on a Perkin-Elmer 2400C instrument. $^1$H NMR spectra were recorded in $D_2O$ on a Bruker AV600 spectrometer. $^{13}$C NMR spectra were obtained in $D_2O$ on a Varian UNITYplus 400 NMR spectrometer. Circular dichroism and UV-vis spectra were performed in a conventional quartz cell (light path 10 mm) on a spectropolarimeter or a spectrophotometer equipped with a temperature controller to keep the temperature at 25 °C.

### Synthesis of complex 1

As shown in Scheme 1, an ethanol solution of 4-HAB (1 mmol, 10 mL) was added dropwise to an aqueous solution of β-CD (1 mmol, 40 mL), and the reaction mixture was stirred at 50 °C for 5 h. After cooling to room temperature, the precipitate was collected by filtration to give a yellow powder. The crude product was dissolved in hot water to make a saturated solution. After removing the insoluble substances by filtration, a small amount of water was added to the filtrate. The resultant solution was kept at room temperature for several days, and the yellow crystal **1** was collected along with its mother liquor for X-ray crystallographic analysis. Data for **1**: yield 68%. $^1$H NMR (600 MHz, $D_2O$, TMS, ppm): $\delta$ = 3.49–3.87 (m, 42H), 4.97–4.98 (m, 7H), 6.99–7.01 (d, 2H), 7.44–7.50 (m, 3H), 7.69–7.71 (d, 2H), 7.74–7.75 (d, 2H). $^{13}$C NMR ($D_2O$, TMS, ppm): $\delta$ 161.4, 154.3, 144.7, 132.7, 129.2, 124.8, 118.9, 104.7, 76.0, 74.9, 74.7, 63.1. Anal. Calcd. for $C_{54}H_{80}O_{36}N_2\cdot 6H_2O$: C 45.00, H 6.43, N 1.94. Found: C 44.91, H 6.34, N 1.91%.



**Scheme 1** Schematic representation of the formation of complexes **1** and **2**.

CCDC reference number 224219. See http://www.rsc.org/suppdata/ob/b4/b415946b/ for crystallographic data in .cif or other electronic format.

### Synthesis of complex 2

Inclusion complex **2** was prepared from 4-AAB (1 mmol, 10 mL) and β-CD (1 mmol, 40 mL), according to a similar procedure as described above. Data for **2**: yield 73%. $^1$H NMR (600 MHz, $D_2O$, TMS, ppm): $\delta$ = 3.40–3.82 (m, 42H), 4.93–4.94 (m, 7H), 6.81–6.82 (d, 2H), 7.29–7.40 (m, 3H), 7.60–7.72 (m, 4H). $^{13}$C NMR ($D_2O$, TMS, ppm): $\delta$ 153.2, 147.5, 141.1, 135.7, 133.2, 127.4, 122.3, 104.8, 83.9, 76.0, 74.9, 74.7, 63.0. Anal. Calcd. for $C_{54}H_{81}O_{35}N_3\cdot 5H_2O$: C 45.60, H 6.45, N 2.95. Found: C 45.63, H 6.41, N 2.92%.

CCDC reference number 244422. See http://www.rsc.org/suppdata/ob/b4/b415946b/ for crystallographic data in .cif or other electronic format.

## Results and discussion

### Crystal structures

The β-CD complexes **1** and **2** were synthesized by the reaction of β-CD with 4-HAB and 4-AAB respectively in yields of about 70%. The crystallographic data of **1** and **2** were collected from a well-formed, prismatic crystal sealed in a glass capillary to prevent loss of the water of crystallization. The crystal data, experimental and refinement parameters of **1** and **2** are shown in Table 1.

Fig. 1 shows the crystal structure of **1**, which is triclinic system with the space group *P*1. Seen from Fig. 1, one asymmetric unit of **1** contains two β-CD moieties (2 : 2 stoichiometry between β-CD and 4-HAB in the crystal structure), each of which has an approximate 7-fold axis and maintains the round shape of the macrocycle. Every glucose residue of β-CD has a $^4C_1$ chair conformation, and seven glycosidic oxygen atoms are coplanar within 0.0159 Å (or 0.0136 Å). Moreover, two 4-HAB molecules with *trans* conformation are respectively embedded in two β-CD cavities in different directions to form the head-to-head dimer arrangement, and the hydroxyl group of 4-HAB molecule points to the primary side of the β-CD cavity. The dihedral angle between the plane of the *a* (or *a′*) ring and the heptagons composed of seven glycosidic oxygen atoms in β-CD is 58.1° (or 61.1°), and the dihedral angle between the aromatic rings *a* (or *a′*) and *b* (or *b′*) in 4-HAB is 11.6° (or 19.2°). This unusual dimerization behavior is attributed to the cooperative interactions of eight hydrogen bonds between the secondary hydroxyl groups of two adjacent CD units, as well as the π–π interaction between *b* and *b′* rings (1.1° dihedral angle and 3.637 Å centroid separation).

It is noteworthy that, as can be seen from Fig. 2, each dimer tightly connects with the adjacent dimers through a relatively complicated interdimer hydrogen bond system involving the CD's C6–OHs, the hydroxyl groups of 4-HAB molecules, and

**Table 1** The crystal data, experimental and refinement parameters of **1** and **2**

| | Crystal **1** | Crystal **2** |
|---|---|---|
| Molecular formula | $C_{108}H_{192}N_4O_{88}$ | $C_{108}H_{205}N_6O_{91.5}$ |
| $M_r$/g mol$^{-1}$ | 2954.66 | 3051.78 |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P*1 | *P*2(1) |
| *Z* | 1 | 2 |
| *a*/Å | 15.440(2) | 15.460(4) |
| *b*/Å | 15.483(2) | 32.209(8) |
| *c*/Å | 17.971(3) | 15.512(4) |
| $\alpha$/° | 112.852(3) | 90 |
| $\beta$/° | 99.090(3) | 103.096(4) |
| $\gamma$/° | 103.334(3) | 90 |
| *V*/Å$^3$ | 3702.6(9) | 7523(3) |
| $\rho_{calcd}$/g cm$^{-3}$ | 1.325 | 1.347 |
| *F* (000) | 1572 | 3254 |
| *T*/K | 293(2) | 293(2) |
| $\mu$(Mo K$_\alpha$)/mm$^{-1}$ | 0.116 | 0.119 |
| Crystal dimensions/mm | 0.24 × 0.20 × 0.08 | 0.24 × 0.22 × 0.20 |
| Range scanned $\theta$/° | 1.28–25.00 | 1.35–25.00 |
| Index range | $-18 < h < 18$<br>$-14 < k < 18$<br>$-21 < l < 19$ | $-18 < h < 18$<br>$-38 < k < 37$<br>$-18 < l < 18$ |
| No. of reflections collected | 20586 | 50667 |
| No. of unique reflections | 13004 | 13507 |
| $R_{int}$ | 0.0368 | 0.0614 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0820 | 0.0972 |
| $wR_2$ (all data) | 0.2006 | 0.2595 |
| ($\Delta\rho$)max./e Å$^{-3}$ | 0.780 | 0.647 |
| ($\Delta\rho$)min./e Å$^{-3}$ | −0.478 | −0.442 |

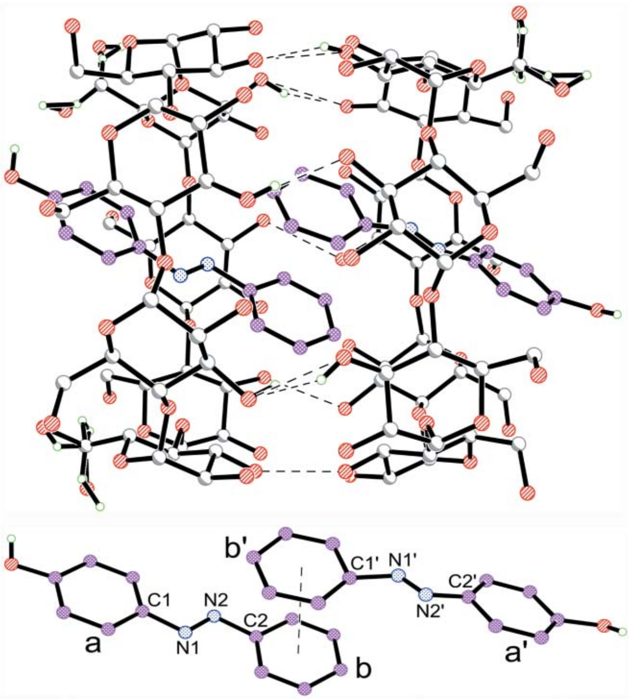


**Fig. 1** The head-to-head dimer of β-CD/4-HAB complexes. The 4-HAB molecules are colored by atom type, purple: carbon atoms, red: oxygen atoms, blue: nitrogen atoms, and green: hydrogen atoms. The β-CD dimers are also colored by atom type, gray: carbon atoms, red: oxygen atoms, and green: hydrogen atoms involved hydrogen-bonding interactions.

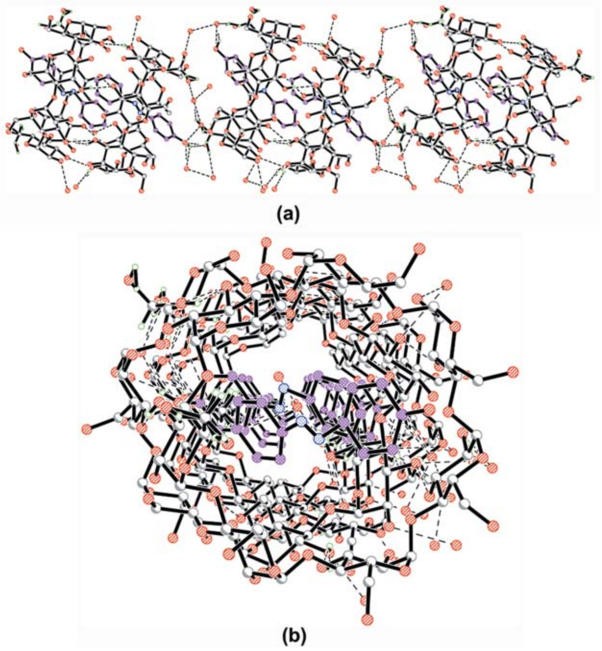


**Fig. 2** The (a) side view and (b) top view of the linear supramolecular aggregate (AAAA type) of **1** constructed by the head-to-head dimers.

water molecules. These interconnections consequently enable the β-CD/4-HAB dimers to form a linear supramolecular aggregate in the solid state (AAAA type).

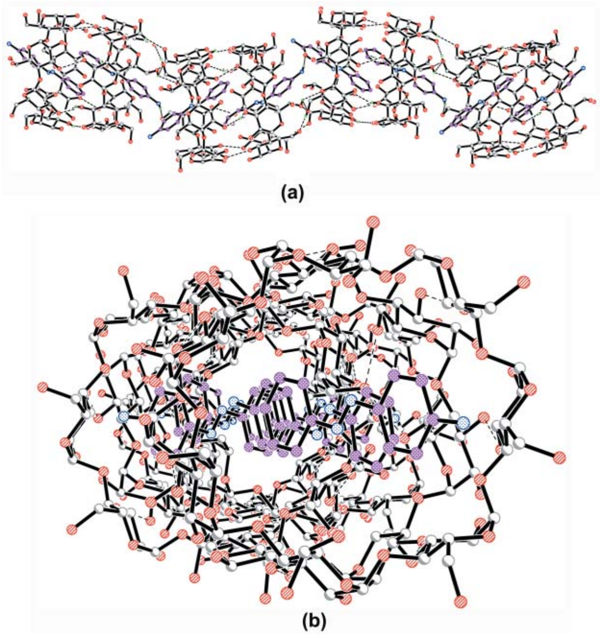


**Fig. 3** The (a) side view and (b) top view of the wave-type aggregate (ABAB type) of **2** constructed by the head-to-head dimers. The 4-AAB molecules are colored by atom type, purple: carbon atoms, red: oxygen atoms, blue: nitrogen atoms, and green: hydrogen atoms. The β-CD dimers are also colored by atom type, gray: carbon atoms, red: oxygen atoms, and green: hydrogen atoms involved hydrogen-bonding interactions.

Interestingly, by switching the 4-HAB molecule in complex **1** to a 4-AAB molecule, we obtain a wave-type supramolecular aggregate assembled from complex **2** (Fig. 3). Similar to complex **1** (Fig. 2), two *trans* 4-AAB molecules in β-CD/4-AAB dimer are also embedded into the β-CD cavities by two different directions with the amino group of the 4-AAB molecule pointing to the primary side of the β-CD cavity (2 : 2 stoichiometry between β-CD and 4-AAB in the crystal structure). However, compared with the corresponding data for complex **1**, the dihedral angle between the plane of the *c* (or *c*′) ring and the heptagons composed of seven glycosidic oxygen atoms in β-CD increases to 63.5° (or 65.1°), and the dihedral angle between the aromatic rings *c* (or *c*′) and *d* (or *d*′) in 4-AAB decreases to 2.2° (or 6.9°). These jointly lead to a less tilted orientation of the included 4-AAB relative to the $C_7$ axis of β-CD than the case for complex **1**. Moreover, two β-CD/4-AAB complexes are connected by seven hydrogen bonds (coming from the hydroxyl groups at the secondary sides of the β-CDs) and the π–π interaction between two benzene rings in a head-to-head arrangement (dihedral angle between *d* and *d*′: 3.8°, centroid separation between *d* and *d*′: 3.669 Å) to form a dimer unit (Fig. 4). More interestingly, two adjacent head-to-head β-CD/4-AAB dimers in the aggregate adopt different orientations, which consequently result in the formation of wave-type polymeric supramolecules (ABAB type)

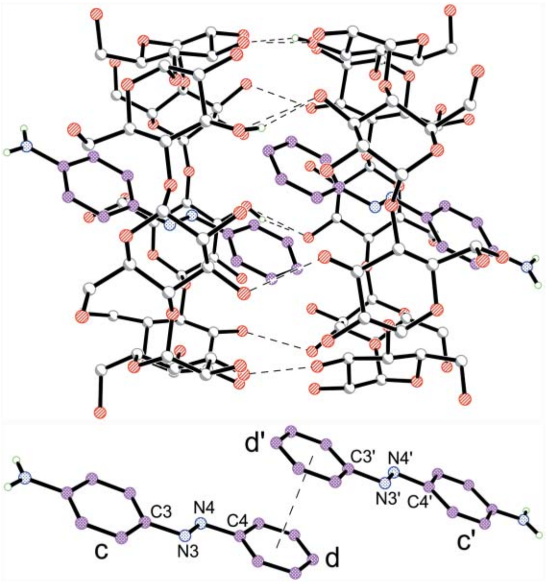


**Fig. 4** The head-to-head dimer of β-CD/4-AAB complexes.

through the interdimer hydrogen bonds between the CD's C6–OHs as well as the O···H–N interactions between the amino group at the *c′* ring of 4-AAB and the C6–OH of the adjacent β-CD ($d_{O\cdots H–N} = 3.140$ Å).

Each asymmetric unit is distributed with 16 water molecules for crystal **1** and 21.5 water molecules for crystal **2**, and these water molecules are all located on the exterior of the β-CD cavities, which indicates the presence of stronger hydrophobic interactions between the CD cavities and guests. The disparity of water molecule numbers in the asymmetric units of **1** and **2** is important in the formation of structures of different types.[18] On the other hand, the strong hydrogen bond network formed by the hydroxyl groups of the β-CD, substituent groups of azobenzene, and intervening water stabilize the aggregations of **1** and **2** and further extend the aggregation to a more complicated level.

According to the crystal structures of **1** and **2**, we can also deduce that the different arrangements of two guest molecules (4-HAB and 4-AAB) in β-CD cavities are ascribed to the disparity of substituent groups on the azobenzenes. In the β-CD/4-HAB dimer, two hydroxyl groups of the included 4-HAB molecules both participate in the formation of the interdimer hydrogen bonds, accordingly leading to an ordered spatial arrangement of the resultant aggregates (AAAA type). However, two 4-AAB molecules in a β-CD/4-AAB dimer provide only one amino group at the *c′* ring to form the interdimer hydrogen bond, which leads to the "less-ordered" spatial arrangement of the aggregate (ABAB type). Therefore, these interesting results provide valuable insight for understanding the spatial topology of biotic acceptors with different model substrates in the solid state, and the inclusion complexation mechanism of CDs with functional guests.

## NMR and ICD spectra

In order to comprehensively examine the structural features of these CD complexes and deeply understand the assembly process, the solution structures of **1** and **2** were investigated by means of NMR and circular dichroism (CD) spectroscopy, which show certain consistency with those in the solid state. Generally, the chemical shift values of the guest protons tend to show appreciable changes if the guest molecules are included in the CD cavities.[48] Therefore, $^1$H NMR spectra of complexes **1** and **2** are performed at 25 °C in $D_2O$ and compared with those of 4-HAB and 4-AAB. As can be seen from Fig. 5, the $\delta$ value of $H_a$ protons of the 4-HAB unit in **1** ($7.0 \times 10^{-4}$ mol dm$^{-3}$) shifts downfield *ca.* 0.01 ppm, and the $\delta$ values of $H_b$, $H_c$, and $H_d$ protons shift upfield *ca.* 0.05, 0.04, and 0.03 ppm respectively, as compared with the corresponding values for free 4-HAB ($1.0 \times 10^{-4}$ mol dm$^{-3}$). Similar phenomena are also observed in the case of complex **2**. The $\delta$ values of $H_e$, $H_f$, $H_g$, and $H_h$ protons of the 4-AAB unit in **2** ($7.6 \times 10^{-4}$ mol dm$^{-3}$) shift upfield *ca.* 0.01, 0.05, 0.05, and 0.06 ppm respectively as compared with the corresponding values for free 4-AAB ($1.5 \times 10^{-4}$ mol dm$^{-3}$). These results indicate that a host–guest inclusion complex is formed between 4-HAB (or 4-AAB) and β-CD in aqueous solution.

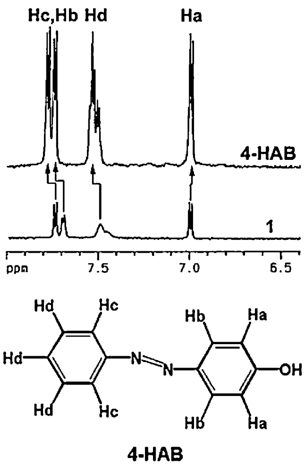


**Fig. 5** $^1$H NMR spectra of 4-HAB ($1.0 \times 10^{-4}$ mol dm$^{-3}$) and complex **1** ($7.0 \times 10^{-4}$ mol dm$^{-3}$) in $D_2O$ at 25 °C.

Another useful piece of information about the solution structure of complexes **1** and **2** comes from 2D NMR experiments. Recently, 2D NMR spectroscopy has become an essential method for the study of the structures of organic compounds since one can conclude that two protons are closely located in space if a NOE correlations is detected between the relevant proton signals in the NOESY or ROESY spectrum. Therefore, if the guest molecule is included into the β-CD cavity, the NOE correlations between the protons of the guest and the interior protons of the β-CD cavity (H3 and H5) should be observed. According to the relative intensity of these correlations, it is possible to estimate the orientation of the guest molecule within the β-CD cavity.[48] As shown in Fig. 6a, the ROESY spectrum of **1** displays clear NOE correlations between the H5 protons of β-CD and the $H_b$ protons of 4-HAB (peaks B), as well as the correlations between the H3 protons of β-CD and the $H_c$ protons of 4-HAB (peaks D), which indicates that the 4-HAB molecule is embedded into the CD cavity. Moreover, the NOE correlations between the H6 protons of β-CD and the $H_a$ (peaks A) as well as $H_b$ (peaks C) protons of 4-HAB are also observed. Considering the structural features of the CD cavity, where the H6 protons are located at the narrow side of cavity, the H5 protons near the narrow side, and the H3 protons near the wide side, we can deduce a possible inclusion complexation geometry of complex **1** as illustrated in Fig. 6b. In the case of complex **2** (Fig. 7a), the strong correlations (peaks E) between the CD's H5 protons and the $H_f$ and/or $H_g$ protons of 4-AAB, the relatively weak correlations (peaks F) between the CD's H3 protons and the $H_f$ and/or $H_g$ protons of 4-AAB, and the correlations (peaks G) between the CD's H6 protons and the $H_e$, $H_f$, and/or $H_g$ protons of 4-AAB unequivocally indicate that the 4-AAB is accommodated in the β-CD cavity from the narrow side, as illustrated in Fig. 7b.

In addition to the NMR results, circular dichroism spectroscopy also provides some useful information about the inclusion complexation geometry of β-CD with 4-HAB or 4-AAB, since achiral organic compounds (in this case, 4-HAB and 4-AAB) can show an induced circular dichroism (ICD) signal around their corresponding transition band in cases where there is a chiral microenvironment such as a CD cavity. As can be seen from Fig. 8, either **1** or **2** shows a positive Cotton effect peak in the circular dichroism spectrum; the $\Delta\varepsilon$ values are 1.57 dm$^{-3}$ mol$^{-1}$ cm$^{-1}$ at 343 nm for **1** and 1.26 dm$^{-3}$ mol$^{-1}$ cm$^{-1}$ at 365 nm for **2**. In the control experiments, neither 4-HAB nor 4-AAB displays any appreciable circular dichrosim signals in the wavelength range from 200–500 nm (results not shown). According to Kajtár's proposal[49] and some reported studies on the circular dichrosim spectra of CD/azo complexes,[50,51] we can deduce that the azobenzene moiety of 4-HAB (or 4-AAB) is included longitudinally in the β-CD cavity. On the other hand, the UV-vis spectrum of **2** in aqueous solution shows a low-energy absorption band at about 430 nm with an extinction coefficients with a magnitude of $10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$, which is assigned as a bigger conjugated system occurring between two benzene rings in 4-AAB, that is to say, the two benzene rings are almost located in the same plane. However, only a weak low-energy absorption band at about 425 nm with an extinction coefficient with a magnitude of $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ is observed in the UV-vis spectrum of **1**, which suggests that the conjugation degree between two benzene rings in 4-HAB is lower than that in 4-AAB. One possible explanation for this phenomenon may come from the crystal structure of **1** and **2**, in which two benzene rings

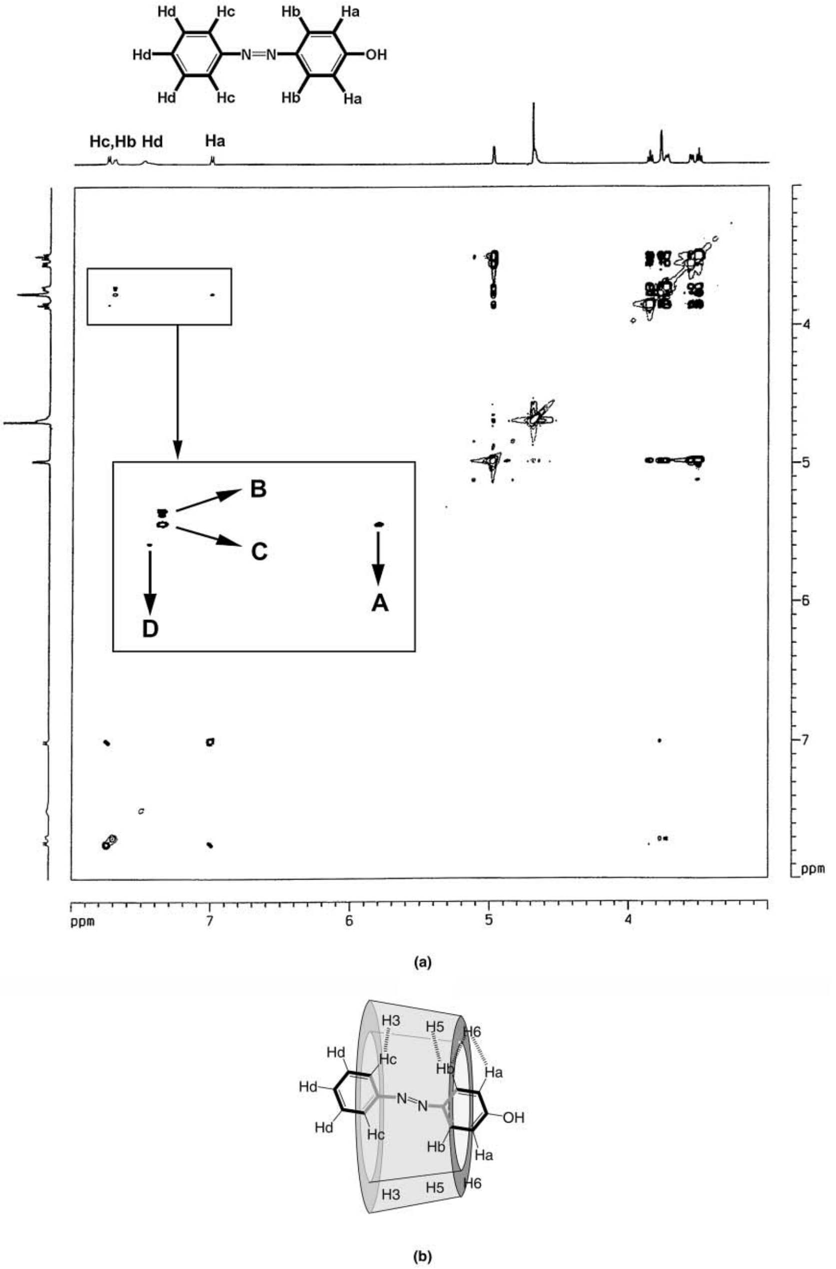


**Fig. 6** (a) ROESY spectrum of **1** ($2.0 \times 10^{-3}$ mol dm$^{-3}$) in $D_2O$ at 25 °C with a mixing time of 200 ms, (b) possible structure of **1** in solution.

of the included 4-AAB molecule in **2** display a smaller dihedral angle than the corresponding value for the 4-HAB molecule in **1**.

## Binding abilities

For a quantitative assessment of the association of CD with azobenzene derivatives in aqueous solution, UV-vis spectral titrations were performed at 25 °C in a phosphate buffer (pH 7.20) to give the binding constants ($K_S$) and Gibbs free energy change ($-\Delta G°$) for the inclusion complexation of 4-HAB and 4-AAB with β-CDs. In the UV-vis spectra of 4-AAB ($2.0 \times 10^{-5}$ mol dm$^{-3}$) with β-CD, the UV absorption intensity of 4-AAB at 436.0 nm gradually decreases upon the addition of varying amounts of β-CD. Moreover, the appearance of the isosbestic point at 407.0 nm further confirms the simple one-step transformation from the free 4-AAB to the inclusion complex. Using the nonlinear least squares curve-fitting method,[52,53] we obtain the complexation stability constants ($K_S$: 840 M$^{-1}$ for 4-HAB and 2130 M$^{-1}$ for 4-AAB) and Gibbs free energy changes ($-\Delta G°$: 16.7 kJ mol$^{-1}$ for 4-HAB and 19.0 kJ mol$^{-1}$ for 4-AAB) for each host–guest combination from the analysis of the sequential changes of absorption intensity ($\Delta A$) at various β-CD concentrations. A typical curve-fitting plot for the titration of 4-AAB with β-CD is shown in the ESI,† which gives good fits between the experimental and calculated data. In the repeated measurements, the $K_S$ values were reproducible within an error of ±6%.

Many researches demonstrate that the host–guest size/shape matching and hydrogen bond interactions can dominate the stability of complex formed between β-CD and model substrates, leading to stronger van der Waals and hydrophobic interactions, since these interactions are closely related to the distance and contacting surface area between the host and guest.[54] According to the obtained results, the inclusion complexation of 4-AAB with β-CD affords a higher stability constant up to 2130 M$^{-1}$, which is 2.5 times as high as that of the 4-HAB/β-CD complexation (840 M$^{-1}$). The result may be attributed to the size/shape fit between the guest 4-AAB and the β-CD cavity. In the former section, we have demonstrated that the included

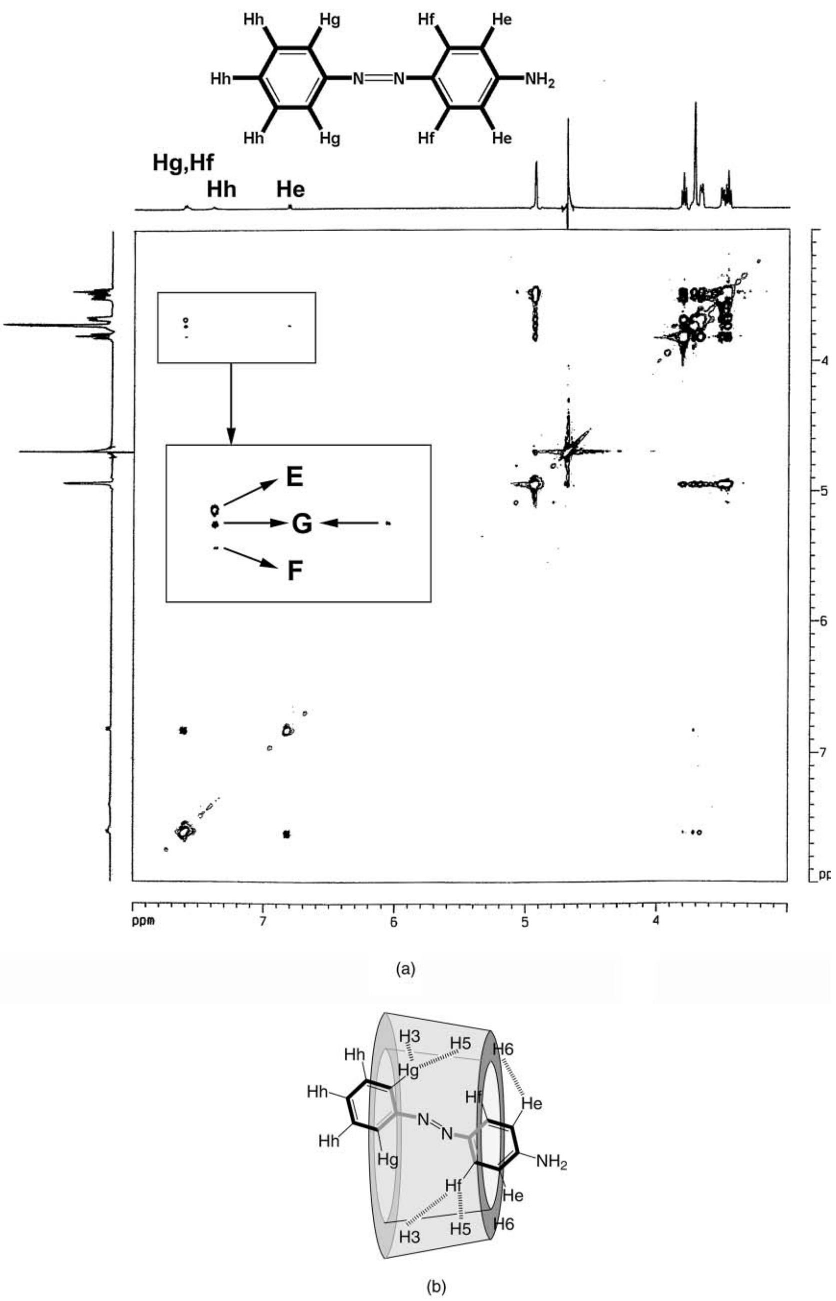


**Fig. 7** (a) ROESY spectrum of **2** ($1.8 \times 10^{-3}$ mol dm$^{-3}$) in $D_2O$ at 25 °C with a mixing time of 200 ms, (b) possible structure of **2** in solution.

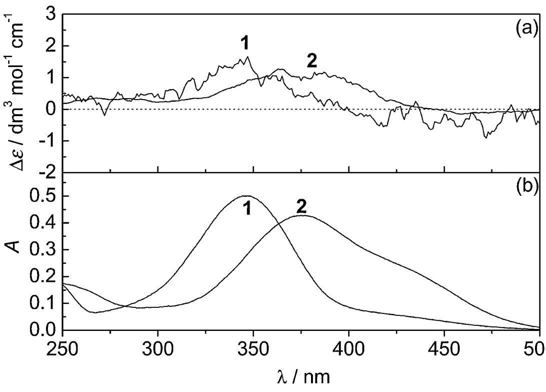


**Fig. 8** (a) Circular dichroism and (b) absorption spectra of **1** ($2.1 \times 10^{-5}$ mol dm$^{-3}$) and **2** ($2.0 \times 10^{-5}$ mol dm$^{-3}$) in phosphate buffer aqueous solution (pH 7.20).

4-AAB molecule in the crystal of **2** adopts a less tilted orientation relative to the $C_7$ axis of β-CD than the case of 4-HAB in **1**. This conformation will further exploit the geometric requirement of longitudinal incorporation of the linear guest within the β-CD cavity, which consequently results in the strong van der Waals and hydrophobic interactions between the host and guest. Owing to these strengthened host–guest interactions, complex **2** gives a larger $K_S$ value than that of **1**.

## Conclusions

Two one-dimensional polymeric supramolecular architectures possessing a triclinic system (*P*1) for **1** and a monoclinic system (*P*2(1)) for **2** are constructed by the self-assembly of β-CD/azobenzene complexes. The crystallographic studies show that the β-CD/azobenzene complexes can form a head-to-head dimer structure through the linkage of the interdimer π–π and hydrogen bond interactions. Subsequently, the interdimer hydrogen bond interactions link the discrete dimers into infinite linear or wave-type aggregate with AAAA type (for **1**) or ABAB type (for **2**) spatial arrangements. Further investigations by

UV-vis, circular dichroism, and NMR spectroscopy elucidate the structural similarity of **1** and **2** in both solution and the solid state. These observations, along with the easy synthesis of β-CD/azobenzene complexes, indicate that, with judicious design, highly ordered supramolecular arrays can be achieved conveniently in a controllable way.

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