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ORIGINAL ARTICLE

Interaction between cucurbit[6]uril and bispyridinecarboxamide

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Abstract The interaction between cucurbit[6]uril and *N*,*N*′-(m-bispyridinecarboxamide)-1,n-alkane (m = 2, 3, 4; n = 4, 6, 8) has been investigated by ^{1}H-NMR, ESI-MS and single crystal X-ray diffraction method. The results show that cucurbit[6]uril can form pseudorotaxanes with *N*,*N*′-(m-bispyridinecarboxamide)-1,6-hexane (m = 2, 3, 4) easily. When the alkyl chain length increases (n = 8), the binding mode is identical, but the binding ability of the host towards guest decreases. In both two cases cucurbit[6]uril shows no selectivity towards positional isomers. However, in the case of n = 4, the binding mode is different, having relations with positional substitution of the guest. Only *N*,*N*′-(m-bispyridinecarboxamide)-1,4-butane (m = 2) can form pseudorotaxane with cucurbit[6]uril, while the other two (m = 3, m = 4) form external complex with cucurbit[6]uril. The possible reason for the difference has been discussed.

Keywords Bispyridinecarboxamide · Cucurbit[6]uril · Pseudorotaxane · Supramolecular assembly

Introduction

Cucurbit[6]uril (CB[6]), a macrocyclic compound comprising six glycoluril units and twelve methylene groups, has a hydrophobic cavity similar to α-cyclodextrin in size which is accessible from the exterior by two carbonyl fringed-portals [1], as shown in Fig. 1a [2]. The unique structure makes CB[6] a very effective receptor for many neutral molecules to be accommodated into the cavity and a good ligand to coordinate with various cations, especially metal ions and ammonium ions. Wide investigation about its host-guest chemistry has been done by Mock et al. [3], Buschmann et al. [4], Kim et al. [5] and other research groups [6]. And it was found out that CB[6] has particularly high selectivity towards protonated alkyl- and aryl-diamines because of the cooperation of hydrophobic interaction and ion-dipole interaction. This property is often utilized in constructing supramolecular architectures such as (pseudo)rotaxanes, main-chain and side-chain (pseudo)polyrotaxanes [7], 1D, 2D, 3D polyrotaxanes with transition metal ions and molecular necklaces [8], molecular switches [9] and so on. Although elegant work has been done in this area, it is still of importance and significance in constructing new kinds of supramolecular assemblies with novel structures and special properties. Bispyridinecarboxamide is a kind of bidentate ligand [10], both the nitrogen of the pyridine and the oxygen of the carbonyl group can coordinate with metal. However, to the best of our knowledge, no metalo-rotaxane or other supramolecular assemblies based on this kind of guest and CB[6] has been reported so far. Furthermore, no detailed investigation of the interaction between these guests and CB[6] has been reported. Here, we present the study of the interaction of CB[6] and *N*,*N*′-(m-bispyridinecarboxamide)-1,n-alkane (m = 2, 3, 4; n = 4, 6, 8; Fig. 1b) by ^{1}H-NMR analysis. The results show that CB[6] can form different complexes with different bispyridinecarboxamide, and the binding mode is dependent on the chain length and the

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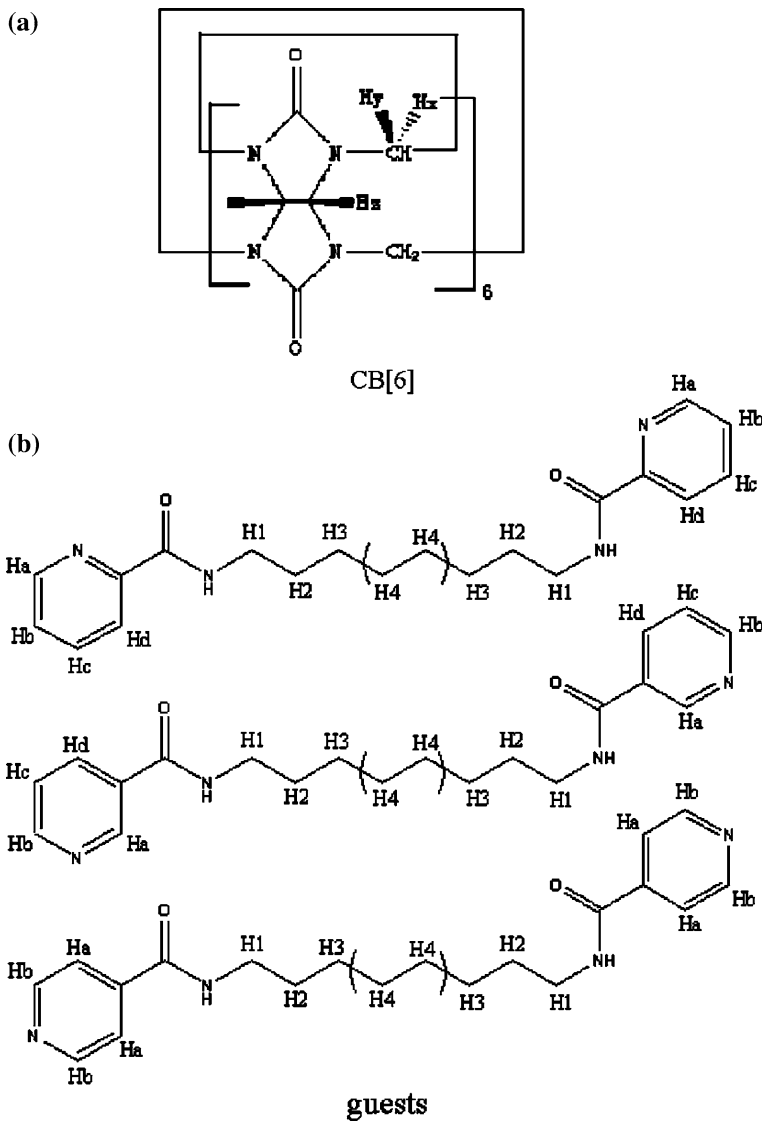

Fig. 1 (**a**) Structure of Cucurbit[6]uril, (**b**) Structures of the guests

positional substitution of the guest, this is supported by ESI-MS analysis. A pseudorotaxane based on *N*,*N*′-(4-bispyridinecarboxamide)-1,6-hexane and CB[6] has been prepared and characterized by single crystal X-ray diffraction.

Experimental

Elemental analysis was performed using a VarioEL III Elemental Analyzer. ^{1}H-NMR measurement was conducted on a Mercury VX-300 (Varian, 300 MHz) spectrometer immediately after mixing a certain amount of host and guest in 20% DCl/D_2O with $(CH_3)_3SiCH_2CH_2CH_2SO_3^-Na^+$(DSS) as internal standard at room temperature. ESI-MS measurement was performed on Thermo Finnigan LCQ advantage at room temperature in CH_3COOH/H_2O solution. FAB-MS spectra were obtained on a VG ZAB-3F-HF mass spectrograph.

CB[6] and the nine guests used were synthesized according to the literatures [11] and [12] method, respectively, and characterized by ^{1}H-NMR, FAB-MS, elemental analysis.[1]We abbreviated *N*,*N*′-(2-bispyri-

[1] CB[6]: ^{1}H-NMR (20%DCl/D2O): 4.495 (Hx, d, 12H, J=15.6Hz), 5.645 (Hy, s, 12H), 5.706 (Hz, s, 12H). FAB-MS: m/z 997 $[M+H]^+$. Anal. calcd. for $C_{36}H_{36}N_{24}O_{12}\cdot 4H_2O$: C, 40.45; H, 4.12; N, 31.46. Found: C, 40.61; H, 4.29; N, 31.61. 2-H_2BPBu: ^{1}H-NMR (20% DCl/D_2O): 1.817 (H2, s, 4H), 3.570 (H1, s, 4H), 8.342 (Hb, t, 2H), 8.724 (Hc, d, 2H), 8.849 (Hd, t, 2H), 9.019 (Ha, d, 2H). FAB-MS: m/z 299 $[M+H]^+$. Anal. calcd. for $C_{16}H_{18}N_4O_2$: C, 64.43; H, 6.04; N, 18.79. Found: C, 64.46 ; H, 6.54 ; N, 18.85. 2-H_2BPH: ^{1}H-NMR (20% DCl/D_2O): 1.456 (H3, s, 4H), 1.714 (H2, s, 4H), 3.510 (H1, t, 4H), 8.344 (Hb, t, 2H), 8.715 (Hc, d, 2H), 8.849 (Hd, t, 2H), 9.019 (Ha, d, 2H). FAB-MS: m/z 327 $[M+H]^+$. Anal. calcd. for $C_{18}H_{22}N_4O_2$: C, 66.26; H, 6.74; N, 17.18. Found: C, 66.24; H, 6.79;

dinecarboxamide)-1,4-butane as 2-H_2BPBu, *N*,*N*′-(3-bispyridinecarboxamide)-1,6-hexane as 3-H_2BPH, for convenience, and the rest may be deduced by analogy.

X-ray crystallography

The crystal structure of psesudorotaxane formed by CB[6] and 4-H_2BPH was determinated using a Bruker SMART APEX II CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 293 (2) K in the range of $1.83° < \theta < 27.50°$. The structure was solved by direct method (SHELXL-97) and refined against F^2 in anisotropic approximation (SHELXL-97). The SQUEEZE procedure was used because the included solvent was unordered. Crystal data: $C_{36}H_{36}N_{24}O_{12} + C_{18}H_{22}N_4O_2$, Mr = 1,323.28, monoclinic, space group P2(1)/n, a = 14.0014(9) Å, b = 15.9367 (10) Å, c = 15.7331(10) Å, α = 90°, β = 97.4590(10)°, γ = 90°, V = 3480.9(4) Å^3, Z = 2, ρ_{cal} = 1.263 Mg/m^3, μ = 0.095 mm^{-1}, number of reflections measured = 24,854, number of independent reflections = 7,932 (R_{int} = 0.0531), R_1 = 0.0652 ($I > 2\sigma(I)$), wR_2 = 0.1571 (($I > 2\sigma(I)$); R_1 = 0.1177 (all data), wR_2 = 0.1782 (all data).

CCDC reference number 626911.

Footnote 1 continued
N, 17.17. 2-H_2BPO: ^{1}H-NMR (20% DCl/D_2O): 1.361 (H3, H4, s, 8H), 1.682 (H2, s, 4H), 3.488 (H1, t, 4H), 8.342 (Hb, t, 2H), 8.711 (Hc, d, 2H), 8.848 (Hd, t, 2H), 9.019 (Ha, d, 2H). FAB-MS: m/z 355 $[M+H]^+$. Anal. calcd. for $C_{20}H_{26}N_4O_2$: C, 67.42; H, 7.30; N, 15.73. Found: C, 67.26; H, 7.43; N, 15.63. 3-H_2BPBu ^{1}H-NMR (20% DCl/D_2O): 1.795 (H2, s, 4H), 3.523 (H1, s, 4H), 8.279 (Hc, t, 2H), 9.035 (Hb, Hd, t, 4H), 9.276 (Ha, s, 2H). FAB-MS: m/z 299 $[M+H]^+$. Anal. calcd. for $C_{16}H_{18}N_4O_2$: C, 64.43, H, 6.04, N, 18.79. Found: C, 64.73; H, 5.99; N, 18.66. 3-H_2PBH: $_1$H-NMR (20% DCl/D_2O): 1.448 (H3, s, 4H), 1.689 (H2, s, 4H), 3.450 (H1, t, 4H), 8.249 (Hc, t, 2H), 9.006 (Hb, Hd, t, 4H), 9.225 (Ha, s, 2H). FAB-MS: m/z 327 $[M+H]^+$. Anal. calcd. for $C_{18}H_{22}N_4O_2$: C, 66.26; H, 6.74; N, 17.18. Found: C, 66.24; H, 6.79; N, 17.17. 3-H_2BPO: ^{1}H-NMR (20% DCl/D_2O): 1.359 (H3, H4, s, 8H), 1.659 (H2, s, 4H), 3.430 (H1, s, 4H), 8.249 (Hc, t, 2H), 9.002 (Hb, Hd, d, 4H), 9.219 (Ha, s, 2H). MS: m/z 355 $[M+H]^+$. Anal. calcd. for $C_{20}H_{26}N_4O_2$: C, 67.42; H, 7.30; N, 15.73. Found: C, 67.78; H, 7.25; N, 15.67. 4-H_2BPBu ^{1}H-NMR (20% DCl/D_2O): 1.796 (H2, s, 4H), 3.531 (H1, s, 4H), 8.452 (Ha, d, 4H), 9.047 (Hb, d, 4H). FAB-MS: m/z 299 $[M+H]^+$. Anal. calcd. for $C_{16}H_{18}N_4O_2$: C, 64.43 ; H, 6.04; N, 18.79. Found: C, 64.25; H, 6.212; N, 18.83. 4-H_2BPH. ^{1}H-NMR (20% DCl/D_2O): 1.453 (H3, s, 4H), 1.698 (H2, s, 4H), 3.468 (H1, t, 4H), 8.435 (Ha, s, 4H), 9.044 (Hb, s, 4H). FAB-MS: m/z 327 $[M+H]^+$. Anal. calcd. for $C_{18}H_{22}N_4O_2$: C, 66.26; H, 6.74; N, 17.18. Found: C, 66.24; H, 6.79; N, 17.17. 4-H_2BPO ^{1}H-NMR (20% DCl/D_2O): 1.360 (H3, H4, s, 8H), 1.662 (H2, s, 4H), 3.434 (H1, t, 4H), 8.394 (Ha, d, 4H), 9.006 (Hb, d, 4H). FAB-MS: m/z 355 $[M+H]^+$. Anal. calcd. for $C_{20}H_{26}N_4O_2$: C, 67.42; H, 7.30; N, 15.73. Found: C, 67.69; H, 7.288; N, 15.68.

Results and discussion

Investigation of the interaction of CB[6] and *N*,*N*′-(m-bispyridinecarboxamide)-1,6-hexane (m = 2, 3, 4)

As we know, the hollow cavity of CB[6] can serve as a proton-shielding region and make guests included exhibit a higher field signal compared to the unbound ones. NMR technique has proven to be a powerful method to investigate the host-guest interaction. Fig. 2 is the ^{1}H-NMR spectra of interaction between CB[6] and the three guests. The proton connected to the amide nitrogen doesn't appear in the spectra because it's exchangeable with D_2O. It can be clearly observed a new set of NMR signals of guests, which come from the guests bound with the host. That means the exchange between the bound guests and free ones is slow enough to be checked by NMR time scale. The signals of H1, H2, and H3 in the three isomers all shift upfield about 0.1, 0.8, 0.9 ppm, respectively, indicating that the alkyl chain is located inside the cavity of the host. At the same time, the proton signals of the pyridine group shift downfield, indicating the endgroup protrude outside of the cavity. This information shows that CB[6] can form pseudorotaxane with 2-H_2BPH, 3-H_2BPH, and 4-H_2BPH, respectively. The binding behavior is almost the same, irrespective of positional isomers. This result is further confirmed by ESI-MS as the molecular ion peak of the pseudorotaxane appearing in the corresponding spectrum (Fig. 3). The ratios of bound guests to free ones are about 6/1. All these indicate that the formation of pseudorotaxane is easy, fast and high yielded as the spectra were recorded immediately after the two reactants were mixed. The structure was also confirmed by single crystal X-ray diffraction analysis.

The crystal structure (Fig. 4) of the pseudorotaxane CB[6]·4-H_2BPH indicates that one guest threads through one CB[6] molecule to form a [2] pseudorotaxane. The hexyl chain is included in the cavity, and both amide groups slightly protrude from the portal, consequently, the carbonyl groups of the guest are located away from the portal. Two oxygen atoms of the carbonyl group of CB[6] form hydrogen bonds with the amide hydrogen (N(14)–H(14A)···O(3)) and methylene hydrogen (C(25)–H(25B) ··O(6)) of the guest respectively within one pseudorotaxane molecule. The hydrogen bond lengths and bond angles for the pseudorotaxane are listed in Table 1. All the bond distances of amide (N–H···O) hydrogen bonds (d(D–H), d(H···A) and d(D···A)) are shorter than the corresponding one of methylene (C–H···O) hydrogen

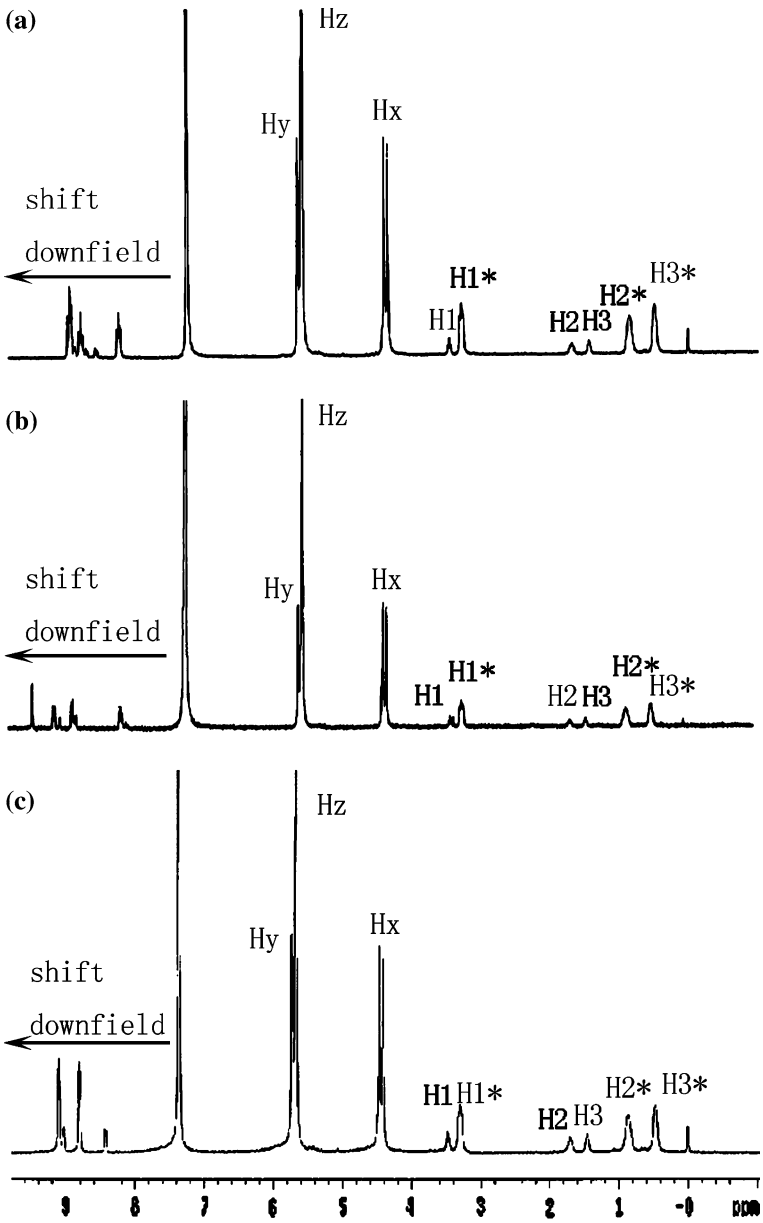

Fig. 2 The ^{1}H-NMR spectra of (**a**) 2-H_2BPH:CB[6] = 1:1, (**b**) 3-H_2BPH: CB[6] = 1:1, (**c**) 4-H_2BPH: CB[6] = 1:1 in 20% DCl/D_2O (Peaks marked with asterisks (*) represent guests complexed with CB[6])

bonds. And the bond angle for N(14)–H(14)...O(3) is very close to 180°. These indicate the amide (N–H···O) hydrogen bonds are stronger than the methylene (C–H···O) hydrogen bonds and may contribute more to the complex stabilization. The combination of hydrophobic interaction and the hydrogen bonds makes the complex stable.

Investigation of interaction of CB[6] and *N*,*N*′-(m-bispyridinecarboxamide)-1,8-octane (m = 2, 3, 4)

Figure 5 is the ^{1}H-NMR spectra of CB[6] and *N*,*N*′-(m-bispyridinecarboxamide)-1,8-octane (m = 2, 3, 4). It can be observed that H2, H3, H4 of guests shift upfield about 0.4, 0.6, 0.9 ppm, respectively, whereas H1 doesn't show any shift. This indicates the alkyl chain is a little longer than the axial distance of the cavity of CB[6], thus making H1 away from the influence of CB[6]. The proton signals of the pyridine shift downfield as expected. It indicates that CB[6] can form pseudorotaxanes with H_2BPO, too, and has no selectivity towards three positional isomers. The result is also confirmed by ESI-MS (Fig. 6). It also can be found out that the proton signals of CB[6] in the pseudorotaxanes shift upfield and be differentiated from that of free ones clearly, it may be caused by the pyridine

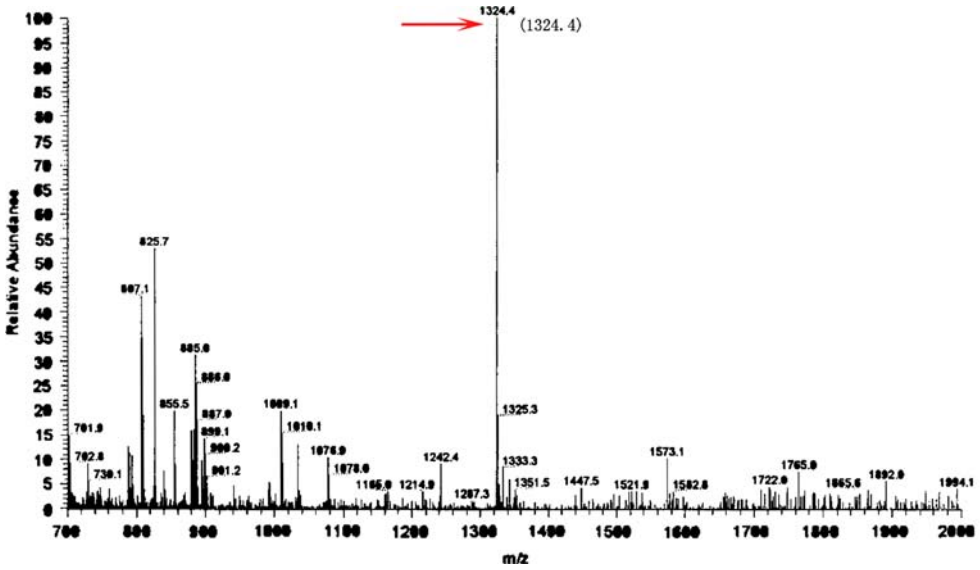

Fig. 3 ESI-MS spectrum of CB[6] and 3-H_2BPH (the peak indicated with red arrow is [CB[6]+3-H_2BPH+ H]$^+$)

group in the adjacent pseudorotaxane molecule extending close to the periphery of CB[6] due to the longer octyl chain and increasing the electron cloud density around CB[6].The integration ratio of CB[6] shifting upfield to guests shifting upfield is about 1:1. The integration ratio of the bound H_2BPO to unbound one is 1/2, indicating the binding ability of CB[6] towards H_2BPO decreased compared to that of CB[6] and H_2BPH as they were performed under the same experimental condition. The difference may be caused by the absence of amide (N-H...O) hydrogen bonds formation in the case of H_2BPO because the longer octyl chain keeps amide group far way from the carbonyl of CB[6], which is unfavorable to form hydrogen bonds.

Investigation of interaction of CB[6] and *N*,*N*′-(m-bispyridinecarboxamide)-1,4-butane (m = 2, 3, 4)

The ^{1}H-NMR spectra of CB[6] and H_2BPBu shows the interaction mode of the three positional isomers with CB[6] is different. In the case of 2-H_2BPBu and CB[6] (Fig. 7), there are obviously two sets of signals which can be assigned to the bound guests and free ones, respectively. Proton H1 and H2 shift upfield about 0.6, 0.8 ppm, respectively. The integration ratio of the bound 2-H_2BPBu to the unbound one is 1/3, less than that of H_2BPH and H_2BPO with CB[6]. Besides, Hx and Hy of CB[6] also shift upfield slightly and split into two sets. It indicates undoubtedly that CB[6] formed pseudorotaxane with 2-H_2BPBu. However, it is different in the case of 3-H_2BPBu and 4-H_2BPBu (Fig. 8), there is only one set of signal each for host and guest. When the concentration of CB[6] increases, the signals of all protons of 3-H_2BPBu and 4-H_2BPBu shift downfield slightly. The molecular ion peak of 1:1 complex of the host and guest was found in the ESI-MS spectrum (Fig. 9). We presume that a one-dimensional external complex supermolecule formed, based on the following consideration: (1) Neither of the ^{1}H-NMR spectra of the guests (3-H_2BPBu and 4-H_2BPBu) shows the characteristic upfield chemical shift, only an averaged signal shifting slightly downfield is observed; (2) The ESI-MS results show they indeedly formed a 1:1 complex; (3) Since the host and guest are symmetrical in structure, both ends of the host will bind a guest and vice versa, as a result a one-dimensional external complex supermolecule formed.

This result is completely different from that of *N*,*N*′-(bispyridylmethyl)-1,4-diaminobutane and CB[6] reported by Kim et al.[8a–c, h, i]. And why CB[6] has selectivity towards 2-H_2BPBu, 3-H_2BPBu, 4-H_2BPBu, whereas it has no selectivity towards H_2PBH isomers and H_2BPO isomers? The polarity of carbonyl group of the guest may be responsible for the reason, because butyl chain is not long enough to match the axial distance of CB[6] well, and the inclusion of this polar group will lead to an energetically unfavorable state, consequently, the inclusion complex of 3-H_2BPBu and 4-H_2BPBu with CB[6] is unstable and easy to decompose. As for 2-H_2BPBu, the orientation of pyridine nitrogen makes it suitable to bind with carbonyl group of CB[6] through ion-dipole interaction. The cooperation of hydrophobic interaction and ion-dipole

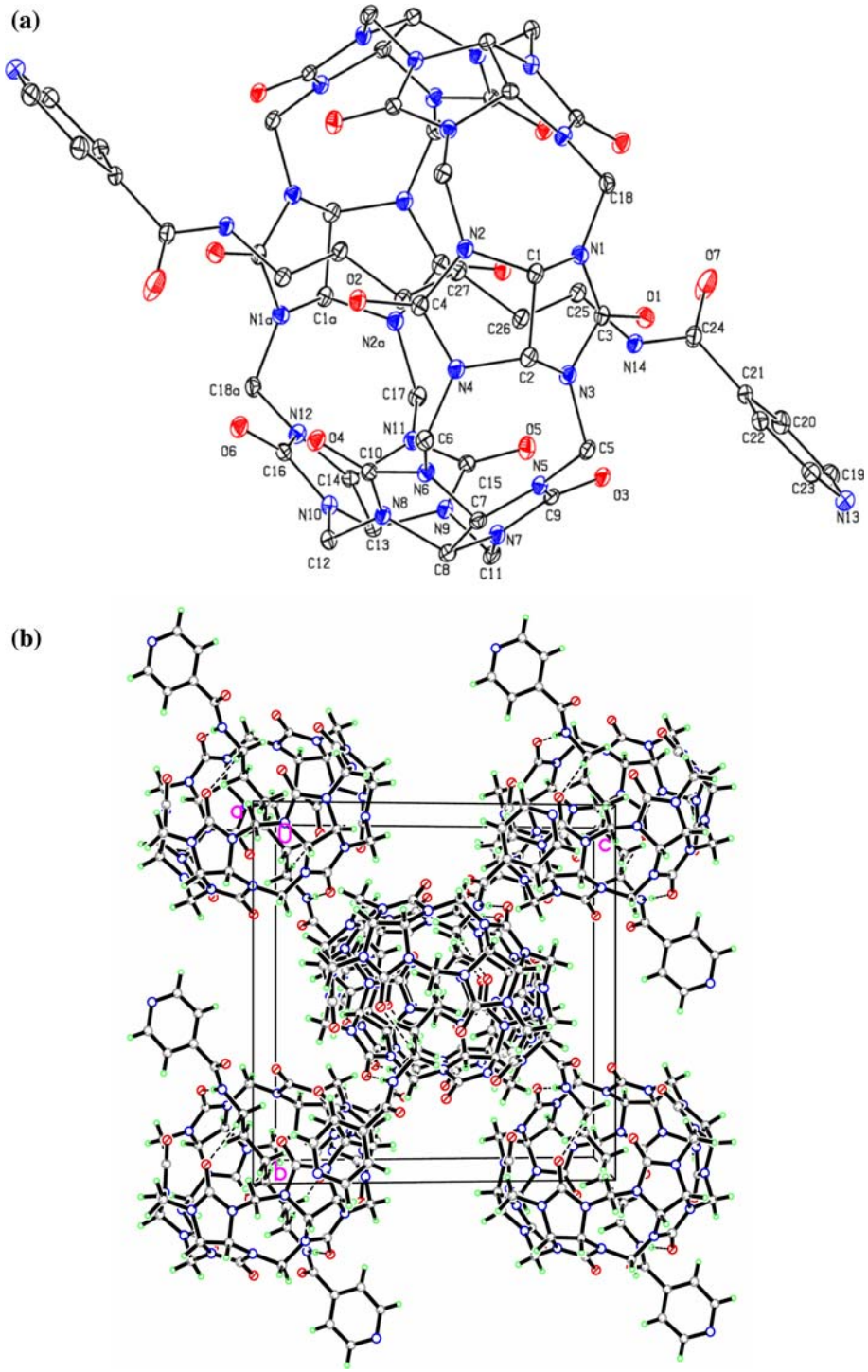

Fig. 4 (**a**) ORTEP view of the pseudorotaxane with hydrogen atoms omitted for clarity, (**b**) Stacking diagram of the pseudorotaxane

Table 1 Selected distances (Å) and angles (deg) of hydrogen bonding for the pseudorotaxane

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(14)–H(14) ···O(3)	0.8600	2.0800	2.929(3)	171.00
C(25)–H(25B) ···O(6)#1	0.9700	2.5400	3.451(3)	156.00

Symmetry code: #1 1–x, –y, –z

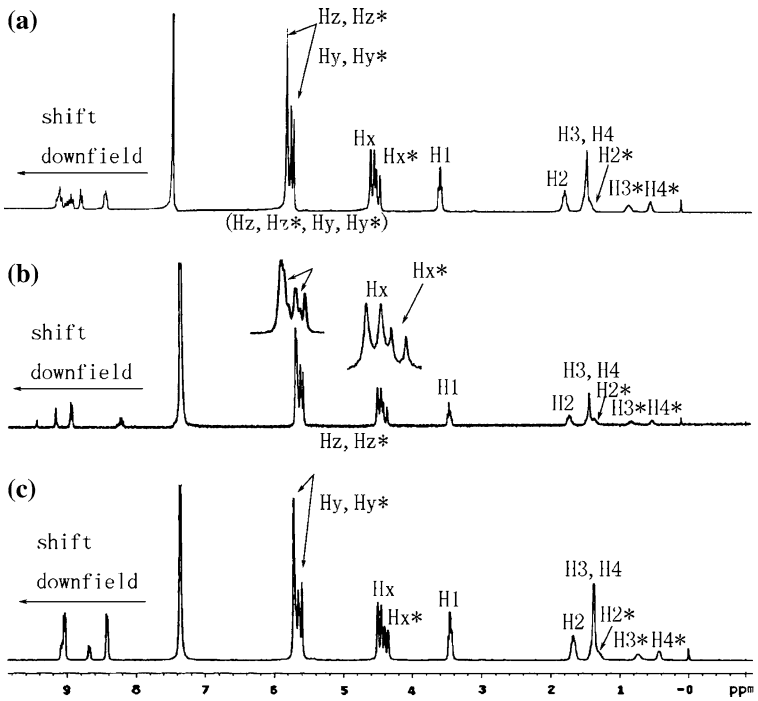

Fig. 5 The ^{1}H-NMR spectra of (**a**) 2-H_2BPO:CB[6] = 1:1, (**b**) 3-H_2BPO:CB[6] = 1:1, (**c**) 4-H_2BPO:CB[6] = 1:1 in 20% DCl/D_2O (Peaks marked with asterisks (*) represent guests complexed with CB[6])

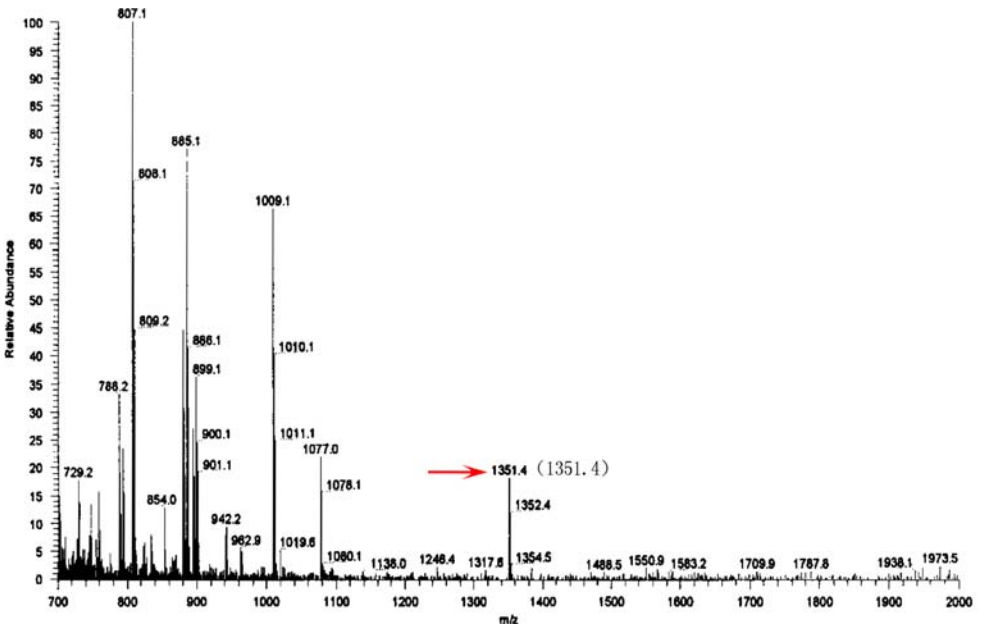

Fig. 6 ESI-MS spectrum of CB[6] and 3-H_2BPO (the peak indicated with red arrow is [CB[6]+3-H_2BPO+ H]$^+$)

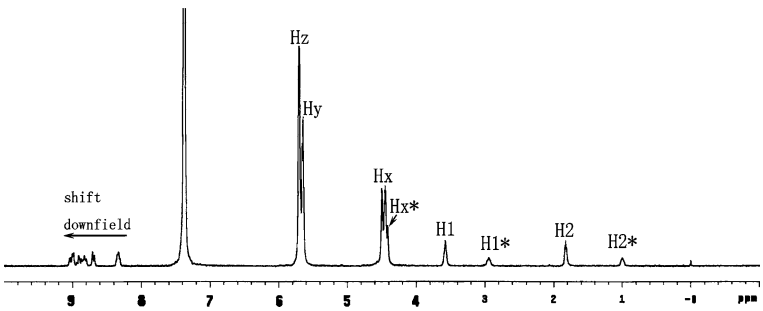

Fig. 7 The ^{1}H-NMR spectrum of 2-H_2BPBu: CB[6]=1:1 in 20%DCl/D_2O (Peaks marked with asterisks (*) represent guests complexed with CB[6])

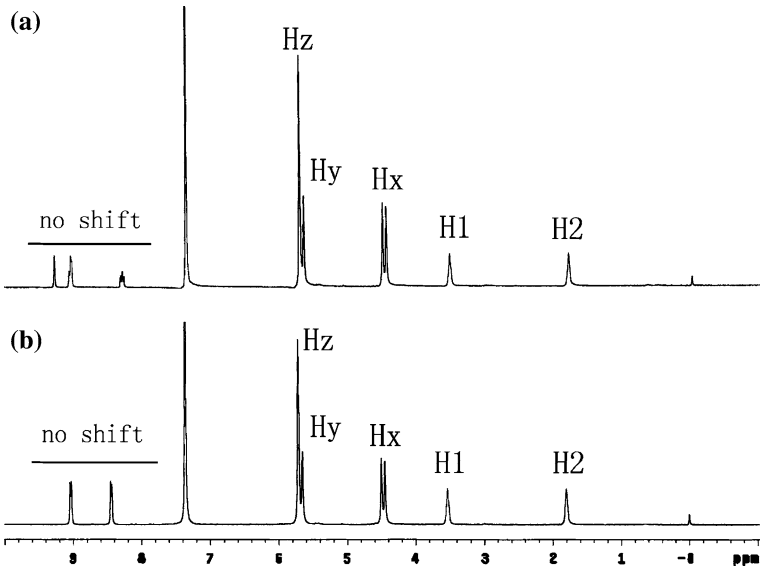

Fig. 8 The ^{1}H-NMR spectra of (a) 3-H_2BPBu:CB[6] = 1:1, (b) 4-H_2BPBu:CB[6] = 1:1

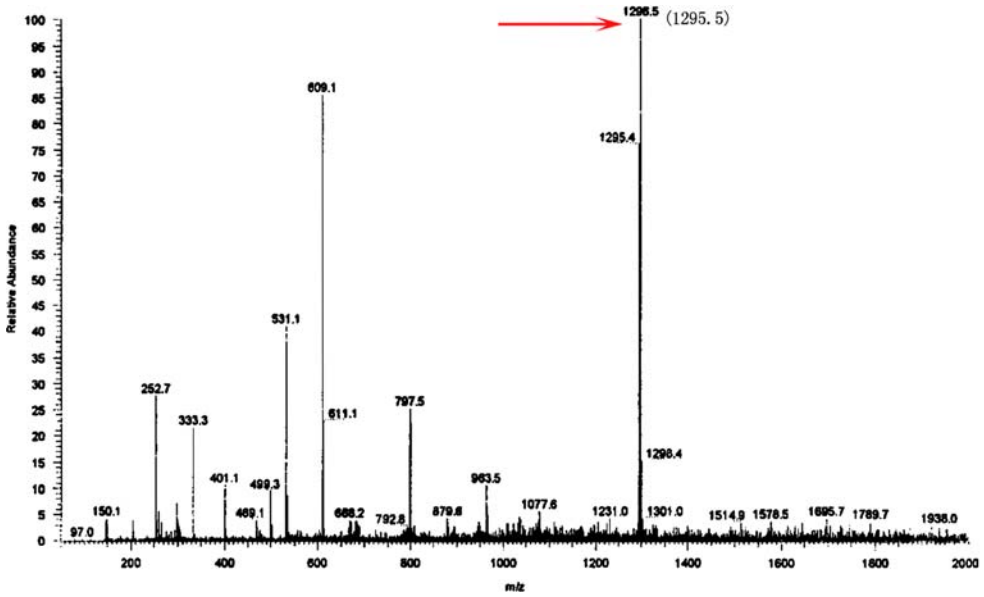

Fig. 9 The ESI-MS spectrum of 4-H_2BPBu and CB[6] (the peak indicated with red arrow is [CB[6]+ 4-H_2BPBu+H]$^+$)

interaction makes the inclusion complex of 2-H_2BPBu and CB[6] stable. When the alkyl chain becomes longer, the carbonyl groups of the guests are located far away from the portal (as we see from the crystal structure); they have no effect on the interaction of the host and guests.

Conclusion

The results show that CB[6] can form pseudorotaxanes with both m-H_2BPH (m = 2, 3, 4) and m-H_2BPO (m = 2, 3, 4) easily with no selectivity towards positional isomers. But CB[6] has higher selectivity towards the former than the later because of size match. Kim et al. [8a–c, h, i] reported a series of supramolecular assemblies based on *N*,*N*′-(bispyridylmethyl)-diaminobutane and CB[6]. According to their investigation, *N*,*N*′-(bispyridylmethyl)-1,4-diaminobutane can threads through CB[6] to form a pseudorotaxane. However, when methylene group is replaced by carbonyl group, the interaction between the guests and host changed markedly in our experiment. Only 2-H_2BPBu can form pseudorotaxane with CB[6], whereas the other two (3-H_2BPBu and 4-H_2BPBu) form external complexes with CB[6]. The difference may be caused by the polar carbonyl group of the guest. When the alkyl chain is long enough, the

carbonyl group will be far away from the portal of the host. It has no effect on the interaction. In the case of H_2BPBu, the butyl chain is not so long, when the chain threads through the cavity, the carbonyl group will be located in it, which is energetically unfavorable. So, 3-H_2BPBu and 4-H_2BPBu took the external binding mode. Whereas 2-H_2BPBu formed inclusion complex with CB[6] because there exist not only hydrophobic interaction but also ion-dipole interaction between pyridine nitrogen and carbonyl group of CB[6] due to the orientation of the pyridine nitrogen. The combination of the two acting force stabilizes the inclusion complex.

We have studied the interaction of the nine guests and CB[6], and it was found out that H_2BPH and H_2BPO are suitable to construct metalo-rotaxanes. The following work is in progress.

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