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A new type of pseudorotaxanes based on cucurbit[6]uril and bis-cyanopyridyl alkane compounds

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Using bis-cyanopyridyl alkane compounds as guests, three cucurbit[6]uril-based new pseudorotaxanes (**2a**, **2b** and **2c**) were synthesised and characterised. The crystal structures for **2a** and **2c** have been determined and discussed. In addition, formation constants and thermodynamic parameters in aqueous solution, as well as thermal decomposition behaviour in solid state, have been studied by ^{1}H NMR and TGA techniques, respectively.

Keywords: cucurbituril; bis-cyanopyridyl alkane; pseudorotaxane; X-ray diffraction; ^{1}H NMR

Introduction

Rotaxane and pseudorotaxanes, a type of very important supramolecular assemblies, prepared by threading linear guests into the cavities of cyclic hosts, have attracted much interest because of their topological importance and potential applications (*1*). Usually, pseudorotaxanes are used as intermediates to prepare rotaxanes, whose linear guests have enough bulky end groups as 'stoppers' to prevent unthreading. An important method to synthesise them is to combine two or more correlative organic molecules by means of self-organisation. Cucurbit[6]uril (CB[6]) is a hexameric macropolycyclic organic compound constructed by an acid-catalysed condensation reaction of glycoluril and formaldehyde. It has been found that a hydrophobic inner cavity of CB[6] can selectively recognise and bind linear chain-like diaminoalkane guests. The easy preparation, rigid structure and capability of holding guest molecules tightly make CB[6] a useful candidate for a ring part in the preparation of pseudorotaxane (*2*). In the previous works about rotaxanes and pseudorotaxanes based on CB[6], the 'stopper' of linear chain alkyl diamine guest often use pyridine (Py) ring as their end group (*2*, *3*). However, except paraquat derivatives and diquat, the other Py salts have been rarely reported. Therefore, it is still a challenge to create such supramolecular assembly with new type of alkyl diamine guest and to investigate their behaviour of molecular recognition in aqueous solution. Herein, we reported a type of long-chain alkyl diamine guests with cyanopyridine as end group, i.e. [4-CNpy-$(CH_2)_5$-4-CNPy]Br_2 **1a**, [4-CNpy-$(CH_2)_{10}$-4-CNPy]Br_2 **1b** and [3-CNpy-$(CH_2)_6$-3-CNPy]Br_2 **1c** (CNPy, cyanopyridine). They were assembled with CB[6] to obtain a kind of new CB[6]-based pseudorotaxanes **2a** (Br_2C5N4/CB[6]), **2b** (Br_2C10N4/CB[6]) and **2c** (Br_2C6N3/CB[6]) (Scheme 1), respectively. Crystal structures of **2a** and **2c** are determined. Influence of guest molecules and intermolecular weak interaction on the architectures of structures and packing style of pseudorotaxanes crystals are discussed. The complexation behaviours between CB[6] and these guests in aqueous solution and the thermal stabilities in solid state are also investigated.

Results and discussion

Crystal structures of pseudorotaxanes 2a and 2c

The ORTEP diagrams of **2a** and **2c** are shown in Figure 1(a), (b), respectively, and the bond lengths and angles are listed in Tables 1 and 2, respectively. Usually, CB[6] presumes a high D_{6h} symmetrical structure. However, in **2a** and **2c**, CB[6] is slightly distorted. The degree of distortion of CB[6] was judged by the difference of distance between the opposite carbon atoms of the CH groups in CB[6] (*4*), thus the degrees of distortion of CB[6] in **2a** are 0.29 Å, which is a little larger than that of **2c** (0.19 Å).

It can be seen from Figure 1 that the alkylene chains of **1a** (Br_2C5N4) and **1c** (Br_2C6N3) were threaded into the cavity of CB[6] to form the pseudorotaxanes, in which two CNPy groups exclude outside the cavity. In **2a** two pyridyl planes of alkandiamine guest have an angle 59.47°, while they are parallel in **2c**. The dihedral angle between the plane of six portal carbonyl O atoms of CB[6] and the plane of pyridyl group of alkylene chains are 65.58° for **2a** and 60.27° for **2c**, respectively. Probably, alkylene chain length and the position of CN group at Py of guests cause the above structural difference. Such effect was also found in the packing style of **2a** and **2c**. In 2D packing structure

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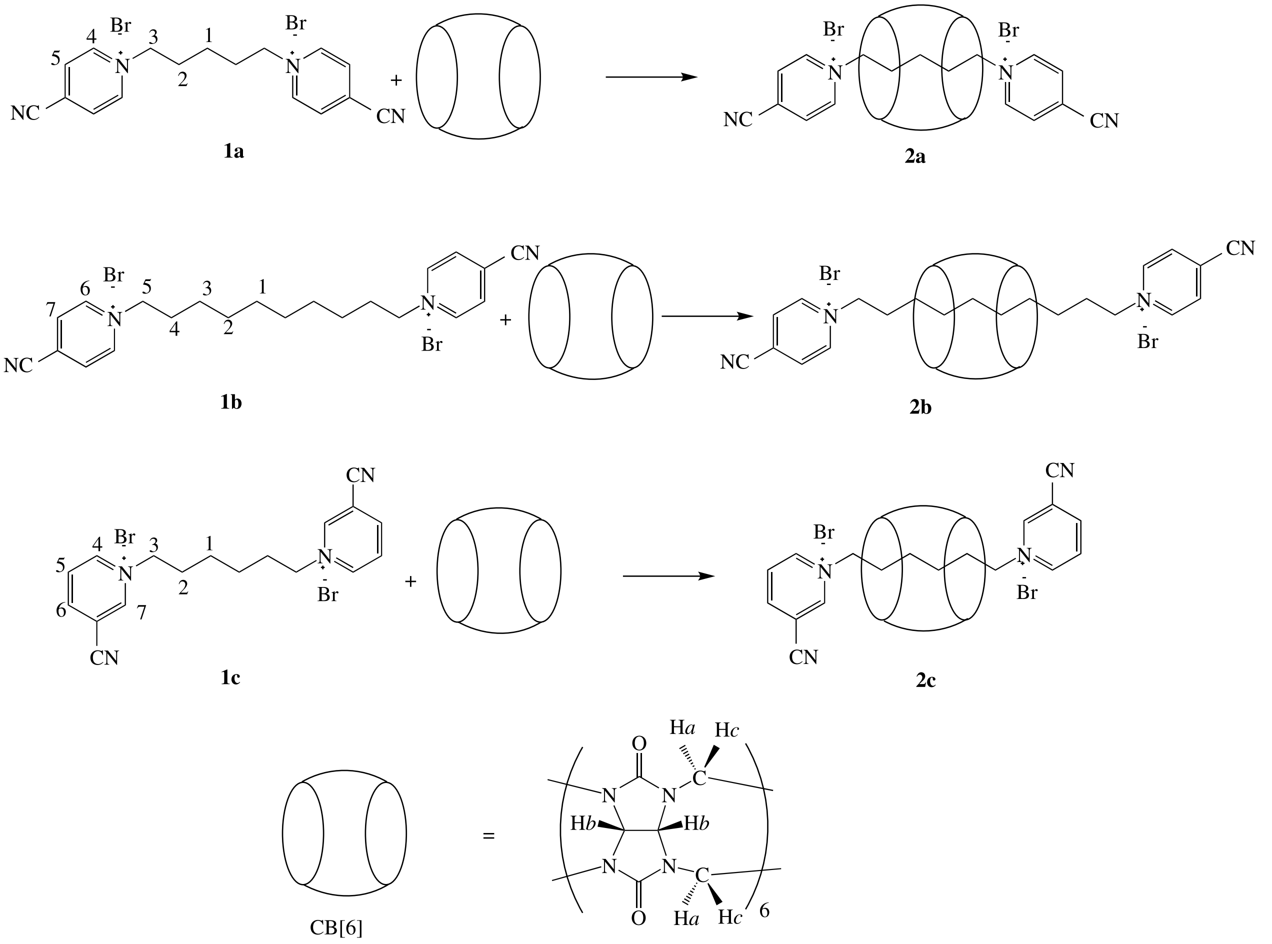

Scheme 1. Preparation of the pseudorotaxanes **2a**–**c**.

of **2a**, the parallel arrangement of CB[6] rings was in a way of regular cored hexagonal in the *ab* plane (see the Supporting Material). The space between the pseudorotaxane molecules is filled with water molecules, which is H-bonded to CB[6] carbonyl, the guest molecules, Br atoms and other water molecules (Figure 2(a)). While the crystal stacking of **2c** is more loose than that of **2a**, where the CB[6] rings array with angle 73.58° and no 2D H-bond net existed (Figure 2(b)).

There are many intra- and intermolecular interactions contributing to the self-assembling process. Measured interatomic distances of **2a** and **2c** are listed in Tables 3

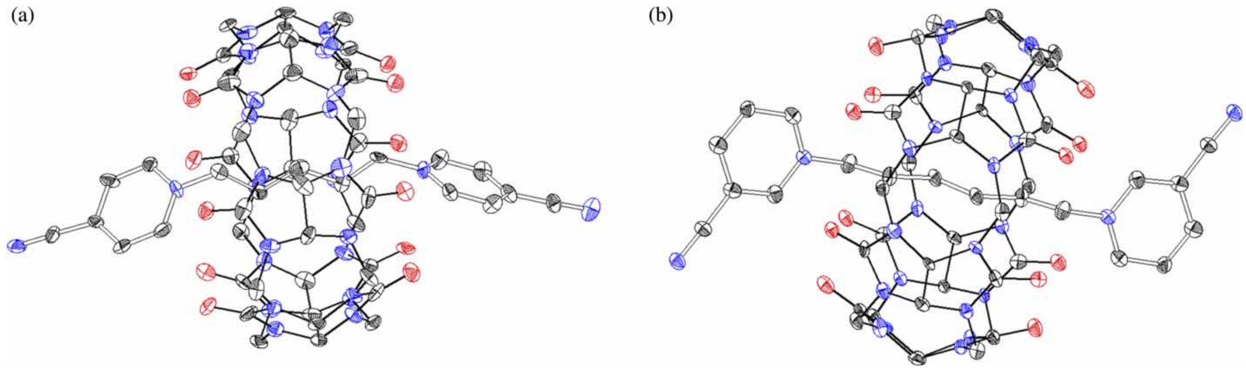

Figure 1. ORTEP diagram of pseudorotaxanes (a) **2a** and (b) **2c** (thermal ellipsoids are drawn at 30% probability level; hydrogen atoms, solvent molecules and disordered atoms are omitted; bonds of guest molecules are hollow for clarity).

Table 1. Bond lengths (Å) and angles (°) for **2a***.

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
O1—C1	1.272(5)	N9—C5	1.355(5)	N14—C23	1.390(6)
O5—C5	1.228(5)	N9—C17	1.434(4)	N14—C25	1.462(4)
N1—C1	1.273(5)	N10—C9	1.410(6)	C19—C20	1.390(5)
N1—C13	1.470(5)	N10—C5	1.321(5)	C20—C21	1.390(6)
N1—C9	1.448(5)	N10—C18	1.572(6)	C21—C24	1.412(5)
N2—C1	1.388(6)	C9—C10	1.560(6)	C21—C22	1.390(6)
N2—C14	1.416(5)			C22—C23	1.390(5)
N2—C10	1.408(5)	N13—C24	1.169(5)	C25—C26	1.493(5)
N9—C10	1.428(4)	N14—C19	1.390(5)	C26—C27	1.488(5)
Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C1—N1—C13	125.8(3)	O1—C1—N2	121.9(4)	C19—N14—C23	120.0(3)
C1—N1—C9	111.5(3)	N1—C1—N2	111.8(4)	C19—N14—C25	119.9(3)
C9—N1—C13	120.9(3)	O5—C5—N9	123.7(4)	C20—C21—C24	117.1(4)
C1—N2—C10	110.1(3)	N9—C5—N10	107.6(3)	C22—C21—C24	122.7(4)
C1—N2—C14	124.4(3)	O5—C5—N10	128.7(4)	C21—C22—C23	120.0(4)
C10—N2—C14	124.0(3)	N1—C9—N10	115.1(4)	N14—C23—C22	120.0(4)
C5—N9—C17	123.6(3)	N10—C9—C10	102.3(3)	N13—C24—C21	177.2(5)
C5—N9—C10	112.8(3)	N1—C9—C10	102.8(3)	N14—C25—C26	117.3(3)
C10—N9—C17	122.2(3)	N2—C10—C9	103.2(3)	C25—C26—C27	109.5(3)
C5—N10—C9	114.7(3)	N9—C10—C9	102.0(3)	C26—C27—C26b	116.3(4)
C5—N10—C18	118.9(3)	N2—C10—N9	115.0(3)	N14—C19—C20	120.0(4)
C9—N10—C18	125.8(3)			C19—C20—C21	120.0(4)
O1—C1—N1	126.2(4)	C23—N14—C25	120.1(3)	C20—C21—C22	120.0(3)

*Data for one glycoluril ring of CB[6] and the guest molecule.

and 4, respectively. In the structure of **2a** (Table 3; Figure 3(b)), the oxygen atoms (O2, O3, O4 and O5) of carbonyls in the portal of CB[6] are unusually close to C19 and C23, which belong to the Py ring of the guest, with the distances of about 0.05–0.39 Å less than the normal sum of van der Waals radius (3.12 Å). This indicates that there are C—H···O hydrogen bonds or π–π interactions between host and guest. Considering the angle's difference,

Table 2. Bond lengths (Å) and angles (°) for **2c***.

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
O1—C1	1.240(4)	N2—C13	1.388(5)	N14—C27	1.178(5)
O4—C4	1.261(5)	N7—C15a	1.411(5)	C19—C20	1.380(5)
N8—C16	1.466(4)	N7—C4	1.381(4)	C20—C27	1.387(5)
N8—C8	1.415(4)	N7—C7	1.417(4)	C20—C21	1.412(7)
N1—C1	1.346(5)	N8—C4	1.345(5)	C21—C22	1.338(6)
N1—C18a	1.457(5)	C7—C8	1.576(4)	C22—C23	1.415(5)
N1—C7	1.514(4)	N13—C24	1.510(5)	C24—C25	1.528(6)
N2—C1	1.370(4)	N13—C19	1.339(5)	C25—C26	1.529(5)
N2—C8	1.413(4)	N13—C23	1.275(5)	C26—C26b	1.557(6)
Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C1—N1—C18a	126.4(3)	N1—C1—N2	110.0(3)	C19—N13—C23	123.8(3)
C1—N1—C7	111.0(3)	O1—C1—N2	125.9(3)	C19—N13—C24	116.9(3)
C7—N1—C18a	120.4(3)	O4—C4—N8	126.7(3)	N13—C19—C20	119.8(4)
C1—N2—C8	112.5(3)	O4—C4—N7	124.0(4)	C19—C20—C27	120.5(4)
C1—N2—C13	121.5(3)	N7—C4—N8	109.3(3)	C19—C20—C21	118.3(4)
C8—N2—C13	125.0(2)	N1—C7—C8	100.7(2)	C21—C20—C27	121.0(4)
C4—N7—C7	110.6(3)	N1—C7—N7	113.3(2)	C20—C21—C22	117.5(4)
C4—N7—C15a	123.2(3)	N7—C7—C8	103.9(2)	C21—C22—C23	122.1(4)
C7—N7—C15a	124.5(3)	N8—C8—C7	102.4(2)	N13—C23—C22	117.8(4)
C8—N8—C16	121.1(3)	N2—C8—C7	104.9(2)	N13—C24—C25	111.8(3)
C4—N8—C8	113.1(3)	N2—C8—N8	118.6(2)	C24—C25—C26	109.4(3)
C4—N8—C16	125.2(3)			C25—C26—C26b	109.7(3)
O1—C1—N1	124.0(3)	C23—N13—C24	118.5(3)	N14—C27—C20	177.3(4)

*Data for one glycoluril ring of CB[6] and the guest molecule.

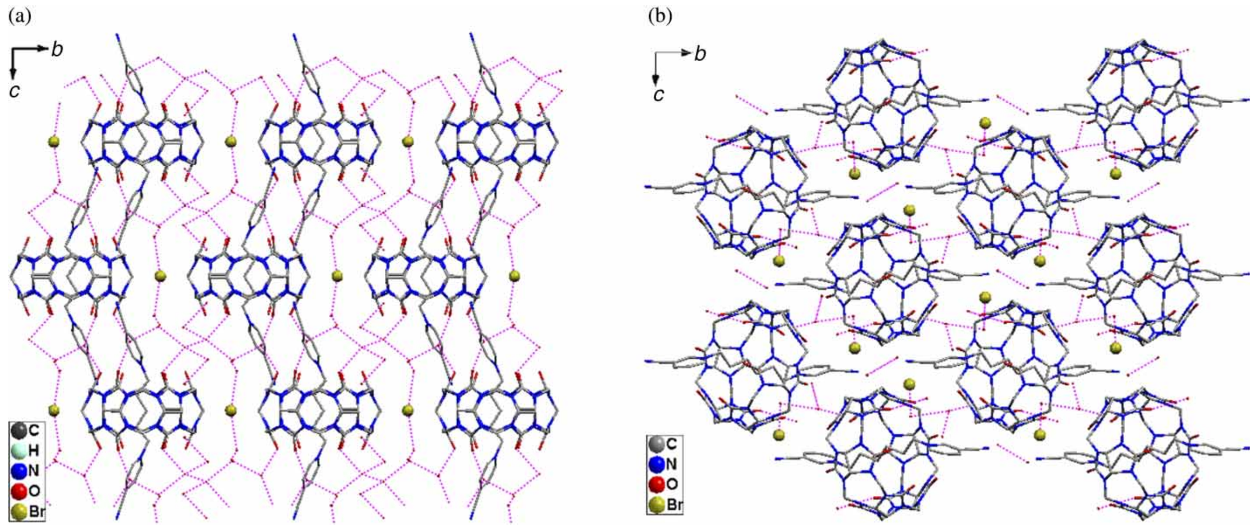

Figure 2. Packing style of (a) **2a** and (b) **2c** taken from the *bc* plane viewing along *a* axial. The purple lines indicate hydrogen bonding.

Table 3. Measured interatomic distances of **2a** (in Å).

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
O2—C23	2.855(11)	O5—C19	3.015(7)	N13—N3	3.154(6)
O3—C23	3.074(5)	N13—C11	3.171(7)	N13—N4	3.200(9)
O4—C19	2.727(7)	N13—C12	3.206(10)	C24—C2	3.456(9)
O1—C25	3.254(7)	N13—C2	3.090(6)	C24—C5	3.450(15)
O6—C25	3.090(4)				

O4···C19 and O3···C23 (almost vertical Py plane) are a kind of C—O···π interaction, while O2···C23 and O5···C19 (parallel to Py plane) are hydrogen bondings. In addition, distances between O1, O6 and C25 at alkyl chain of guest are also in the range of hydrogen bond (Table 3). Thus, the six carbonyl oxygens at portal of CB[6] all have non-bonding interactions with C atom at Py or alkylene part of the guest. It is noteworthy that in **2a,** the distances between N13 of cyano and the atoms of neighbouring glycoluril ring are in the range of 3.090(6)–3.206(10) Å, forming a novel penta-pyramid ferrocene-like structure, and the distances of cyano C24 and adjacent C2 and C5 of glycoluril are 3.456(9) and 3.450(15) Å, respectively (Table 3; Figure 2(b)). Therefore, there are π–π interactions between cyano and neighbouring glycoluril ring of CB[6].

Similarly, the above-mentioned inter- and intramolecular weak interactions were also found in **2c** (Figure 4), such as H-bond (O3···C23, O6···C19, O4···C24, O5···C24, etc.) or C—O···π interaction (O2···C23 and O6···C19) between carbonyl of CB[6] and alkyl chain or Py part of the guest, which play an important role in binding the guest molecule with CB[6] tightly. In the mean time, π–π interaction between cyano and the adjacent glycoluril ring of CB[6] also existed, since distances between N14 or C27 of cyano and C9 or C10 or C5 atoms of adjacent glycoluril ring of CB[6] are in the range of 3.180(2)–3.366(2) Å (Table 4).

NMR study

The ^{1}H NMR is one of the useful techniques to verify the formation of inclusion complex between host and guest

Table 4. Measured interatomic distances of **2c** (in Å).

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
O1—C19	2.904(6)	O6—C19	3.071(2)	N14—N3	3.273(3)
O2—C23	3.032(5)	N14—C9	3.180(2)	N14—N10	3.264(4)
O3—C23	3.11(00)	N14—C10	3.215(5)	C5—C27	3.366(2)
O4—C24	3.223(5)	N13—C2	3.090(6)	C24—C5	3.450(15)
O5—C24	3.286(1)				

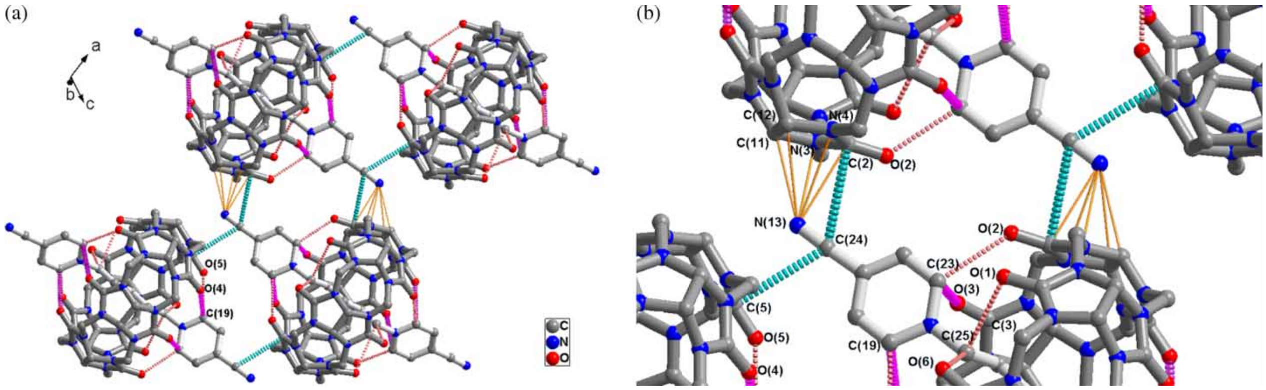

Figure 3. Weak interactions among pseudorotaxane **2a** molecules (C—H···O interactions are indicated by yellow dashed lines, other hydrogen bonding interactions are indicated by green dashed lines and π–π conjugation effects are indicated by orange thick dashed lines).

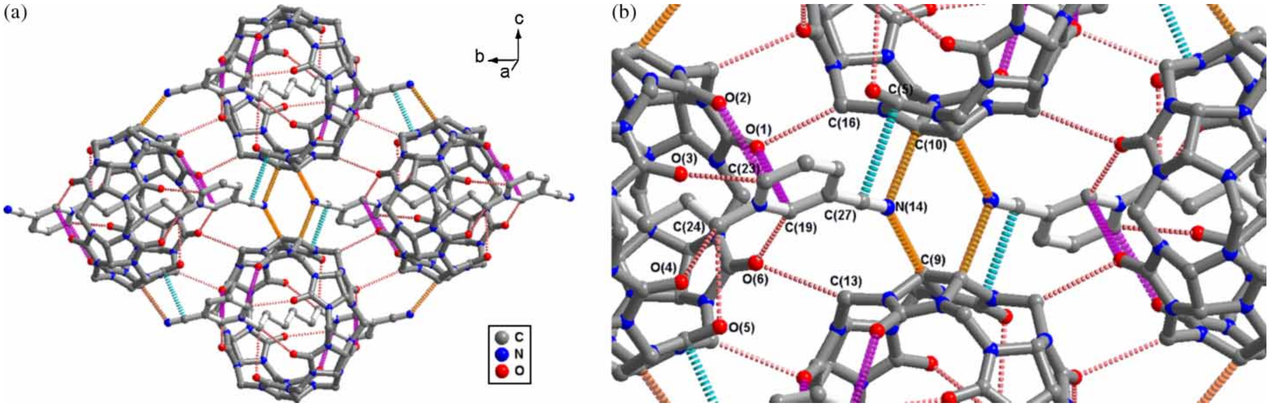

Figure 4. Weak interactions between molecules **2c** (C—H···O interactions are indicated by yellow and purple dashed lines, other hydrogen bonding interactions are indicated by green dashed lines and π–π conjugation effects are indicated by orange thick dashed lines).

molecules in aqueous solution. Table 5 gives all data of chemical shifts in aqueous solution for **2a–c**, respectively. It can be seen that chemical shifts for those protons in the alkyl chain of the guest molecule are significantly moved upfield after forming pseudorotaxanes. Among them the signals of central protons *H*1 and *H*2 are changed mostly because of the strong shielding effect from the ring of cucurbituril, while the chemical shifts for *H*4 of **2a** and **2c**, *H*6 of **2b** and *H*7 of **2c** in pyridyl group are moved downfield, since they are located in the deshielding region. However, only a little change is found in the chemical shifts for protons of CB[6] host (δ_{H_a}, δ_{H_b} and δ_{H_c}; Table 5), because they are all located on the outer surface of CB[6]. Figure 5 showed the NMR spectra changes for the formation of pseudorotaxane **2b**.

It is noted that the guest in **2a** and **2b** was similar and only different in methylene chain lengths. Although we have not got the single crystal of **2b**, through ^{1}H NMR study, we can obtain quantitative data of the formation constant (*5*) to examine the molecular recognition effect

Table 5. Chemical shifts (δ) of pseudorotaxanes (**2a–c**) and their difference (Δδ) with guest (or host) compounds (ppm, in D$_2$O).

		*H*1	*H*2	*H*3	*H*4	*H*5	*H*6	*H*7	H_a	H_b	H_c
2a	δ	0.68	1.24	4.12	9.59	8.45	–	–	4.37	5.60	5.72
	Δδ	− 0.84	− 0.90	− 0.62	0.42	− 0.05	–	–	0.17	0.12	0.12
2b	δ	0.60	0.90	0.92	1.78	4.75	9.41	8.40	4.24	5.45	5.74
	Δδ	− 0.65	− 0.40	− 0.38	− 0.23	− 0.08	0.26	− 0.08	0.04	− 0.03	0.14
2c	δ	0.49	1.11	4.49	9.56	8.80	8.14	9.98	4.23	5.48	5.66
	Δδ	− 0.83	− 0.82	− 0.09	0.52	− 0.02	− 0.01	0.59	0.03	0.00	0.06

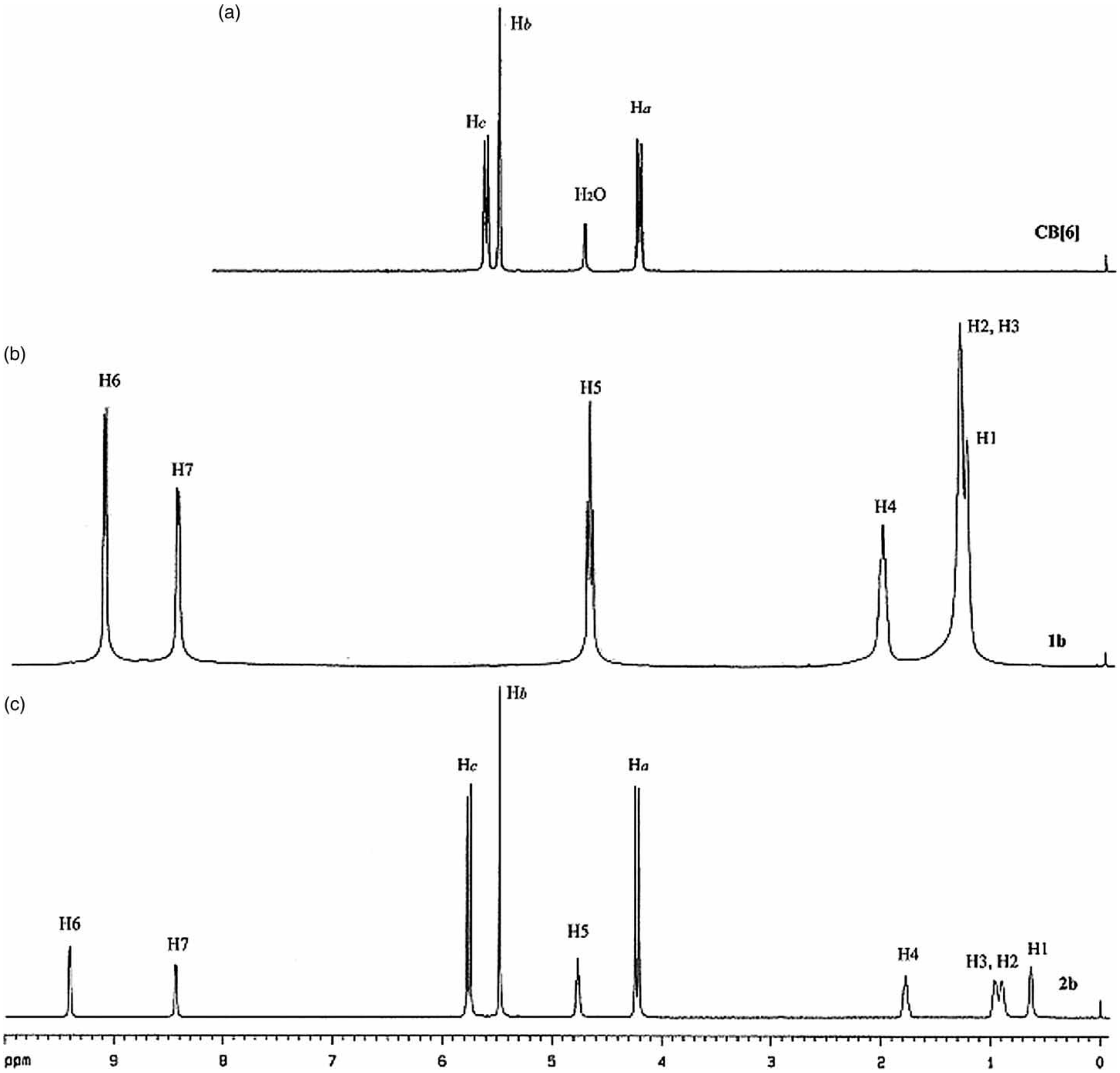

Figure 5. The ^{1}H NMR spectra of (a) CB[6], (b) **1b** and (c) **2b** in D_2O (500 MHz).

of different methylene chain lengths of guest in aqueous solution. Data for **2a** and **2b** at different temperatures are summarised in Table 6.

The results show that the formation constant for **2a** is larger than that of **2b** at the same temperature. It means that CB[6] cavity matches the C5 chain of **1a** better than the C10 chain of **1b**. Therefore, pseudorotaxane **2a** is more stable than **2b** in aqueous solution. The thermodynamic parameters derived from Van't Hoff plot showed that ΔH_{2a} ($8.18\,\mathrm{kJ\,mol^{-1}}$) $> \Delta H_{2b}$ ($2.38\,\mathrm{kJ\,mol^{-1}}$) > 0 and ΔS_{2a} ($150\,\mathrm{J\,mol^{-1}\,K^{-1}}$) $> \Delta S_{2b}$ ($119\,\mathrm{J\,mol^{-1}\,K^{-1}}$) > 0, which indicates that the formation of pseudorotaxane is an endothermic process, and increasing temperature is in favour of the pseudorotaxane formation.

TGA study

TGA experiments were performed to examine the thermal behaviour of pseudorotaxane in solid state (diagrams were given in the Supporting Material). The DTA temperatures for guest **1a** and **1c** are 247 and 252°C, while for **2a** and **2c** they increased to 434 and 418°C, respectively; both are

Table 6. Value of $\log K_f$ for the formation of pseudorotaxanes **2a** and **2b** at different temperatures.

T (K)	278	291	303	313
$\log K_f$ of **2a**	6.29	6.36	6.43	6.46
T (K)	283	293	303	313
$\log K_f$ of **2b**	5.80	5.81	5.83	5.84

close to the decomposition temperature of CB[6] (482°C). This result indicates that after the guest molecules thread into CB[6], their thermal stabilities are largely increased.

In conclusion, bis-cyanopyridinyl alkane compounds were used as guests to assemble with CB[6] forming a new kind of pseudorotaxanes. According to the crystal structure analysis and ^{1}H NMR studies, it has been found that the guest molecules with an alkyl chain of five or six methylene units are more likely to form crystallised pseudorotaxanes with CB[6], while the pseudorotaxane with longer chain guest is less stable in aqueous solution, and its single crystal is also difficult to obtain. It is noteworthy that intra- and intermolecular weak interactions, such as hydrogen bond, ion dipole and $\pi-\pi$ conjugation, play an important role in the crystallisation of the pseudorotaxanes. The position of cyano group at terminal Py and the length of the methylene chain of guest may affect the crystal structure and packing style of the pseudorotaxanes. TGA experiment shows that after forming pseudorotaxanes, the thermal stability of guest molecules has been increased.

Experimental section

The host molecule CB[6] was prepared from glycoluril and excess formaldehyde by the method of Freeman (*2a*). The three guest compounds **1a**, **1b** and **1c** were prepared from 4-cyanopyridine or 3-cyanopyridine and relevant dibromo-alkyl compounds in a molar ratio of 2:1 in *N*,*N*′-dimethylformamide by the method of Atalla (*6*). All compounds gave satisfactory spectral and analytical results.

Compound **1a**. Yield 43.4%; Anal. calcd (%) for $C_{17}H_{18}N_4Br_2$: C, 46.60; H, 4.14; N, 12.79; found: C, 46.19; H, 4.07; N, 12.62; ^{1}H NMR (500 MHz, D_2O): δ 9.17 (4H, s, H_4), 8.50 (4H, s, H_5), 4.74 (4H, t, H_3), 2.14 (4H, m, H_2) and 1.52 (2H, m, H_1) (signal of H_2O: 4.78); ESI-MS *m*/*z*: 356 (358) ($[M-Br^-]^+$).

Compound **1b**. Yield 31.5%; Anal. calcd (%) for $C_{22}H_{28}N_4Br_2$: C, 51.95; H, 5.51; N, 11.02; found: C, 51.71; H, 5.58; N, 11.02; ^{1}H NMR (500 MHz, D_2O): δ 9.15 (4H, s, H_6), 8.48 (4H, s, H_7), 4.83 (4H, t, H_5), 2.01 (4H, m, H_4), 1.30 (8H, m, H_3-H_2) and 1.25 (4H, m, H_1) (signal of H_2O: 4.80); ESI-MS *m*/*z*: 426 (428) ($[M-Br^-]^+$).

Compound **1c**. Yield 33.0%; Anal. calcd (%) for $C_{18}H_{20}N_4Br_2$: C, 47.81; H, 4.46; N, 12.39; found: C, 47.88; H, 4.60; N, 12.35; ^{1}H NMR (500 MHz, D_2O): δ 9.39 (2H, s, H_7), 9.04 (2H, s, H_4) 8.82 (2H, s, H_5), 8.15 (2H, s, H_6), 4.58 (4H, t, H_3), 1.93 (4H, m, H_2) and 1.32 (4H, m, H_1) (signal of H_2O: 4.70); ESI-MS *m*/*z*: 370 (372) ($[M-Br^-]^+$).

The pseudorotaxanes of **2a**–**c** were synthesised by self-assembly of the guest compounds with CB[6] in aqueous solution. General procedure for the preparation of pseudorotaxanes **2a**–**c**: 0.1 mmol of CB[6](s) was added to a solution of **1a**–**c**, respectively (0.1 mmol) in water (10 ml). The solution was stirred at 70°C for 3 h. There is no precipitate in the solution. Then the solution was allowed to stand at room temperature for several weeks. Colourless transparent square crystals were collected and were dried *in vacuo* at the presence of P_2O_5 prior to the ^{1}H NMR experiment and element analysis. Yield ~30%.

Compound **2a**. Anal. calcd (%) for $C_{53}H_{54}N_{28}O_{12}Br_2$: C, 44.36; H, 3.79; N, 27.33; found: C, 44.24; H, 3.82; N, 27.26; ^{1}H NMR (500 MHz, D_2O): δ 9.59 (4H, s, H_4), 8.45 (4H, s, H_5), 5.72 (12H, d, H_c), 5.60 (12H, s, H_b), 4.37 (12H, d, H_a), 4.12 (4H, t, H_3), 1.24 (4H, m, H_2) and 0.68 (2H, m, H_1) (signal of H_2O: 4.80); ESI-MS *m*/*z*: 637.5 ($[M-2Br^-]^{2+}$).

Compound **2b**. Anal. calcd (%) for $C_{58}H_{64}N_{28}O_{12}Br_2$: C, 46.28; H, 4.29; N, 26.06; found: C, 46.07; H, 4.32; N, 25.92; ^{1}H NMR (500 MHz, D_2O): δ 9.41 (4H, s, H_6), 8.40 (4H, s, H_7), 5.74 (12H, d, H_c), 5.45 (12H, s, H_b), 4.75 (4H, t, H_5), 4.24 (12H, d, H_a), 1.78 (4H, m, H_4), 0.92 (4H, m, H_3), 0.90 (4H, m, H_2) and 0.60 (4H, m, H_1) (signal of H_2O: 4.80); ESI-MS *m*/*z*: 672.5 ($[M-2Br^-]^{2+}$).

Compound **2c**. Anal. calcd (%) for $C_{54}H_{56}N_{28}O_{12}Br_2$: C, 44.76; H, 3.90; N, 27.07; found: C, 44.59; H, 3.92; N, 26.97; ^{1}H NMR (500 MHz, D_2O): δ 9.98 (2H, s, H_7), 9.56 (2H, s, H_4), 8.80 (2H, s, H_5), 8.14 (2H, s, H_6), 5.66 (12H, d, H_c), 5.48 (12H, s, H_b), 4.49 (4H, t, H_3), 4.23 (12H, d, H_a), 1.11 (4H, m, H_2) and 0.49 (4H, m, H_1) (signal of H_2O: 4.70); ESI-MS *m*/*z*: 644.5 ($[M-2Br^-]^{2+}$).

Table 7. Crystallographic data for crystals **2a** and **2c**.

Crystal	**2a**	**2c**
Chemical formula	$C_{53}H_{54}N_{28}O_{12}Br_2\cdot 12H_2O$	$C_{54}H_{56}N_{28}O_{12}Br_2\cdot 6H_2O$
Formula weight	1651.25	1557.16
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2(1)/*c*
a (Å)	25.669(5)	14.174(2)
b (Å)	14.329(3)	20.234(3)
c (Å)	24.572(4)	14.845(2)
α (°)	90.00	90.00
β (°)	117.913(9)	114.635(3)
γ (°)	90.00	90.00
V (Å^3)	7986(3)	3870.0(10)
Z	4	2
λ (Å)	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.373	1.336
T (K)	293	293
μ (Mo Kα) (mm^{-1})	1.101	1.126
Unique reflns	7847	7557
Observed reflns	5610	6002
Parameters	501	487
R_{int}	0.0349	0.0425
$R\ [I > 2\sigma(I)]$[a]	0.0633	0.0582
$wR\ [I > 2\sigma(I)]$[b]	0.1685	0.1594

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2) + (0.09P)^2 + 1.95P]$. $P = (F_o{}^2 + 2F_c{}^2)/3$.

Single-square X-ray quality crystals of **2a** and **2c** were obtained by slow evaporation of the aqueous solution of them.

Crystallography

The intensity data for crystals were collected on a Bruker Smart Apex CCD area detector diffractometer at 293 K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with SHELXTL (Bruker, 2000). All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. The hydrogen atoms were generated geometrically. Details of the crystal parameters, data collection and refinements for crystals **2a** and **2c** are summarised in Table 7. Detailed crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication nos CCDC-267529 (**2a**) and CCDC-267528 (**2c**).

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