

Materials and Measurements

All starting materials were purchased from commercial sources and used without further purification. ^1H NMR spectra were recorded on a Varian Mercury VX-300 spectrometer. The IR spectra (in KBr pellets) were recorded on a Shimadzu FT-IR 157 spectrophotometer. ESI-MS measurement was performed on Thermo Finnigan LCQ advantage at room temperature. Thermogravimetric studies were carried out with a NETZSCH STA 449C at a heating rate of 5 K/min under nitrogen. X-ray powder diffractograms were measured (Cu KR) using a D/max-rA model Philips Analytical X-ray diffractometer.

1. Synthesis

CB[6] was prepared according to the literature.[1]

1,1'-(hexane-1,6-diyl)dipyridinium-4-carboxylate(HBPC): A solution of 20mmol of 1,6-dibromohexane dissolved in 20ml of acetonitrile was added dropwise, over a period of 1h, to a refluxing solution of 50mmol of the isonicotinate in 25ml of acetonitrile. After gentle refluxing for 3-4h, acetonitrile was removed in vacuo yielding a dark yellow solid, which was the product **1**(1,1'-(hexane-1,6-diyl)bis(4-ethoxycarbonylpyridinium bromide). Product **1** washed with acetone and dried under vacuum with yield of 85%[2]. The solution of product **1**(10mmol) was dissolved in 15% HCl (10ml) and refluxed for 5 h, then the solvent was removed in vacuum. The residue was solved in minimum amount of water and treated with 1, 2-epoxypropane until pH=7. After the solvent was removed under vacuum, the colorless product BPHC was obtained from recrystallization of the residue in $\text{H}_2\text{O}/\text{EtOH}$ and dried under vacuum with yield of 68%[3].

Pseudorotaxane: A mixture of **CB[6]** (1.20 g, 1.20 mmol) and 1,1'-(hexane-1,6-diyl)-dipyridinium-4-carboxylate (0.328 g, 1.0 mmol) in water (30 ml) was heated at 80 °C for 8 h.

After stirring at room temperature over night, the residue of CB[6] was filtered off. The mixture heated at 120 °C in the reactor for 2 days, then slowly cooled to the room temperature and produced X-ray quality yellow crystals of pseudorotaxane with yield of 83%.

2. Characterization

CB[6]: ^1H NMR (300 MHz, 0.2 mol/L NaCl / D_2O) δ 4.269 (Hb, d, 12H, $J=14.7$ Hz), 5.560 (Hc, s, 12H), 5.624 (Ha, d, 12H, $J=16.2$ Hz); IR: (KBr) ν/cm^{-1} 1734 (C=O stretching frequency of CB[6], characteristic peak of CB[6]), 3003, 2937 (C-H stretching frequency of bridged CH_2); ESI-MS: $m/z = 998.1$ [$\text{CB}[6] + \text{H}$] $^+$.

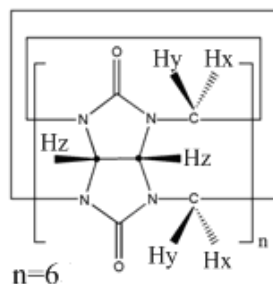


Figure1. The structure of CB[6].

Product 1: ^1H NMR (300 MHz, D_2O) δ 1.258-1. (H1 and H7, m, 10H), 1.891 (H2, m, 4H), 4.318 (H6, q, 4H $J_1=7.2$ Hz, $J_2=7.5$ Hz, $J_3=6.3$ Hz), 4.503 (H3, t, 4H $J_1=7.5$ Hz, $J_2=7.2$ Hz), 8.359 (H5, s, 4H $J=5.7$ Hz), 8.874 (H4, s, 4H $J=6.6$ Hz); IR: (KBr) ν/cm^{-1} 3118, 3051, 3113 (=C-H of pyridine), 2936 (CH_2 of alkyl chain), 1724 (carboxylate, C=O), 1636 (C=N), 1573, 1458, 1369 (skeleton stretching frequency of pyridine), 1295 (C-O-C), 1114 (C-N $^+$); ESI-MS: $m/z=497.2$ [$\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_4\text{Br}^+ + \text{MeOH}$].

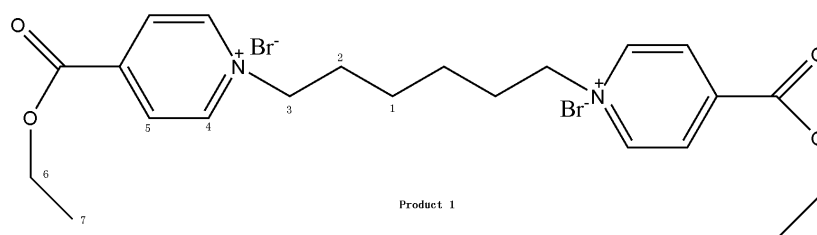


Figure 2. The structure of product **1**

HBPC: $^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 1.275 (H1, m, 4H), 1.893 (H2, m, 4H), 4.518 (H3, t, 4H, $J_1=7.5$ Hz, $J_2=7.2$ Hz), 4.862 (H4, d, 4H $J=6.6$ Hz) 8.176 (H5, s, 4H $J=6.6$ Hz); IR: (KBr) ν/cm^{-1} 3042 (=C-H of pyridine), 2931, 2962 (CH_2 of alkyl chain), 1644 (C=N, C=O, broad peak), 1513, 1450, 1395, 1346, 1254 (skeleton stretching frequency of pyridine), 1460 ([O-C-O] $^-$), 1159(C-N $^+$); ESI-MS: $m/z=329.0$ [$\text{Mr}+\text{H}$] $^+$.

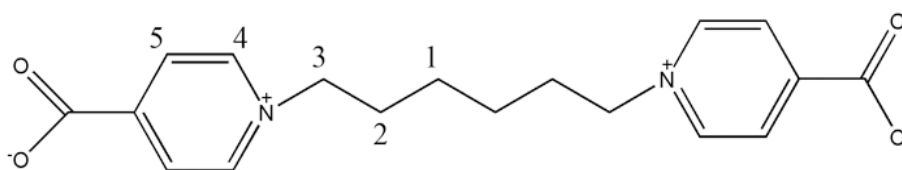


Figure 3. The structure of BPHC

Pseudorotaxane: $^1\text{H NMR}$ (300 MHz, 0.2 mol/L NaCl/ D_2O) δ 0.440(H1, m, 4H), 1.065 (H2, m, 4H), 4.381 (H3, t, 4H, $J_1=9.3$ Hz, $J_2=7.5$ Hz), 9.428 (H4, s, 4H, $J=6.6\text{Hz}$), 8.215 (H5, s, 4H, $J=6.6\text{Hz}$), 4.184 (Hb, d, 12H, $J=15.6\text{Hz}$), 5.397 (Hc, s, 12H), 5.662 (Ha, d, 12H, $J=16.2\text{Hz}$); IR (KBr) ν/cm^{-1} :3459 (the O-H stretching frequency of water cluster), 1739 (C=O of CB[6]), 1620 (C=N stretching frequency of pyridine), 1470 ([O-C-O] $^-$), 1423, 1374, 1326, 1235 (skeleton stretching frequency of pyridine), 1189(C-N $^+$); ESI-MS: $m/z=663.7$ [$\text{Mr}+2\text{H}$] $^{2+}/2$.

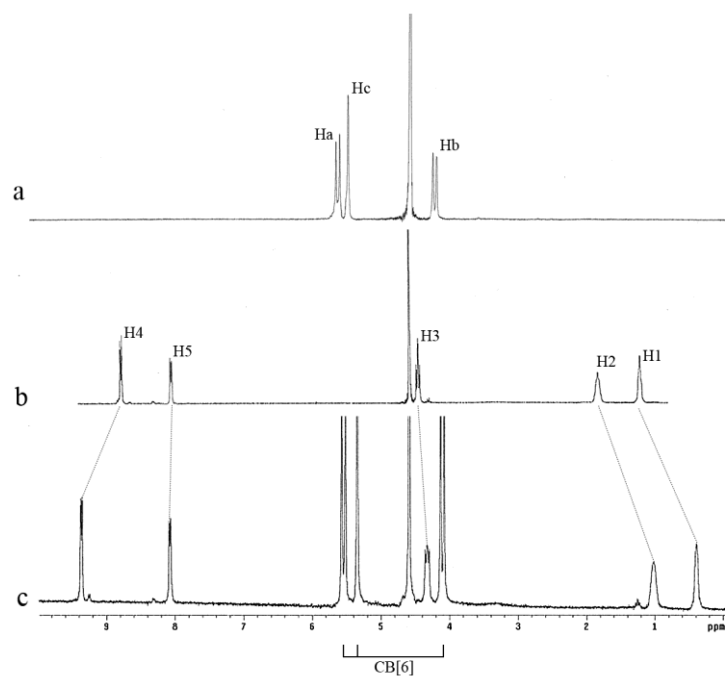


Figure 4. ¹H NMR spectra in 0.2 mol/L NaCl/D₂O. a: the host molecular CB[6]. b: the guest molecule HBPC. c: the pseudorotaxane.

IR of pseudorotaxane:

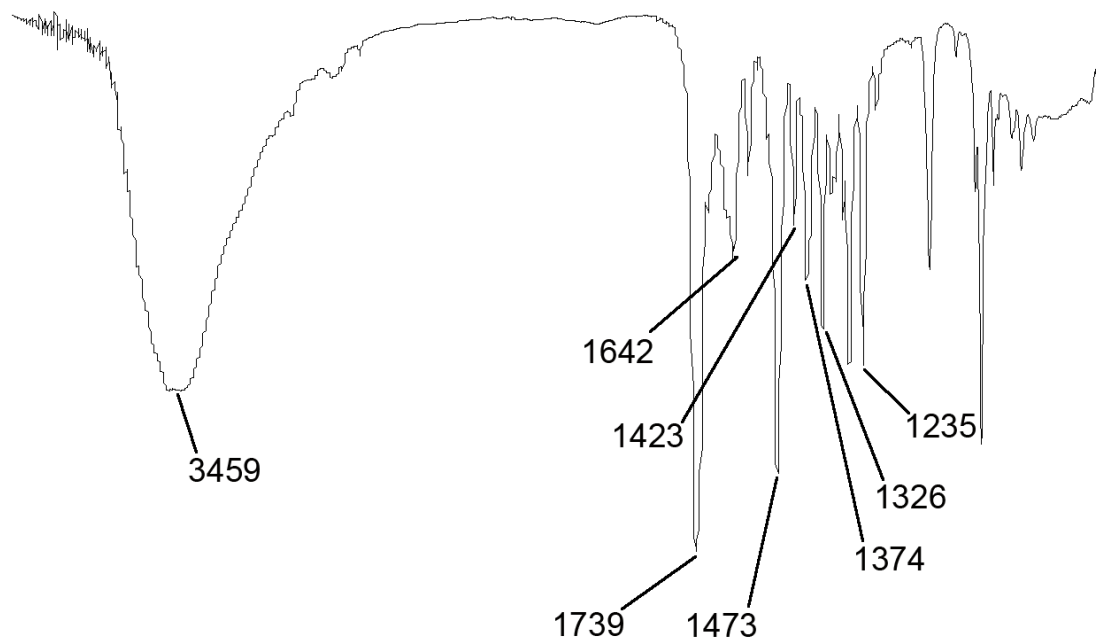


Figure 5. IR of pseudorotaxane.

The TGA curve of Pseudorotaxane:

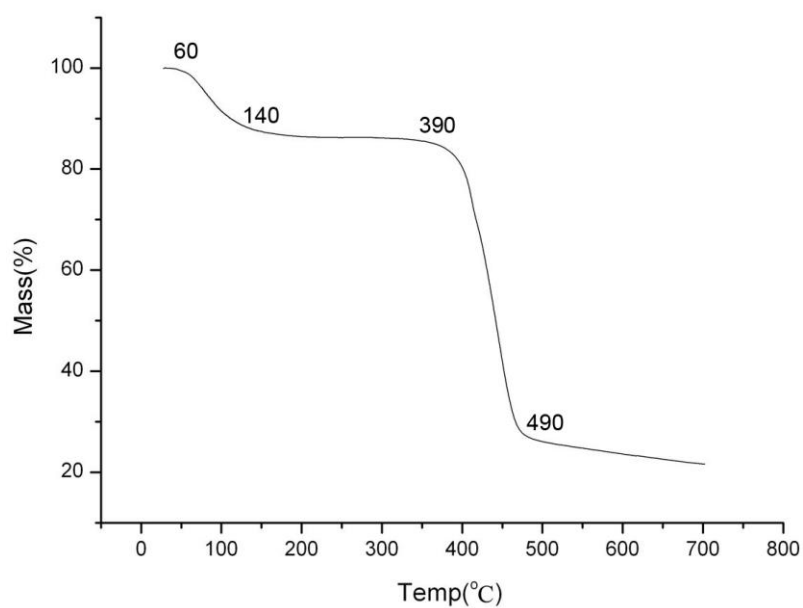


Figure 6. The TGA curve of pseudorotaxane in N₂ atmosphere.

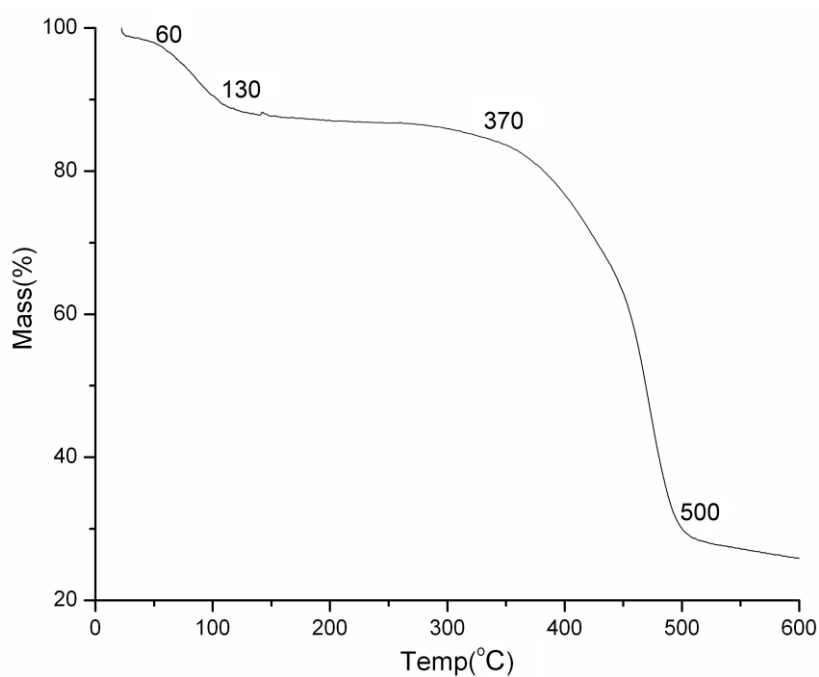


Figure 7. The TGA curve of rehydrated pseudorotaxane in N₂ atmosphere.

The TGA curve of the dehydrated sample placed in a humidity container for 3 days show that the mass loss is similar to the pseudorotaxane. A mass loss is observed at 60 to 130°C corresponding to the loss of twelve water molecules (14.0% calcd, 13.9% obsd). Heating from 130°C to 390°C, the platform implies the high stability of the host of pseudorotaxane. Heating

beyond 370°C, a more gradual mass loss occurs to 500 °C corresponding to the loss of pseudorotaxane.

X-Ray Crystallography

The crystal structure of pseudorotaxane formed by CB[6] and BPHB was determined using a Bruker SMART APEX II CCD diffractometer with Mo KR radiation (λ) 0.71073 Å at 200(2) K in the range of $2.44^\circ < \theta < 27.58^\circ$. The structure was solved by direct method (SHELXL-97) and refined against F^2 in anisotropic approximation (SHELXL-97). More details of the crystal data are shown in Table 1.

Table 1. The crystal data of pseudorotaxane.

Empirical formula	$C_{36}H_{36}N_{24}O_{12} + C_{18}H_{20}N_2O_4 + 12H_2O$
Formula weight	1541.44
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 30.4423(12)$ Å $\alpha = 90^\circ$. $b = 12.3940(4)$ Å $\beta = 128.822(1)^\circ$. $c = 21.4045(8)$ Å $\gamma = 90^\circ$.
Volume	$6292.0(4)$ Å ³
Z	4
Density (calculated)	1.627 Mg/m ³
Absorption coefficient	0.333 mm ⁻¹
$F(000)$	3240
Crystal size	0.16 x 0.10 x 0.10 mm ³
Theta range for data collection	2.44 to 27.58°.
Index ranges	$-32 \leq h \leq 36$, $-14 \leq k \leq 14$, $-25 \leq l \leq 25$
Reflections collected	22274
Independent reflections	5515 [$R(\text{int}) = 0.0550$]
Completeness to $\theta = 27.00^\circ$	99.7 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9868 and 0.9790
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5515 / 0 / 487
Goodness-of-fit on F^2	1.042

Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0635$, $wR_2 = 0.1831$
R indices (all data)	$R_1 = 0.0789$, $wR_2 = 0.1949$
Largest diff. peak and hole	0.630 and -0.965 e.Å ⁻³

Table 2. Hydrogen bonds of intramolecular for pseudorotaxane [Å and °]^a

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C21--H21...O4	0.9500	2.2200	3.127(3)	160.00
C22--H22...O3#1	0.9500	2.1600	3.082(4)	162.00
C24--H24A...O6	0.9900	2.4300	3.297(3)	146.00
C24--H24B...O1#1	0.9900	2.4600	3.362(5)	151.00

^aSymmetry transformations used to generate equivalent atoms: #1 1/2-x,3/2-y,2-z

Table 3. Hydrogen bonds of (COO)₂(H₂O)₁₀ anion water clusters [Å and °]^a

D-H...A	d (D-H)	d (H...A)	d (D...A)	< (DHA)
O9--H9B...O10	0.8200	2.1700	2.844(15)	139.00
O9--H9B...O12	0.8200	2.5700	3.204(7)	135.00
O10--H10A...O6	0.8200	1.9800	2.775(14)	162.00
O10--H10B...O11#6	0.8200	2.0400	2.443(16)	109.00
O11--H11C...O7	0.8200	2.0200	2.797(6)	158.00
O11--H11D...O13	0.8200	2.0630	2.841(7)	158.00
O12--H12C...O10	0.8200	2.1600	2.644(17)	118.00
O12--H12C...O13	0.8200	2.1800	2.929(6)	152.00
O12--H12D...O1#1	0.8200	2.1600	2.974(5)	170.00
O13--H13B...O11#6	0.8200	2.5400	2.843(11)	104.00

^aSymmetry transformations used to generate equivalent atoms: #1 1/2-x,3/2-y,2-z, #6 x,1+y,z

Table 4. Hydrogen bonds of (H₂O)₂ water clusters and C (1)-H (1)...O (9W), C (5)-H (5A)...O (7 acetate), C (6)-H (6B)...O (10W), C (7)-H (7)...O (11W), C (11)-H (11A)...O (14W), C (17)-H (17A)...O (12W), C (17)-H (17B)...O (14W) [Å and °]^a

D-H...A	d (D-H)	d (H...A)	d (D...A)	< (DHA)
O(14 W)--H(14AW)...O2	0.8200	2.5100	3.011(3)	121.00
O(14W)--H(14BW)...O(14W)	0.8200	2.6320	3.056(7)	113.00
C (1)-H (1)...O (9W) #8	1.0000	2.5500	3.306(6)	132.00
C (5)-H (5A)...O (7 acetate) #8	0.9900	2.5200	3.149(5)	122.00
C (6)-H (6B)...O (10W) #9	0.9900	2.3900	3.355(16)	165.00
C (7)-H (7)...O (11W) #10	1.0000	2.3300	3.304(11)	164.00

C (11)-H (11A)...O (14W) #6	0.9900	2.4400	3.395(4)	162.00
C (17)-H (17A)...O (12W) #11	0.9900	2.3200	3.270(6)	161.00
C (17)-H (17B)...O (14W) #1	0.9900	2.5800	3.548(4)	164.00

^aSymmetry transformations used to generate equivalent atoms: #1 $1/2-x, 3/2-y, 2-z$, #6 $x, 1+y, z$, #8 $x, 1-y, 1/2+z$,

#9 $-x, y, 3/2-z$, #10 $-x, 1+y, 3/2-z$, #11 $1/2-x, 1/2+y, 3/2-z$.

Reference

1. (a) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540-541. (b) A. I. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094-8100. (c) F. J. Huo, C. X. Yin and P. Yang, *J. Incl. Phenom. Macrocycl. Chem.* 2006, **56**, 193-196. (d) Y. W. Yang, Y. Chen and Y. Liu, *Inorg. Chem.* 2006, **45**, 3014-3022.
2. F. H. Huang, C. Slebodnick, E. J. Mahan and H. W. Gibson, *Tetrahedron*, 2007, **63**, 2875-2881.
3. Y. Z. Zhao, S. L. Li, L. H. Weng, M. J. Zhang and Y. F. Xiao, *Chin. J. Inorg. Chem.* 2001, **17**, 691-698.