

## Highly Cesium Selective Calix[6]arene Receptors: Synthesis, Structure and Cesium Binding Properties of Calix[6]arene Biscrown

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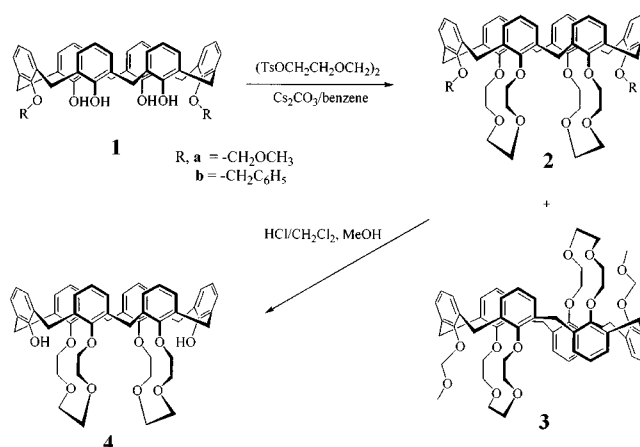
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Cesium-137 is a relatively abundant nuclear fission product and constitutes a major source of heat in nuclear wastes<sup>1,2</sup> along with strontium-90. Much effort has been made to the development of improved processes<sup>3,4</sup> for the removal of cesium-137 from nuclear wastes. For the efficient removal of cesium, several crown ethers have been prepared and their binding properties were investigated. For the development of a selective ligand for cesium ion, calix[6]arenes have been utilized as a receptor. When six ester groups were introduced at the lower rim, a high binding property for cesium ion was reported.<sup>5</sup> But selectivity over potassium and rubidium is not quite high. The lack of selectivity has been attributed into the flexibility of the parent calix[6]arene moieties. The most effective approach to make them immobile is to build a bridge at the lower. Since Gutsche's lower rim-bridged calix[6]arene<sup>6</sup> in 1993, several lower rim-multibridged calix[6]arenes and their ion binding properties were reported.<sup>7-9</sup> Recently, calix[6]arene bis-crown-4 was synthesized and it showed a high selectivity for cesium.<sup>10</sup> For the purpose of developing cesium selective ion receptors, we prepared three new calix[6]arene biscrowns and investigated their structural and metal binding properties.

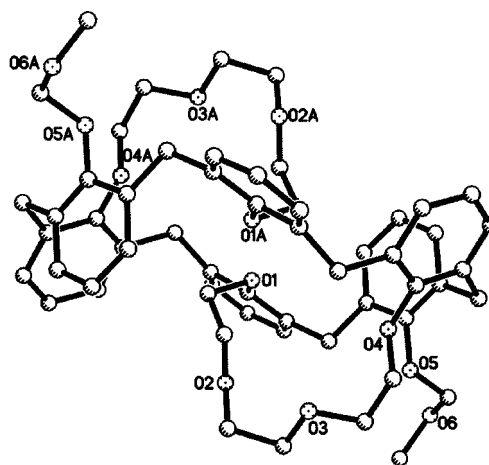
In order to increase ion binding strength, two methoxymethyl substituents(-CH<sub>2</sub>OCH<sub>3</sub>) at the 1,4-position of calix[4]arene are introduced by treating calix[6]arene with methoxymethyl chloride in the presence of (CH<sub>3</sub>)<sub>3</sub>SiOK.<sup>11</sup> Benzyl derivative was also prepared for comparison. A mixture of calix[6]arene biscrown **2a** and **3a** were synthesized when **1a** was treated with tri-ethylene glycol ditosylate in the presence of Cs<sub>2</sub>CO<sub>3</sub> in benzene as shown in Figure 1. The total amount of two conformers was consistently about 35% of the reaction mixture and the two isomers were isolated by column chromatography. Two conformers can be identified from <sup>1</sup>H NMR spectra.<sup>8</sup> The cone conformation was clearly demonstrated by presence of two AB quartets for the ArCH<sub>2</sub>Ar protons (2 : 1 ratio) in the <sup>1</sup>H NMR spectrum at δ 4.6, 3.6 and 3.4. On the other hand, the methylene protons of 1,2,3-alternate conformation appeared as an AB quartet for *syn*-oriented aromatic rings and a singlet for *anti*-oriented rings. But only cone conformer **2b** was obtained when benzyl derivative **1b** treated under the same condition, indicating that substituents R could play an important role for the formation of 1,2,3-alternate conformer. Free hydroxy calix[6]arene biscrown **4** is obtained when R groups are



**Figure 1.** Synthesis of calix[6]arene-bis-crown-4.

removed by treating **2a** and **3a** with HCl in CH<sub>2</sub>Cl<sub>2</sub> and MeOH, indicating that the fixed 1,2,3-alternate and cone conformers could exist only when the large R groups were present to prevent the rotation.

Figure 2 showed a X-ray structure of 1,2,3-alternate calix[6]arene biscrown **3a**. Two crown units as well as two methoxymethyl groups stayed at the opposite side of calixarene circle, indicating that the inversion point existed



**Figure 2.** Crystal structure of **3a**. Solvent molecules (four molecules of benzene) and hydrogen atoms have been omitted for clarity.

**Table 1.** Crystal data and structure refinement for **3a**

Empirical formula	C60H66C16O12
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.2536(13) Å $\alpha$ = 102.215(3)° b = 13.0158(16) Å $\beta$ = 92.621(3)° c = 23.641(3) Å $\gamma$ = 104.494(3)°
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Goodness-of-fit on F <sup>2</sup>	0.911
Final R indices [I > 2σ(I)]	R1 = 0.0880, wR2 = 0.1873
R indices (all data)	R1 = 0.3317, wR2 = 0.2860
Largest diff. peak and hole	0.343 and -0.354 e.Å <sup>-3</sup>

**Table 2.** Percentage extraction (%) of alkali picrates from water into CH<sub>2</sub>Cl<sub>2</sub> at 25°C<sup>a</sup>

	%E				
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
<b>2a</b>	0	0	0	3	57
<b>2b</b>	0	0	0	4	33
<b>4</b>	0	0	0	3	11

<sup>a</sup>1 × 10<sup>-4</sup> M receptor solution in CH<sub>2</sub>Cl<sub>2</sub> was shaken (1 hr) with 1 × 10<sup>-4</sup> M picrate salt solution in H<sub>2</sub>O and the percentage extraction was measured from the resulting absorbance at 355 nm.

at the center of calixarene framework. It is believed that this is the first example of the X-ray structure of 1,2,3-conformer of calix[6]arene so far. Table 1 showed the detail data for X-ray structure **3a**.

The alkali metal binding properties were investigated from two phases extraction experiment where aqueous solutions of the picrate salts are shaken with methylene chloride solutions of ligands. The amount of metal ion was determined from picrate absorption in the UV spectrum. Table 2 showed the percent extraction of metal picrate salts by **2a**, **2b**, **3a** and **4**. 1,2,3-Alternate conformer **3a** showed no metal extraction at all. The cone conformer **2a** extracted 57% of the cesium picrate from aqueous solution into the methylene chloride solution of the host at a 1 : 1 ratio, but only 3% of the rubidium and almost none of the others such as Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> salts. Extraction percentage of cesium salt decreased to 33% for **2b**, indicating that the large benzyl groups could inhibit the cesium binding from two crown units. Further decrease of cesium extraction to 11% was observed when free hydroxy groups are present with host **4**, indicating that free OH groups could compete the alkali metal binding for ligand as expected. ISE experiments are in progress using PVC membrane electrodes.

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- Some representative spectroscopic data for **2a**, **2b**, **3a** and **4** are as follows. **2a**: mp = 238-241 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.59-7.57 (d of d, 4H, ArH, *J* = 6.69 Hz), 7.13-7.09 (d of t, 8H, ArH), 6.31 (t, 2H, ArH, *J* = 7.68 Hz), 6.05 (d, 4H, ArH, *J* = 7.68 Hz), 5.14 (s, 4H, -OCH<sub>2</sub>-), 4.61 (d, 2H, ArCH<sub>2</sub>Ar, *J* = 13.23 Hz), 4.60 (d, 4H, ArCH<sub>2</sub>Ar, *J* = 16.29 Hz), 4.03 (t, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-, *J* = 9.09 Hz), 3.83-3.73 (m, 12H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.71 (s, 6H, -OCH<sub>3</sub>), 3.62 (d, 4H, ArCH<sub>2</sub>Ar, *J* = 16.29 Hz), 3.57-3.39 (m, 6H, ArCH<sub>2</sub>Ar and -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.13 (d, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-, *J* = 10.74 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.67, 153.49, 135.13, 134.25, 133.31, 130.77, 129.56, 126.14, 123.87, 123.35 and 99.07 (Ar), 73.59, 71.51, 70.75 and 57.25 (-OCH<sub>2</sub>-), 31.41 and 27.17 (ArCH<sub>2</sub>Ar). **3a**: mp = 250-252 °C <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.21-7.18 (d of d, 4H, ArH, *J* = 7.29 Hz), 7.16-7.13 (d of d, 4H, ArH, *J* = 7.62 Hz), 7.02 (t, 4H, ArH, *J* = 7.44 Hz), 6.69 (t, 2H, ArH, *J* = 7.47 Hz), 6.52 (d, 4H, ArH, *J* = 6.62 Hz), 5.04 (s, 4H, -OCH<sub>2</sub>-), 4.56 (d, 4H, ArCH<sub>2</sub>Ar, *J* = 15.3 Hz, *syn*), 4.01 (s, 4H, ArCH<sub>2</sub>Ar, *anti*), 3.65 (s, 6H, -OCH<sub>3</sub>), 3.58-3.54 (m, 6H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.49-3.41 (m, 10H, ArCH<sub>2</sub>Ar and -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.23 (m, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.11 (m, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.02 (m, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 156.42, 152.92, 134.65, 133.96, 133.62, 130.23, 129.74, 126.60, 124.00, 123.86, 123.47 and 99.82 (Ar), 72.72, 70.85, 70.06 and 57.67 (-OCH<sub>2</sub>-), 31.77 and 31.55 (ArCH<sub>2</sub>Ar). **2b**: mp = 234-236 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.63 (d, 4H, ArH, *J* = 6.72 Hz), 7.55 (t, 4H, ArH, *J* = 4.62 Hz), 7.43-7.34 (m, 6H, ArH), 7.09-7.07 (d of t, 8H, ArH), 6.33 (t, 2H, ArH, *J* = 7.65 Hz), 6.09 (d, 4H, ArH, *J* = 7.65 Hz), 5.05 (s, 4H, -OCH<sub>2</sub>-, benzyl), 4.69 (d, 4H, ArCH<sub>2</sub>Ar, *J* = 16.2 Hz), 4.60 (d, 2H, ArCH<sub>2</sub>Ar, *J* = 13.32 Hz), 3.99 (t, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-, *J* = 8.73 Hz), 3.83-3.69 (m, 12H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.54-3.38 (m, 10H, ArCH<sub>2</sub>Ar and -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.18 (d, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-, *J* = 10.74 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.68, 154.00, 138.16, 135.15, 134.37, 133.28, 130.70, 129.53, 128.40, 127.67, 126.17, 123.81 and 123.21 (Ar), 73.59, 73.49, 71.47 and 70.68 (-OCH<sub>2</sub>-), 30.87 and 27.14 (ArCH<sub>2</sub>Ar). **4**: mp = 190 °C dec.; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.72 (s, 2H, OH), 7.03 (br. s, 4H, ArH), 6.86 (br. s, 4H, ArH), 6.77 (t, 2H, ArH, *J* = 7.44 Hz), 6.59 (br. s, 8H, ArH), 4.10 (m, 14H, ArCH<sub>2</sub>Ar and -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.80 (m, 11H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.56 (m, 11H, ArCH<sub>2</sub>Ar and -OCH<sub>2</sub>CH<sub>2</sub>O-). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 154.36, 152.35, 133.79, 133.27, 129.08, 128.68, 128.39, 128.19, 124.57 and 120.07 (Ar), 72.85, 70.27 and 70.12 (-OCH<sub>2</sub>-), 31.67 and 29.61 (ArCH<sub>2</sub>Ar).