

Phenylene Bridged Calix[6]arenes: Cesium Selective Ionophores

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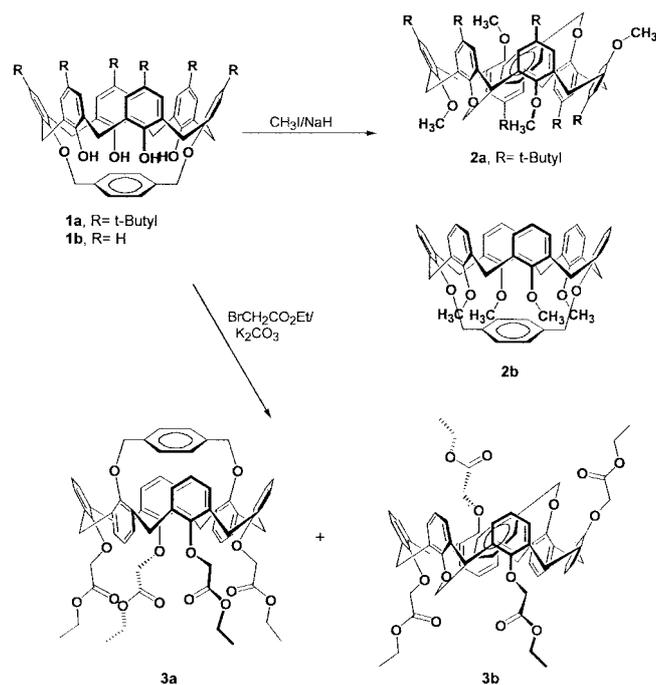
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Cesium-137 constitutes a major source of heat in nuclear wastes¹ along with strontium-90. Much effort has been made to the development of improved processes^{2,3} for the removal of cesium-137 from nuclear wastes. For the efficient removal of cesium, several crown ethers and calixcrowns⁴⁻⁸ have been prepared and their binding properties were investigated. Recently, Shinkai⁹ reported that the triply bridged calix[6]arene also showed a high selectivity for cesium. Although the triply bridged calix[6]arene and calixcrowns showed a high selectivity for cesium over other alkali metals, the Shinkais compound required a difficult separation procedure for the trimethylation and the relatively long steps were needed for the synthesis of calixcrowns. For the development of a simple method for cesium selective ionophore we utilized two step reaction from calix[6]arene and obtained four phenylene bridge derivatives and investigated their alkali metal binding properties by UV, ¹H NMR and solvent extraction.

Results and Discussion

The bridging reaction was performed by the reaction of calix[6]arene with 1,4-bis(bromomethyl)benzene in the pre-



Scheme 1

sence of $(\text{CH}_3)_3\text{SiOK}$ as reported^{10,11} and the alkyl derivatives of phenylene bridge calix[6]arene **2a**, **2b**, **3a** and **3b** were obtained by treating **1** with alkylating reagents as shown in Scheme 1. Gutsche reported that **2a** exist as a self-anchored rotaxane^{10,12} based on the ¹H NMR spectrum analysis. But the ¹H NMR spectrum of **2b** which has no *t*-butyl group at the *para* position showed several broad peaks, indicating that **2b** could exist as a slow moving conformational isomer. When **1b** treated with ethyl bromoacetate in the presence of K_2CO_3 , two conformational isomers **3a** and **3b** (2 : 1 ratio, overall 75% yield) were separated. The ¹H NMR spectrum of **3a** in Figure 1 shows a singlet at δ 5.94 for the four phenylene protons,¹³ which indicate that phenylene protons in **3a** is located at the shielding area. We do not have a clear evidence for the exact conformation of **3a**, but one possibility could be up-down conformation as shown in Scheme 1 rather than cone. On the other hand the ¹H NMR spectrum of **3b** shows a typical self-anchored rotaxane characteristics.¹⁰

It is well known¹⁴ that calixarene ester derivatives show the metal selectivity dependent on the calixarene ring size: that is, calix[4]arene derivatives show very high Na^+ selectivity, on the other hand calix[6]arene derivatives show broad alkali metal selectivity with K^+ , Rb^+ , and Cs^+ . This is

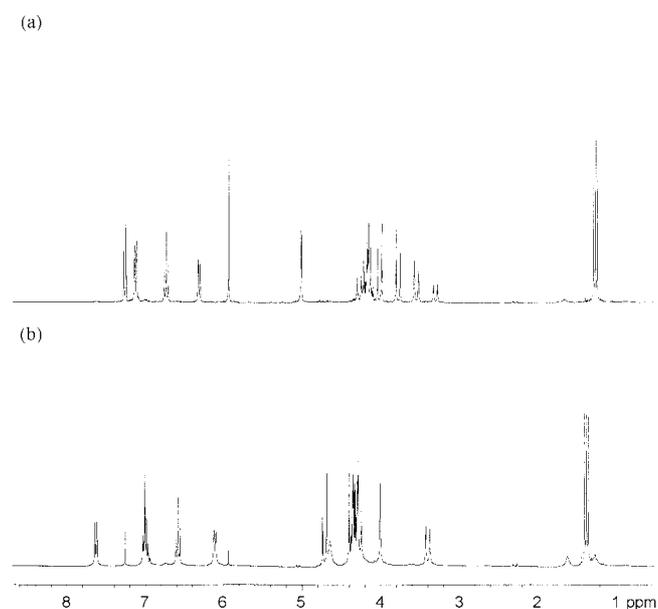
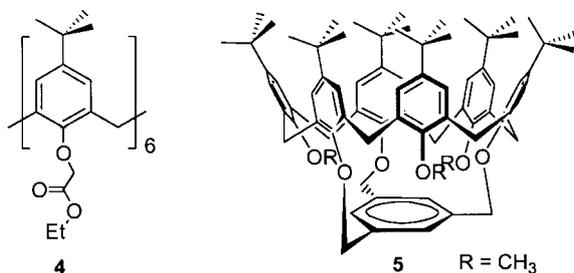


Figure 1. (a) ¹H NMR spectrum of **3a** in CDCl_3 . (b) ¹H NMR spectrum of **3b** in CDCl_3 .

related to the rigidity of the calix[6]arene ring framework, which inevitably features the induced-fit-type metal complexation.



Solvent extraction of alkali metal cations with picrate ion into dichloromethane was performed and the extraction value are compared with those of conformationally mobile calix[6]arene ester **4**¹¹ and Shinkai's triply bridged calix[6]arene **5**.⁹ Table 1 indicates that **2b** shows extremely high selectivity toward Cs⁺ over sodium and potassium ions, but selectivity falls down with rubidium ion. It extracts Cs⁺ 80%, but 8% Rb⁺ and shows no affinity with K⁺ and Na⁺ comparable to Shinkai's triply bridged calix[6]arene **5**. On the other hand **2a**, **3a** and **3b** exist as a conformation which might not be good for the metal binding. That is why metal extraction values of **2a**, **3a** and **3b** are poor. They extract Cs⁺ at about 5-34%. Due to the presence of four ester groups, **3a** and **3b** were expected a high extraction value with cesium, but conformation does not allow to bind to cesium easily.

Inoue found¹⁵ that the ion pair tightness in solution could be evaluated by the bathochromic shift of the absorption band of the picrate anion extracted into organic phase with a macrocyclic ligand from aqueous metal picrate solution. We

Table 1. Percent extraction of alkali picrates into dichloromethane at 25 °C

ligand	2a	2b	3a	3b	4 ^a	5 ^b
Li ⁺	0	0	0	0	11	0
Na ⁺	7	0	0	0	50	0
K ⁺	13	1	0	0	86	5
Rb ⁺	13	8	6	5	89	8
Cs ⁺	34	80	5	6	100	77

^aCited from Ref. 14. ^bCited from Ref. 9.

Table 2. Bathochromic shifts (λ_{\max}) of alkali picrates extracted into the dichloromethane phase^a

ionophore	λ (nm)			
	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
18-crown-6 ^b	367	369	368	369
[2,2,1]cryptand ^b	375	375	375	375
[2,2,2]cryptand ^b	375	375	375	376
5	377	378	378	378
2b	— ^c	— ^c	— ^c	377

^a25 °C. ^bCited from Ref. 15. ^cUnable to measure due to weak extraction.

investigated the absorption spectra of alkali picrate in the dichloromethane phase after two-phase solvent extraction and found a large bathochromic shift of picrate anion in the presence of **2b**. As shown in Table 2, the λ_{\max} of cesium picrate shift 354 nm to 377 nm in the presence of **2b**. The 23nm bathochromic shift is comparable with that of **5** and larger than those induced by 15 nm of 18-crown-6, 21 nm of [2,2,1]cryptand, and 22 nm of [2,2,2] cryptand, indicating that the metal picrate ion pair is highly separated. Cesium ion could be surrounded by a bridge phenylene and calixarene aromatic rings, but picrate is located outside the calixarene. Therefore, the picrate anion of the **2b** · M⁺Pic⁻ complex could behave as a highly solvent separated anion which was observed by the large bathochromic shift.

In conclusion, we prepared four phenylene bridge calix[6]arenes by the simple two step reaction from calix[6]arene and **2b** showed an exceptional selectivity for cesium ion over other alkali metals. Ester derivatives of **3a** and **3b** were expected to give a strong bind with cesium, but obviously conformation did not allow to bind metal ion properly. For the development of alkali metal sensor, ISE experiments are in progress.

Experimental Section

5,11,17,23,29,35 - Hexa-tert-butyl-37,38,40,41-tetrahydroxy-39-42-(p-xylylenedioxy) calix[6]arene 1a was prepared by the previously known procedure.¹¹

37,38,40,41-Tetrahydroxy-39-42-(p-xylylenedioxy) calix[6]arene 1b was prepared by the previously known procedure.¹¹

5,11,17,23,29,35 - Hexa-tert-butyl-37,38,40,41-tetramethoxy-39-42-(p-xylylenedioxy) calix[6]arene 2a was prepared by the previously known procedure.¹¹

37,38,40,41-Tetramethoxy-39,42-(p-xylylenedioxy)calix[6]arene 2b. To a solution of 2.81 g (3.8 mmol) of **1b** and 1.12 g (46 mmol) of NaH (60% dispersion in oil) in 300 mL of THF, 2.92 mL (31 mmol) of (CH₃)₂SO₄ was added and stirred for 48 h at room temperature in a nitrogen atmosphere. Aqueous ammonia solution (6 mL) was added and neutralized with 2N HCl and extracted with ether (100 mL × 2). The solvents were removed and the residue was triturated with methanol. Filtration and air dry yield 2.2 g (72%) of **2b** in a white powder. mp > 296 °C dec; ¹H NMR (CDCl₃) δ 7.26-6.33 (br m, 22H, ArH), 4.77-3.32 (br m, 28H, ArCH₂Ar, -OCH₃, ArCH₂O-). ¹³C NMR (CDCl₃) δ 155.84, 134.58 (broad peak), 133.76, 132.01 (broad peak), 130.44, 128.31, 127, 44, 123, 60 (broad peak) and 123.03 (Ar), 71.00 (broad peak) and 60.31 (-OCH₂- and OCH₃), 31.47 and 27.70 (two broad peaks, ArCH₂Ar).

37,38,40,41-Tetrakis(ethoxycarbonylmethoxy)-39,42-(p-xylylenedioxy)calix[6] arene 3a, 3b. To a solution of 1 g (1.3 mmol) of **1b** and 10 g of potassium carbonate in 250 mL of acetone, 1.2 mL (10 mmol) of ethylbromoacetate was added and refluxed for 24 h at in a nitrogen atmosphere. The solvent was removed and the residue was triturated with methanol. Column chromatography (eluent; chloroform :

hexane : ethyl acetate = 6 : 5 : 0.5) yielded 0.70 g (50%) of **3a** and 0.35 g (25%) of **3b**.

Compound 3a; mp 179-182 °C; $^1\text{H NMR}$ (CDCl_3) δ 7.27 (d, 4H, ArH, $J = 7.2$ Hz), 7.13 (d, 6H, ArH, $J = 7.2$ Hz), 6.74 (t, 4H, ArH, $J = 7.8$ Hz), 6.32 (d, 4H, ArH, $J = 7.2$ Hz), 5.94 (s, 4H, ArH from phenylene unit), 5.02 (s, 4H, $\text{ArCH}_2\text{O}-$), 4.30-3.28 (m, 28H, ArCH_2Ar , $-\text{OCH}_2\text{CO}_2-$, $-\text{CO}_2\text{CH}_2-$), 1.26 (t, 12H, $J = 7.2$ Hz); $^{13}\text{C NMR}$ (CDCl_3) δ 169.08, 156.28, 154.2, 135.68, 134.57, 133.78, 131.26, 130.14, 128.27, 127.67, 123.94, 123.40, 70.74, 69.76, 60.73, 31.82, 26.99, 14.11.

Compound 3b; mp 240-242 °C; $^1\text{H NMR}$ (CDCl_3) δ 7.63 (d, 4H, ArH, $J = 10.7$ Hz), 7.04-6.94 (m, 6H, ArH), 6.58 (t, 4H, ArH, $J = 7.5$ Hz), 6.11 (d, 4H, ArH, $J = 7.5$ Hz), 4.74-3.37 (m, 36H, ArCH_2Ar , $-\text{OCH}_2\text{CO}_2-$, $-\text{CO}_2\text{CH}_2-$, ArOCH_2 , ArH), 1.37 (t, 12H, $J = 7.2$ Hz); $^{13}\text{C NMR}$ (CDCl_3) δ 169.24, 153.98, 152.47, 134.37, 133.56, 133.32, 133.06, 131.33, 128.66, 127.53, 124.34, 122.27, 72.74, 70.38, 61.22, 31.23, 29.10, 14.22.

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