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Highly Selective Li^+ Ion Transport by Bridged Calix[4]arenes

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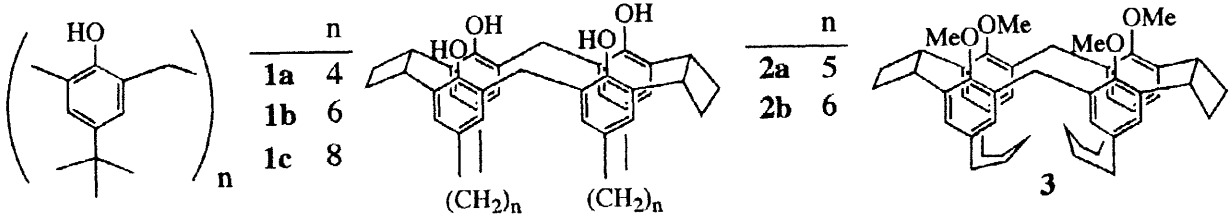
Abstract: Bridged Calix[4]arenes can transport Li^+ ion considerably and the selectivity for Li^+ over Na^+ is about 15 and 30, respectively, in the weak basic and neutral solution. © 1998 Elsevier Science Ltd. All rights reserved.

Many artificial ionophores have been known to exhibit the interaction with the medium size ions such as Na^+ and K^+ ions, which are very important cations in biological systems, as well as Mg^{2+} and Ca^{2+} ones.[1] For the industrial applications some selective ionophores for the small ion like Li^+ or large ones like Rb^+ and Cs^+ have been developed.[2] They are often disclosed in the families of crown ethers,[3] spherands,[4] and calixarenes,[5,6] and exhibit the unique ion selectivity.

The derivatives of calix[n]arenes **1** (n=4 - 8) having several functional groups on hydroxy groups or at *para* position have been known to bind many ions and organic molecules.[7] Although parent calixarenes **1** do not play an important role as ionophores (see Chart 1),[8,9] they do transport alkali metal ions through the liquid membrane phase only in a strong basic solution and give the selective transport of Cs^+ ion over other alkali metal ions due to the lower level of hydration energy. The order of Cs^+ flux of **1** for transport was **1c**>**1b**>**1a** and the Cs^+ selectivity of **1** for transport was **1a**>**1b**>**1c**. The cation transport rate below pH 12, however, is too small to be used, because of the weak ion-dipole interaction between hydroxy groups of **1** and metal ions. The higher cation affinity of **1** compared with phenol derivatives is considered to be a result of the cooperative effect of adjacent oxygen donor atoms in binding the large alkali metal ions.

We previously reported the marked Li^+ ion template effect when bridged calix[4]arene **2a** was formed by the base-catalyzed condensation of two metacyclophanes with paraformaldehyde.[10a] Moreover, it was found that the distance and hydrogen bonding interaction between its four hydroxy groups can be modified.[10] Since these findings suggest us some probabilities of bridged calix[4]arenes as a selective carrier whose abilities can be tunable, we were prompted to investigate their transport of alkali metal ions. We report here the first observation of highly selective Li^+ ion transport by bridged **2**.

Chart 1



	n
1a	4
1b	6
1c	8

	n
2a	5
2b	6

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Table I. Cation transport rate by calixarenes **1** and **2** at 25 °C.[a)]

Source phase		Transport rate (x 10^{-5}mol/l•h)			
M^+	pH	**1a**	**1b**	**2a**	**2b**
Li^+	12.0	5.09	5.03	14.7	4.18
	10.0	1.71	3.92	12.0	4.50
	7.3	0.98	0.89	9.30	4.40
Na^+	14.0	5.40	10.5	10.2	4.89
	12.0	2.53	1.76	3.68	3.60
	10.0	0.69	0.48	0.73	0.65
	7.0	0.30	0.27	0.35	0.32
K^+	14.0	10.8	23.7	23.2	24.1
	12.0	2.00	13.2	4.39	4.39
	9.9	<0.05	<0.05	<0.05	<0.05
Rb^+	14.0	39.3	46.3	38.4	33.0
	12.0	5.20	17.7	8.50	7.65
	10.0	<0.05	<0.05	<0.05	<0.05
Cs^+	14.0	58.9	89.2	55.8	56.7
	12.0	14.0	27.0	12.3	11.5
	10.5	0.08	0.09	0.12	0.20
	6.9	<0.05	<0.05	<0.05	~0.0

a) Source phase: $[M^+]$=1.0 M, anion=NO_3^-/OH^-. Membrane phase: 1.0 x 10^{-3} M of a carrier in the $CHCl_3$ solution. Receiving phase: distilled water. Stirring rate: 100 ± 10 rpm. Experimental error: < ± 10%.

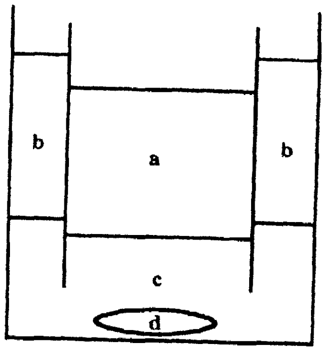

Figure 1 Liquid membrane cell: (a) source phase: 10 ml. (b) receiving phase: 10 ml. (c) membrane phase: 30 ml. (d) magnetic stirring bar.

The alkali metal ion selectivity of bridged **2** was examined in the transport experiments in $CHCl_3$ solution due to their low solubility in CH_2Cl_2 or CH_2Cl_2/CCl_4 (see Figure 1).[8] Calix[4]- and [6]arenes **1** were also used as the reference compounds. The results are summarized in Table I.

In the strong basic solution at pH 14, all calixarenes **1** and **2** selectively transported Cs^+ ion in the series of Na^+ to Cs^+. This result demonstrates again that the lower dehydration energy of Cs^+ cation governs the ion selectivity of all calixarenes under this condition.[8a] Calix[6]arene **1b** recorded the higher transport rate (ca. 1.5 times) than calix[4]arene **1a** and bridged **2** for Rb^+ and Cs^+ ions. This result implies that the cooperative effect of donor moieties, which depends on the number of oxygen atoms, works more than the molecular structure.[8a] The order of Cs^+ ion transport is **1b**>**1a**≈**2a**≈**2b**. The ion selectivity of **2a** for large ions (Rb^+ and Cs^+) resembles **1a**, while that for medium size ions (Na^+ and K^+) resembles **1b**. And also, the ion selectivity of **2b** for alkali metal ions except for K^+ resembles that of **1a**. In fact, calixarenes **1b** and **2** gave almost the same rate for K^+ ion. Their rates are considerably larger (2.2 times) than that for **1a**. Moreover, **1b** and **2a** showed around the same rate for Na^+ ion. Again their rates are considerably larger (ca. 2 times) than those for **1a** and **2b**. Accordingly, the molecular structure of calixarenes considerably contributed the transport for medium size ions like Na^+ and K^+. Hence, the characteristics of bridged calix[4]arenes **2** for ion selectivity come from the preorganization of hydroxy groups by the bridging, which is adjustable by changing the methylene chain length.[10b,e] Note that the hydrogen bonding interaction of four hydroxy groups can be tunable by changing the distance between them, using the bridged calixarene structure.

In the basic solution at pH 12, calix[6]arene **1b** recorded the higher transport rate than other calixarenes for Cs$^+$ among alkali metal ions.[8a] Although the transport rates at this pH region is obviously reduced more than those at pH 14 due to the weak ion-ion interaction, the ion selectivity of **1b** from K$^+$ to Cs$^+$ ion became high compared with that of **1a** and **2**. The order of Cs$^+$ ion transport was **1b**>**1a**≈**2a**≈**2b**. Bridged **2** can play as a carrier to have the nature of both calix[4]- and [6]arenes from Na$^+$ to Rb$^+$ ions and showed the smaller ion selectivity for Li$^+$ and Na$^+$. Especially, **2a** had the higher Li$^+$ ion selectivity than others. It means that **2a** strongly interacts with Li$^+$ ion even at the high pH region. The order of Li$^+$ ion transport was **2a**>**1a**≈**1b**≈**2b**. The transport behavior of bridged calix[4]arenes **2** as carriers is considerably different from that of calixarenes **1**, which reflects the structural rigidity.

In the weak basic solution at pH 10, all calixarenes gave no significant ion transport of Na$^+$ to Cs$^+$ owing to the dependence on the ion-dipole interaction.[8a] Bridged **2** can transport Li$^+$ ion faster than **1**. The Li$^+$ ion transport rates of **2** were almost as same as those at pH 12. The selectivity of **2a** for Li$^+$ over Na$^+$ is about 15. Especially, **2a** showed the rate higher by 3 - 10 times than **1**. The order of Li$^+$ ion transport was **2a**>**2b**>**1b**>**1a**. Hence, calix[4]- and [6]arenes transport only the lower level of Li$^+$ ion due to the size incomplementary in the basic solution. Accordingly, the ion selectivity of calixarenes at pH 10 is greatly governed by the difference of their molecular structures. It is stressed that bridged calixarenes **2** can act as an excellent Li$^+$ carrier at this pH region.

In the neutral solution at pH 7, bridged calix[4]arenes **2** still transported Li$^+$ ion, although **1** hardly transported any alkali metal ions. The transport rates of Li$^+$ ion only a little decreased from those of pH 12 to 7. In particular, **2a** transported Li$^+$ ion about 10 times faster than **1**. The order of Li$^+$ ion transport was **2a**>**2b**>**1a**≈**1b**. These results show that the hydroxy groups of **2** are well arranged to take the ion-dipole interaction with Li$^+$ ion.[11] As shown in Figure 2, **2a** can exclusively transport Li$^+$ ion below pH 12. The Li$^+$ ion selectivity of **2a** over other alkali metal ions is more than 30. Accordingly, **2a** can be said to be the best Li$^+$ carrier among all calixarenes examined.

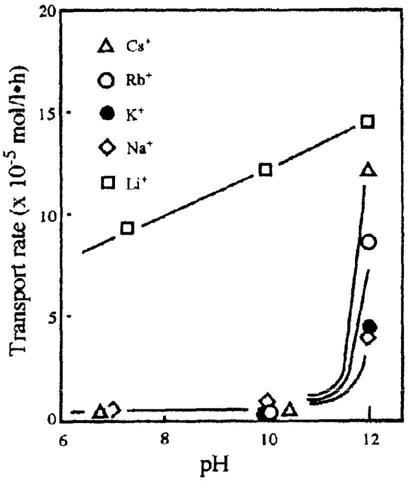

Figure 2 A plot of transport rate of calixarene **2a** as a function of source phase pH.

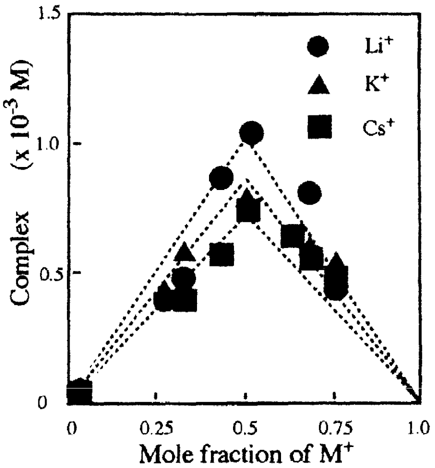

Figure 3 Job's plots of complex between **3** (3.0 mmol/l) and alkali metal thiocyanates in $CDCl_3/CD_3OD$ (7/3).

Since bridged calix[4]arenes **2** had the high Li^+ ion selectivity in the neutral solution, we studied the nature of their bindings to clarify the ion selectivity. Ether analog **3** was used in this experiment to avoid any effect of proton dissociation and to evaluate the detailed ion-dipole interaction between oxygen moieties and alkali metal ions in the neutral media.[10b] The stoichiometry for the complexation was examined by Job's plots between **3** and alkali metal thiocyanates in $CDCl_3/CD_3OD$ (7/3) (see Figure 3). When the mole fraction of **3** was 0.5, the complex concentration reached to maximum for all alkali metal ions. This result clearly demonstrates that **3** forms a 1:1 complex with alkali metal ions. Furthermore, the binding constant for Li^+ ion with **3** recorded the largest value among the alkali metal thiocyanates in $CDCl_3/CD_3OD$ (8/2). The order is Li^+ (Ka=674) > Na^+ (512) > K^+ (343) > Rb^+ (162) > Cs^+ (87).[12] This result suggests that smaller alkali metal ions (Li^+ and Na^+) more strongly interact with **3** than larger ones (K^+, Rb^+, and Cs^+) in the neutral media. In fact, CPK model examinations showed that the oxygen-end cavity diameter across the methylene bridges is only ca. 1.4 Å to fit the smaller ions like Li^+ (1.36 Å) and Na^+ (1.90 Å). This is one of the most sophisticated modification of calix[4]arene geometry, which dramatically changed the ion selectivity.

In conclusion, bridged calix[4]arenes **2** having a unique structure strongly interact with smaller alkali metal ions more than larger ones. They can exclusively transport Li^+ ion even in the neutral media. Therefore, it can be said that the bridging of calix[n]arenes is a useful method to change the geometry of the binding sites and give the high ion selectivity. Further investigation including calix[n]arenes and resorc[n]arenes fused cyclobutane ring by bridging is now in progress and will be reported elsewhere.

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