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Highly Efficient Separation of Lithium Chloride from Seawater

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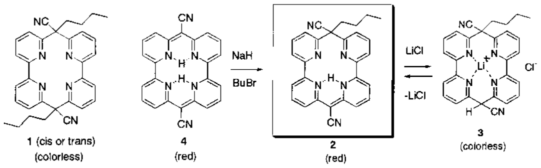
Lithium has attracted intense interest for use in the lithium cell, atomic power, alloy technology, and hydrogen storage technology with nanotubes. In particular, since the utilization of the lithium cell as the energy source for a car creates neither air pollution nor greenhouse gas emissions, enormous amounts of lithium will be required soon. Thus, an environmentally friendly method for lithium separation and recycling is crucial to this development, and therefore, much effort has been devoted to this purpose. One such endeavor is the utilization of membrane technology and lithium separation from seawater. However, no practical methods for lithium separation by liquid membrane have yet been developed, though the liquid membrane system is one of the widely recognized methods of membrane science.[1,2] The most important problem to be solved for the realization of lithium separation by liquid membrane is synthesizing efficient carrier molecules, which can transport the lithium ion without the lipophilic anion. The most successful method studied to date was to design new ionophores or to functionalize crown ether.[3] However, the physical and chemical details of transport and selectivity of these compounds remain largely obscure, and enough ability to separate *lithium chloride* has not been realized with use of crown ether derivatives. Additionally, the usual requirement for a lipophilic anion like perchlorate has limited the utility of this approach.[4]

Recent studies have demonstrated that the new complexing reagent **1** synthesized by us is capable of exhibiting high selectivity for binding to the lithium ion.[5,6] The synthetic success of this highly Li-selective compound **1** permits the design of compounds that possess properties as a carrier molecule of lithium chloride. That is, compound **1** is the macrocycle being composed of two bipyridine moieties, which have the cavity to provide high selectivity for binding to the lithium ion among alkali and alkaline earth metal ions.[6] However, the complexing interaction between macrocycle **1** and the lithium ion is too strong for its use as a carrier in the liquid membrane. An attempt to weaken this interaction is the introduction of the hydrogen atom into the cavity of the macrocycle, though major principles to catch the lithium ion are applied in its design; this is due to the possible prevention of direct interaction between the macrocycle and the lithium ion. The original idea of introducing the hydrogen atom into the cavity came from our approach for developing a color-switching molecule,[7] and this color-switching molecule was applied to this purpose. Synthesis of our macrocycle **2** based on the above fundamental principles was accomplished by monoalkylation of macrocycle **4**, previously reported by us as shown below.[6,7]



Examination for the properties of macrocycle **2** showed that the reaction rate of macrocycle **2** with lithium chloride is much slower than that of macrocycle **1**, and therefore our approach was successful. Macrocycle **2** exhibited the desirable property of being a carrier molecule of *lithium chloride*.

To explore a variety of abilities of macrocycle **2** as the carrier, transport experiments by the liquid membranes containing macrocycle **2** were carried out and the structure of the apparatus, which was an open-ended double cylindrical glass cell, is shown in Figure 1. The organic phase was mechanically agitated at 150 rpm, and the amounts of metal chlorides transported were determined by atomic absorption analysis; other detailed methods were described previously.[8,9] The selectivities obtained under competitive transport conditions, in which a source phase included equimolar Li^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} cations, were shown in Table 1. Lithium chloride was transported quickly compared with other metal chlorides (Na^+, K^+, Ca^{2+}, and Mg^{2+}) under competitive transport conditions, and high selectivity for lithium chloride was obtained (Table 1).[9] The selectivity was also found to have a relationship with the concentrations of various metals in the source phase (Table 1).

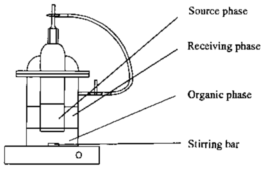


Figure 1. The structure of the transport apparatus.

The striking characteristic of macrocycle **2** is that the Li^+ ion is transported quickly without the lipophilic anion; chloride can be used as a gegen anion. It appears that functionally and structurally, the chloride ion is caught easily by the macrocycle **2** Li complex. Most of the Li^+-selective compounds reported required the lipophilic anion to be used as the carrier of the liquid membrane.[3,4] To the best of our knowledge, new macrocycle **2** is the *first example* that can efficiently transport the lithium ion through liquid membranes *without the lipophilic anion*.[10]

As is stated above, the most notable difference in the two structures **1** and **2** is that macrocycle **2** has one hydrogen atom in the core of the nonplanar macrocyclic ring. Spectroscopic results provided strong evidence for the fact that the hydrogen atom moves from the core to the ring, as shown in macrocycle **3** of the scheme, when macrocycle **2** reacts with lithium chloride. This is the reason the formation of lithium complex **3** is more difficult compared with the case of direct coordination on the nitrogen atoms such as our

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Table 1. Selectivities of Metal Chloride through a Dichloromethane Membrane Containing Macrocycle 2

	selectivity[c]		selectivity[c]
(1)[a] LiCl/NaCl	200	(4)[b] LiCl/$MgCl_2$	300
(2)[b] LiCl/NaCl	100	(5)[b] LiCl/$CaCl_2$	1450
(3)[b] LiCl/KCl	300		

[a] Source phase: water, 20 mL; LiCl, 0.15 M; NaCl, 0.15 M. Receiving phase: water, 10 mL. Organic phase: dichloromethane, 30 mL; macrocycle **2**, 5×10^{-4} M. [b] Source phase: water, 20 mL; LiCl, 0.06 M; NaCl, 0.06 M; KCl, 0.06 M; $MgCl_2$, 0.06 M; $CaCl_2$, 0.06 M. Receiving phase: water 10 mL. Organic phase: dichloromethane, 30 mL; macrocycle **2**, 5×10^{-4} M. [c] The concentrations of metal ions in the receiving phase were determined by the atomic absorption analyses.

Table 2. The Lithium Separation by the Liquid Membrane System from Seawater[a]

metal chlorides[b]	I	II	III	metal chlorides[b]	I	II	III
LiCl	0.005	2.7	79.7	$MgCl_2$	10.1	15.2	5.6
NaCl	86.2	43.9	9.3	$CaCl_2$	1.8	33.9	3.9
KCl	1.8	4.3	1.5				

[a] The change of the ratios (mol %) of various metal chlorides: (I) the ratios of metal chlorides in the sea water, (II) after one separation by liquid membrane, and (III) after two separations by liquid membrane. [b] The following ratios (mol %) of metal chlorides were used as the model of the seawater:[18] LiCl (0.005%), NaCl (86.1%), KCl (1.8%), $MgCl_2$ (10.1%), $CaCl_2$(1.8%).

first macrocycles **1**. Accordingly, this process of hydrogen transfer is a very important factor in the role of the carrier of the Li^+ ion. Macrocycle **2**, prepared for the present study, therefore offers a new synthetic strategy for designing carrier molecules.[12]

Another noteworthy characteristic of macrocycle **2** is that the color of the solution changes *from red to colorless* with the formation of lithium complex **3**,[7] and therefore this macrocycle **2** can be used as a monitor of the transport process.

These facts clearly suggest that the property of macrocycle **2** is a desirable one for use in a carrier. The selectivity, which was observed for the system including equimolar alkali and alkaline earth metal chlorides in the source phase, was particularly superior to those of other systems. Therefore, lithium chloride separation from the seawater including 2.88×10^{-5} mol/L of LiCl (0.005 mol % of total amount of LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$) is expected to be realized by the liquid membrane containing macrocycle **2**. Attempts were therefore made, using macrocycle **2**, to explore whether LiCl can be separated from seawater, and the experimental results are summarized in Table 2. The experimental method with liquid membranes is the same as that reported in Table 1. The condition of the source phase used in this transport experiment is described in Table 2. The ratio of metal ions in the initial source phase (Table 2, I) was the same as those of the seawater, and the ratio of sodium ion (86.2%) was 17 000 times as high as that of the lithium ion (0.005%). Surprisingly, after one separation by our liquid membrane system, the ratio of the lithium ion in the receiving phase increased from 0.005% to 2.7% (Table 2, II). In contrast, the ratio of the sodium ion in the receiving phase decreased and was almost half of that in the source phase. Two separations obtained with use of the resulting receiving phase gave a *strikingly high ratio (80%)* of LiCl, which exhibits the enhanced efficiency of separation (Table 2, III). Accordingly, pure LiCl can be obtained by several repetitions of this operation, and in addition, LiCl as a solid is recovered by evaporation of the receiving phase.

Some carrier molecules previously reported have several advantages for cooperative binding of Li^+ ion.[3,4,13,14] For example, various receptor compounds that have an intramolecular carboxylate or phosphate have been reported as interesting candidates.[15] Higher selectivities for the Li^+ ion seem to be found for phenanthroline and armed crown ether derivatives; oligomethylene-bridged bisphenanthroline offered the higher selectivity (Li/Na = 1850) by chloroform membrane[4c] and double armed diaza-12-crown-4 derivatives transported the Li^+ ion with the selectivity of 12.4 (for Li/Na).[4a] However, since these compounds required the lipophilic anions, such as ClO_4^- and SCN^-, direct LiCl separation from seawater could not be carried out. In contrast, using macrocycle **2**, *pure LiCl can be separated directly from seawater*. Exact direct comparisons of transport rate and selectivity between macrocycle **2** and compounds previously reported have not been carried out yet.[16] However, macrocycle **2**, whether its rate and selectivity are higher than the previously reported compounds or lower, will become a part of important carriers for the Li^+ ion, because the highly efficient separation of LiCl from seawater can be carried out directly by macrocycle **2**, which has been designed by our unique synthetic strategy, and this performance is the key if one wants to use the liquid membrane for practical purposes.

References

(1) Gokel, W. W.; Schall, O. F. In *Comprehensive Supramolecular Chemistry*; Pergamon Press: New York, 1996.

(2) (a) Dugas, H. In *Bioorganic Chemistry Frontiers*; Springer-Verlag: New York, 1990. (b) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

(3) (a) Paquette, L. A.; Tae, J.; Hickey, E. R.; Roger, R. D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1409. (b) Burger, M. T.; Armstrong, A.; Guarneri, G.; McDonald, D. Q.; Still, W. C. *J. Am. Chem. Soc.* **1994**, *116*, 3593. (c) Nijenhuis, W. F.; van Doorn, A. R.; Reichwein, A. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 3607. (d) Olsher, U.; Izatt, R. M.; Bradshaw, J. S.; Dalley, N. K. *Chem. Rev.* **1991**, *91*, 137.

(4) (a) Tsukube, H.; Shinoda, S.; Mizutani, Y.; Okano, M.; Takagi, K.; Hori, K. *Tetrahedron* **1997**, *53*, 3487. (b) Sakamoto, H.; Kimura, K.; Shono, T. *Anal. Chem.* **1987**, *59*, 1513. (c) Sugiura, H.; Collin, J. P.; Hiratani, K. *Chem. Lett.* **1997**, 615. (d) Olsher, U. *J. Am. Chem. Soc.* **1982**, *104*, 4006.

(5) (a) Takano, K.; Furuhama, A.; Ogawa, S.; Tsuchiya, S. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1063. (b) Ogawa. S.; Tsuchiya, S. *Chem. Lett.* **1996**, 709.

(6) (a) Ogawa, S.; Uchida, T.; Uchiya, T.; Hirano, T.; Saburi, M.; Uchida, Y. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1649. (b) Ogawa, S.; Narushima, R.; Arai, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5760.

(7) Ibrahim, R.; Tsuchiya, S.; Ogawa, S. *J. Am. Chem. So*c. **2000**, *122*, 12174.

(8) (a) Tsuchiya, S.; Seno, M. *J. Phys. Chem.* **1994**, *98*, 1682. (b) Tsuchiya. S.; Seno, M. *J. Phys. Chem.* **1994**, *98*, 13680.

(9) When the agitation rate was very fast, the interface between the organic phase and the aqueous phase was not stationary by the agitation. The rate of 150 rpm was the maximum rate necessary to maintain the stationary state of the interface. The transport rates of metal cations decreased with the decrease of the agitation rate.

(10) A number of investigations[11] on Li^+-selective ionophores dispersed in an organic solvent in a PVC matrix for ion-selective electrodes have shown high Li/Na selectivity in the range 100−1000.

(11) (a) Sawada, S.; Torii, H.; Osakai, T.; Kimoto, T. *Anal. Chem.* **1998**, *70*, 4286. (b) Suzuki, K.; Tamada, H.; Sato, K.; Watanabe, K.; Hisamoto, H.; Tobe, Y.; Kobiro, K. *Anal. Chem.* **1993**, *65*, 3404.

(12) The idea to catch lithium chloride by this hydrogen transfer process is considered to led new concepts.

(13) (a) Kimura, K.; Shono, T. In *Cation Binding By Macrocycles*; Marcel Dekker: New York, 1990 (b) Tsukube, H. *Coord. Chem. Rev.* **1996**, *148*, 1.

(14) (a) Bradshaw, J. S.; KraKowiak, K. E.; Izatt, R. M. In *Aza-Crown Macrocycles*; John Wiley and Sons: New York, 1993 (b) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. D. *Chem. Rev.* **1991**, *91*, 1721.

(15) (a) Akabori, S.; Miura, Y.; Yotsumoto, N.; Uchida, K.; Kitano, M.; Habata, Y. *J. Chem. Soc., Perkin Trans.* **1995**, 2589. (b) Habata, Y.; Ugajin, H.; Akabori, S. *J. Org. Chem.* **1994**, *59*, 676. (c) Walkowiak, W.; Kang, S. I.; Stewart, L. E.; Ndip, G.; Bartsch, R. A. *Anal. Chem.* **1990**, *62*, 2022. (d) Inoue, Y.; Gokel, G. W. *Cation Binding by Macrocycles*; Marcel Dekker: New York, 1990. (e) Czech, B. P.; Czech, A.; Son, B.; Koo Lee, H.; Bartsch, R. A. *J. Heterocycl. Chem.* **1986**, *23*, 465.

(16) To the best of our knowledge, the recent data about the transport rate and selectivity of LiCl by using *seawater* and the *liquid membrane* that we obtained in this study have not been published. We obtained some information about oligomethylene-bridged bisphenanthrolines;[4c] metal chlorides were not transported by these compounds.[17] The exact comparison of the transport rate and selectivity by macrocycle **2** with those by other compounds would be able to be clarified by direct comparisons between the data using macrocycle **2** and those using our transport apparatus, seawater, and the previously reported compounds, because there is the possibility that the shape and the size of transport apparatus and the agitation method contribute largely to the transport rate and selectivity of metal chlorides. Unfortunately, we do not have the previously reported compounds now.

(17) Private communication with authors.

(18) In *National Astronomical Observatory*; Maruzen Co. Ltd. Publishing: Tokyo, Japan, 1998.

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