THE EFFICIENT SEPARATION OF LITHIUM CHLORIDE BY ACYCLIC CARRIER MOLECULES

Junko Morita,[a] Shinji Tsuchiya,[b] Misa Ifuku,[a] Makie Kobayashi,[a] Eriko Araki,[a] Zhenxia Zhu,[c] Keiko Takano,[c] and Shojiro Ogawa*,[a]

[a] The School of Human Environmental Science, Graduate School of Humanities and Sciences, Ochanomizu University, 2-1-1, Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan, [b] Institute of Industrial Science, The University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo 106-0032, Japan, and [c] Department of Chemistry, Faculty of Sciences, Ochanomizu University, 2-1-1, Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan

E-mail: sogawa@cc.ocha.ac.jp

Abstract – A new acyclic carrier molecule (**1**) (2,9-didodecanoylamino-1,10-phenanthroline) for the separating purpose of lithium chloride was synthesized by a simple, short synthetic route. Carrier (**1**) exhibited the high selectivity for binding to the Li^+ ion, and has enough ability to form a stable complex consisting of one carrier (**1**) and one Li^+ ion. LiCl is separated efficiently from the mixture of various alkali metal chlorides by using liquid membranes containing carrier (**1**). The transport rate and selectivity by carrier (**1**) can are changed by the concentration of metal salts and the properties of anion in the source phase. Two different transport mechanisms are proposed for the explanation of this transport result and molecular orbital calculations on two proposed carrier (**1**)-Li^+ complexes provide a possibility of supporting above explanation. The numerical simulation of Li^+ transport using the rate equation of a simple model suggests that the transport by carrier (**1**) is promoted due to the diffusion limited process and this property is similar to other previously reported macrocyclic carrier molecules. These results indicate an important fact that simple, acyclic compounds have enough ability as LiCl carrier, though the complicated macrocycles with small cavity have been known as Li^+ ion selective carriers.

This paper is dedicated to Professor Steven M. Weinreb on the occasion of his 65th birthday.

INTRODUCTION

Current applications of lithium have been directed at the energy sources, because users require rechargeable, portable, and longer lasting batteries for mobile electronic devices.   For instance, lithium ion battery is the most important one for cell phones and computer appliances, which are now the most widely used tools.   In addition, the utilization of this carbon free energy source for a car creates neither the pollution caused by harmful emission gases nor the global warming by green house effect.

The practical uses of lithium require the efficient separation and subsequent purification, and recycling. The development of membrane science over the past 30 years has provided a novel method for lithium separation, such as the liquid membrane separation system which has been known to be an environmentally friendly method.[1]   To separate lithium by liquid membranes, a good carrier molecule for use in it has to be prepared.   Therefore a large variety of carriers for separating purposes of the Li^+ ion have been developed by investigators of a variety of fields for many years.[2]   For example, crown ether derivatives often exhibited much higher transport rates of the Li^+ ion than the Na^+ and K^+ ions by using lipophilic anions.[3]   However, one area that researchers have particularly been focusing on is more efficient system for the LiCl separation, because LiCl is very difficult to extract the aqueous phase due to the high enthalpy of hydration of Li^+ and Cl^-.   To the best of our knowledge, LiCl separation system by liquid membranes still has not made its industrial debut despite its promise.   The realization of practical LiCl separation system is very important, because such facts would enable use of Li^+ selective molecules to flourish.   The creation of tailoring carrier molecules for separating purposes of only LiCl thus is a key factor of this research.

We recently developed highly Li^+ ion-selective aza macrocycles (**2** and **3**), which have a small cavity ringed by four pyridine moieties that is a good binding site to the Li^+ ion.[4]   We reported success in making the LiCl separation system by the liquid membranes using macrocycles (**3**); pure LiCl was able to be separated directly from seawater.[4a]   However, the synthetic routes of these macrocycles were multi-step.   Therefore we became interested in the development of new compounds by using a simple, short synthetic method that is of great interest for practical uses.   Our searches also indicated macrocycle (**4**) for purpose of investigation of unsymmetrical effect to interact strongly with the Li^+ ion.[5]

(**2**)   (**3**)   (**4**)
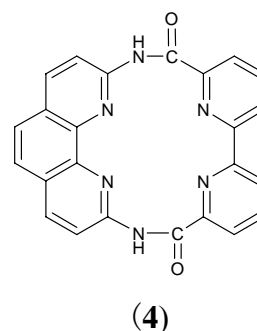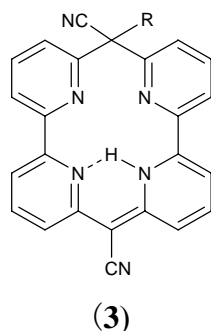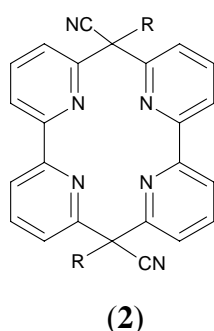
This suggested that 1,10-phenanthroline moiety has enough ability to catch the Li^+ ion and more enhanced binding efficiency of 1,10-phenanthroline could be very suitably exploited by proper assimilation of the side arms with the oxygen atoms into the 1,10-phenanthroline moiety. The use of phenanthroline derivatives for Li/Na selectivity and the ability of amide group to enhance this effect have also been reported.[9] Our approach is therefore based on the combination of 1,10-phenanthroline and carbonyl moieties. Li^+ ion-selective acyclic carriers with the coordination site consisting of both oxygen and nitrogen atoms have not been reported, and the cavity created by these atoms are expected to lead to a bigger role than ever for selectivity in the Li^+ ion binding and transport processes. This fundamental principle to catch the Li^+ ion was applied in our molecular design, and with 2,9-diamino-1,10-phenanthroline developed by us as a starting compound [6], new carrier (**1**) based on this design was synthesized.

The particularly noticeable feature of carrier (**1**) is the structural simplicity of carrier (**1**), which is the product by a simple, short synthetic route. In spite of simple molecule, the transport experiments indicated carrier (**1**) to be one of the excellent compounds for separating purposes of LiCl. The final goals of this research are to evaluate its ability as the Li^+ ion selective carrier and to explore the possibility of practical application.

Herein we report syntheses of carrier (**1**) and related carriers, and results obtained from transport experiments by liquid membrane systems. The transport mechanism was discussed by the molecular orbital calculations (*ab initio*) and the numerical simulation using the equation of diffusion limited process. The transport studies using related compounds were carried out to compare with ability of other previously reported carriers and to evaluate strictly the ability of new carrier (**1**).
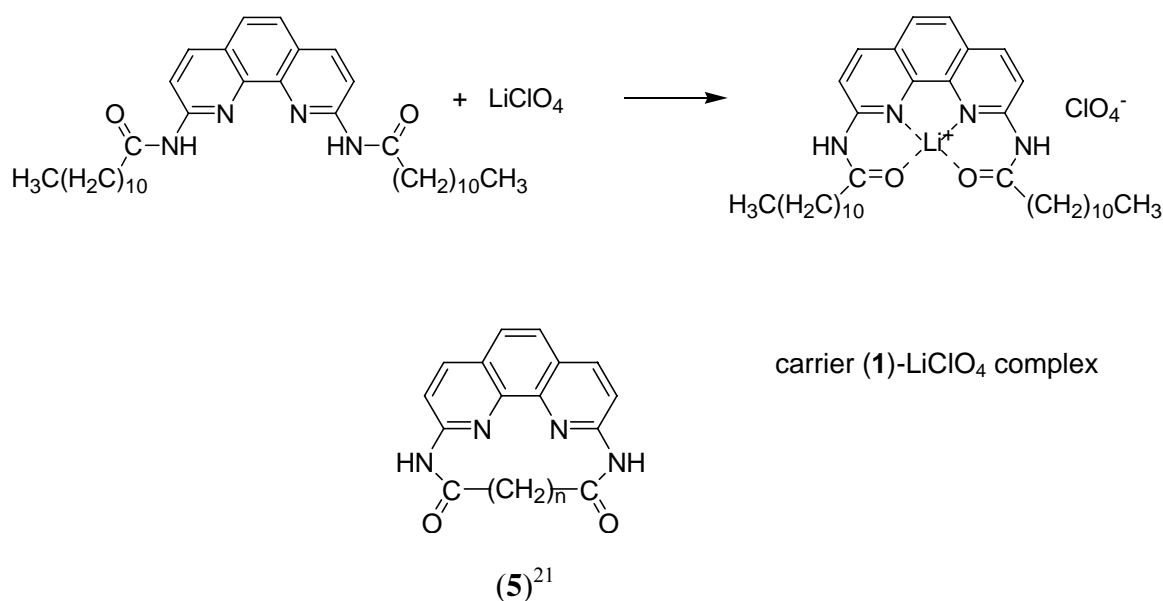
RESULTS AND DISCUSSION

The synthetic procedure of new carrier molecule (**1**) and the structure of carrier (**1**)-$LiClO_4$ complex are shown in the following Scheme 1.

Scheme 1

2,9-diamino-1,10-phenanthroline

carrier (**1**)

carrier (**1**)-LiClO$_4$ complex

$(5)^{21}$
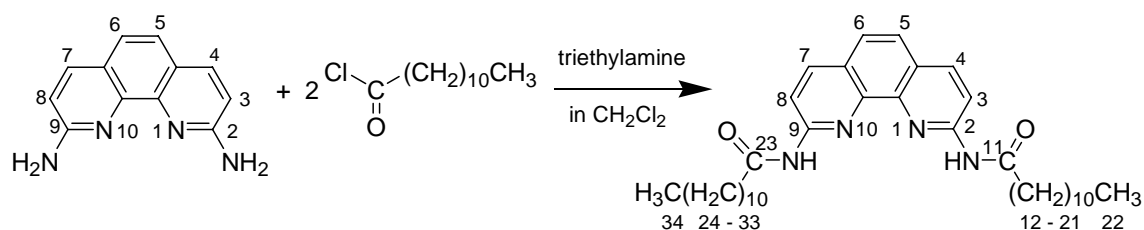
2,9-Diamino-1,10-phenanthroline was prepared by our synthetic procedures[6] and the spectroscopic data of carrier (**1**) were summarized in the experimental section.   The ν (C=O) absorptions of infrared spectra of carrier (**1**) and carrier (**1**)-LiClO$_4$ complex were observed at 1703 and 1677 cm^{-1}, respectively. This indicated the structure of carrier (**1**)-LiClO$_4$ complex as a solid state shown in above scheme to be reasonable, because the C=O stretching is weakened by the interaction between the Li$^+$ ion and the oxygen atoms.

The transport experiments of liquid membrane by carrier (**1**) were carried out by using an open-ended double cylindrical cell and the amounts of metal cations transported were determined by atomic absorption analyses and UV-Visible spectroscopy.[7]   The transport rates and their selectivities obtained by this transport experiment were summarized in Tables 3, 4, 5, and 6, in which the experimental conditions were shown.   Since the difference in the transport rates is extremely larger compared to the experimental errors, detailed discussion using these data is possible.

Though the searches have afforded various Li$^+$ion selective compounds, these reported compounds often have several weak points such as being difficult and expensive to prepare, and are not sufficiently efficient and selective to transport LiCl for practical purpose. [3,4,8,9,11]

We pointed out that replacing one or two N-H bonds of 2,9-diamino-1,10-phenanthroline with N-COR bonds can produce dramatic changes in the chelating properties of this compound.[6]   Specifically, we were fascinated by this simple synthetic route and have turned to further development of this phenanthroline to provide new carrier molecules by one step from starting materials.   The previous searches provide a useful fact that both nitrogen and oxygen atoms have enough capacity to interact with the Li$^+$ion.   These led us to think about making simple molecules that can support LiCl transport by design rather than by accident.   We have therefore designed carrier (**1**), of which such acyclic ONNO

structure may offer the unique potential of being specifically tailored to serve as Li carriers.

The main purpose of the present study is the transport experiments of LiCl by liquid membrane systems containing carrier (**1**).   However, before discussion about results obtained from transport experiments, we report the properties of carrier (**1**).

Conformation Analysis of Carrier (1) by ^{1}H-NMR.   As shown in Scheme 2, two conformations (A) and (B) are possible for carrier (**1**) having two side chains (carbonyl arms).

Scheme 2

(A)   (B)
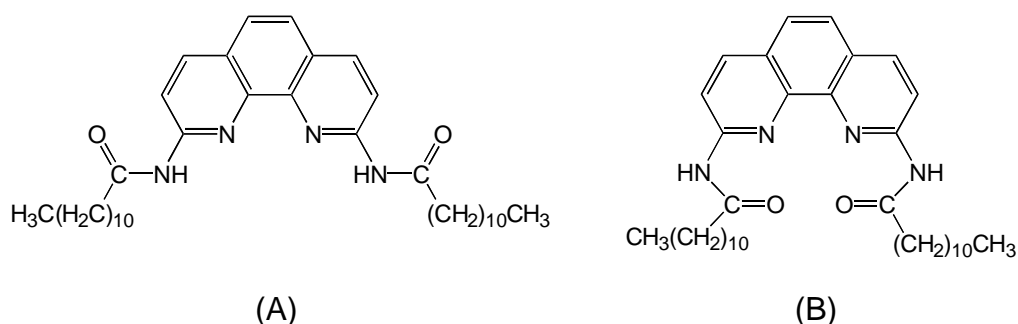
To obtain the information to make determination of the conformation of carrier (**1**) in solution, we have measured the ^{1}H-NMR spectra of carrier (**1**) and starting compound (2,9-diamino-1,10-phenanthroline) in various solvents.   These ^{1}H-NMR spectra were shown in Figure 1.

The spectrum of 2,9-diamino-1,10-phenanthroline in DMSO-d_6 showed two doublet signals for $H_{4,7}$ (δ 7.92 ppm) and $H_{3,8}$ (δ 6.85 ppm) due to neighboring proton coupling and the $H_{5,6}$ protons resonated at δ 7.33 ppm (singlet).   On the other hand, the signals of carrier (**1**) appeared at δ 8.42 ppm (d, $H_{3,8}$ and $H_{4,7}$), and δ 7.82 ppm (s, $H_{5,6}$) in DMSO-d_6.[12]   The most interesting aspect of this ^{1}H-NMR is the finding that the $H_{3,8}$ signals of carrier (**1**) appear at much lower field than those of the starting compound (2,9-diamino-1,10-phenanthroline) in the same solvent.   As shown in Figure 1, the shift of $H_{3,8}$ signals of carrier (**1**) in other solvents such as CD$_3$CN, acetone-d$_6$, and CD$_2$Cl$_2$ is much larger, though the $H_{3,8}$ signals in DMSO-d$_6$ are somewhat broad because of overlap of $H_{4,7}$ signals.   This dramatic change of $H_{3,8}$ signals was caused by the introduction of the carbonyl arms into phenanthroline moiety.   Therefore this marked shift would arise from the deshielding effect of the carbonyl group of side chains (carbonyl arm) to the 3,8-protons of phenanthroline moiety, because the deshielding effect arising from the carbonyl group that can be measured as the chemical shift has been known.   The predominant conformation that the $H_{3,8}$ signals are heavily influenced by the deshielding effect is conformation (A) and then, carrier (**1**) adopts conformation (A).   The signals from the minor conformation (B) were not clearly visible.
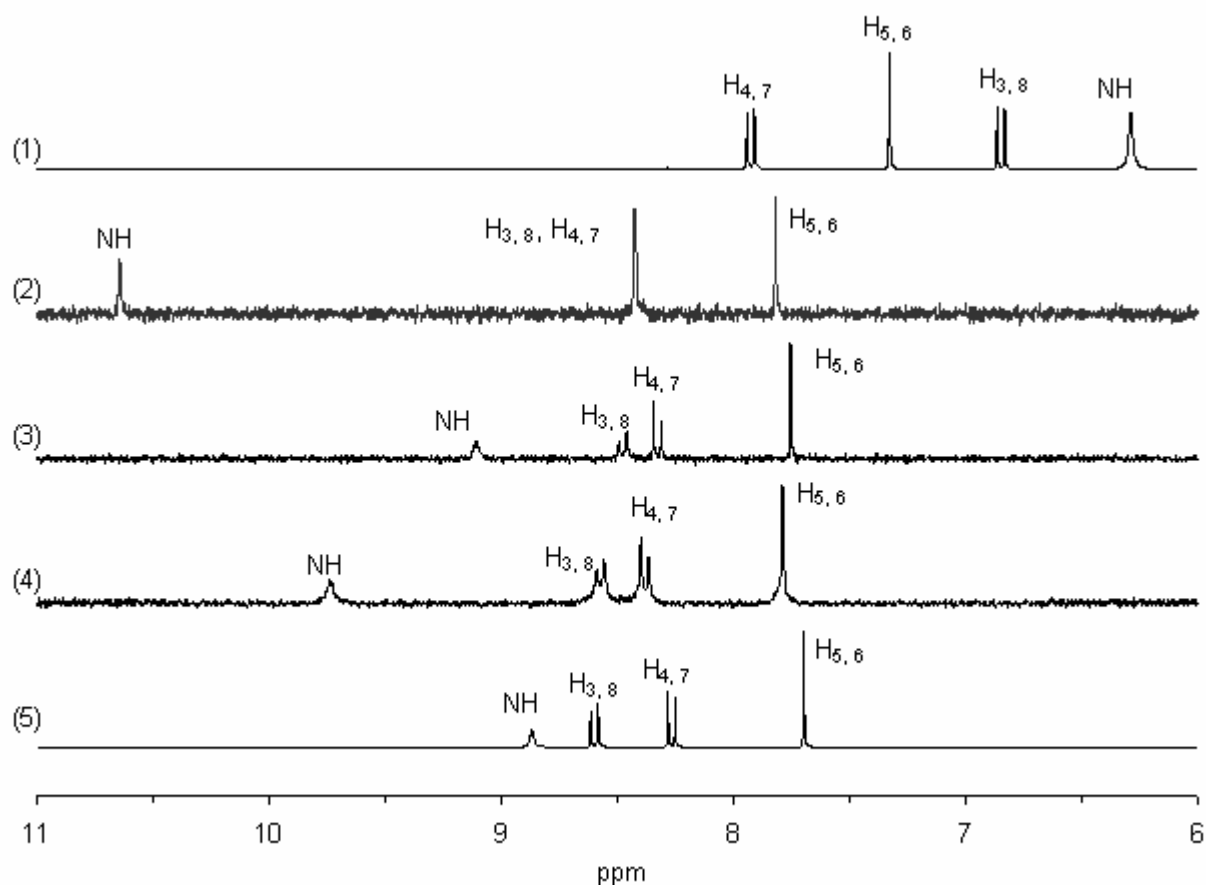
Figure 1. ^{1}H-NMR (270 MHz) spectra of 2, 9-diamino-1,10-phenanthroline in DMSO-d_6 (1) and carrier (**1**) in DMSO-d_6 (2), CD$_3$CN (3), acetone-d_6 (4), and CD$_2$Cl$_2$ (5) at 298 K. Numbering scheme is shown in Scheme 1.

The effect of solvent on the conformation of carrier (**1**) is extremely evident: Figure 1 exhibits that the solvent has a big effect on the peak positions of H$_{3,8}$ protons.   The degree of lower field shift for H$_{3,8}$ depends on the solvent, thus suggesting the conformational change of carrier (**1**) due to the interaction between carrier (**1**) and solvent.   Though the systematic survey of phenanthroline derivatives with different lengths of hydrocarbon chains may provide the information to understand this problem, we did not try such project.

Evidence of the Formation of Carrier (1)-Li^{+} Complex Revealed by ^{1}H-NMR.   The investigation using ^{1}H-NMR was carried out in an attempt to find the evidence about Li^{+} complexatrion.   The ^{1}H-NMR spectrum of the complex by the reaction of carrier (**1**) with LiClO$_4$ in acetone-d_6 was presented in Figure 2 and its data were summarized in Table 1.
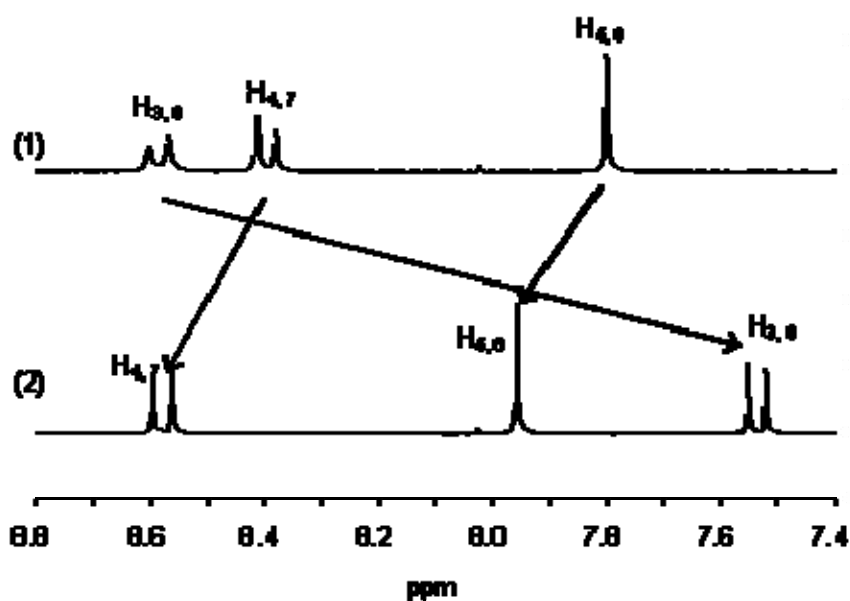
Figure 2. ^{1}H-NMR spectra (270 MHz) of carrier (**1**) (1) and carrier (**1**)–LiClO$_4$ complex (2) in acetone-d_6 at 298 K.

Table 1. ^{1}H-NMR Data for carrier (**1**) and carrier (**6**) and their LiClO$_4$ complex (270 MHz). ^{a}

Carrier (**1**) and its LiClO$_4$ complex

	δ (ppm)		
Compound	H$_{3,8}$	H$_{4,7}$	H$_{5,6}$
carrier (**1**)	8.59	8.40	7.80
complex	7.54	8.58	7.96

^{a} Spectra were recorded in acetone-d_6 at 298 K with SiMe$_4$ as internal reference. Chemical shifts downfield from SiMe$_4$ are defined as positive. The complex was formed by mixing of the solutions of carrier (**1**) (8.3 x 10^{-3} M) and excess LiClO$_4$ (2.08 x 10^{-2} M).   Numbering scheme is shown in Scheme 1.

Carrier (**6**) and its LiClO$_4$ complex

Compound	δ (ppm)							
	NH	H$_8$	H$_7$	H$_4$	H$_6$	H$_5$	H$_3$	NH$_2$
carrier (**6**)	10.18	8.50	8.23	8.01	7.60	7.52	7.00	6.14
complex	10.52	7.44	8.50	8.18	7.78	7.66	7.14	6.54

^{a} Spectra were recorded in acetone-d_6 at 298 K with SiMe$_4$ as internal reference. Chemical shifts downfield from SiMe$_4$ are defined as positive. The complex was formed by mixing of the solutions of carrier (**6**) (8.3 x 10^{-3} M) and LiClO$_4$ (8.3 x 10^{-3} M).   Numbering scheme is shown in Chart 1.

These spectra showed significant changes on complexation and their signals appeared to be very convenient to probe for possible interaction between carrier (**1**) and Li$^+$ ion: The spectrum of carrier (**1**)-Li$^+$ complex showed two doublet signals (H$_{4,7}$ and H$_{3,8}$) with a intensity ratio of approximately 1:1

and one singlet signal ($H_{5,6}$).   A dramatic change from 8.59 to 7.54 ppm was observed in the $H_{3,8}$ signals of phenanthroline protons.   The signals of $H_{4,7}$ and $H_{5,6}$ moved to slightly lower field (from 8.40 to 8.58 ppm and from 7.80 to 7.96 ppm, respectively).   The shift of aromatic protons to lower field by Li^+ coordination was observed in our previous studies on tetra-aza macrocycles containing 2,2'-bipyridines,[4c,4f] but the shifted values for $H_{4,7}$ and $H_{5,6}$ of carrier (**1**)-$LiClO_4$ complex were much larger than previous one.   This lower field shift is thought to be due to the decrease of electron density by the coordination of Li^+ ion.   In contrast, the large higher field shift for the $H_{3,8}$ of carrier (**1**)-$LiClO_4$ complex is unexpected result.   However, this spectral pattern shown in Figure 2 (2) is the same as that of 2,9-diamino-1,10-phenanthroline shown in Figure 1 (1).   This spectral pattern for Li^+ complex indicates that the deshielding effect by the carbonyl group does not occur in carrier (**1**)-$LiClO_4$ complex.   This means that the conformation of carrier (**1**) is transformed from conformation (A) to (B) with the interaction between the oxygen atoms of carbonyl groups and the Li^+ ion, and as a result, the location of the carbonyl group is not close enough to occur the deshielding effect on the 3,8 positions of phenanthroline moiety of the complex.   This conformation (B) is the same as the carrier (**1**)-$LiClO_4$ complex in solid state revealed by infrared data, indicating the coordination of the oxygen atoms of carbonyl groups toward the Li^+ ion.[13]   The spectra of carrier (**1**) and its Li^+ complex shown in Figure 2 are definite evidence that the conformational change of carrier (**1**) is occurring upon the Li^+ ion coordination: Its conformation transforms from (A) to (B), thus indicating the ONNO coordination of the Li^+ ion.

High Field Shift of the $H_{3,8}$ Peak by Li^+ Complexation .   As mentioned above, the Li^+ complexation of carrier (**1**) affords a fact; the $H_{3,8}$ signals at 3 and 8 positions of phenanthroline moiety is shifted largely to higher field from 8.59 to 7.54 ppm by the ONNO coordination of the Li^+ ion.   If the same tendency can be established in analogous compounds, this higher field shift would make ^{1}H-NMR a very useful probe of Li^+ complexation, thus meaning the conformation probe.   Further investigation on this higher field shift will be needed.   Using analogous compounds, the trials to explore the shift of $H_{3,8}$ signals by Li^+ complexation are as follows.

Since the transition metals are believed to be readily coordinated by oxygen atoms and in fact, many transition metal complexes having the ONNO coordination (conformation (B)) have been reported, it is supposed that the coordination of carrier (**1**)-Zn^{2+} complex in acetonitrile-d_3 is the ONNO type.   The ^{1}H-NMR spectra of carrier (**1**)-$LiClO_4$ and carrier (**1**)-Zn^{2+} complex in acetonitrile-d_3 were presented in Figures 3 and 4.   These illustrate that the spectral pattern of carrier (**1**)-Li^+ complex is the same as that of carrier (**1**)-Zn^{2+} complex.   This fact is further evidence that higher field shift of $H_{3,8}$ protons occurs due to Li^+ ion complexation of carrier (**1**).   More beautiful example would be phenanthroline with one carbonyl arm.   In the case of carrier (**1**) with two carbonyl arms, two carbonyl groups can interact with

two H_3 and H_8 hydrogen atoms.   In contrast, in the case of phenanthroline with one carbonyl arm, one carbonyl arm can interact with one hydrogen atom.   As a result, the chemical circumstance of H_3 proton is quite different from that of H_8 proton and the large difference in the behavior of signal shift between H_3 and H_8 must be observed.   To confirm this idea, new carrier (**6**) (2-amino-9-dodecanoylamino-1,10-phenanthroline) was synthesized. ^{1}H-NMR spectra of carrier (**6**) and carrier (**6**)-Li$^+$ complex in acetone-d$_6$ were presented in Figure 5 and their data were summarized in Table 1.

Chart 1
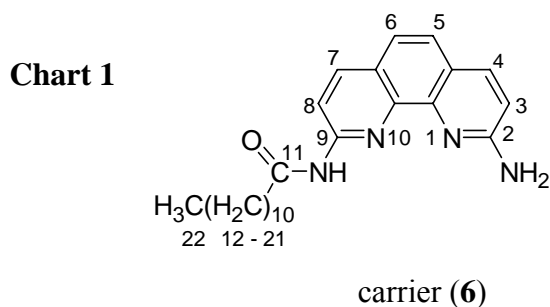
carrier (**6**)

^{1}H-NMR spectrum of carrier (**6**) showing six proton signals is more complicate compared to that of carrier (**1**) (Figure 1).   For instance, though two protons of H_3 and H_8 of carrier (**1**) appeared at the same position as one signal, the H_8 signal of carrier (**6**) appeared at lower field position (8.50 ppm) by the deshielding effect of the carbonyl group in comparison to that (7.00 ppm) of the H_3 signal.   By Li$^+$ complexation of carrier **6**, the direction of signal shift for each H_3 and H_8 is completely reverse.   That is, the H_3 signal moved to lower field (7.14 ppm), indicating Li$^+$ complexation of phenanthroline moiety. Other four signals (H_4, H_5, H_6, and H_7) were, of course, shifted to lower field due to the same reason.   In contrast, the H_8 signal moved to higher field from 8.50 to 7.44 ppm, indicating no shielding effect caused by the coordination of carbonyl group to the Li$^+$ ion.   This lower field shift of H_3 and higher field shift of H_8 strengthens beyond doubt the evidence that the high field shift occurs with Li$^+$ complexation.   This spectrum is a very beautiful example how Li$^+$ complexation can lead the proton shift.   This high field shift is able to be certified by using simple compound (**7**) (2-dodecanoylaminopyridine). ^{1}H-NMR spectra of compound (**7**) and its Li$^+$ complex were presented in Figure 6, indicating the higher field shift of signal at 3 position of pyridine moiety by Li$^+$complexation.   This is *a striking fact* that simple molecule, which can be synthesized by one step from commercially available materials, is able to catch the Li$^+$ ion.[14]

Chart 2

compound (**7**)   compound (**7**)-LiClO$_4$
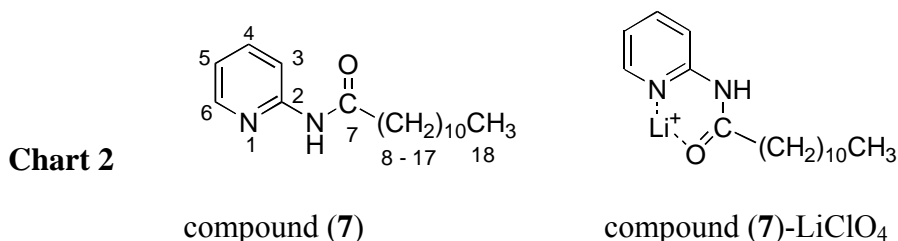
Another Evidence of Carrier (1)-Li$^+$Complex by UV-Visible Spectroscopy.   The complementary method to confirm Li$^+$ complexation of carrier (**1**) is to measure UV-Visible spectra of carrier (**1**) and its

Li$^+$ complex.   The spectral changes with formation of carrier (**1**)-Li$^+$ complex upon treatment with lithium perchlorate were shown in Figure 7.   UV- Visible spectrum of Li$^+$ complex was quite different from that of metal free carrier (**1**), and these indicated the spectral changes experienced by carrier (**1**) in accommodating LiClO$_4$ to be 20% decrease of the peak intensity at 310 nm and the disappearance of peak at 295 nm and the increase of intensity at 247 nm.   This also indicates carrier (**1**) to have the highly desirable capacity as Li$^+$ ion ionophores.   However, the readiness with which carrier (**1**) forms Li$^+$ complex may well foreshadow the capacity to engage in the complexation reaction with other alkali metal ions.   A possible interaction was studied by using Na$^+$ perchlorate and K$^+$ perchlorate, but UV-Visible spectra involving carrier (**1**) and Na$^+$ perchlorate or carrier (**1**) and K$^+$ perchlorate did not provide any evidences for the formation of their complexes.   This fact can be supported by ^{1}H-NMR spectra shown in Table 2.[15]   These results indicate carrier (**1**) to exhibit the extraordinary selectivity of its binding to the Li$^+$ ion.

Table 2.   The difference in chemical shift between carrier (**1**) and its metal ion complexes (270 MHz).[a]

Complex	$\Delta\delta$ (ppm)		
	$H_{3,8}$	$H_{4,7}$	$H_{5,6}$
carrier (**1**)-LiClO$_4$	-0.301	+0.677	+0.057
carrier (**1**)-NaClO$_4$	-0.039	+0.002	+0.004
carrier (**1**)-KClO$_4$	0	0	0
carrier (**1**)-LiCl	-0.015	+0.003	+0.003
carrier (**1**)-NaCl	+0.001	+0.002	+0.004
carrier (**1**)-KCl	-0.001	-0.001	+0.001

[a] Spectra were recorded in CD$_2$Cl$_2$ at 298 K with SiMe$_4$ as internal reference. Chemical shifts downfield from SiMe$_4$ are defined as positive. The complex was formed by mixing of the solutions of carrier (1) (0.010M) and excess metalic salts ([LiClO$_4$] =0.088M,[NaClO$_4$]=0.087M, [KClO$_4$] = 0.135M, [LiCl] = 0.038M, [NaC]l = 0.135M, [KCl] = 0.135M). Numbering scheme is shown in Scheme 1.

Stoichiometry of Carrier (1)-Li$^+$ Complex.   The important information about carrier (**1**)-Li$^+$ complex we need is the stoichiometry of this complex.   UV-Visible spectrum measurements of carrier (**1**) and its Li$^+$ complex in acetonitrile were carried out to determine the stoichiometry of carrier (**1**)-Li$^+$ complex, because carrier (**1**) and its Li$^+$ complex are very soluble in acetonitrile.[22]   As shown in Figure 8, a plot of UV-Visible absorbance versus [LiClO$_4$]/[carrier (**1**)] indicated that when the ratio of molar concentration of carrier (**1**) to the Li$^+$ ion is 1, the absorbance of Li$^+$ complex becomes constant.   Thus, this observation indicates that the ratio of carrier (**1**) to the Li$^+$ ion in the complex is determined as 1:1.   In

addition, we must consider whether a stable carrier (**1**)-Li$^+$ complex is formed in solution.   From the results of determination on the stoichiometry of the complex, we can conclude that the following equilibrium (1) exists.

$$\text{carrier (\textbf{1})} \quad + \quad \text{Li}^+ \quad \underset{}{\overset{K}{\rightleftharpoons}} \quad [\text{carrier (\textbf{1})-Li}^+ \text{ complex}] \qquad (1)$$
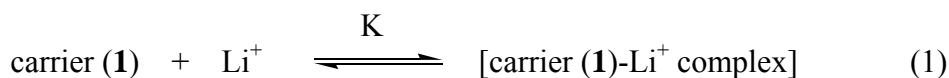
Analysis of the equilibrium constant (K) by Rose and Drango's method [10] gave K = 3.3 x 10^4 M^{-1}, indicating the formation of the stable 1:1 complex.

The stoichiometry of the carrier (**1**)-Li$^+$ complex can be also determined by ^{1}H-NMR.   The ^{1}H-NMR spectral changes with the variation of the ratio of carrier (**1**) to LiClO$_4$ in acetonitrile-d_3 was presented in Figure 3.   When the ratio of molar concentration of the Li$^+$ ion to carrier (**1**) was 1.25, the large spectral change appeared.   In addition, when the ratio was changed from 1.25 to 2.5, little or no change for ^{1}H-NMR spectrum was observed as shown in Figure 3.   This result by ^{1}H-NMR suggests the formation of the 1:1 complex in acetonitrile-d_3 as well as that by UV-Visible method.   Figure 4 showing transient ^{1}H-NMR spectra of the reaction of carrier (**1**) with ZnI$_2$ also exhibits the 1:1 complex formation because of the appearance of H$_{3,8}$ proton peak in the range of higher fields at the equimolar concentration of carrier (**1**) and ZnI$_2$.   The experimental results described in above sections indicate carrier (**1**) to have enough ability to form the stable 1:1 complex in solution.
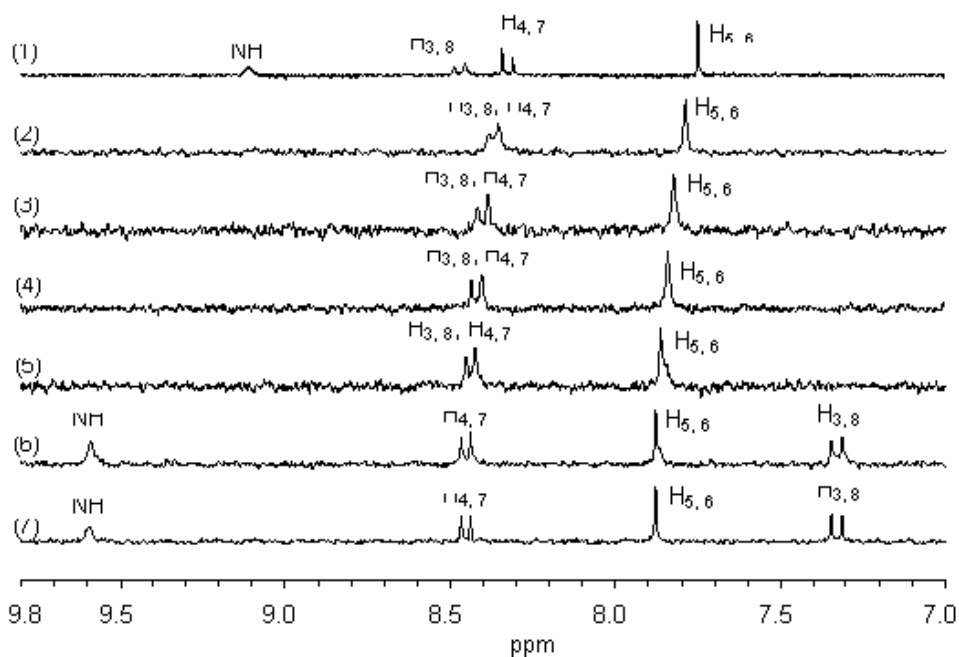

Figure 3. ^{1}H-NMR spectra (270 MHz) of carrier (**1**) (1) and carrier (**1**)-LiClO$_4$ complex (2)-(7) in CD$_3$CN at 298K.   The complex was formed by mixing of both solutions of carrier (**1**) and LiClO$_4$. The concentration of carrier (**1**) in CD$_3$CN was 5.00 x 10^{-4} M. The concentrations of LiClO$_4$ in CD$_3$CN were as follows. (1);0, (2);1.25 x 10^{-4} M, (3); 2.50 x 10^{-4} M , (4); 3.75 x 10^{-4} M, (5); 5.00 x 10^{-4} M, (6); 6.25 x 10^{-4} M, (7); 7.50 x 10^{-4} M. Numbering scheme is shown in Scheme 1.
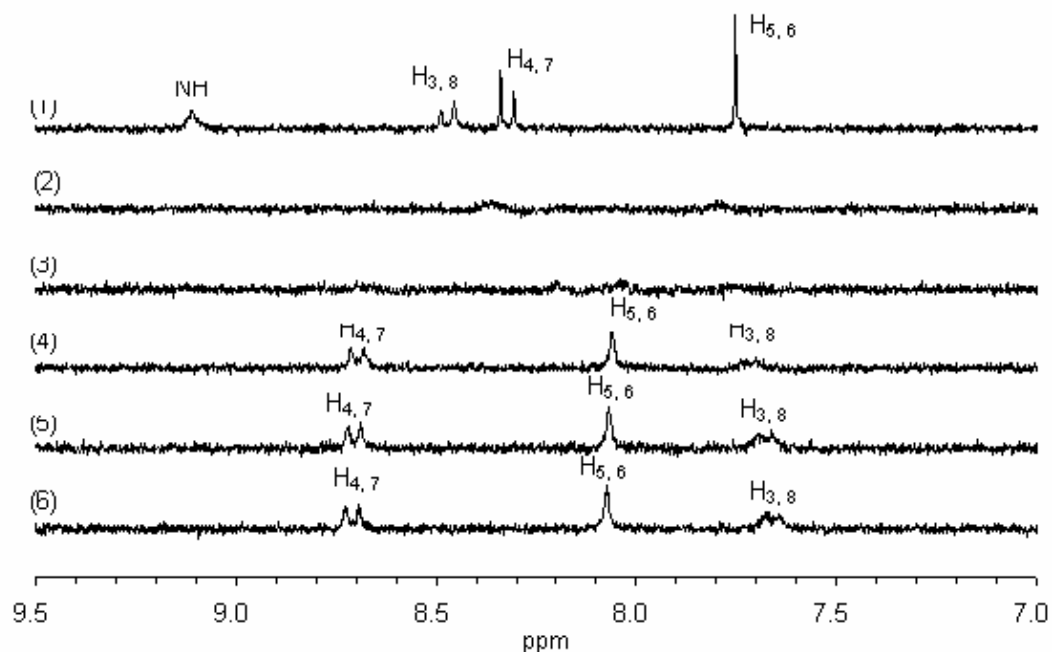
Figure 4. ^{1}H-NMR spectra (270 MHz) of carrier (**1**) (1) and carrier (**1**)-ZnI complex (2)-(6) in CD$_3$CN at 298K.　The complex was formed by mixing of both solutions of carrier (**1**) and ZnI.　The concentration of carrier (**1**) in CD$_3$CN was 5.00 x 10^{-4} M. The concentrations of LiClO$_4$ in CD$_3$CN were as follows. (1); 0, (2); 1.25 x 10^{-4} M, (3); 3.75 x 10^{-4} M, (4); 5.00 x 10^{-4} M, (5); 6.25 x 10^{-4} M, (6); 7.50 x 10^{-4} M.　Numbering
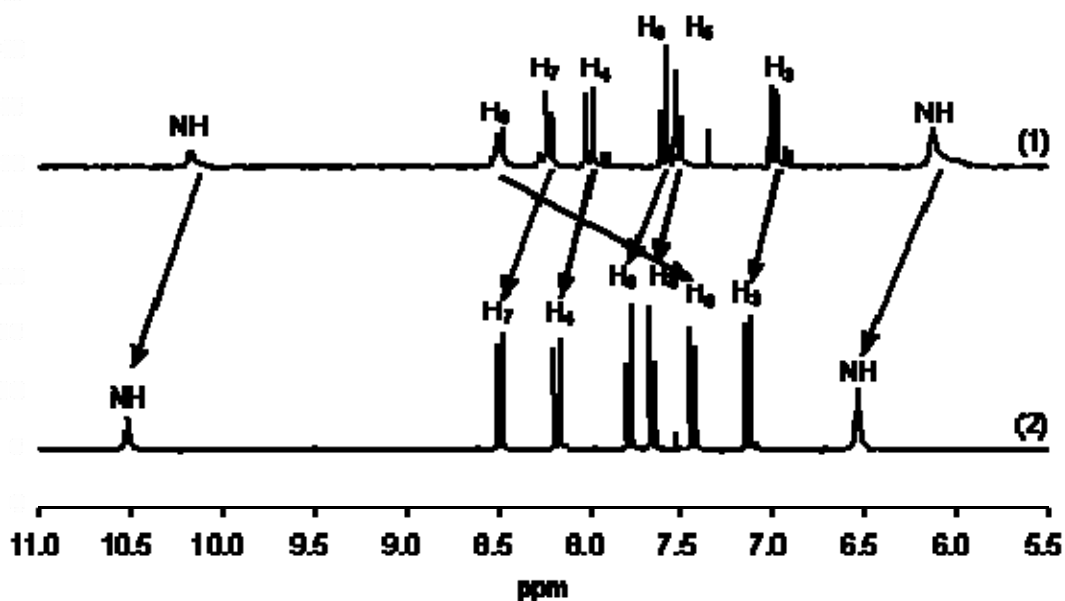

Figure 5. ^{1}H-NMR spectra (270 MHz) of carrier (**6**) (1) and carrier (**6**)–LiClO$_4$ complex (2) in acetone-d_6 at 298 K.　Numbering scheme is shown in Chart 1.
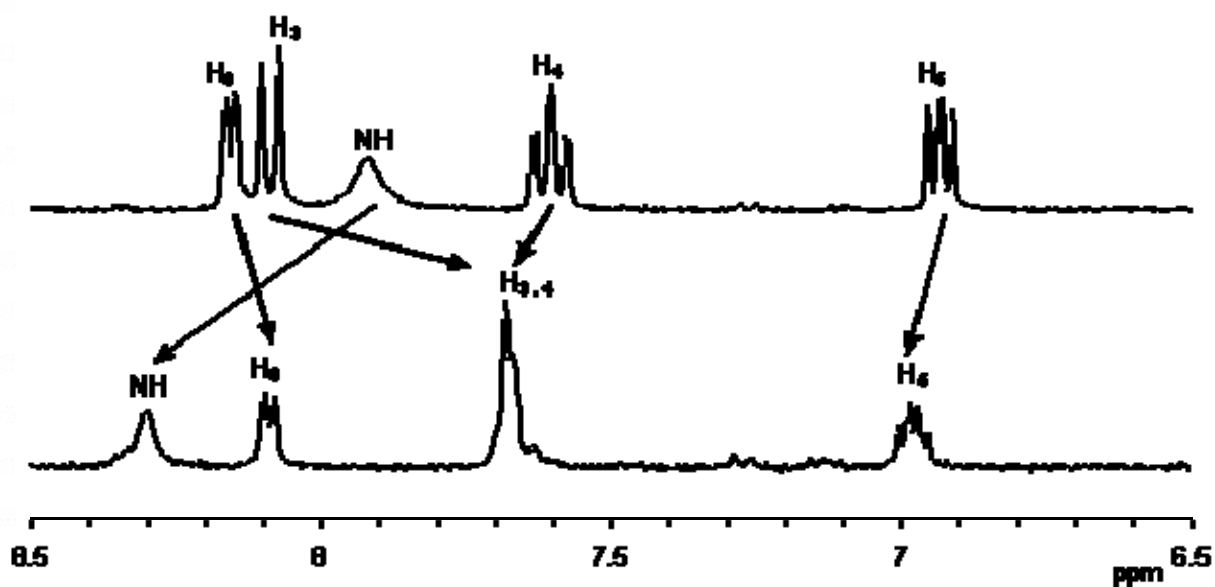
Figure 6. ^{1}H-NMR spectra (270 MHz) of compound (**7**) (1) and compound (**7**)–LiClO$_4$ complex (2) in CD$_2$Cl$_2$ at 298 K. Numbering scheme is shown in Chart 2.

Figure 7. UV-Visible spectra of carrier (**1**) and its Li$^+$ complex in CH$_2$Cl$_2$. (1); carrier (**1**), (2); carrier (**1**)-LiClO$_4$ complex. The concentration of carrier (**1**) in CH$_2$Cl$_2$ used in this experiment was 2.50 x 10^{-5} M. The complex was formed by mixing of both solutions of carrier (**1**) (2.5 x 10^{-5} M) and LiClO$_4$ (7.7 x 10^{-2} M).
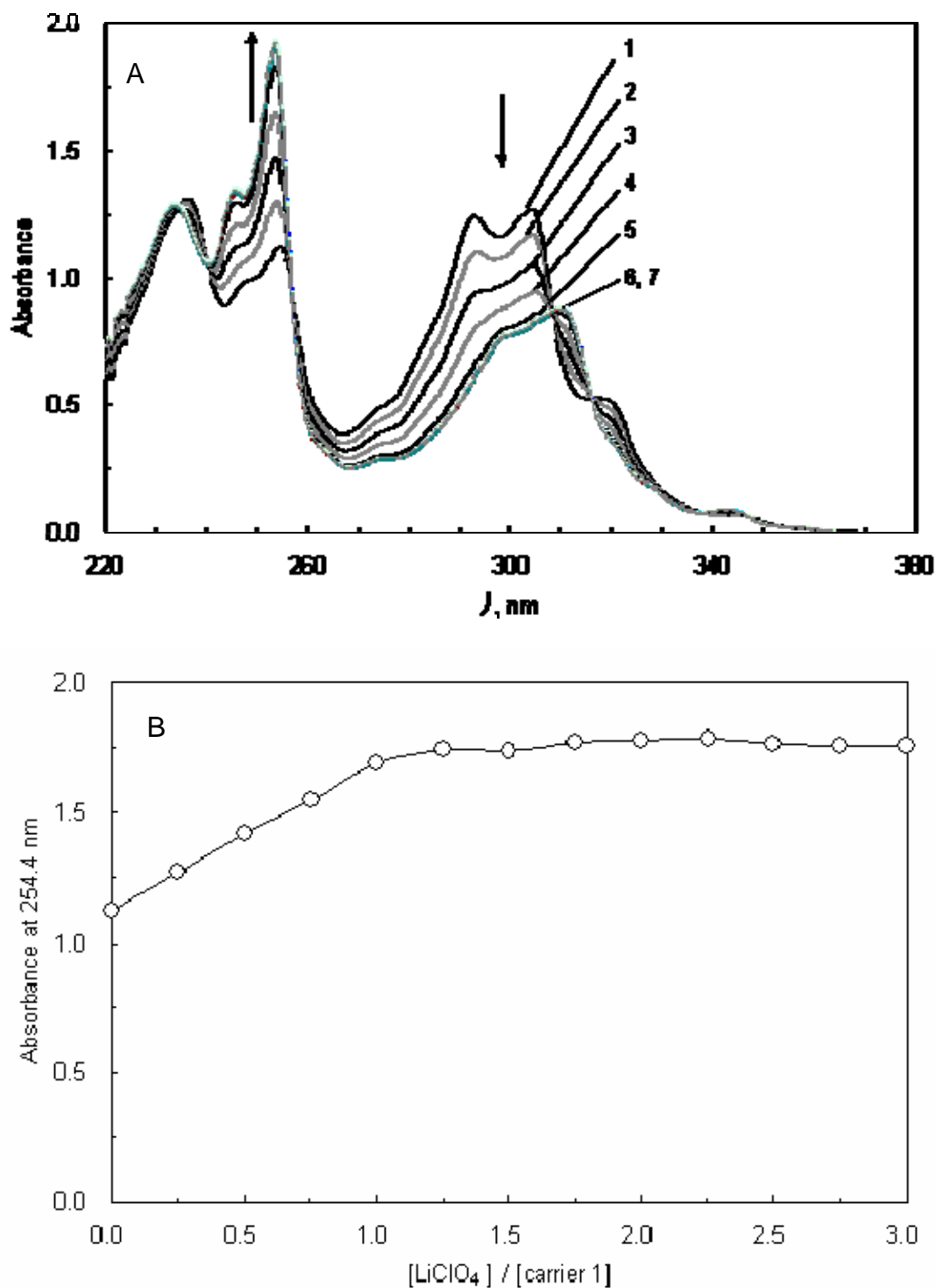
Figure 8. (A) UV-Visible spectra changes of carrier (**1**) and its Li$^+$ complex in CH$_3$CN.
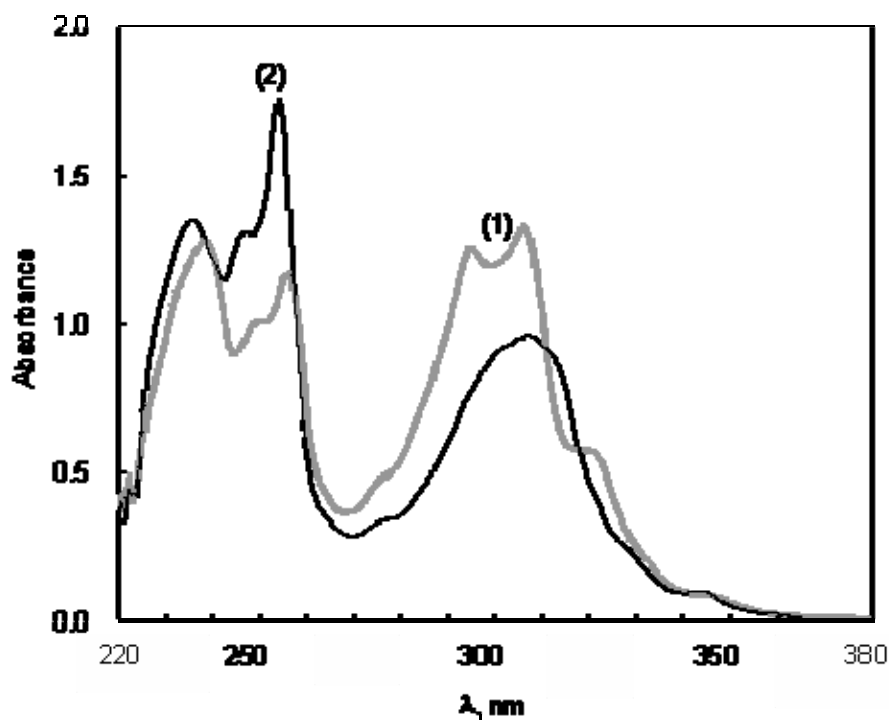The concentration of carrier (**1**) in CH$_3$CN used in this experiment was 3.01 x 10^{-5} M.   The amounts of
LiClO$_4$ added to the solution were as follows. (1); 0 M, (2); 7.53 x 10^{-6} M ([LiClO$_4$] / [carrier (**1**)]= 0.25),
(3); 1.51 x 10^{-5} M ([LiClO$_4$] / [carrier (**1**)] = 0.5), (4); 2.26 x 10^{-5} M ([LiClO$_4$] / [carrier (**1**)] = 0.75), (5);
3.01 x 10^{-5} M ([LiClO$_4$] / [carrier (**1**)]= 1.0), (6); 6.02 x 10^{-5} M ([LiClO$_4$] / [carrier (**1**)] = 2.0), (7); 9.03
x 10^{-5} M ([LiClO$_4$] / [carrier (**1**)] = 3.0).
(B) Absorbance at 254.4 nm vs [LiClO$_4$] / [carrier (**1**)] in CH$_3$CN.

Figure 9. UV-Visible spectra of carrier (**1**) (1) and carrier (**1**)–LiCl complex (2) in CH_2Cl_2. The complex was formed by mixing of both solutions of carrier (**1**) (2.5 x 10^{-5} M) and $LiClO_4$ (2.4 x 10^{-1} M).

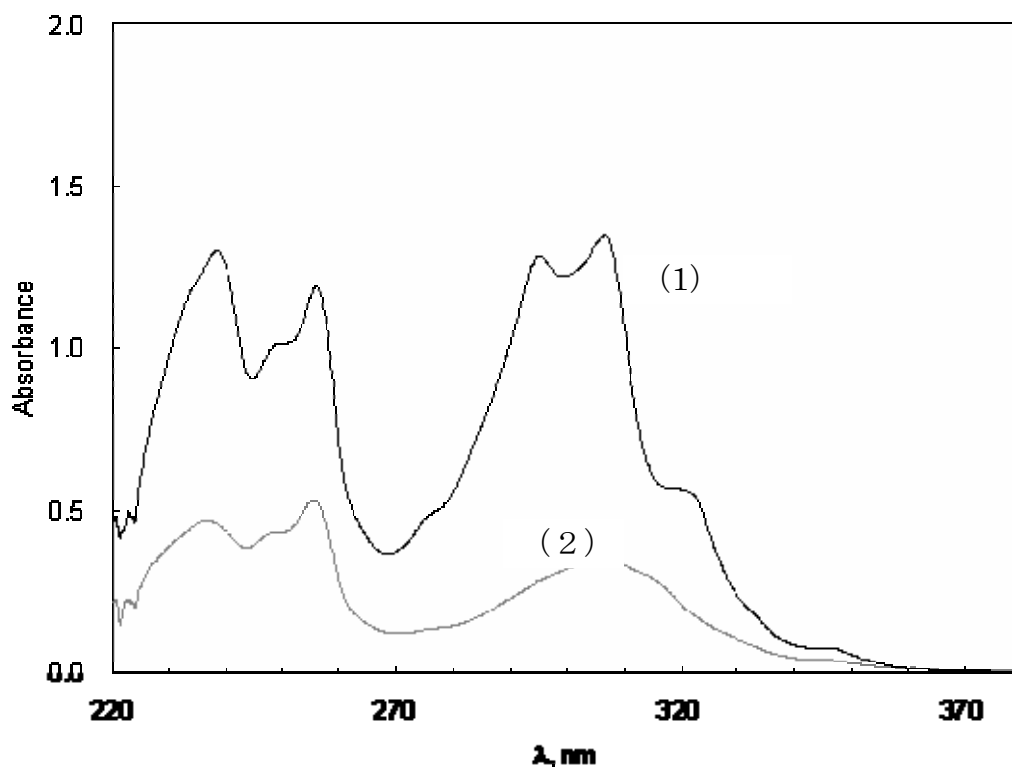**Advantage of Acyclic ONNO Coordination to Catch the Li^+ Ion.** To the best of our knowledge, this hybrid coordination (ONNO type) is a novel acyclic system to catch the Li^+ ion. Although the size-match selectivity is known to be most important factor to realize the selective metal ion binding, the presence of *carbonyl arm*s also provides positive inducement for selective ion complexation. As discussed elsewhere, the double armed crown ethers are known to have the Li^+ ion selective ionophoric property.[11] The coordination modes of these compounds are *lariat* type: Two sidearms interact with the Li^+ ion from the upper and/or lower sides of the plane of crown ether. However, the Li^+ ion in carrier (**1**)-Li^+ complex is coordinated by nitrogen and oxygen atoms on the plane formed by phenanthroline and carbonyl moieties. In the cases of macrocyclic compounds, Li^+ complex would be formed, when the stereochemical and spatial arrangements satisfy those structural requirements conductive to the Li^+complexation. In contrast, the coordination of ONNO type formed for carrier (**1**) has much more advantages for binding of the Li^+ ion, because the binding system of acyclic carrier (**1**) can have much higher freedom of coordination. Additionally, the ability to catch the Li^+ ion may be heavily influenced by the conformation and the molecular motion of double dodecyl groups. The control of *carbonyl arm*s *with the amide bonds and the long hydrocarbon chains* which would enhances the ability of carrier (**1**) is believed to be key to acting as effective and selective binding to the Li^+ ion.

Effect of Counterion on Li⁺ Complexation.   In the experiments of the complexation reaction of carrier (**1**) with the Li⁺ ion in above section, the perchlorate was used as the anion.   This perchlorate is a convenient counterion that provides greater solubility to Li⁺ complex than do other anions.   However, the occurrence and strength of interaction between the Li⁺ ion and carrier (**1**) are thought to be controlled by the geometry of the complex, which may vary as the counterion is changed.[8]   It has been reported that the electrostatic cation-anion interaction depends on the properties of anion, such as its charge, size, shape, and polarizability.[8a]   Therefore the selectivity for formation of carrier (**1**)-alkali metal perchlorate complex may differ significantly from that for carrier (**1**)-alkali metal chloride complex, that would restrict the applicability of liquid membranes.   For this reason, the "anion effect" on the complexiation between carrier (**1**) and alkali metal cation is needed to investigate.   The change of formation ability of the Li⁺complex with the anion variation was studied by the UV-Visible measurements and their results were shown in Figures 7 and 9.   As shown in these figures, the large difference in the peak intensity and shape was observed, when the anion was changed from ClO_4^- to Cl^-: The decrease of peak intensity was enhanced in the case of complexation reaction of carrier (**1**) with LiCl.   A definite explanation for the difference in two results obtained by UV-Visible measurements is rather difficult at present and exact estimation of the contribution from anion to changes observed for the UV-Visible spectrum with carrier (**1**)-LiCl complex relative to that with carrier (**1**)-LiClO₄ complex would require more extensive investigation which is outside the scope of the present work.   Nevertheless, the pronounced change found in two UV-Visible spectra is definite evidence for the "anion effect".   This anion effect on the formation of carrier (**1**)-Li⁺ complex can be confirmed by ¹H-NMR spectroscopy.   As shown in Table 2, the differences in chemical shift of aromatic protons of phenanthroline moiety between carrier (**1**) and carrier (**1**)-LiClO₄ complex are much larger than those between carrier (**1**) and carrier (**1**)-LiCl complex. One of the aim of this survey is to control the formation reaction of the complex by the anions and to explore the possibility of transport control, though the transport control has been known to carry out by the light or pH, that have been studied as the model of active transport. [1,7]

Li⁺ Ion Selective Transport through Liquid Membranes.   Previous studies have shown that the affinity differences for ion binding to Li⁺ and other metals on the uptake side of liquid membrane provide efficient and selective transport.[1, 2, 7, 8, 9, 11, 17]   The membrane system containing carrier (**1**) is expected to have the high Li⁺ affinity because of the higher selectivity of carrier (**1**) for binding to the Li⁺ ion.   The main purpose of the present study is to explore the ability of carrier (**1**) and the effect of factors on selectivity and efficiency of carrier (**1**), investigating how they would be affected by the conformation of carrier (**1**) and the concentration of metal ion pair (M^+X^-) on the uptake side.

Their transport rates and selectivities obtained under competitive transport conditions, in which a source phase included equimolar Li⁺, Na⁺, and K⁺ cations, were shown in Table 3.   The Li⁺ ion was transported

quickly compared with Na^+ and K^+ ions as shown in this table.   Perchlorate and chloride were used as the anion to probe the effect of anion on transport rate and selectivity.

Table 3.   The transport rate and selectivity of metal perchlorate by carrier (**1**) through a dichloromethane membrane.

Concentration of metal salt (M)	Metal ion	Transport rate (10^{-10} mol/h)	Selectivity (v_{Li}^+/v_M^+)
0.05	Li^+	4.27×10^2	-
	Na^+	8.58	49.8
	K^+	1.67	255
0.01	Li^+	5.35×10	-
	Na^+	2.70	19.8
	K^+	8.23×10^{-1}	65.0

Source phase: distilled water, 15mL, LiClO$_4$; NaClO$_4$; KClO$_4$. Receiving phase: distilled water, 15mL. Organic phase: CH$_2$Cl$_2$, 30mL, Carrier (1) (3.1 x 10^{-3}M).

In the case using perchlorate as the counterion, higher selectivity for the Li^+ ion was observed as shown in Table 3.   The selectivity for the Li^+ ion was enhanced as the concentration of metal perchlorate in the source phase increased.   For example, when the concentration of metal perchlorate was changed from 0.01 M to 0.05 M, the selectivity for Li/Na was enhanced from 19.8 to 49.8.   These changes in selectivities on going from 0.01 M to 0.05 M were more dramatic in those for Li/K; namely this selectivity changed from 65.0 to 255.   It seems difficult to explain this fact by a simple mechanism. This transport is dynamic phenomenon and include the interface; especially, it is difficult to understand accurately what the transfer phenomenon occurs at the interface.   However, one factor is supposed to be the change of coordination type to the metal ion, because the number of atoms coordinated to the metal ion and their interactions are one of most important factors that carriers discriminate between various metal cations.   Thus, there is a possibility that the observed trend on selectivity could be explained by differing the coordination type of the carrier (**1**)-alkali metal perchlorate complex, that is produced by the change of conformation of carrier (**1**).   As described above, the results by infrared (solid state) and ^{1}H-NMR measurements of carriers (**1**, **6**, **7**), and their metal complexes in various solvents offered the evidence that the conformation of carrier (**1**)-LiClO$_4$ complex is (B).   ^{1}H-NMR measurements require higher concentration of carrier (**1**) and LiClO$_4$, but the concentration used for the transport experiments is much lower.   Thus, the following conformational changes of carrier (**1**) are supposed to occur at the interface between the organic phase and the source phase with the variation of concentration in the source

phase. In the case of higher concentration, there exists a strong interaction between carrier (**1**) and LiClO$_4$, that produces the conformation (B) of carrier (**1**). In contrast, a weak interaction between carrier (**1**) and LiClO$_4$ occurs under lower concentration, and the conformation of carrier (**1**) becomes (A) as well as that of metal free carrier (**1**) and this conformation is kept during low concentration transport. The coordination type (ONNO coordination) of conformation (B) due to strong interaction would lead the higher selectivity, because the alkali metal cation is discriminated by four atoms coordinated (ONNO). In the case of the coordination type (NN coordination) of conformation (A) due to weak interaction, lower selectivity would be observed because of the discrimination by only two nitrogen atoms. Since we do not have evidence that two NN coordination occurs during this transport system, this is simply a supposition on low selectivity observed at low concentration. However, NMR spectrum showed that the NN coordination (type (A)) occurs in LiCl transport that is stated as follows. Though the transport rate is considered to be related to the stability of the complex, the higher stability of the complex leads faster transport rate in this system.

On the other hand, in the case of chloride as counterion, the selectivity was extremely lower than that by perchlorate and the transport rate was also very slower. That is, as shown in Tables 3 and 4, the system including 0.1 M LiCl exhibited 27 and 102 times lower selectivities for Li/Na and Li/K than those including 0.05 M LiClO$_4$, though the concentration of LiCl in the source phase is two times higher than that of LiClO$_4$. In addition, the transport rate by the system including 0.1 M LiCl was 191 times as slow as that by 0.05 M LiClO$_4$. The fact that the selectivity and rate vary significantly with the anion indicates that the interaction between carrier (**1**) and metal cation anion pair not only depends on the cation type and its concentration, but also may be influenced strongly by the properties of the anion.[8] In particular, the slow rate for LiCl from 0.01 M to 0.1 M are noteworthy. This suggests a weak interaction between carrier (**1**) and LiCl, indicating the N N coordination type. To explore the interaction between carrier (**1**) and LiCl, ^{1}H-NMR spectra during complexation process were measured and its spectra were presented in Figure 10. This experiment demonstrated that the spectrum of carrier (**1**)-LiCl complex differs significantly from that for carrier (**1**)-LiClO$_4$ complex of Figure 2 (2). As stated above section, the UV-Visible spectra observed in the complexation process of carrier (**1**) and LiCl was also very different from those of carrier (**1**) and LiClO$_4$. This feature may cause unexpected complication in the estimation of metal ion transport propensities by carrier (**1**). However, ^{1}H-NMR spectrum (Figure 10) of carrier (**1**)-LiCl complex is very similar to that of carrier (**1**) itself (Figure 1 (5)). This fact leads to a plausible explanation for the spectrum of carrier (**1**)-LiCl complex. That is, since the conformation of carrier (**1**) itself is (A), carrier (**1**)-LiCl complex also adopts (A). It appears likely that the interaction between carrier (**1**) and LiCl is located in the nitrogen atom region rather than in both nitrogen and oxygen atoms.
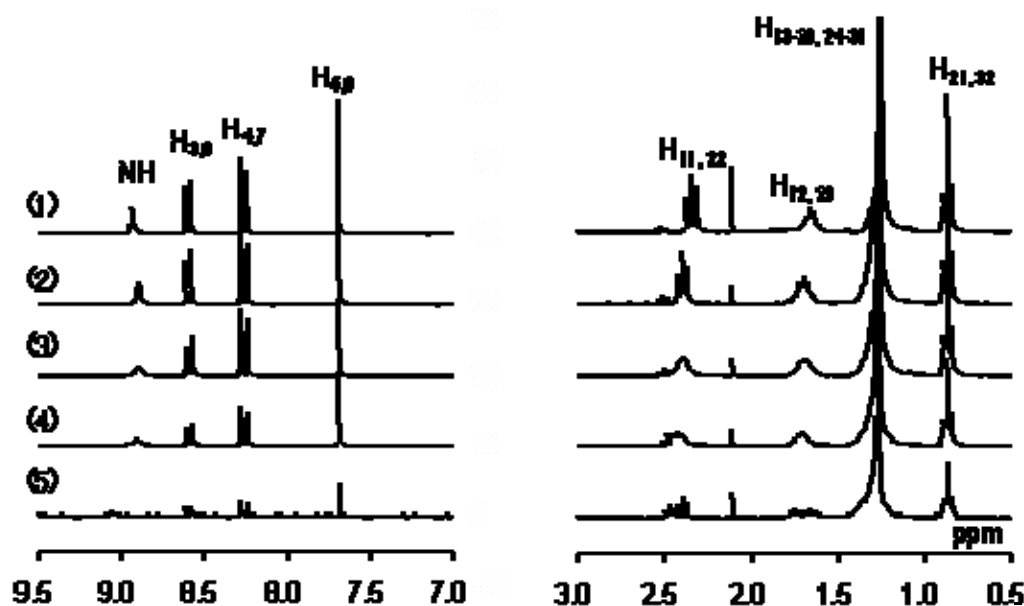
Figure 10. ^{1}H-NMR (270 MHz) spectral changes of carrier (**1**)–LiCl complex in CD$_2$Cl$_2$ with time. (1); metal free, (2); immediately after mixing with LiCl, (3); 1 day after, (4); 3 days after, (5); 9 days after. The complex was formed by mixing of both dichloromethane solutions of carrier (**1**) (1.0 x 10^{-2} M) and LiCl (3.8 x 10^{-2} M).

Therefore this also affords the assessment for overall stability of carrier (**1**)-LiCl complex: The stability of carrier (**1**)-LiCl complex is much lower than that of carrier (**1**)-LiClO$_4$ complex. One of the reasons why this difference in the interaction occurs may be the solubility of the complex, because its solubility may be related with the mobility of carbonyl arms. Additionally, when the concentration of LiCl changed from 0.01 M to 0.1 M, the selectivity did not change within the experimental errors (Table 4). During these concentrations, the carbonyl arms of carrier (**1**) are not able to act as an effective binder of the Li$^+$ ion, and therefore there exists the weak interaction between carrier (**1**) and LiCl, indicating the NN coordination type. As a result, lower selectivity and slower rate seem to be observed. This result suggests that when the interaction increases, the selectivity and transport rate are enhanced. One of the causes that produce above results is similar to those that create a barrier to LiClO$_4$ transport: The transport experiments using LiClO$_4$ demonstrated that when the concentration of LiClO$_4$ in the source phase decreases, lower selectivity and slower rate for the Li$^+$ ion are observed as shown in Table 3. Thus, an option to enhance the interaction between carrier (**1**) and LiCl is to increase the concentration of LiCl in the source phase. This allows us to carry out the transport experiments using higher concentration of LiCl and the results of transport experiment using 1 M LiCl were shown in Table 4.[16] When the concentration of LiCl in the source phase was changed from 0.1 M to 1M, the selectivity was enhanced

from 1.85 to 22.4 and the transport rate became faster from 2.24 x 10^{-10} to 1.63 x 10^{-8} mol/h.   Though higher selectivity and faster transport rate suggest some contribution of the ONNO coordination type, the reason why ^{1}H-NMR spectrum of carrier (**1**)-LiCl complex does not show the contribution from this type could be lower solubility of carrier (**1**)-LiCl complex to the solvent (CD$_2$Cl$_2$).   This fact supports our above explanation for the selectivity and transport rate of alkali metal ions observed in this experiment.

Table 4.   The transport rate and selectivity of metal chloride by carrier (**1**) through a dichloromethane membrane.

Concentration of metal salt (M)	Metal ion	Transport rate (10^{-10} mol/h)	Selectivity (v_{Li}^+/v_M^+)
1	Li$^+$	1.63 x 10^2	-
	Na$^+$	7.28	22.4
	K$^+$	1.64	99.4
0.1	Li$^+$	2.24	-
	Na$^+$	1.21	1.85
	K$^+$	8.91 x 10^{-1}	2.51
0.01	Li$^+$	6.60 x 10^{-1}	-
	Na$^+$	3.78 x 10^{-1}	1.75
	K$^+$	5.56 x 10^{-1}	1.19

*Source phase: distilled water, 15mL, LiCl; NaCl; KCl. Receiving phase: distilled water, 15mL. Organic phase: CH$_2$Cl$_2$, 30mL, Carrier (**1**) (3.1 x 10^{-3}M).*

Table 5.   The transport rate and selectivity of metal chloride by carrier (**1**) through a dichloromethane membrane; the effect of the concentration of carrier (**1**).

Concentration of carrier (**1**) (M)	Metal ion	Transport rate (10^{-10} mol/h)	Selectivity (v_{Li}^+ / v_M^+)
5.0 x 10^{-3}	Li$^+$	2.65 x 10^2	-
	Na$^+$	1.77 x 10	15.0
3.1 x 10^{-3}	Li$^+$	1.63 x 10^2	-
	Na$^+$	7.28	22.4
5.0 x 10^{-4}	Li$^+$	1.60 x 10	-
	Na$^+$	6.96 x 10^{-1}	23.0

*Source phase: distilled water, 15mL, LiCl (1.0M); NaCl (1.0M); KCl (1.0M). Receiving phase: distilled water, 15mL. Organic phase: CH$_2$Cl$_2$, 30mL, carrier (**1**).*

Another route, which enhances the interaction at the boundary between the organic phase and the source phase, is to increase the carrier concentration in the organic phase. The experimental results with the variation of concentration of carrier (**1**) are summarized in Table 5. As shown in this data, the increase of concentration of carrier (**1**) from 5 x 10^{-4} M to 5 x 10^{-3} M produces 17 times faster rate for LiCl, and there is a linear relationship between the concentration of carrier **1** and the transport rate of LiCl.

As is stated above, the selectivity and rate would depend on the interaction between carrier (**1**) and alkali metal cations. This interaction is controlled by the following three factors; the concentration of alkali metal salt (M^+X^-) in the source phase, the concentration of carrier (**1**), and the anion. These processes proposed above could be summarized in the strong interaction by ONNO coordination and the weak interaction by NN coordination. We do not mean to imply, however, that the interaction between carrier (**1**) and metal cation anion pair alone as proposed above determines the selectivity and the rate. Though the interaction between these species must, of course, play an important role in allowing selective transport system, many other factors such as the shape cavity size and conformational flexibility are probably involved in determining overall selectivity and transport rate. For example, the selectivity of carrier (**1**) for Li/Na decreased with the increase of the concentration of carrier (**1**) as shown in Table 5. This fact suggests that the ability of carrier (**1**) to discriminate between different alkali metal cations is very sensitive to the environment of carrier (**1**) itself. Additionally, the effect of water on the coordination at the interface would be important. Using usual spectroscopic methods, accurate characterization of lithium-alkali metal ion complexes at the interface that would play the important role in this dynamic process therefore seems to be impossible, but one possible mechanism is presented above.

As described above, carrier (**1**) mediated highly selective and efficient transport of the Li^+ ion across the dichloromethane membrane. We are particularly motivated by the observation that LiCl is transported by carrier (**1**), though other previously reported systems contain the lipophilic ion as the counter ion. ^{1}H-NMR spectrum of carrier (**1**)-LiCl complex did not show definite evidence about the interaction between LiCl and the carbonyl arms of carrier (**1**) as stated above. However, the results by transport experiment of alkali metal chlorides raise the possibility that a sort of interaction between the Li^+ ion and the carbonyl arms would probably occur, because the selectivities of Li^+/Na^+ and Li^+/K^+ increases at higher concentration (1M) of source phase as shown in Table 4, and these higher selectivities would be caused by the discrimination four nitrogen and oxygen atoms (ONNO) rather than nitrogen atoms. If some conditions that LiCl can interact stronger with the carbonyl arms explore, LiCl transport system with much higher selectivity and faster rate could be found.

Molecular Orbital Studies on Stabilities of Carrier 1-Li$^+$ Complexes. The assessment for overall stabilities of Li^+ complexes from the transport data suggests the stability of carrier (**1**)-Li^+ complex with the ONNO coordination to be much higher than that with the NN coordination. We need further

information for a convincing validation of the difference in stability between two Li$^+$ complexes, and then have tried the possibility of explaining such properties by using a theoretical method. Geometry optimization of energy minimum structures was carried out by *ab initio* RHF method with 6-31G(d) basis sets. Figure 11 shows the optimized structures of two carrier (**1**)-Li$^+$ complexes with the ONNO coordination and the NN coordination obtained by RHF/6-31G(d) calculations with C$_{2v}$ symmetry. The calculated total energies for the optimized energy minimum structures indicate carrier (**1**)-Li$^+$ complex with the ONNO coordination to be more stable than carrier (**1**)-Li$^+$ complex with the NN coordination. The difference in stabilization energy between two complexes is 45.0 kcal/mol.[18] This calculated result is in good agreement with our conclusion obtained from the ^{1}H-NMR and transport experiments. A noticeable fact obtained by this calculation is that frontier orbitals of the carrier (**1**)-Li$^+$ complex with the NN coordination are quite different from those of the carrier (**1**)-Li$^+$ complex with the ONNO coordination (Figure 12), suggesting the difference in the property between two complexes. What is unclear is whether these results obtained from molecular orbital calculations can be applied directly for the stability of the complex. However, present results would provide a possibility of supporting our explanation using two kinds of complexes (ONNO coordination and NN coordination) for the transport experiments.
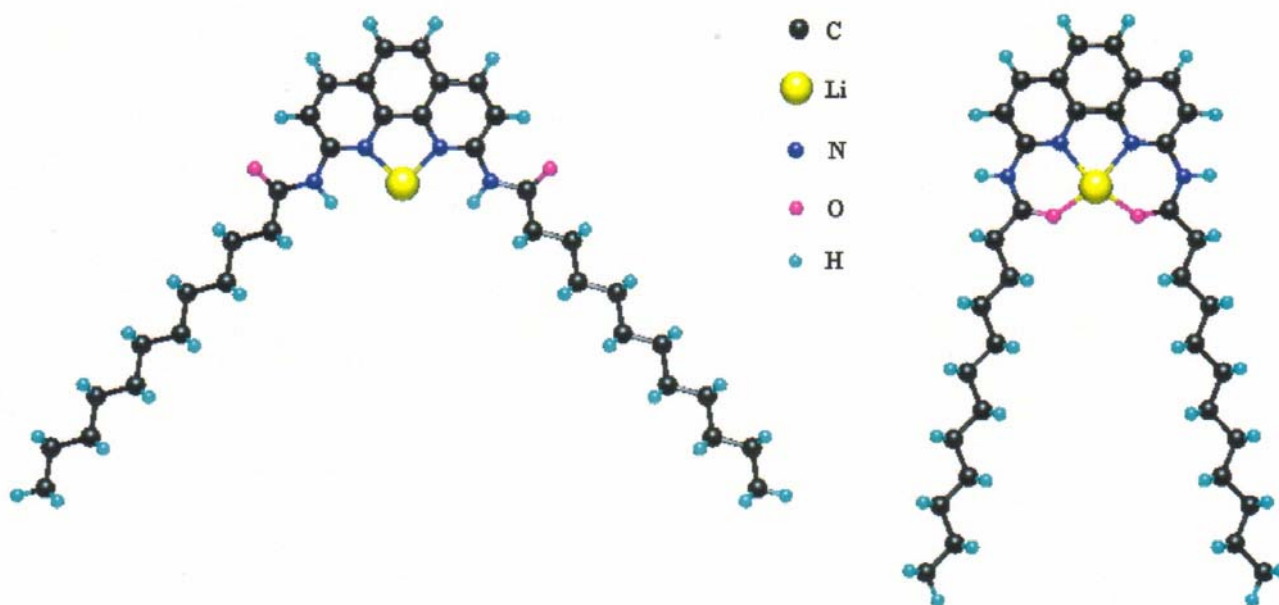

Figure 11. Optimized structures of carrier (**1**)-Li$^+$ complexes with the NN coordination (a) and the ONNO coordination (b).
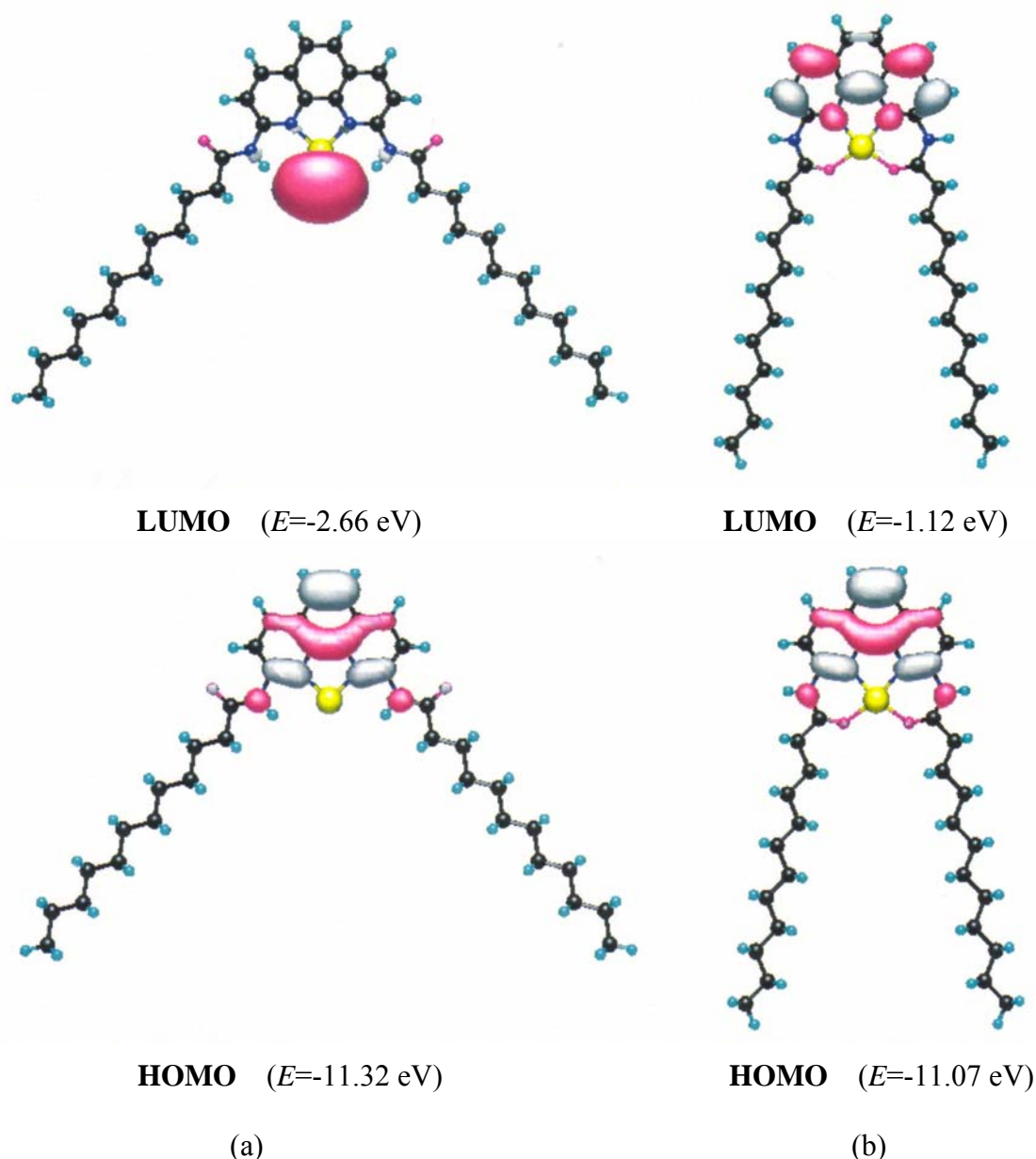
LUMO   (*E*=-2.66 eV)   LUMO   (*E*=-1.12 eV)

HOMO   (*E*=-11.32 eV)   HOMO   (*E*=-11.07 eV)

(a)   (b)

Figure 12.   Frontier orbitals of carrier (**1**)-Li$^+$ complexes with the NN coordination (a) and the ONNO coordination (b).

Effect of Oxygen Atoms on Selectivity   The ability of carrier (**1**) to discriminate between Li$^+$ and Na$^+$ ions would be enhanced by oxygen of amide carbonyl arms.   An attempt to explore this oxygen effect is to synthesize carrier (**1**) analogue without the carbonyl group.   2,9-Dihexylamino-1,10-phenanthroline (carrier (**8**)) was therefore synthesized from 2,9-dichloro-1,10-phenanthroline as shown in Scheme 3.[19] ^{1}H-NMR spectrum of carrier (**8**) in CDCl$_3$ was presented in Figure 13 and this spectral pattern was the same as 2,9-diamino-1,10-phenanthroline and carrier (**1**)-Li$^+$ complex.   This is reasonable, because the deshielding effect of H$_{3,8}$ signals by carbonyl group is not operative.   The transport data by carrier (**8**) were summarized in Table 6, including the data by carrier (**1**).
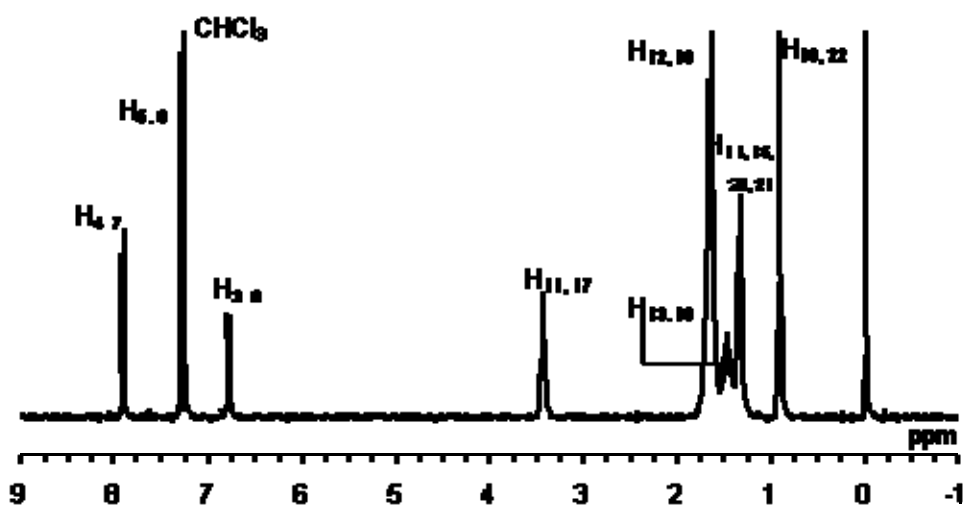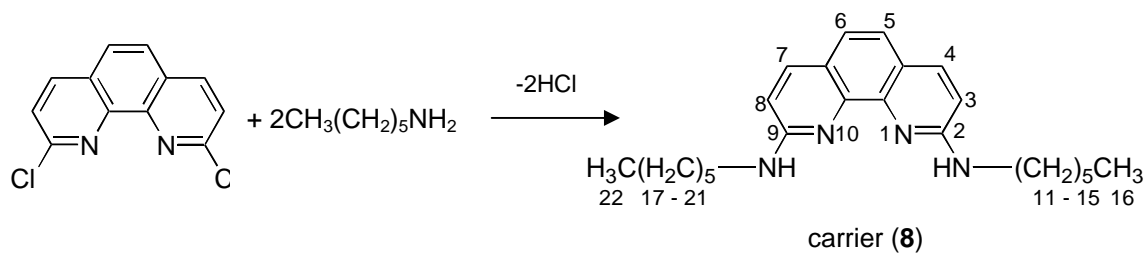
Scheme 3

Figure 13. ^{1}H-NMR spectrum (270 MHz) of 2,9-dihexylamino-1,10-phenanthroline (carrier (**8**)) in CDCl$_3$ at 298 K.   Numbering scheme is shown in Scheme 3.

Table 6.   **The transport rate a**nd selectivity of metal ion by carriers (**1** and **8**) through a dichloromethane membrane; the effect of the anion.

Anion	Carrier	Metal ion	Transport rate $(10^{-10}$ mol/h)	Selectivity (v_{Li}^{+} / v_{M}^{+})
ClO$_4^{-\,a}$	carrier (**1**)	Li$^+$	5.35×10^1	-
		Na$^+$	2.70	19.8
	carrier (**8**)	Li$^+$	4.19×10^2	-
		Na$^+$	1.16×10^2	3.61
Cl$^{-\,b}$	carrier (**1**)	Li$^+$	1.63×10^2	-
		Na$^+$	7.28	22.4
	carrier (**8**)	Li$^+$	3.47×10^2	-
		Na$^+$	6.22×10	5.58

a Source phase: distilled water, 15mL, LiClO$_4$ (0.01M); NaClO$_4$ (0.01M). Receiving phase: distilled water, 15mL. Organic phase: CH$_2$Cl$_2$, 30mL, carrier (1) or carrier (8) (3.1 x 10^{-3}M).

b Source phase: distilled water, 15mL, LiCl (1.0M); NaCl (1.0M). Receiving phase: distilled water, 15mL. Organic phase: CH$_2$Cl$_2$, 30mL, carrier (1) or carrier (8) (3.1 x 10^{-3}M).

The examination for the selectivity of Li/Na showed that the enhancement of selectivity by the oxygen atoms is quite apparent; namely the selectivity by carrier (**1**) for both LiCl and LiClO₄ are much higher than that by carrier (**8**).
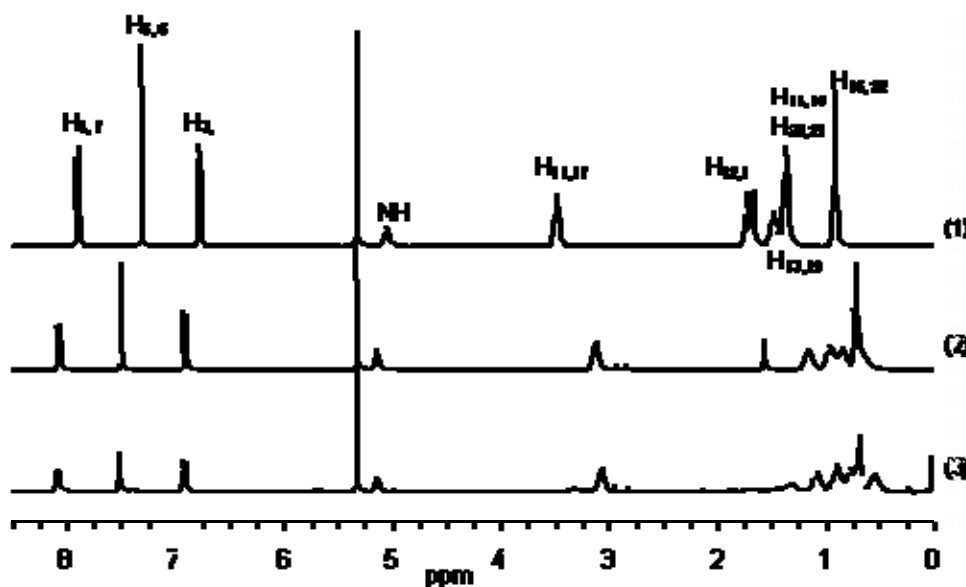

Figure 14. ¹H-NMR (270 MHz) spectral changes of carrier (**8**)–LiClO₄ complex in CD₂Cl₂ at 298 K with time. (1);metal free, (2); 1 hour after mixing with LiClO₄, (3); 6 days after. The complex was formed by mixing of both dichloromethane solutions of carrier (**7**) (1.1 x 10⁻² M) and excess amounts of LiClO₄ (9.5 x 10⁻² M). Numbering scheme is shown in Scheme 3.

Another noticeable fact seen in this Table 6 is faster rates of Li⁺ and Na⁺ ions by carrier (**8**).   ¹H-NMR spectrum of carrier (**8**)-LiClO₄ complex was measured to explore the reason why this rate is faster.   As shown in Figure 14, the change by Li⁺ complexation is the higher field shift of α-methylene protons of the side chains.   This shift was not observed for carrier (**1**)-LiClO₄ complex.   In the case of previously reported other phenanthroline derivatives having two alkyl groups, the formation of 2:1 complex with the Li⁺ ion in solution had been reported (phenanthroline derivative : Li⁺ ion = 2 : 1) and the Li⁺ ion was found to be wrapped with two phenanthroline derivatives by X-Ray analysis.[9]   Therefore, the complex having similar structure is considered to be formed.   If this is the case, the large shift ($\Delta \delta = 0.413$ ppm) of α-methylene signals seems to be reasonable: This shift is caused by the phenanthroline moiety, which would be located beside the α-methylene protons of the side chains.   These data suggest the formation of 2:1 complex consisting of carrier (**8**) and LiClO₄.   Since this indicates the structure of carrier (**1**)-LiClO₄ complex to be entirely different from carrier (**8**)-LiClO₄ complex, the estimation of transport rates by direct comparisons between carriers (**1** and **8**) seems to be very difficult.   However, we can lead the plausible explanation for faster rates by carrier (**8**): The faster rates would be arisen from the stronger

interaction, because the Li^+ ion is expected to be coordinated by two molecules of carrier (**8**). Another possible explanation about this is that Li-carrier (**8**) complex becomes more lipophilic due to the wrappings of two phenanthroline moieties and is easy to travel in the liquid membrane.

As stated above, the metal ion in carrier (**1**)-metal complex is coordinated by two oxygen and two nitrogen atoms.   In contrast, the metal ion in carrier (**8**)-metal complex is ringed by four nitrogen atoms. The fact that the selectivity of Li/Na by carrier (**1**) is much higher than that by carrier (**8**) suggests that the oxygen atoms play an important role in making a discrimination between Li^+ and Na^+ ions, though their stereochemical structures and stoichiometry differs each other.   As seen in carrier (**8**), the stronger interaction between carrier and metal ion may create a barrier to release metal ion on the side of the receiving phase.   Thus, the application of the coordination of ONNO type would bridge the gap between the disadvantage of transport rate and the advantage of selectivity.   The use of ONNO coordination may be a way of realizing the liquid membrane system where the selective properties are dramatically modified with respect to the Li^+ ion.

Eventually, the features of carrier (**1**) mentioned above would arise from the oxygen atom of carbonyl arm and this is an advantage over the previous reported transport systems.   However, we could synthesize better carriers:Various substituents are introduced systematically into the ONNO coordination system to improve sterical and geometrical disadvantages.   Not only does this improvement lead to enhanced transport rate, but also maximizes the ability of carrier to discriminate the Li^+ ion from other metal ions.

Studies on Transport Mechanism by Numerical Simulations.   To explore the behavior of transport process, researchers are continually trying to find more exact transport mechanism through liquid membranes.   This requires that the theoretical analysis becomes more exact.   However, it becomes more and more difficult to clarify the mechanism by theoretical method as the carrier has more functionalized ability.   Additionally, we have to find a simple way to pass metal ions through the interface, but a tremendous amount of work still needs to estimate the exact boundary conditions.   The most typical method on this approach comes from the diffusion limited transport.[7,20]   This model makes it relatively easy to do the theoretical treatment and this attempt offers a possibility for clarifying the transport mechanism of the Li^+ ion by carrier (**1**).   Thus, we made an attempt to explore the mechanism of our transport experiments by using this model.   The rate equation used is as follows.[20]

$$V = \frac{D}{2l}(KL_o)\left(\frac{S_{out}^{\;2} - S_{in}^{\;2}}{\left(1 + KS_{out}^{\;2}\right)\left(1 + KS_{in}^{\;2}\right)}\right) \tag{2}$$

Where V = transport rate; D = diffusion coefficient; K = overall extraction equilibrium constant; L_0 = total concentration of carrier (**1**); S_{out} = concentration of lithium picrate in the source phase; S_{in} = concentration

of lithium picrate in the receiving phase. The experiments for this treatment were carried out by using Li$^+$picrate, because the picrate anion is brightly colored which allows for spectrophotometric determination of concentrations and is a convenient counterion that provides greater membrane transport rates for the Li$^+$ ions.   The value of K was measured under the conditions of transport experiments and its observed value was 0.712 M^{-1}.   The result of a calculation using equation (2) is shown in Figure 15, which includes the experimental results.   Since the result of the numerical simulation is in good agreement with the experimental result, the transport of Li$^+$ picrate by carrier (**1**) would proceed in obedience to the diffusion limited process.   This result indicates the ability of carrier (**1**) as the carrier to be similar to other reported macrocyclic carrier molecules.   The transport system of LiCl is expected to display similar behavior (diffusion limited process).   However, relevant measurements have not been yet made, because the convenient method to trace the concentration change of LiCl in all phases is not available.
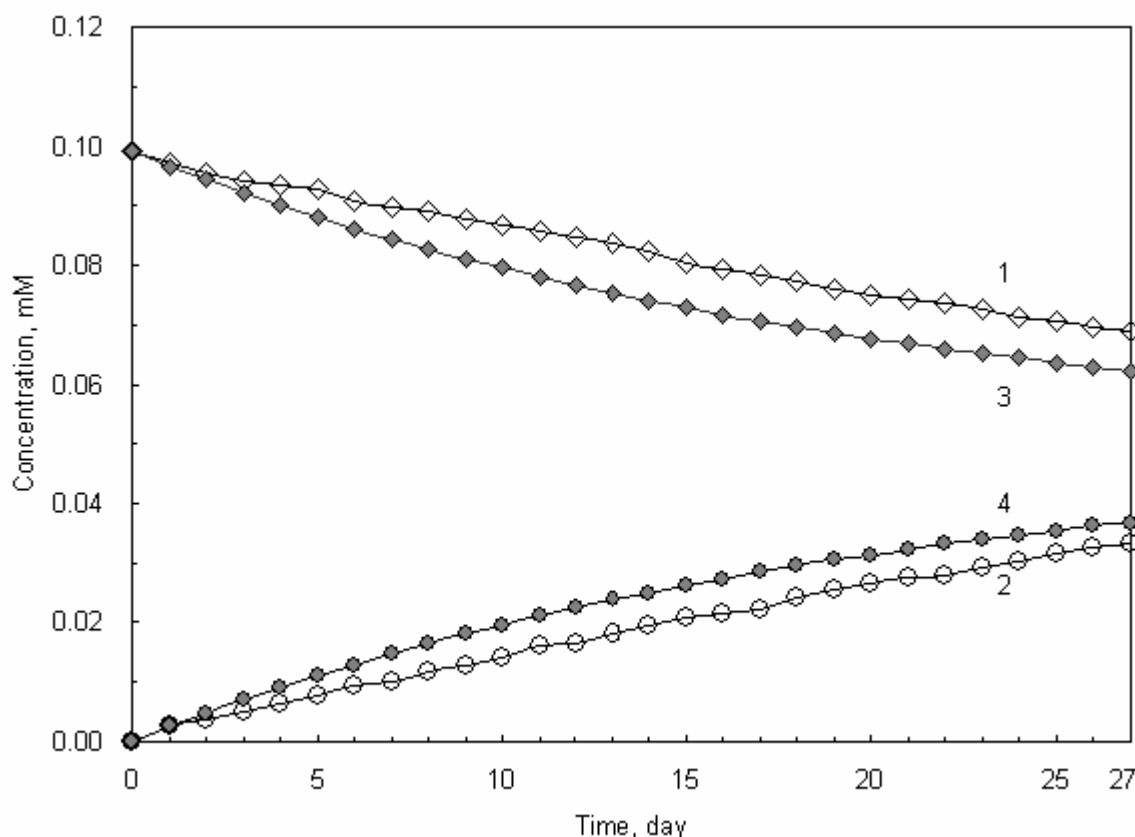

Figure 15.   Transport behavior of Li$^+$ picrate by carrier (**1**) and their numerical simulations. (1, 2) Experiment,[a] (3, 4) calculation;[b] (1, 3) source phase, (2, 4) receiving phase.   [a] The experimental data were shown in Table 9.   [b] These data were calculated by eq (2). The experimental data of *V* for the first day were used for determination of *(D/l)(L$_o$)* value. The values of organic phase were gained from the transport experiments.   Source phase: Tris buffer, 15mL; Li$^+$ picrate (9.9 x 10^{-5} M). Receiving phase: Tris buffer, 15mL. Organic phase: CH$_2$Cl$_2$, 30mL; carrier (**1**) (3.1 x 10^{-5} M).   *K* = 7.12 x 10^{-1}M^{-1}.

CONCLUSION

Carbonyl arm phenanthroline (**1**) was prepared in which two dodecanoylamino moieties were attached as the sidearms to phenanthroline.   A particularly striking feature of carrier (**1**) is the structural simplicity and the synthesis by short route, and hence carrier (**1**) is accessible.   The novelty of the strategy developed by us is the exploitation of acyclic ONNO coordination system to the Li^+ ion.   Various measurements for probing the properties of carrier (**1**) and its lithium complex provided the evidence that carrier (**1**) interacts strongly with the Li^+ ion.

The evaluation of this molecule (**1**) as the carrier afforded notable aspects.   That is, the amide bonds and long hydrocarbon chains in the sidearms cause this acyclic molecule to generate enhanced Li^+ selective ionophoric functions: This carrier (**1**) was able to transport the Li^+ ion with excellent selectivity and fast rate through liquid membranes.   The advantage of this carrier (**1**) compared to other approaches such as the most commonly studied crown ethers is that LiCl is transported efficiently, though LiCl is very difficult to extract the aqueous phase and much of the research focuses on using the lipophilic anion to improve overall transport performance.   The capacity as the carrier depended on the concentration of alkali metal salts in the source phase.   Two transport mechanisms such as strong and weak interaction are proposed for the results of transport experiments.   Molecular orbital studies on two carrier (**1**)-Li^+ complexes with ONNO and NN coordination used in these mechanisms would provide a possibility of supporting our explanation.   The numerical simulation using the rate equation of a simple model suggested that the transport of Li^+ ion by carrier (**1**) proceeds due to the diffusion limited process.   The exploration of the oxygen effect indicates the oxygen atoms of carrier (**1**) to play an important role in making a discrimination between Li^+ and Na^+ ions, though other factors such as size effect and coordination number as ascribed above would contribute to the discrimination.

2,9-Diamino-1,10-phenanthroline synthesized by us has the ease and feasibility of introducing active substituents into the amino groups to realize active carrier, and these simple, acyclic products are capable of binding the lithium ion and has enough capacity to transport only the lithium ion through liquid membranes.   Therefore this new concept found in this study would provide a means to design Li^+selective carrier molecules.

In conclusion, new carrier molecules we present in this paper have the capability to discriminate efficiently only LiCl among various alkali metal chlorides, and hence have the potential to provide practical system of LiCl separation by liquid membranes.   In addition、 the synthetic method by short route also offers access to practical uses.

EXPERIMENTAL

Instruments.   IR spectra were measured on a Perkin-Elmer FT-IR 1720 X spectrometer with a KBr method.   UV-Visible spectra were obtained on a Shimadzu UV-1600 spectrometer at room temperature

in 1-cm quartz cell. ^{1}H-NMR spectra were measured on a JEOL JNM GX-270 spectrometer (270 MHz).   Chemical shifts were reported with ppm units with SiMe$_4$ as an internal standard.   Mass spectra (MS) were taken in a JEOL JMS-700 spectrometer.   Atomic absorption analyses were carried out by a Shimadzu AA-680 spectrometer.

Syntheses.   The reagents used in this study were purchased from Wako Pure Chemical Industries, Ltd. and Kanto Kagaku Co.   Dichloromethane was distilled from calcium hydride under an argon atmosphere. Triethylamine was dried with sodium hydride.   Lauloyl chloride was purchased commercially and used without further purification.   2,9-Diamino-1,10-phenanthroline and 2,9-dichloro-1,10-phenanthroline were prepared by the procedures published by us.[6]

2,9-Didodecanolyamino-1,10-phenanthroline (carrier (1)).   2,9-Diamino-1,10-phenanthroline[6] (0.525 g, 2.50 mmol) was dispersed in dry dichloromethane (30 mL) and triethylamine (1.4 mL, 10 mmol), followed by the slow, dropwise addition of lauroyl chloride (2.4 mL, 10 mmol) under an argon atmosphere.   The solution was stirred at room temperature for 5 h and then, 30 mL of distilled water was added.   The organic layer was separated, washed with distilled water, and evaporated to dryness. The product isolated as solid was purified by column chromatography (silica-gel, 200 Mesh, chloroform), washed with methanol for removal lauroyl chloride, and recrystallized from methanol.   The yield was 74.2 % (1.065 g).   mp 75 – 78 ^{o}C; ^{1}H-NMR (CDCl$_3$, 298K) δ 8.65 (d, H$_{3,8}$), 8.49 (s, NH), 8.27 (d, H$_{4,7}$), 7.70 (s, H$_{5,6}$), 2.44 (t, H$_{12,24}$), 1.77 (m, H$_{13,25}$), 1.27 (H$_{14-21, 26-33}$), 0.88 (t, H$_{22,34}$), J_{34} =J_{78}=8.91 Hz; HRMS (EI$^+$) m/z calcd for C$_{36}$H$_{54}$O$_2$N$_4$: 574.4246, found: 574.4230; IR (KBr) (cm^{-1}) 3291, 2880, 1703, 1657, 1611, 1596, 1577, 1495; UV-vis (CH$_2$Cl$_2$) λ$_{max}$ (ε) 236.2 nm, (35356), 256.2 (32132) 306.0 (35648), 345.6 (1884), 367 (128).

2,9-Didodecanoylamino-1,10-phenanthroline-LiClO$_4$ Complex. (carrier (1)-LiClO$_4$ Complex)
2,9-Didodecanoylamino-1,10-phenanthroline (0.0144g, 5mmol) and LiClO$_4$ (0.0054g, 10mmol) were dissolved in 5 mL of acetone and left for 24 h and the resulting precipitates were collected.   IR (KBr) (cm^{-1}) 2919, 2850, 1677, 1569, 1474.   The trials to obtain the single crystals of carrier (**1**)-LiClO$_4$ complex and related compounds (derivatives of carrier (**1**) with short side chains) were carried out to confirm the structure as solid state by X-Ray structure determination, but these were unsuccessful.

2-Amino-9-dodecanoylamino-1,10-phenanthroline (carrier (6))   2,9-Diamino-1,10-phenanthroline (0.100 g, 0.476 mmol) was dispersed in dry dichloromethane (30 mL) and triethylamine (0.20 mL, 1.44 mmol), followed by the slow, dropwise addition of lauroyl chloride (0.65 mL, 2.73 mmol) under an argon atmosphere.   The solution was stirred at room temperature for 2.5 h and then, 30 mL of distilled water was added.   The organic layer was separated, washed with distilled water, and evaporated to dryness. The product isolated as solid was purified by column chromatography (silica-gel, 200 Mesh, chloroform). The yield was 53.5 % (0.100g).   mp 122.5 – 125.9 ^{o}C; ^{1}H-NMR (CDCl$_3$, 298K) δ 8.57 (d, H$_8$, NH),

8.21 (d, H_7), 7.98 (d, H_4), 7.56 (d, H_6), 7.52 (d, H_5), 5.09 (s, NH_2), 2.43 (t, H_{12}), 1.76 (t, H_{13}), 1.31 (H_{14-21}), 0.88 (t, H_{22}), J_{34} = 8.64Hz, J_{78}=8.91 Hz; MS(EI$^+$) m/z 392; IR (KBr) (cm^{-1}) 3333, 2924, 2852, 1689, 1631, 1446, 1422, 1380; UV-vis (CH$_2$Cl$_2$) λ_{max} (ε) 237.2 nm, (35774), 254.6 (32499), 300.2 (35861).

2-Dodecanoylaminopyridine (Compound (7)) 2-Aminopyridine (0.430 g, 4.57 mmol) was dispersed in dry dichloromethane (50 mL) and triethylamine (1.45 mL, 10.4 mmol), followed by the slow, dropwise addition of lauroyl chloride (1.30 mL, 5.47 mmol) under an argon atmosphere. The solution was stirred at room temperature for 6 h and then, 50 mL of distilled water was added. The organic layer was separated, washed with distilled water, and evaporated to dryness. The product isolated as solid was purified by column chromatography (silica-gel, 200 Mesh, chloroform and hexane). The yield was 5.56 % (0.0702 g). mp 46.2 – 47.3 ^{o}C; ^{1}H-NMR (CDCl$_3$, 298K) δ 8.59 (s, NH), 8.25 (d, H_3), 8.21 (d, H_6), 7.71 (t, H_4), 7.03 (t, H_5), 2.41 (t, H_8), 1.71 (t, H_9), 1.26 (H_{10-17}), 0.88 (t, H_{18}), J_{34} =8.64Hz, J_{45} = 7.29Hz, J_{56} = 5.13Hz, J_{35} = 1.08Hz, J_{46}= 0.81 Hz; HRMS(EI$^+$) m/z calcd for C$_{17}$H$_{28}$ON$_2$: 276.2202, found: 276.2200; IR (KBr) (cm^{-1}) 3354, 2918, 2850, 1687, 1580, 1471, 1437; UV-vis (CH$_2$Cl$_2$) λ_{max} (ε) 235.6 nm (12712), 278.0 (6389).

2,9-Dihexylamino-1,10-phenanthroline (carrier (8)) 2,9-Dichloro-1,10-phenanthroline[6] (0.25g, 1.00 mmol) was added to hexylamine (7 mL, 5.29 mmol) and the mixture was heated at reflux for 6h under nitrogen atmosphere. After cooling, 200mL of distilled water was added. The resulting precipitates were collected and purified by recrystallization from hexane. The yield was 89.6% (0.340g). mp 65 – 68 ^{o}C; ^{1}H-NMR (CDCl$_3$) δ 7.91 (d, $H_{4,7}$), 7.31 (s, $H_{5,6}$), 6.77 (d, $H_{3,8}$), 5.14 (s, NH), 3.42 (m, $H_{11,17}$), 1.69 (m, $H_{12,18}$), 1.46 (m, $H_{13,19}$), 1.35 (m, $H_{14-15, 20-21}$), 0.91 (t, $H_{16,22}$), $J_{3,4}$=$J_{7,8}$=8.91 Hz; HRMS(EI$^+$) m/z calcd for C$_{24}$H$_{34}$N$_4$: 378.2783, found: 378.2767; IR (KBr) (cm^{-1}) 3425, 3263, 2928, 2856, 1618, 1529, 1478, 1439, 1356.

Method of Molecular Orbital Calculations. Geometry optimization of energy minimum structures was carried out at the RHF level of theory with 6-31G (d) basis set for the carrier (**1**)-Li$^+$ complexes with the ONNO coordination and the NN coordination. Gaussian 98 program suite was used for all the calculations reported in this paper on the linux computer, Dell Dimension 8200 in our laboratory.

Transport Measurements[7] Liquid membrane experiments were conducted using open-ended double cylindrical glass cell. The top of this cylinder was covered with a glass lid containing a three way stopcock to minimize evaporation of solvents. A dichloromethane solution (30 mL) containing the carrier (0.5 mmol – 5 mmol) was placed at the base of the cell. The source phase (15 mL) was the aqueous solution containing metal salts, and this was added carefully on the dichloromethane solution in the inner cylinder. The receiving phase was the distilled water (15 mL) which was placed in the outer cylinder. The organic phase was stirred magnetically with 150 rpm. The areas of the inner cylinder

and the outer cylinder were 5.31 and 7.45 cm^2, respectively.   The glass vessel of transport was maintained at 20° C.   After stirring for 72 h, the receiving phase was taken out and the amount of the metal ions transported was measured by atomic absorption analysis (relative error of calibration curve < 1% .   When the picrate was used as the counterion, the amount of the metal picrates transported was analyzed by UV-Visible spectrum measurements.

REFERENCES AND NOTES

1.   (a) N. Sabatini, M. Guardigli, and J. M. Lehn, *Coord. Chem. Rev.,* 1993, **123**, 201. (b) C. Kaes, A. Katz, and M. W. Hosseini, *Chem. Rev*., 2000, **100**, 3553. (c) E. Abel, G. E. M. Maguire, E. S. Meaduws, O. Murillo, T. Jin, and G. W. Gokel, *J. Am. Chem. Soc.,* 1997, **119**, 9061. (d) R. M. Izatt and J. J. Christensen, *Synthetic Multidentate Macrocyclic Compounds*; Academic press: New York, 1978.   (e) L. X. Dang and P. A. Kollman, *J. Am. Chem. Soc.,* 1990, **112**, 5716. (f) ed. by F. Vogtle, *Host Guest. ChemistryII*; Springer-Verlag: Berlin-Heidelberg, 1982. (g) Z. F. Ye, Y. P. Wang, Y. S. Liu, Z. L. Jiang, X. Shen, L. G. Zhu, and X. F. Shi, *J. Memb. Sci*., 1999, **163**, 367. (h) P. Ramirez, A. Alcaraz, S. Mafe, and J. Pellicer, *J. Membr. Sci*., 1999, **161**, 143. (i) G. C. Sahoo, A. C. Ghosh, and N. N. Dutta, *Process Biochem*., 1997, **32**(4), 265. (j) G. C. Sahoo, A. C. Ghosh, N. N. Dutta, and R. K. Mathur, *J. Membr. Sci*., 1996, **112**, 147. (k) I. Tabushi, Y. Kobuke, and J. Imuta, *J. Am. Chem. Soc*., 1980, **102**, 1744. (l) L. A. Frederick, T. M. Fyles, V. A. Malik-Diemer, and M. Whitfield, *J. Chem. Commun*., 1980, 1211. (m) A. P. De Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice, *Chem. Rev*., 1997, **97**, 1515.

2.   (a) M. Erich, D. Rene, and S. Wilhelm, *Anal. Chem*., 1987, **59**, 1600. (b) M. Erich, A. Daniel, A. Robert, and S. Wilhelm, *Anal. Chem*., 1986, **58**, 132. (c) A. Zeevi and R. Margalit, *J. Membr. Biol*., 1985, **86,** 61. (d) J. D. Lamb, R.M. Izatt, D. G. Garrick, J. S. Bradshaw, and J. J. Christensen, *J. Membr. Sci*., 1981, **9**, 83. (e) Y. Kobuke, K. Hanji, M. Asada, Y. Nakayama, and J. Furukawa, *J. Am. Chem. Soc*., 1976, **98**, 7414. (f) Y. Nakatsuji, M. Inoue, M. Matsumoto, A. Masuyama, and T. Kida, *J. Membr. Sci.,* 1995, **104**, 165.

3.   (a) Z. Chen, O. F. Schall, M. Alcalo, Y. Li, G. W. Gokel, and L. Echegoyen, *J. Am. Chem. Soc*., 1992, **114**, 444. (b) N. Malhotra, P. Roepstoff, T. K. Hansen, and J. Becher, *J. Am. Chem. Soc*., 1990, **112**, 3709. (c) J. Rebeck, Jr., B. Askew, D. Nemeth, and K. Parris, *J. Am. Chem. Soc*., 1987, **109**, 2432. (d) K. Kobiro, *Cood. Chem. Rev*., 1996, **148,** 135. (e) Y. Habata, and S. Akabori, *Cood. Chem. Rev*., 1996, **148**, 97. (f) H. Tsukube, *Cood. Chem. Rev*., 1996, **148**, 1.

4.   (a) S. Tsuchiya, Y. Nakatani, R. Ibrahim, and S. Ogawa, *J. Am. Chem. Soc*., 2002, **124**, 4936. (b) A. Furuhama, K. Takano, S. Ogawa, and S. Tsuchiya, *Bull. Chem. Soc. Jpn.,* 2001, **74**, 1241. (c) R. Ibrahim, S. Tsuchiya, and S. Ogawa, *J. Am. Chem. Soc*., 2000, **122**, 12174. (d) K. Takano, A. Furuhama, S. Ogawa, and S. Tsuchiya, *J. Chem. Soc., Perkin Trans. 2,* 1999, 1063. (e) S. Ogawa

and S. Tsuchiya, *Chem. Lett.*, 1996, 709. (f) S. Ogawa, T. Uchida, T. Uchiya, T. Hirano, M. Saburi, and Y. Uchida, *J. Chem. Soc., Perkin Trans.1*, 1990, 1649. (g) S. Ogawa, R. Narushima, and Y. Arai, *J. Am. Chem. Soc.*, 1984, **106**, 5760.

5. S. Tsuchiya, and S. Ogawa, Presented at the CSJ Chemical Meeting, Yokohama, March 1999. The detailed results about new macrocycle (**4**) we synthesized will be published in the future.

6. S. Ogawa, T. Yamaguchi, and N. Gotoh, *J. Chem. Soc., Perkin Trans. 1*, 1974, 976.

7. (a) S. Tsuchiya, Y. Yamada, and M. Seno, *J. Chem. Soc. Chem. Commun.,* 1983, 995. (b) S. Tsuchiya and M. Seno, *J. Phys. Chem.* 1994, **98**, 1682. (c) S. Tsuchiya and M. Seno, *J. Phys. Chem.*, 1994, **98**, 13680.

8. (a) U. Olsher, *J. Am. Chem. Soc.*, 1982, **104**, 4006. (b) J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt, *J. Am. Chem. Soc.,* 1980, **102**, 3399. (c) H. Sun and M. Tabata, *Talanta,* 1999, **49**, 603. (d) H. Sakamoto, K. Kimura, and T. Shono, *Anal. Chem.*, 1987, **59**, 1513.

9. (a) H. Sugihara, and K. Hiratani, *Cood. Chem. Rev.*, 1996, 285. (b) H. Sugihara, J. P. Collin, and K. Hiratani, *Chem. Lett.*, 1994, 397.(c) K. Hiratani, M. Nomoto, H. Sugihara, and T. Okada, *Chem. Lett.*,1990, 43: *Analyst*, 1992, **117**, 1491.

10. N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, 1959, **81**, 6138.

11. H. Tsukube, S. Shinoda, Y. Mizutani, M. Okano, K. Takagi, and K. Hori, *Tetrahedron*, 1997, **53**, 3487.

12. The ^{1}H-NMR peaks of carrier (**1**) can be also assigned by using Figure 2 as follows. The singlet peak (δ 7.80 ppm) of carrier (**1**) should be assigned to $H_{5,6}$ protons because of equivalent H_5 and H_6 protons. There is the possibility that the doublet signal at the lowest field in the spectrum of carrier (**1**) is assigned to either $H_{3,8}$ or $H_{4,7}$ protons. If the doublet signal of the lowest field is assigned to $H_{4,7}$, this doublet signal should be found in much lower field by Li^+ complexation. However, the positions of the lowest field signal (δ 8.58 ppm) of carrier (**1**)-$LiClO_4$ complex (Figure 2 (2)) and the lowest field signal (δ 8.59 ppm) of carrier (**1**) (Figure 2 (1)) remain essentially unchanged in chemical shift, and this is not in agreement with the decrease of electron density by Li^+ complexation. Therefore, this assignment is not correct. On the other hand, if the middle doublet signal (δ 8.40 ppm) in the spectrum of carrier (**1**) (Figure 2 (1)) and the doublet signal (δ 8.58 ppm) of the lowest field in the spectrum of carrier (**1**)- $LiClO_4$ complex (Figure 2 (2)) are assigned to $H_{4,7}$, the peak position (δ 8.58 ppm) in the spectrum of carrier (**1**)-$LiClO_4$ complex can be explained as the result of the lower field shift of $H_{4,7}$ protons by Li^+complexation. Thus, this assignment for $H_{4,7}$ is more reasonable. This conclusion using Figure 2 is the same as that in Figure 1. The fact that carrier (**8**), which does not have the carbonyl group, does not exhibit the deshielding effect of $H_{3,8}$ signals also indicates the peak assignment for carrier (**1**) to be reasonable.

13. The infrared data indicated the evidence that the oxygen atoms of the carbonyl groups interact with

the Li$^+$ ion in the solid state.   We need to explore whether or not the interaction of this type is persisted in solution.   It is possible to obtain this information by infrared measurements using liquid cell.   Attempts were therefore made, but any definite evidence was not observed.   It seems rather difficult to explain this result, though there is a possibility that some technical problems occur.

14. This simple experiment with well-known materials has serious implication for the design of Li$^+$ ion selective carriers and this may show our understanding of the ligands to stabilize the Li$^+$ ion is still in the primitive stage.

15. The ^{1}H-NMR measurements of the mixture of carrier (**1**) and Na$^+$ perchlorate in dichloromethane-d_2 also afforded the same conclusion (Table 2): Remarkable changes in the chemical shift on complexation of carrier (**1**) with Na$^+$ perchlorate were not observed.

16. The solubility of LiClO$_4$ to the water is low and thence, the source phase containing 1 M LiClO$_4$ was not prepared.   However, the source phase containing 1 M LiCl was prepared because of higher solubility of LiCl.

17. I. Tajima, M. Okada, and H. Sumitomo, *J. Am. Chem. Soc.,* 1981. **103**, 4096.

18. The detailed interpretation of carrier (**1**)-Li$^+$ complexes from the quantum chemical viewpoints is in progress and will appear elsewhere.

19. M. Ifuku, E. Araki, M. Kobayashi, S. Tsuchiya, and S. Ogawa, Presented at the CSJ Chemical Meeting, Kobe, March 2001.

20. J. P. Behr, M. Kirch, and J. M. Lehn, *J. Am. Chem. Soc.,* 1985, **107**, 241.

21. Macrocycle (**5**) has been designed to ascertain the functionality of carrier (**1**) and to fortify the assignment of their ^{1}H-NMR spectra.   The trials to prepare pure macrocycle (**5**) are in progress and the data about its synthesis and property will be published in our following papers.

22. These lithium complex and lithium chloride do not have enough solubility to carry out this experiment in dichloromethane.   This experimental result using acetonitrile as the solvent suggests that carrier (**1**) has enough ability to form a 1:1 complex in the organic solvents.

23. T. Kametani and T. Honda, 'Advances in Heterocyclic Chemistry: Application of Aziridines to the Synthesis of Natural Products,' Vol. 39, ed. by A. R. Katritzky, Academic Press, Inc., London, 1986, pp. 181-236.

24. T. Kametani, K. Katoh, M. Tsubuki, and T. Honda, *J. Am. Chem. Soc.*, 1986, **108**, 7055; M. Ihara, K. Noguchi, T. Ohsawa, K. Fukumoto, and T. Kametani, *J. Org. Chem.*, 1983, **48**, 3150; T. Kametani, H. Yukawa, Y. Suzuki, and T. Honda, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2151.

25. L. M. Jackman, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Inc., New York, 1959.