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1,10-Phenanthroline derivatives as ionophores for alkali metal ions

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Contents

Abstract

A number of 1,10-phenanthroline derivatives such as 2,9-dialkyl phenanthroline derivatives, biscrown derivatives which include crown ether moieties via amide groups at the 2 and 9 positions, and oligomethylene bridged phenanthrolines which work as ionophores have been synthesized. Their properties not only as sensing agents for ion-selective electrodes (ISEs) and fluorometry, but also as agents for selective ion transport have been investigated. It has been found that 2,9-dibutyl-1,10-phenanthroline is an excellent Li^+-sensing agent for both ISEs and fluorometry. 1,6-Bis(9-butyl-1,10-phenanthrolin-2-yl)hexane, which is one of the bridged bisphenanthrolines, exhibits high selectivity toward Li^+ among alkali and alkaline earth metal ions in a liquid membrane system. The phenanthroline derivative with bis(benzo-15-crown-5)

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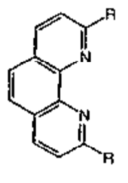
moieties functions as a highly selective K^+ carrier. The relationship between their structure and functions is also discussed.

Keywords: Keywords: Ionophores; 1,10-Phenanthroline; Alkali metals

1. Introduction

1,10-Phenanthroline and its derivatives have been known for a long time to be color reagents for transition metal ions [1], and their selectivity for metal ions largely depends on their substituents at the 2 and 9 positions. 1,10-Phenanthrolines work as bidentate ligands for metal ions. For example, 2,9-dimethyl-1,10-phenanthroline forms a 2:1 complex with many metal ions.

Recently, the rare earth metal ion complex of phenanthroline derivative **3**,



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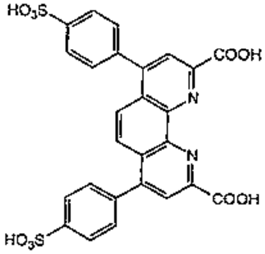
2: R= CH_3



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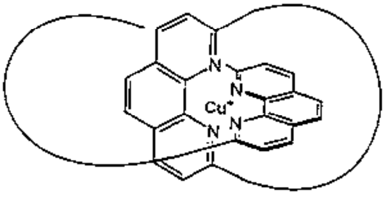
which has dicarboxyl groups at 2 and 9 positions, was reported to be available as a fluorescent reagent for biological systems [2–4]. More recently, phenanthroline derivatives were used as a DNA intercalator [5]. Sauvage's group has studied the synthesis of structurally interesting catenands, knot molecules **4** and **5**,



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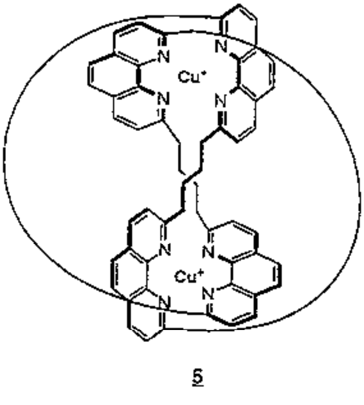

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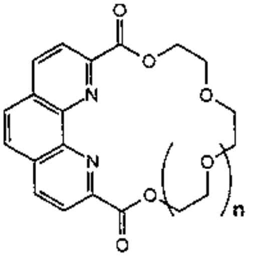
respectively by using a phenanthroline moiety as a building block [6]. Further, macrocyclic compounds containing phenanthroline subunits (**6**, **7**)



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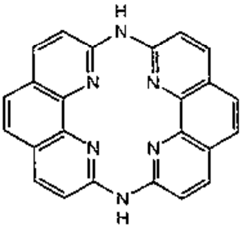

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were synthesized and the characteristics as ionophores were investigated [7–10]. One of the structural features of phenanthrolines is that two nitrogen atoms are immobilized conformationally and as a result they are entropically advantageous in the metal ion complexation. Furthermore, in nucleophilic substitution reactions to the phenanthroline ring, the 2 and 9 positions are more reactive than others so that various substituents could introduce α to the nitrogen.

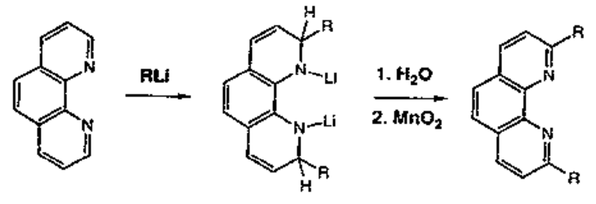
In this article, we mainly review our studies on phenanthroline derivatives which can be applied to separation and detection for some metal ions.

2. Preparation of 1,10-phenanthroline derivatives

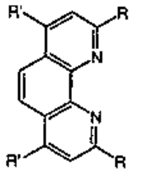
2.1. Preparation of substituted 1,10-phenanthrolines

Compounds having a 1,10-phenanthroline skeleton can be synthesized by the Skraup reaction from *o*-nitroaniline or *o*-phenylenediamine [11]. Substituted phenanthrolines are prepared using substituted precursors [12] or direct introduction of substituents into 1,10-phenanthrolines by substitution or addition reactions. Some direct substitution reactions to phenanthrolines are known, such as nitration at 5 position [13], sulfonylation at 3 and 5 positions [14], bromination at 5 and 6 positions [15].

The characteristics as a ligand for metal ions are known to be largely influenced by the substituents at the 2 and 9 positions of 1,10-phenanthrolines, since these positions are adjacent to ligating nitrogen atoms. However, in order to functionalize the 2 and 9 positions, trihalogenation of 2,9-dimethyl-1,10-phenanthroline using *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) followed by hydrolysis gives carboxylates which can be changed to a variety of carbonyl compounds [2,16]. The methyl groups at 2 and 9 positions can also be oxidized to aldehyde by selenium dioxide [17]. The cyano group can also be introduced at the 2 position [18]. Dietrich-Büchecker et al. achieved direct alkylation or arylation of 1,10-phenanthroline using alkyl or aryl lithium reagents to give 2,9-disubstituted 1,10-phenanthrolines in reasonable yield [19]. In this procedure, as is shown in Scheme 1, addition occurs at 2 and 9 positions of nonsubstituted 1,10-phenanthroline, followed by hydrolysis and rearomatization with manganese dioxide. They introduced a *p*-methoxyphenyl group to phenanthroline, and after removal of the methyl



Scheme 1.



9: R= n-Bu, R'= H
10: R= s-Bu, R'= H
11: R= t-Bu, R'= H
12: R= n-Bu, R'= Ph

Fig. 1. 2,9-Dialkyl-1,10-phenanthroline derivatives.

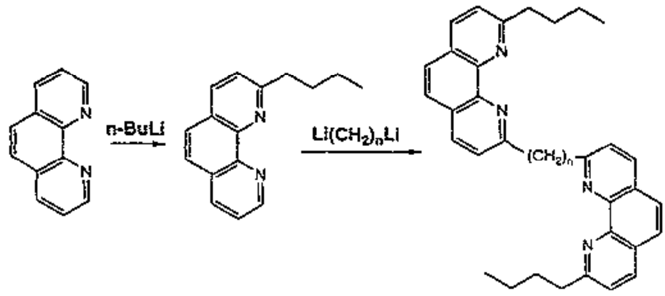
protecting groups, they prepared catenanes and knots in a highly sophisticated manner using Cu(I) as a template [20]. Porphyrines and pyrroles are also introduced in a similar manner [21,22]. We have prepared 2,9-disubstituted phenanthrolines to investigate the relationship between their structure and functions as ionophores. The compounds examined are shown in Fig. 1.

2.2. Preparation of bisphenanthroline derivatives

Recently, the preparation of ligands which contain two or more phenanthroline units has been reported. Bisphenanthrolines bridged with an ethylene chain at 2,2′ or 4,4′ positions were prepared by coupling of two lithiated methyl phenanthrolines [23]. The reaction between 2-(ω-bromoalkyl)-1,10-phenanthroline and lithiated 2-methylphenanthroline also yields bridged phenanthroline. This method was employed in the preparation of bridged trisphenanthrolines [24]. Recently, Cram et al. reported the preparation of a 1,1′-binaphthyl bridged cyclic compound which contains two phenanthroline units [25]. If the method described in the previous paragraph was used in the reaction between α,ω-dilithioalkane [26] and two phenanthrolines, the formation of bisphenanthroline bridged with polymethylene at 2 and 2′ positions was expected, and the reaction proceeded as expected [27]. Bisphenanthrolines bridged with oligomethylenes from tetramethylene to octamethylene were prepared in a similar manner (Scheme 2) [28].

2.3. Preparation of biscrown type ionophores

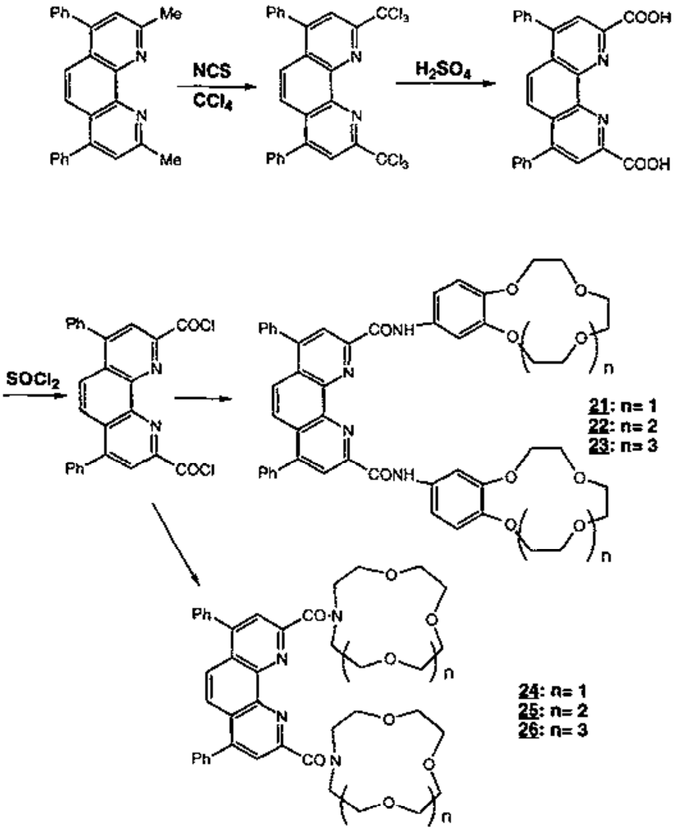
Functional substituents at the 2 and 9 positions of 1,10-phenanthroline might cooperate with each other and exhibit a new function, for the functional groups are juxtaposed in the same direction. We have introduced crown ether moieties, which are well-known units in host–guest chemistry, at the 2 and 9 positions of



Scheme 2.

1,10-phenanthroline. Shono and Kimura et al. have reported that biscrown compounds show good performance as sensing agents for ion-selective electrodes [29].

We prepared 4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxylic acid from 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline as a starting material (Scheme 3) [30].



Scheme 3.

This compound is known to be a fluorescence reagent for detection of protein in biological systems [2–4]. Biscrown type compounds were obtained by the reactions of the acid chloride of phenanthroline and aminobenzocrown ethers or azacrown ethers.

3. Phenanthrolines as ion-sensing agents

3.1. Ionophores for ion-selective electrodes (ISEs)

Ion-selective electrodes (ISEs) have many advantages in the ion activity determining process, i.e., direct and real time monitoring of samples is possible. One of the most popular ISEs is a pH meter using a glass electrode. In these decades, the development of liquid membrane ISEs based on ion exchange liquid or neutral carriers has been carried out [31–33]. Especially, after the development of polymer supported liquid membrane electrodes based on natural ionophores, i.e., valinomycin etc., the design and synthesis of neutral carriers mimicking such natural ionophores has become more important in the field of host–guest chemistry. Although a natural ionophore for a lithium ion, the smallest alkali metal ion in size, is unknown, the preparation of artificial ionophores for a lithium ion has been reported [34]. One of the reasons is that lithium carbonate is used as a medicine to be taken orally for the therapy of manic-depressive psychosis, and the effective concentration and the hazardous concentration are very close in the human body. Therefore, a lithium sensor with high selectivity is required, in order to dose it safely.

We have been engaged in the development of artificial ionophores, especially with the lithium ion, the smallest ion among alkali metal ions, as a target. We found that 2,9-dialkylsubstituted 1,10-phenanthrolines show very high lithium-ion selectivity among alkali metal ions and alkaline earth metal ions [35]. We have investigated the relationship between the structure and selectivity [36].

The performance of ISEs (see Fig. 2) was estimated by determining their selectivity using the following Nicolsky–Eisenman equation by the separate solution method (SSM) and/or the fixed interference ion method (FIM).

$$E = E_0 + (2.3RT/Z_iF \ \log (a_{\mathrm{Li}} + \sum K^{\mathrm{Pot}}_{\mathrm{Li,M}} \, a_{\mathrm{M}}{}^{1/Z_{\mathrm{M}}})$$

where R, a, T, Z and F denote the gas constant, ion activities, absolute temperature, charge of the interfering ion, and Faraday constant, respectively. The selectivity coefficients estimated by SSM are listed in Fig. 3. The response of the electrode based on **9** is shown in Fig. 4. As is shown in Fig. 4(b), in the presence of interfering ions which exist in blood serum, such as sodium and calcium, the electrode showed excellent selectivity. However, this ISE responds to hydrogen ion concentration sensitively, for imide nitrogen atoms tend to be protonated. Therefore, the measurement must be carried out over pH 5. Both with and without phenyl substitutents at the 4 and 7 positions of 1,10-phenanthrolines, the electrodes based on 2,9-dimethyl (**2**) or 2,9-di-*n*-butyl phenanthroline (**9**, **12**) exhibited high lithium selectivity, while the electrodes based on 2,9-di-*sec*-butyl (**10**) or 2,9-di-*tert*-butyl phenanthroline (**11**)

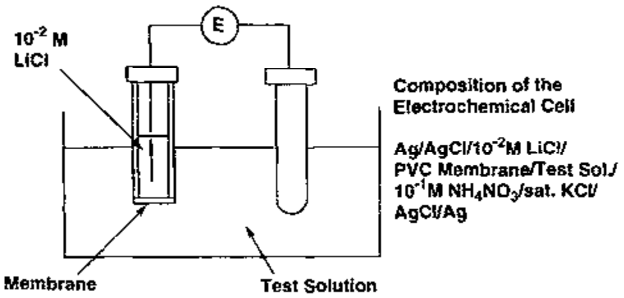


Fig. 2. Schematic model of a membrane electrode measuring circuit and cell.

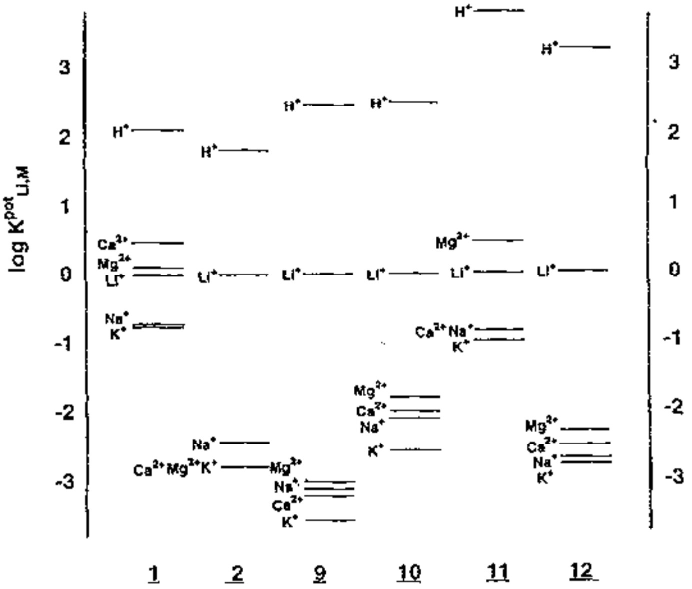


Fig. 3. Selectivity coefficients of the PVC-matrix membrane electrodes based on 1,10-phenanthroline derivatives.

did not show appreciable electromotive response or selectivity. These low responses are due to the steric hindrance of bulky substituents at the 2 and 9 positions of phenanthroline in complexation with lithium ions. The NMR titration showed that 2,9-dimethyl-1,10-phenanthroline and 2,9-di-*n*-butyl-1,10-phenanthroline form complexes in 2:1 stoichiometry with lithium perchlorate [36], and the structures of the complexes were determined by X-ray crystallography, showing the nitrogen atoms of the 1,10-phenanthrolines to be apices of a tetrahedron surrounding a lithium ion, as shown in Fig. 5, while in the case of sec-butyl or tert-butyl substituted phenanthrolines, these substitutents prevent the phenanthroline nitrogen atoms from coming close to each other; consequently, the electrode based on these compounds showed only low responses.

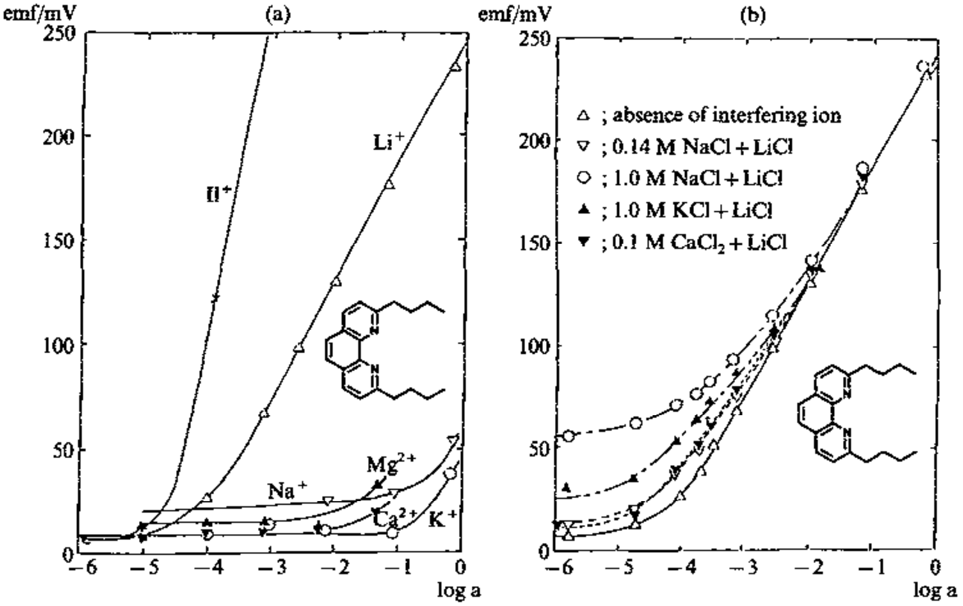


Fig. 4. Calibration curves for the electrode based on **9**. (a) separate solution methods (SSM); (b) fixed interference method (FIM).

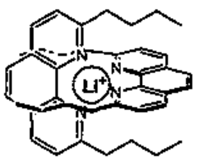
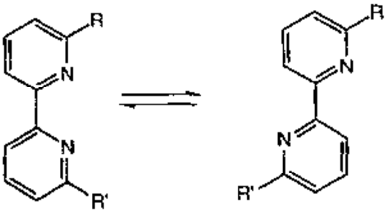


Fig. 5. Schematic representation of 2:1 comples of **9** with Li^+.

Thus, phenanthrolines having methyl or *n*-butyl groups at the 2 and 9 positions were proven to form 2:1 complexes with lithium ions. From this result, we have designed new types of compound which are composed of two phenanthroline units bridged with an oligomethylene chain, expecting an improvement in both complexing ability and selectivity for lithium ions. For this purpose, we prepared several novel bisphenanthrolines with different oligomethylene chain lengths. As a result, the ion sensing electrode based on the 9-*n*-butyl substituted phenanthrolines bridged with oligomethylene at the 2 positions (**15**) showed almost the same selectivity as that based on **9**.

As described above, 2,9-di-*n*-butyl-1,10-phenanthroline (**9**) and bis(9-*n*-butyl-1,10-phenanthrolin-2-yl)hexane (**15**) showed the highest lithium ion-selectivity reported so far.



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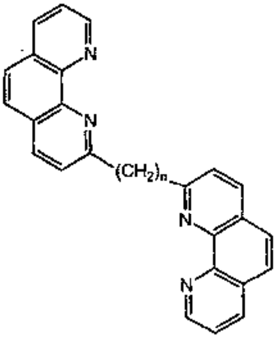

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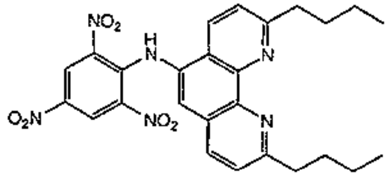
3.2. Phenanthrolines as fluorophores and chromophores

Ionophores which demonstrate fluorescence spectrum or UV-visible spectrum changes upon complexation with ions are called fluorophores and chromophores, respectively. Both are expected to be new probes for optical sensors toward ions [37]. Upon addition of alkali and alkaline metal ions into aprotic solution, i.e., acetonitrile, 1,4-dioxane etc., of 1,10-phenanthroline derivatives, an increase of the fluorescence intensity was observed only upon the addition of lithium ions [38]. The change of fluorescence intensity upon addition of alkali metal ions is shown in Fig. 6.

Fluorescence intensity vs. concentration of alkali metal ions from 10^{-6} M to 10^{0} mol dm^{-3} (=M) are plotted in Fig. 7. Under the concentration range of lithium ion where the fluorescence intensity changes, no interference from added sodium or potassium ion was observed. Therefore compound **9** is a lithium specific fluorophore [39]. The bisphenanthroline with 9-*n*-butyl substituted, bridged with oligomethylene at the 2 positions, showed a similar tendency to nonbridged ones. The complexation constant of 1,6-bis(9-butyl-1,10-phenanthrolin-2-yl)hexane in acetonitrile solution was estimated to be 1.7×10^{6} M^{-1}.

We also developed lithium ion selective chromogenic ionophores composed of 2,9-disubstituted phenanthroline derivatives. Upon addition of lithium ion to the 1,4-dioxane solution of this type of compound, the color of the solution changed from yellow to dark brown [40]. Complexation with lithium ion made the N–H proton of **19** more acidic, which allowed deprotonation under the experimental conditions.



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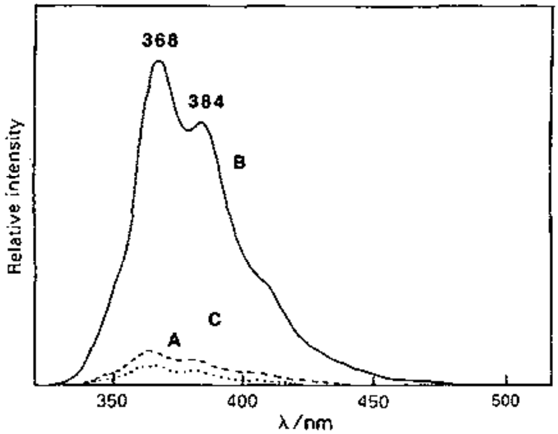


Fig. 6. Effect of the addition of metal ions (0.5 mmol dm^{-3}) on the fluorescent spectra of **9** (0.1 mmol dm^{-3}) in MeCN. Emission spectra excited at 289 nm (23 °C): A, **9** and $\mathbf{9}+Na^+$; B, $\mathbf{9}+Li^+$; and C, $\mathbf{9}+K^+$.

4. 1,10-Phenanthrolines as ion transport agents in liquid membrane systems

4.1. *1,10-Phenanthrolines as lithium ionophores*

Lithium has become more and more important as a material and as an energy resource in the fusion reaction. It is known that tritium, which is a reactant for nuclear fusion, is obtained by irradiation of lithium (atomic weight = 6) by neutrons, and lithium is also used as a coolant for air conditioners or as a coolant for nuclear reactors, as material for batteries, and as a component of an alloy for high performance materials. While inorganic absorbents for lithium harvesting have been studied intensively, we have been trying to develop organic materials for selective lithium ion separation.

We have reported noncyclic polyether carboxylic acid type ionophores as selective lithium ion transporting agents in proton driven uphill transport through liquid membranes. We have also found that several 1,3-bis(quinolyloxy)propane derivatives exhibit appreciable lithium ion selectivity [41,42]. Recently, several phenanthroline derivatives were found to exhibit much better selectivity compared to the lithium ionophores reported so far. Thus, among 1,10-phenanthroline derivatives, 2,9-di-*n*-butyl-1,10-phenanthroline exhibits excellent lithium selectivity compared with non-

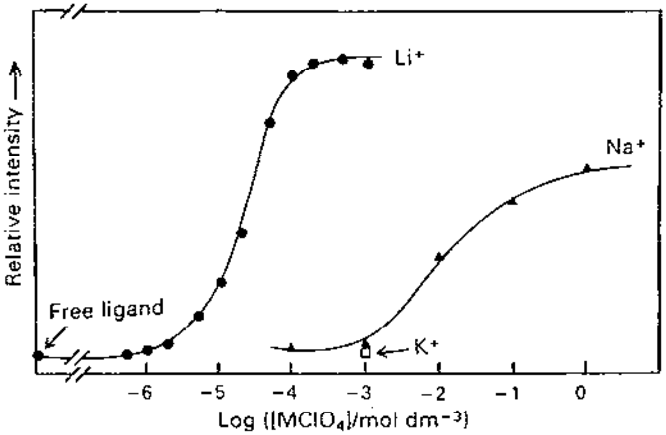


Fig. 7. Plots of fluorescence intensity of 9 (0.1 mmol dm^{-3} in MeCN) versus logarithmic concentration of perchlorate salts of alkali metal ions. Excitation at 289 nm, emission recorded at 368 nm (23 °C). ●, $LiClO_4$; ▲, $NaClO_4$; □, $KClO_4$.

substituted or methyl substituted phenanthrolines. From the results of crystallographic data for 2,9-dimethyl or 2,9-di-*n*-butyl-1,10-phenanthroline, we designed molecules containing two phenanthroline units, which could include a lithium ion in one molecule to form a 1:1 complex with a lithium ion. The compounds with various lengths of bridging oligomethylene were prepared by the reaction path indicated in Scheme 2 [28].

An ion transport experiment through a liquid membrane was carried out using a U-shaped cell. Initial transport conditions were as follows; (source phase) 1.0 mol dm^{-3} of each of LiCl, NaSCN and KSCN in 15 ml of water/(chloroform phase) 0.15 mmol of carrier (0.30 mmol for **9**) in 30 ml of $CHCl_3$/(receiving phase) 15 ml of deionized water; the temperature of the three phases is kept at 25 °C.

The results are shown in Fig. 8 and Table 1. As was expected, a remarkable increase of ion transport rate and ion selectivity was observed for **13**–**17** compared with 2,9-dibutyl-1,10-phenanthroline **9**. Among the various bridge lengths of bisphenanthrolines, tetramethylene to octamethylene, selectivities and transport rates largely depend on the bridge length, and the hexamethylene bridged form showed the highest selectivity for $Li^+/Na^+ = 1850$. This value is extremely high for a liquid membrane ion transport system. Carriers **13** and **14** with a short oligomethylene chain compared with **15** might be unfavorable to form a 1:1 Li^+-complex, thus reducing their Li^+-selectivity. On the contrary, **16** and **17** with a long oligomethylene chain compared with **15** also gave decreased selectivity, probably because of excessive flexibility for the complexation. Although there was little difference in selectivity between the electrode based on 2,9-dibutyl-1,10-phenanthroline and that based on 1,6-bis(9-butyl-1,10-phenanthrolin-2-yl)hexane, there appeared to be a large difference in ion transport selectivity. These results might be explained as follows. While the relative difference of stability reflected the selectivity in ISE, the stability constant

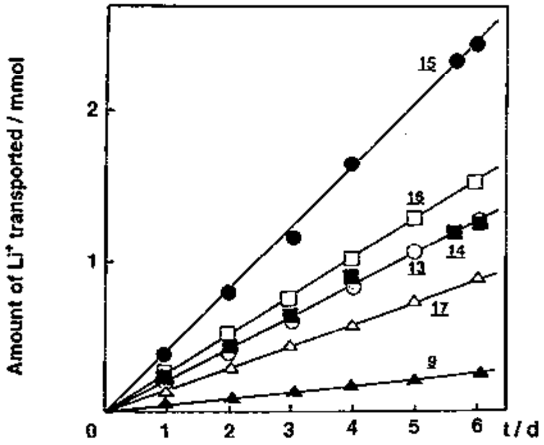


Fig. 8. Plots of amount of Li$^+$ transported by **9**, **13–17** vs. time.

Table 1
Rates of ion transport through chloroform liquid membrane

Phenanthroline derivative	Transport rate (μmol h^{-1} cm^{-2})			Selectivity	
	Li	Na × 10^2	K × 10^2	Li/Na	Li/K
9	1.97	0.33	0.17	600	1160
13	9.19	2.19	0.73	430	1290
14	8.38	8.38	4.16	200	5590
15	17.6	0.95	0.36	1850	4890
16	11.3	0.80	0.80	1410	1410
17	5.90	0.50	0.13	1180	1540

Initial transport conditions (25°C): (source phase) 1.0 mol dm^{-3} of each of LiCl, NaSCN and KSCN in 15 ml water/(chloroform phase) 0.15 mmol of carrier (0.30 mmol for **9**) in 30 ml of $CHCl_3$/(receiving phase) 15 ml of deionized water.

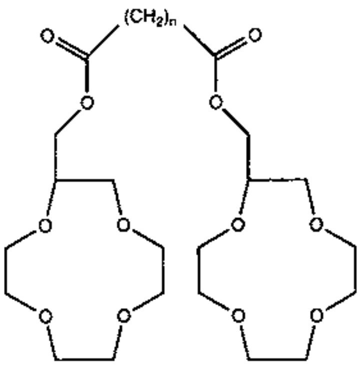
of the complex itself reflected the ion transport rate. The difference should be revealed from a mechanistic point of view.

Bisphenanthroline without substituents showed Mg^{2+} selectivity in its spectroscopic behavior. This is important, since only a few Mg^{2+} selective ionophores have been reported so far.

As shown above, the ion-selectivity varies depending on the structure of substituents on phenanthrolines and the length of the bridging oligomethylene chain. Phenanthrolines are promising candidates for various applications.

4.2. Biscrown type ionophores

In the field of crown ether chemistry, in which cations are captured depending on the sizes of ions and crown ethers, a great deal of work has been done in both fundamental and applicational fields [43]. Compounds which possess two crown ether moieties show excellent properties in their selectivity and ion capturing features compared with monocrown derivatives. For example, bis(14-crown-4)s **20** [29] and bis(15-crown-5)s reported by Shono and Kimura showed sodium and potassium selectivity, respectively, and are useful as ion sensing agents for ion-selective electrodes [44]. In their compounds, the degree of freedom in the rotation of the bridging chain between two crown moieties is relatively large, while our compounds have a restricted degree of freedom because of the rigid structure of phenanthroline as a bridging unit, i.e., two crown ether moieties are juxtaposed in the same direction. Ion transport properties were investigated using compounds **21**–**23**. Compound **22**, which containes benzo-15-crown-5 as cation binding unit, showed good potassium ion selectivity [30] (Fig. 9), while **21** and **23**, which bear benzo-12-crown-4 and benzo-18-crown-6, respectively, did not show an appreciable difference in selectivity.



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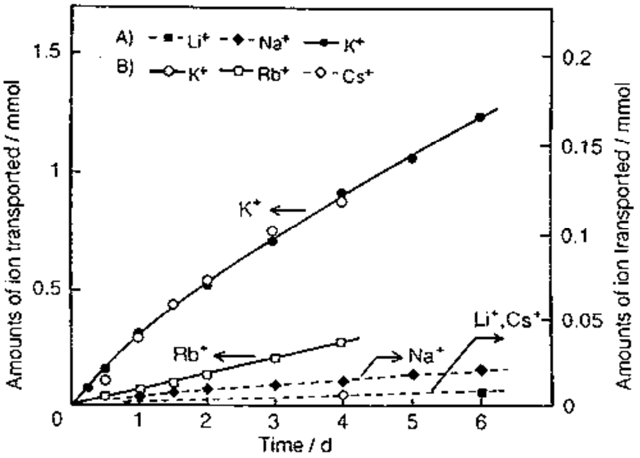

Fig. 9. Time dependence of competitive ion transport with **21**. Initial transport conditions (25 °C): (source phase) 15 ml of (A) 1 M of each of KSCN, NaSCN and LiCL, or (B) 1 M of each of KSCN, RbCL and CsCL, (liquid membrane) 0.1 mmol of **21** in 30 ml of $CHCl_3$, (receiving phase) 15 ml of deionized water.

5. Concluding remarks

We reviewed here our study of phenanthroline derivatives, which we have investigated for several years. 1,10-Phenanthrolines not only with 2,9-alkyl groups but also with 2,9-amide groups have been synthesized and applied to ion-separation and ion-detection. As a sensing reagent, 2,9-di-*n*-butyl-1,10-phenanthroline was found to exhibit excellent selectivity for lithium ion among alkali and alkaline earth metal ions, not only as ion-selective electrodes but also in fluorimetry. As a carrier for ion-separation through liquid membranes, oligomethylene-bridged bisphenanthroline **15** can transport lithium ion with high selectivity.

Thus, we designed and synthesized highly functional phenanthroline molecules, investigating the relationship between their structure and functions.

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