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Highly-selective Li^+ Transport through Liquid Membranes with Oligomethylene-bridged Bisphenanthroline Derivatives

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Newly prepared oligomethylene-bridged bisphenanthrolines have been found to transport lithium ion with excellent selectivity among alkali metal ions through chloroform liquid membrane.

Considerable efforts have been made toward the separation of alkali and alkaline earth metal ions using liquid membranes.1) The separation of Li^+ from other alkali ions, especially from Na^+, is not easy because of its strong hydration and similarity to Na^+. Although no natural Li^+-ionophore is known, a number of synthetic Li^+-ionophores have been reported,2) e.g., spherands3) and cryptands4) as extracting agents, cyclic and noncyclic ethers as ion carriers5,6) in liquid membrane system. Some of them are successfully used in Li^+ sensing systems, e.g., ion selective electrodes7,8) and optical ion sensors.9,10) We have reported that 2,9-dibutyl-1,10-phenanthroline 1 exhibits an excellent Li^+-selectivity when engaged in an ion-selective electrode.11) Compound 1 has been confirmed by NMR titration to form a 2 : 1 complex with Li^+ in solution.9) In the single crystals of 2 : 1 complex with $LiClO_4$, Li^+ was found to be wrapped with two substituted phenanthrolines as depicted in Fig. 1.12)

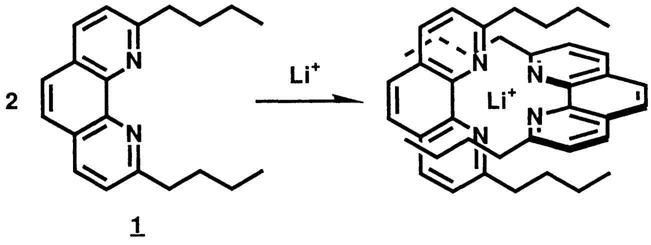

Fig. 1. Schematic representation of 2 : 1 complex of 1 with Li^+.

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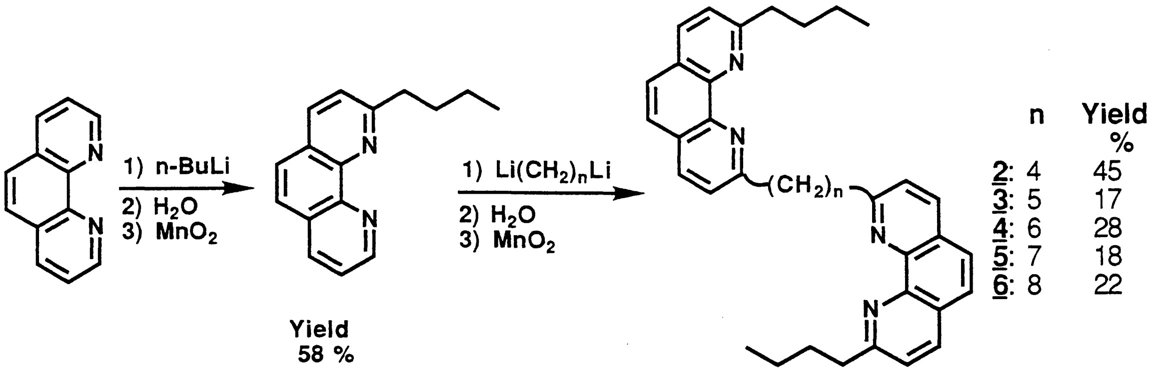
From these results and inspection of CPK molecular models, we have contrived a new type of compounds which are composed of two phenanthrolines bridged with oligomethylene chain expecting the improvement of both complexing ability and selectivity for Li^+. In this work, we report the synthesis of several novel bisphenanthrolines with different length of oligomethylene chain and their ion transport properties in a liquid membrane system. We synthesized the following compounds which could form 1 : 1 complexes with Li^+; 1,4-bis(9-butyl-1,10-phenanthrolin-2-yl)butane(2), 1,5-bis(9-butyl-1,10-phenanthrolin-2-yl)pentane(3), 1,6-bis(9-butyl-1,10-phenanthrolin-2-yl)-hexane(4), 1,7-bis(9-butyl-1,10-phenanthrolin-2-yl)-heptane(5), and 1,8-bis(9-butyl-1,10-phenanthrolin-2-yl)octane(6). 2-Butyl-1,10-phenanthroline was prepared from 1,10-phenanthroline and n-butyl lithium by using a modified procedure previously published.$^{13)}$ Oligomethylene-bridged bisphenanthrolines, 2 - 6,$^{14)}$ were prepared from 2-butyl-1,10-phenanthroline and α,ω-dilithioalkane in a way analogous to previously reported work as depicted in Scheme 1.$^{15)}$



Scheme 1. Preparation of oligomethylene bridged bisphenanthrolines.

Competitive ion transport experiments were carried out under the conditions described in Table 1 by using a U-shaped tube which was kept at 25 °C. Each phase was mechanically agitated at 200 rpm. The amount of ion transported was determined by atomic absorption analysis.

Amount(mmol) of Li^+ transported into the receiving phase is plotted against time in Fig. 2. Even after 6 d, the amount of Li^+ transported increases linearly in all cases. The amounts of Na^+ and K^+ transported are too small to be plotted in this scale. Transport rates for each ion and Li^+ selectivities over Na^+ or K^+ are summarized in Table 1. No ion transport was observed even after 6 d when no carrier was employed. All bisphenanthrolines employed exhibited a good Li^+ selectivity. Both the selectivity and the rate of ion transport varied depending on the length of oligomethylene bridge. The highest selectivity and rate of transport for Li^+ were observed at the hexamethylene-bridged compound 4, which transports

Li^+ 1.85 x 10^3 times faster than Na^+; its turnover number for Li^+ was ca. 2.7 times/d. On the other hand, 2,9-dibutyl-1,10-phenanthroline(1), which showed an excellent selectivity when used in an ion-selective electrode, showed moderate Li^+-selectivity among them.

Carriers, 2 and 3, having short oligomethylene chain compared with 4 might be unfavorable to form 1 : 1 Li^+-complex(cf. Fig. 1), thus reducing their Li^+-selectivity. On the other hand, 5 and 6 having long oligomethylene chain compared with 4 also gave decreased selectivity, probably because of too much flexibility for the complexation.

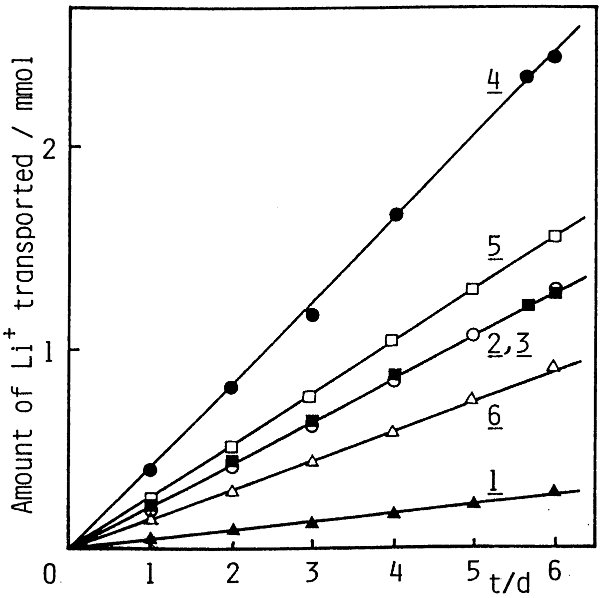


Fig. 2. Plots of amount of Li^+ transported by 1 - 6 vs. time.

Table 1. Rates of ion transport through chloroform liquid membrane[a)]

Phenanthroline Derivatives	Transport rates(μmol/h cm^2)			Selectivity	
	Li	Na x10^2	K x10^2	Li/Na x10^{-3}	Li/K x10^{-3}
1	1.97	0.33	0.17	0.60	1.16
2	9.42	2.19	0.73	0.43	1.29
3	8.39	4.16	0.15	0.20	5.59
4	17.6	0.95	0.36	1.85	4.89
5	11.3	0.80	0.80	1.41	1.41
6	5.90	0.50	0.13	1.18	1.54

a) Initial transport conditions(25 °C):(source phase) 1.0 mol/dm^3 of each LiCl, NaSCN, and KSCN in 15 ml of water/(chloroform phase) 0.15 mmol of carrier(0.30 mmol for 1) in 30 ml of $CHCl_3$/(receiving phase) 15 ml of deionized water.

Thus, oligomethylene-bridged bisphenanthrolines have shown excellent Li^+-selectivity in ion transport through a liquid membrane. Both the rate of ion transport and the ion selectivity largely depended on the length of the oligomethylene chain between two phenanthroline units. Such a type of carriers might find wide applications in analytical and separation science.

References

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14) Compound 2: mp 147.3-147.6 °C; ^{1}H NMR(300 MHz, $CDCl_3$): 8.14(2H, d), 8.13(2H, d), 7.70(4H, s), 7.56(2H, d), 7.51(2H, d), 3.34(4H, t), 3.22 (4H, t), 2.15(4H, m), 1.98(4H, m), 1,53(4H, m), 1.00(6H, t); HRMS Found: 526.3040. Calcd for $C_{36}H_{38}N_4$: 526.3094. Compound 3: mp 150.5-151.4 °C; ^{1}H NMR: 8.14(2H, d), 8.11(2H, d) 7.70(4H, s), 7.53(2H, d), 7.52(2H, d), 3.24 (8H, m), 2.06(4H, m), 1.91(4H, m), 1,70(2H, m), 1.52 (4H, m), 1.00(6H, t); HRMS Found: 540.3229. Calcd for $C_{37}H_{40}N_4$: 540.3250. Compound 4: mp 154.6-155.6 °C; ^{1}H NMR: 8.13(4H, d), 7.70(4H, s), 7.52(2H, d), 7.51(2H, d), 3.22(8H, m), 1.96(8H, m), 1.62 (4H, m), 1.53(4H, m), 1.00(6H, t); HRMS Found: 554.3566. Calcd for $C_{38}H_{42}N_4$ 554.3407. Compound 5: mp 109.5-110.8 °C; ^{1}H NMR: 8.13(4H, d), 7.70(4H, s), 7.51(4H, d), 3.22(8H, t), 1.93(8H, m), 1.58(8H, m), 1,53(4H, m), 1.01(6H, t); HRMS Found: 568.3520. Calcd for $C_{39}H_{44}N_4$: 568.3564. Compound 6: mp 106.7-108.1 °C; ^{1}H NMR: 8.14(4H, d), 7.70(4H, s), 7.52 (4H, d), 3.21(8H, t), 1.93(8H, m), 1.61(8H, m), 1,54(4H, m), 1.01(6H, t); HRMS Found: 582.3639. Calcd for $C_{40}H_{46}N_4$: 582.3720.
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