Sodium-Selective Macrocyclic Polyamine Carriers having Pyridine-Functionalized Sidearms

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A new type of sodium-selective carrier molecule was developed which was characterized by a pyridine-functionalized arm and a parent polyamine ring. Although the parent macrocyclic polyamines are well recognized as potential ligands of 'soft' heavy and transition metal cations, pyridine-armed triamine and tetraamine macrocycles show specific ionophoric activity for the 'hard' Na^+ cation. ^{13}C NMR binding experiments strongly supported the idea that these polyamine carriers completely encapsulated a Na^+ cation *via* sidearm–macroring interaction. Their unique cation-binding properties offered selective and efficient membrane transport of the Na^+ cation. Since their complexation and transport behaviour is largely different from that observed with conventional macrocycles, the present study provides a new possibility for the design of a macrocyclic polyamine carrier exhibiting a specific transport function.

Armed macrocycles represent a family of synthetic cation binders, characterized by a parent macrocyclic ligand and a cation-ligating functionalized sidearm.[1] In this class of compounds, the donor group on the flexible sidearm can provide further co-ordination of a guest cation trapped in the parent macroring. Since these armed macrocycles exhibited three-dimensional and dynamic complexation behaviour, they can be considered as very promising candidates for effective carriers.[2] Macrocyclic polyamines having cation-ligating sidearms are typical examples. The cation-binding property was remarkably modified by the introduction of an additional functionalized sidearm.[3] The parent polyamines are potential ligands for 'soft' metal cations, but some armed macrocyclic polyamines have been presented as three-dimensional ligands for 'hard' metal cations.[4] Although they have rarely been examined as cation carriers, armed macrocyclic polyamines are expected to offer characteristic cation-transport profiles.

Here we report Na^+-selective transport behaviour of new pyridine-armed macrocyclic polyamines.[5] Co-operative binding of a pyridine-functionalized sidearm and a polyamine ring clearly offered a three-dimensional Na^+ complex suitable for effective membrane transport.[6] Since their transport profiles are largely different from those of common polyamine carriers, the present study offers a new strategy for the design of a specific carrier of the macrocyclic polyamine type.

Results and Discussion

Pyridine-armed Macrocyclic Polyamines.—Four kinds of pyridine-armed macrocyclic polyamines, compounds **1a**, **2a**, **3a**

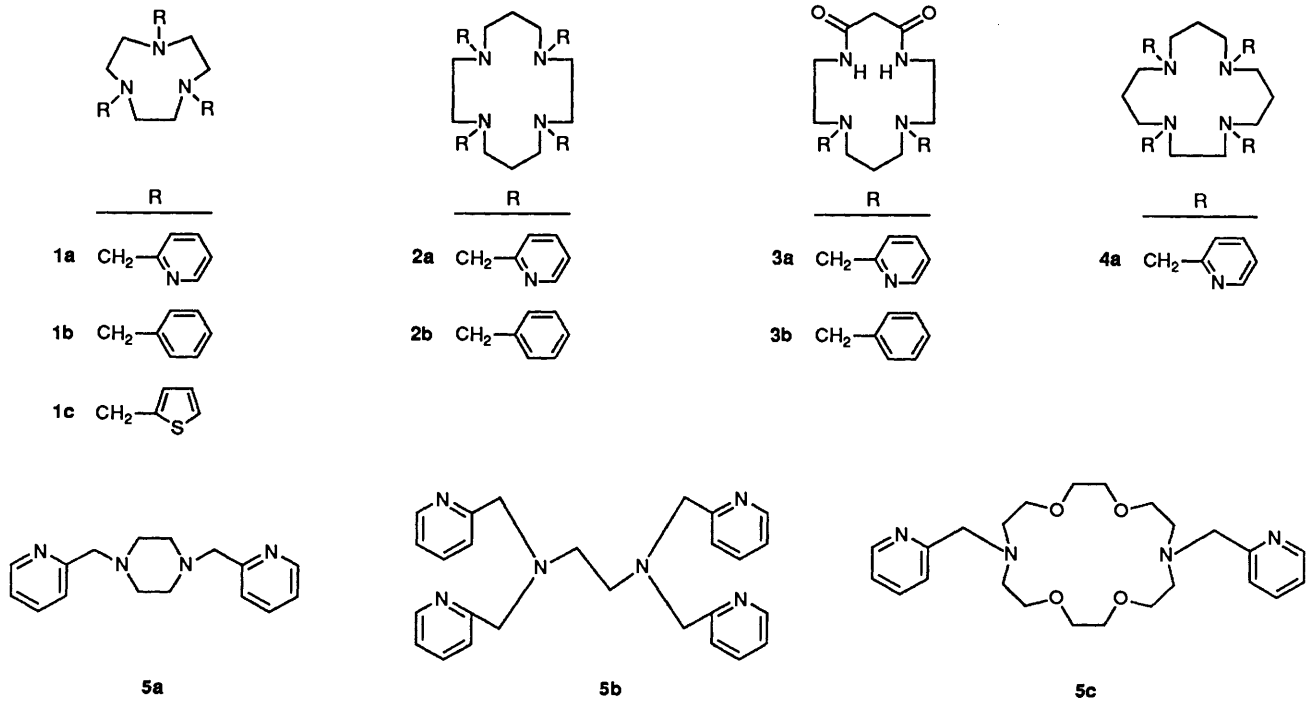


Fig. 1 Molecular structures of pyridine-armed macrocyclic polyamines and related carriers

Table 1 Cation-transport properties of pyridine-armed macrocyclic polyamines and related carriers

Guest cation	Transport rate × 10^6 (mol h^{-1})										
	1a	**1b**	**1c**	**2a**	**2b**	**3a**	**3b**	**4a**	**5a**	**5b**	**5c**
Li^+	*	*	*	0.4	*	*	*	0.4	*	6.2	5.0
Na^+	6.4	*	*	2.2	*	*	*	*	*	3.1	10.5
K^+	*	*	*	*	*	*	*	*	*	*	7.9
Cs^+	*	*	*	*	*	*	*	*	*	*	7.3
Ag^+	*[a]	0.8	0.8	0.4	*	0.4	4.9	*[a]	*	1.0	*
Mg^{2+}	*	*	*	*	*	*	*	*	*	*	*
Ca^{2+}	0.7	*	*	*	*	*	*	*	*	12.8	11.5
Ba^{2+}	1.0	*	*	*	*	*	*	*	*	7.0	3.4
Pb^{2+}	0.9	*	*	*	*	*	*	3.2	0.4	1.1	1.6
Cu^{2+}	3.3	*	*	0.4[a]	0.3[a]	1.2	*	*	*[a]	0.9	2.2[a]
Ni^{2+}	*	*	*	*	*	1.0	*	*	*	*	*
Co^{2+}	*	*	*	0.5[a]	*	*	*	*	*[a]	0.8	0.8[a]
Zn^{2+}	0.7	*	*	*	*[a]	1.4	*	*	*[a]	1.3	4.1

Conditions: Aq. 1: Guest perchlorate (0.50 mmol), water (5 cm^3); Membrane: macrocycle (0.0372 mmol), CH_2Cl_2 (12 cm^3); Aq. 2: water (5 cm^3). * Below limit of detection (< 0.3). [a] A precipitate was observed.

and **4a**, were prepared from the corresponding unsubstituted polyamines (Fig. 1). A combination of a polyamine ring skeleton and a flexible pyridine-functionalized sidearm can offer three-dimensional ligand geometries suitable for the complete envelopment of the guest metal cations. Typically, the pyridine-armed triamine **1a** is expected to provide hexacoordination of guest cations, while tetraamines **2a** and **4a** may form octahedral complexes. The pyridine-armed dioxocyclam **3a** has a somewhat different donor combination, which incorporates amide, amine and pyridine units as cation-binding sites. We compared the cation-binding and transport properties of these pyridine-armed macrocycles with those of the simple polyamines **1b**, **1c**, **2b** and **3b** and the other pyridine-functionalized ligands, **5a**–**5c**.[2e,7] Although some kinds of multiarmed macrocyclic polyamines have been reported to form encapsulated complexes with 'hard' metal cations,[4] their ionophoric functions have rarely been examined. We demonstrated that some armed macrocyclic polyamines acted as specific carriers of a 'hard' Na^+ cation.

Cation-transport Properties of Armed Macrocyclic Polyamines.—Using armed macrocyclic polyamines as synthetic carriers, we performed transport experiments in a CH_2Cl_2 liquid-membrane system.[8] Table 1 summarizes the transport properties of the pyridine-armed macrocyclic polyamines **1a**, **2a**, **3a** and **4a**, and compares them with those of the related polyamines **1b**, **1c**, **2b**, **3b** and **5a**–**5c**. This clearly indicates that pyridine-armed macrocyclic polyamines **1a** and **2a** showed Na^+-selective transport profiles which differed greatly from those of other polyamines.

Pyridine-armed macrocyclic triamine **1a** effectively transported the 'hard' Na^+ cation, while 9-membered triamines **1b** and **1c** having benzene- and thiophene-functionalized arms did little to mediate the transport of any metal cation examined. Although macrocyclic triamines are well known to be potential ligands for 'soft' metal cations,[9] the triamine **1a** exhibited a higher transport rate of 'hard' Na^+ ion than those of 'soft' Pb^{2+}, Cu^{2+} and Zn^{2+} cations. Introduction of the pyridine-functionalized arm clearly enhanced and modified the cation-transport ability of the macrocyclic triamine. Pyridine-armed 14-membered tetramine **2a** also mediated Na^+ transport, but 15-membered tetramine **4a** showed only poor transport of 'hard' metal cations. Hence, the size of the parent polyamine ring should be carefully chosen when the pyridine-functionalized sidearm is attached in order to attain high cation transport. The pyridine-armed dioxocyclam **3a** was also examined. Kimura *et al.* demonstrated that lipophilic dioxocyclam derivatives effectively transported Cu^{2+} cations and protons in opposite directions.[10] Under the conditions employed here, the dioxocyclam **3a** transported 'soft' Ag^+, Cu^{2+}, Ni^{2+} and Zn^{2+} cations together with ClO_4^- anion,* but did little to mediate effective transport of 'hard' alkali and alkaline earth metal cations. The nature of the parent macroring was a major factor in influencing the cation-transport property.

The pyridine-armed ethylenediamine **5b**[7] and the diaza-18-crown-6 **5c**[2e] exhibited higher transport efficiencies for various metal cations than did pyridine-armed macrocyclic polyamines **1a** and **2a**. Since they non-selectively transported both 'soft' and 'hard' metal cations, their transport selectivities were lower than those of polyamines **1a** and **2a**.

Cation-complexation Properties of Armed Macrocyclic Polyamines.—Details of cation-complexation behaviour of pyridine-armed macrocyclic polyamines were obtained *via* ^{13}C NMR binding experiments. Fig. 2 illustrates the Na^+- and K^+-induced changes in the ^{13}C NMR chemical shifts of selected carbon signals of triamines **1a** and **1c** and the ethylenediamine **5b**. The addition of $NaClO_4$ to a dimethylformamide (DMF)-D_2O (4:1) solution of pyridine-armed triamine **1a** caused significant and continuous shifts of the signals for both pyridine and polyamine ring carbons [see Fig. 2(A)]. These titration curves suggest that triamine **1a** forms a three-dimensional and, probably, 1:1 complex with Na^+ cation, in which the pyridine-nitrogen atom on the sidearm effectively co-ordinates with the Na^+ cation trapped in the polyamine ring. On the other hand, this triamine was confirmed to bind K^+ cation very weakly, because the signals for the pyridine and polyamine ring carbons were only slightly shifted even on addition of an excess of $KClO_4$. Hence, pyridine-armed triamine **1a** specifically accommodated a Na^+ cation in the three-dimensional cavity, and effectively transported it across a CH_2Cl_2 membrane. Similar co-operative binding has been observed in the pyridine-armed diaza-crown ether systems.[2e]

Fig. 2(B) indicates that thiophene-armed triamine **1c** poorly binds either Na^+ or K^+ cations. Although it has a polyamine skeleton and a functionalized sidearm, the thiophene-sulphur

* We determined the concentrations of metal cations and cotransported ClO_4^- anion in aq. phase 2. and confirmed that the symport occurred. As reported for the Pb^{II}-dioxocyclam complex, the neutral ligand may form an 'out' complex.[11]

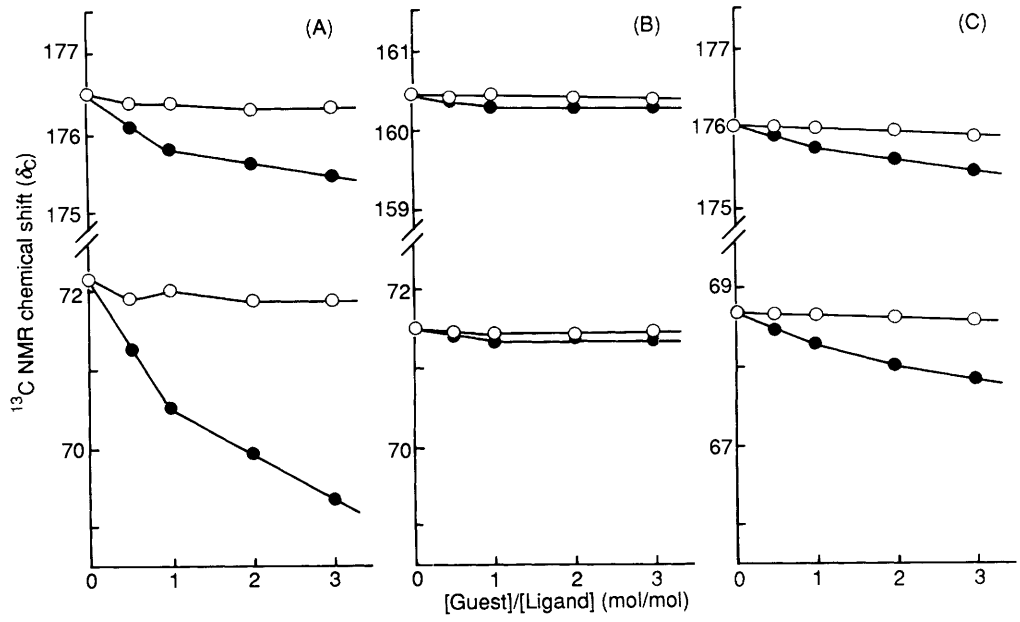
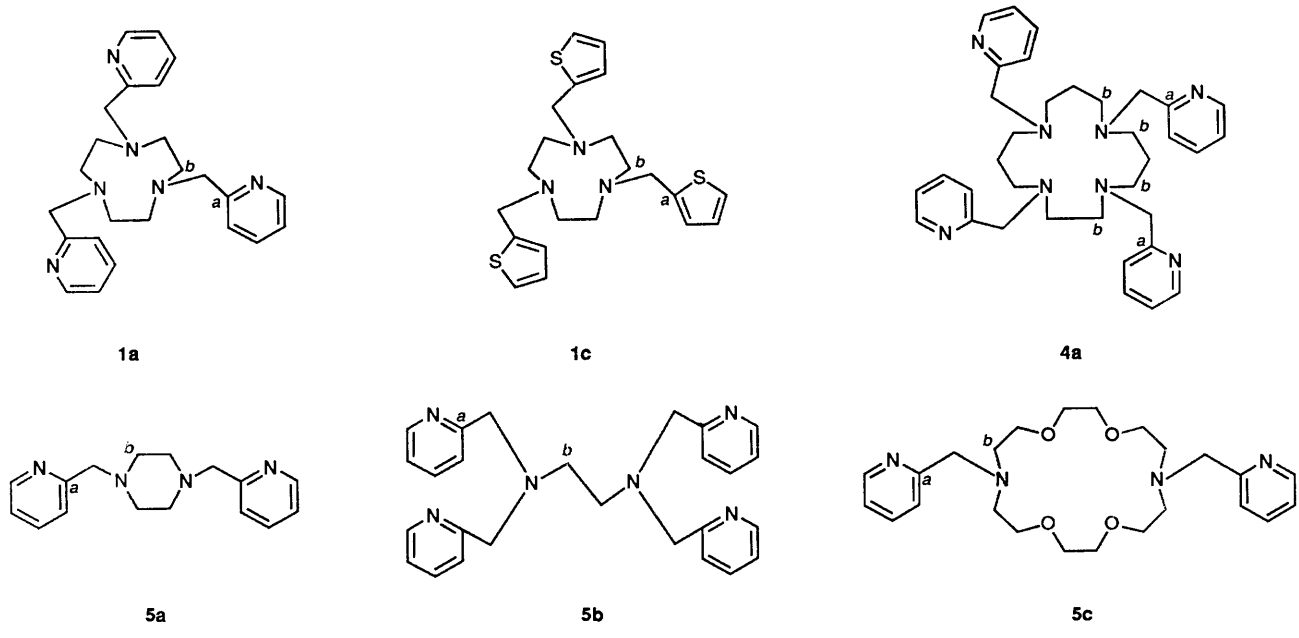


Fig. 2 Na^+- and K^+-induced changes in ^{13}C NMR chemical shifts of pyridine-armed macrocyclic polyamines **1a** (A) and **1c** (B), and the ethylenediamine **5b** (C). Upper and lower lines indicate changes for carbons marked by *a* and *b*, respectively. —●—: Na^+-induced change. —○—: K^+-induced change.



1a **1c** **4a**

5a **5b** **5c**

atom seemed to be an ineffective binding site for these metal cations. In other words, complete inclusion occurs when the macrocyclic polyamine has suitable binding sites on its sidearm. In the pyridine-armed ethylenediamine **5b**–Na^+ cation system [see Fig. 2(C)], the results suggested co-operative binding of pyridine and polyamine nitrogen atoms. Since shallow titration curves were obtained and since the Na^+-induced shift values were small, its complex stability seemed to be lower than that with pyridine-armed triamine **1a**. Therefore, a combination of the triamine macroring and the pyridine-functionalized sidearm offered characteristic cation recognition.

Table 2 summarizes the results of ^{13}C NMR binding experiments for the pyridine-armed macrocyclic polyamines **1a** and **4a** and related ligands **1c**, **5a**, **5b** and **5c** toward Li^+, Na^+, K^+ and Zn^{2+} cations. The data indicate that pyridine-armed triamine **1a** also forms encapsulated complexes with Li^+ and Zn^{2+} cations *via* sidearm–polyamine ring co-operative binding. Although these metal cations induced larger spectral changes than did Na^+ cation, each carbon signal was split into two signals corresponding to the free and complexed forms in the presence of excess of macrocycle (1 > [metal]/[macrocycle]), consistent with slow kinetics of cation exchange on the NMR time-scale. Signals due to the free macrocycle completely disappeared when one equivalent of metal cation was added. This suggests that very static complexes are formed with Li^+ and Zn^{2+} cations. As described above, macrocyclic triamine **1a** transported Na^+ ion much more effectively than Li^+ and Zn^{2+} ions. This supported our hypothesis that dynamic and three-dimensional binding offered fast cation transport. In contrast, polyamines **1c**, **4a** and **5a** were confirmed to bind alkali metal cations only poorly, indicating that stable complexation requires special structural features. The pyridine-armed diaza-18-crown-6 **5c** was confirmed to be a non-selective carrier. This host co-ordinated well with Na^+, K^+ and Zn^{2+} cations and

Table 2 Guest-induced changes in ^{13}C NMR chemical shifts of pyridine-armed ligands

Ligand	Carbon[a]	Induced chemical shift (ppm)			
		Li^+	Na^+	K^+	Zn^{2+}
1a	*a*	−0.8	−0.7	−0.1	br
	b	−4.9	−1.6	−0.1	3.8
1c	*a*	−0.1	−0.2	0	−9.4
	b	−0.1	−0.2	−0.1	−6.6
4a	*a*[b]	−0.2	−0.2	−0.1	br
	b[c]	−0.2	−0.1	−0.1	br
5a	*a*	−0.2	−0.2	−0.2	−2.0
	b	−0.1	−0.2	−0.1	−1.7
5b	*a*	−0.1	−0.3	0	−3.9
	b	−0.1	−0.4	0	4.8
5c	*a*	−0.1	−1.0	−0.9	−3.4
	b	0	−0.2	0.7	4.5

Conditions: Ligand (0.025 mmol). Guest perchlorate (0.025 mmol) in DMF–D_2O (4:1) (0.5 cm^3). Positive is downfield shift. br: These signals were broadened. [a] See structural formulae shown in Fig. 2. [b] The averaged value of two carbon signals. [c] The averaged value of three carbon signals.

effectively transported them.[2e] These observations indicate that, remarkably, arm-functionalization of macrocyclic polyamines provided excellent complexation and transport behaviour toward uncommon guest cations. Further combinations of functionalized sidearms and macrocyclic skeletons are envisaged.

Experimental

^1H NMR spectra were recorded on a JEOL 90A (89.95 MHz) spectrometer for solutions in $CDCl_3$ with Me_4Si as internal reference. ^{13}C NMR spectra were also recorded on the same spectrometer at 25.12 MHz in DMF–D_2O (4:1). Chemical shifts were determined using the peak of the DMF carbonyl carbon (δ_C 180.00) as reference. IR spectra were run on a Hitachi 260–10 spectrometer. M.p.s were measured on a Yanaco MP-3 micro-melting point apparatus and are uncorrected.

Chemical reagents employed were purchased from Nacalai Tesque Inc., Kishida Chemical Co., Tokyo Kasei Co., Kanto Chemical Co., Wako Pure Chemical Industries, Dojindo Laboratories, Alfa Products, and Aldrich Chemical Co. Solvents and the pyridine-armed ethylenediamine **5b** were commercially available and were used without additional purification. Macrocyclic tetraamines **2a** [12] and **2b** [13] and the pyridine-armed diaza-18-crown-6 **5c** [2e] were synthesized by methods described earlier. All new compounds had correct elemental compositions determined by microanalysis (Wako Elemental Analysis Center, Amagasaki, Hyogo) and high-resolution mass spectroscopy (Analytical Center, Department of Chemistry, Kyoto University).

Preparation of Armed Macrocyclic Polyamines.—1,4,7-*Tris*-(2-*pyridylmethyl*)-1,4,7-*triazacyclononane* **1a**. A solution of 1,4,7-triazacyclononane (Aldrich; 1 g, 7.74 mmol), triethylamine (23.37 g, 230 mmol), NaI (1.50 g, 10 mmol) and 2-(chloromethyl)pyridine hydrochloride (18.95 g, 115.5 mmol) in ethanol (20 cm^3) was refluxed for 12 h and then extracted with chloroform. The organic phase was washed with water and dried over Na_2SO_4. The solvent was evaporated off and the residue was purified by column chromatography on alumina with chloroform–hexane (4:1) as eluent (55%, *yellowish oil*): δ_H 2.89 (12 H, s, 3 × NCH_2CH_2N), 3.83 (6 H, s, 3 × CH_2-pyridine) and 7.11, 7.54 and 8.49 (12 H, each m, 3 × pyridine-H); ν_{max}(neat)/cm^{-1} 1590 (Found: M^+, 402.253. $C_{24}H_{30}N_6$ requires *M*, 402.253).

1,4,7-*Tribenzyl*-1,4,7-*triazacyclononane* **1b** was similarly prepared from 1,4,7-triazacyclononane and benzyl bromide (75%; yellowish oil): δ_H 2.80 (12 H, s, 3 × NCH_2CH_2N), 3.57 (6 H, s, 3 × CH_2Ph) and 7.26 (15 H, m, Ph); ν_{max}(neat)/cm^{-1} 1605 (Found: M^+, 399.268. $C_{27}H_{33}N_3$ requires *M*, 399.267).

1,4,7-*Tris*-(2-*thienylmethyl*)-1,4,7-*triazacyclononane* **1c**. To a stirred tetrahydrofuran (THF) solution (20 cm^3) of 1,4,7-triazacyclononane (1 g, 7.74 mmol) and pyridine (3.95 g, 19.9 mmol) was added dropwise thiophene-2-carbonyl chloride (4.54 g, 30.97 mmol). After the mixture had been refluxed for 8 h, the solvent was evaporated off. A $CHCl_3$ solution of the residue was washed successively with aq. HCl and water, and dried over Na_2SO_4. The white solid amide was purified by column chromatography on alumina ($CHCl_3$) and dried *in vacuo*.

The obtained amide was reduced by diborane under dry N_2 as follows: The amide (2.878 g, 6.05 mmol) was suspended in a 1 mol dm^{-3} solution of diborane in THF (100 cm^3). The reaction mixture was refluxed for 8 h. After the usual work-up, the *title material* was purified by column chromatogaphy on alumina with CH_2Cl_2–hexane (2:1) as eluent (40%; yellowish oil: δ_H 2.86 (12 H, s, 3 × NCH_2CH_2N), 3.82 (6 H, s, 3 × CH_2-thiophene) and 6.86 and 7.17 (9 H, 2 × m, 3 × thiophene-H); ν_{max}(neat)/cm^{-1} 690 (Found: M^+, 417.136. $C_{24}H_{30}N_6$ requires *M*, 417.136).

1,11-*Bis*-(2-*pyridylmethyl*)-1,4,8,11-*tetraazacyclotetradecane*-5,7-*dione* **3a** was prepared from 1,4,8,11-tetraazacyclotetradecane-5,7-dione (Aldrich) and 2-(chloromethyl)pyridine hydrochloride and was recrystallized from methylene dichloride–diethyl ether (80%), m.p. 151–152 °C; δ_H 1.68 (2 H, quin, $CH_2CH_2CH_2$), 2.49 and 2.59 (8 H, 2 × t, 4 × pyridyl-CH_2NCH_2), 3.27 (2 H, s, $COCH_2CO$), 3.37 (4 H, t, 2 × $NHCH_2$), 3.68 (4 H, s, 2 × CH_2-pyridine) and 7.26, 7.64 and 8.53 (10 H, each m, 2 × NH + pyridine-H); ν_{max}(Nujol)/cm^{-1} 1680, 1660 and 1590 (Found: C, 64.5; H, 7.4; N, 20.5. $C_{22}H_{30}N_6O_2$ requires C, 64.4; H, 7.4; N, 20.5%).

1,11-*Dibenzyl*-1,4,8,11-*tetraazacyclotetradecane*-5,7-*dione* **3b** was obtained as crystals (85%), m.p. 187–188 °C; δ_H 1.60 (2 H, quin, $CH_2CH_2CH_2$), 2.43 and 2.57 (8 H, 2 × t, 4 × benzyl-NCH_2), 3.20 (2 H, s, $COCH_2CO$), 3.34 (4 H, t, 2 × $NHCH_2$), 3.51 (4 H, s, 2 × CH_2Ph), 6.54 (2 H, br, 2 × NH) and 7.26 (10 H, m, 2 × Ph); ν_{max}(Nujol)/cm^{-1} 1670 and 1630 (Found: C, 70.8; H, 7.8; N, 13.6. $C_{24}H_{32}N_4O_2$ requires C, 70.6; H, 7.9; N, 13.7%).

1,4,8,12-*Tetrakis*-(2-*pyridylmethyl*)-1,4,8,12-*tetraazacyclopentadecane* **4a** was derived from 1,4,8,12-tetraazacyclopentadecane (Aldrich) and was recrystallized from diethyl ether (45%), m.p. 91–92 °C; δ_H 1.71 (6 H, m, 3 × $CH_2CH_2CH_2$), 2.54 (12 H, t, 3 × $NCH_2CH_2CH_2N$), 2.69 (4 H, s, NCH_2CH_2N) 3.66 (8 H, s, 4 × CH_2-pyridine) and 7.09, 7.43 and 8.46 (16 H, each m, 4 × pyridine-H); ν_{max}(Nujol)/cm^{-1} 1580 (Found: C, 72.5; H, 8.1; N, 19.2. $C_{35}H_{46}N_8$ requires C, 72.6; H, 8.0; N, 19.4%).

N,N′-*Bis*-(2-*pyridylmethyl*)*piperazine* **5a** was similarly synthesized, and was recrystallized from hexane (90%), m.p. 96–97 °C; δ_H 2.58 (8 H, s, 2 × NCH_2CH_2N), 3.68 (4 H, s, 2 × CH_2-pyridine) and 7.21, 7.55 and 8.55 (8 H, each m, 2 × pyridine-H); ν_{max}(Nujol)/cm^{-1} 1582 (Found: C, 71.6; H, 7.6; N, 20.8. $C_{16}H_{20}N_4$ requires C, 71.6; H, 7.5; N, 20.9%).

Transport Experiments.—Transport experiments were performed at room temperature (*ca.* 20 °C) in a U-tube glass cell (2.0 cm id). The carrier, dissolved in methylene dichloride, was placed in the base of the U-tube, and two aq. phases were placed in the tube arms, floating on the membrane phase. The membrane phase was constantly stirred with a magnetic stirrer. The transport rates indicated in Table 1 were calculated from

the initial rates of appearance of cotransported ClO_4^- anion into aq. phase 2, which was determined by a ClO_4^- ion-selective electrode (Orion 93–81). The transported amount of each guest cation was also determined by atomic absorption or flame spectroscopy (carried out at Exlan Technical Center Co., Okayama), and was almost equal to that of the cotransported anion. We confirmed that all guest salts were rarely transported in the absence of carrier (transport rate $< 0.3 \times 10^{-6}$ mol^{-1} h).

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