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Transport of Alkali Halides through a Liquid Organic Membrane Containing a Ditopic Salt-Binding Receptor

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A ditopic receptor is shown to have an impressive ability to recognize and extract the ion pairs of various alkali halides into organic solution. X-ray diffraction analysis indicates that the salts are bound in the solid state as contact ion pairs. Transport experiments, using a supported liquid membrane and high salt concentration in the source phase, show that the ditopic receptor can transport alkali halide salts up to 10-fold faster than a monotopic cation or anion receptor and 2-fold faster than a binary mixture of cation and anion receptors. All transport systems exhibit the same qualitative order of ion selectivity; that is, for a constant anion, the cation selectivity order is $K^+ > Na^+ > Li^+$, and for a constant cation, the anion transport selectivity order is $I^- > Br^- > Cl^-$. The data suggest that with a ditopic receptor, the polarity of the receptor–salt complex can be lowered if the salt is bound as an associated ion pair, which leads to a faster diffusion through the membrane and a higher maximal flux.

Introduction

Liquid extraction and liquid membrane transport are two closely related purification processes that can be employed on an industrial scale.[1] The principle of using phase-transfer agents to selectively complex a target ion has been pursued for some time.[2] Indeed, organic soluble salts with lipophilic cations or anions (such as tetraalkylammonium or tetraarylborate salts) are often used as phase-transfer agents that operate by ion-exchange processes.[3] In the case of uncharged phase-transfer agents, such as crown ethers, the process is formally a salt transfer since electrical neutrality must be maintained. Typically in this situation, the cation selectivity is determined by the structure of the crown ether; however, the efficiency of the process is strongly dependent on the structure of the counteranion.[4] Currently, there is an active effort to develop molecular complexation systems that simultaneously bind both the cation and the anion. Two strategies can be envisioned: a binary mixture of cation receptor and anion receptor (dual receptor strategy)[5] or a single ditopic receptor with defined cation and anion binding sites (ditopic receptor strategy).[6] Although there have been a large number of recent reports of ditopic salt-binding systems, very few have attempted to evaluate the effectiveness of the design in extraction and membrane transport.[6a,m−o,7] The most detailed transport study was reported in 1999 by Reinhoudt and co-workers.[7a] They compared the membrane transport properties of ditopic calixarene receptors with different mixtures of cation and anion receptors. In the case of KCl transport, they observed that when the source phase's salt concentration was high enough to saturate the membrane-bound receptor, transport with the dual receptor mixture was

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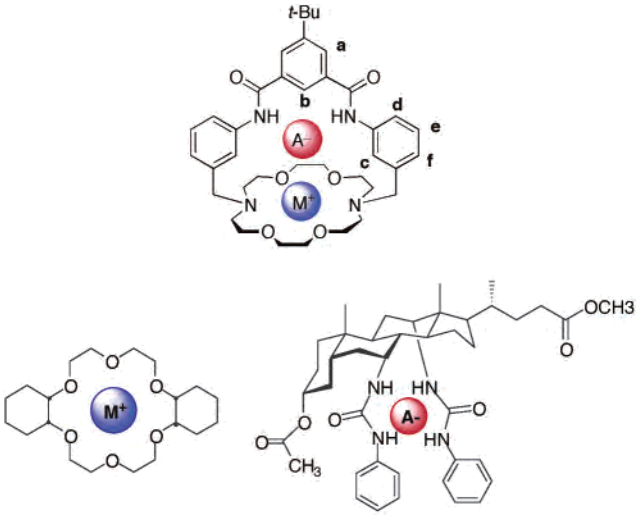
almost 2-fold faster than that with the ditopic receptor. They tentatively attributed the result to the slow diffusion of the zwitterionic, salt-bound ditopic receptor through the liquid organic membrane.

In 2001, we reported the synthesis of ditopic receptor **1** and showed that it has an impressive ability to recognize and extract the ion pairs of sodium and potassium chloride.[8] We now disclose that **1** is able to form organic soluble complexes with many other alkali halide salts. X-ray diffraction analysis shows that these salts are bound as contact ion pairs. We also evaluate the ability of **1** to transport the salts through a liquid organic membrane. We demonstrate that, unlike the Reinhoudt transport system mentioned above, the ditopic receptor **1** is a more effective membrane transporter under salt-saturating conditions than a binary mixture of cation and anion receptors, **2** and **3** (Scheme 1).

Scheme 1. Ditopic Salt Receptor **1** (Top), Monotopic Cation Receptor **2** (Bottom Left), and Monotopic Anion Receptor **3** (Bottom Right)



Results and Discussion

Salt Solubilization Studies. Solid−liquid extraction studies were performed by allowing a solution of **1** in $CDCl_3$ to be exposed to an excess of powdered NaCl, NaBr, NaI, KCl, KBr, or KI. The extractions were monitored by ^{1}H NMR. Peaks corresponding to the receptor−salt complexes grew over time (Figure 1). The changes in the receptor chemical shift (Table 1) are consistent with the formation of a receptor−salt complex, with the salt bound inside the receptor cavity.[8a] Receptor saturation generally took 2 weeks for a 10 mM solution of **1**. Mass spectral analysis of the receptor−salt solutions revealed evidence of 1:1 receptor−salt complexes. For example, a solution of **1** that had been exposed to NaCl showed a peak at *m*/*z* 693 for [**1**·Cl^-]$^-$, *m*/*z* 715 for [**1**·NaCl−H]$^-$ (negative ion FAB), and *m*/*z* 681 for [**1**·Na^+]$^+$ (positive ion FAB). No higher binding stoichiometries were observed.

X-ray Crystal Structures. Slow evaporation of solutions of the receptor−salt complexes in ethyl acetate produced single crystals that were suitable for analysis by X-ray diffraction. The crystal structures for **1**·NaBr, **1**·KBr, **1**·NaI, and **1**·KI are depicted in Figures 2 and 3 (the crystal structures for **1**·NaCl and **1**·KCl have been communicated previously).[8a] In each example, the salts are bound to the receptor as contact ion pairs.[9] A listing of selected supramolecular distances is provided in Table 2. The average cation−crown oxygen distances (M−O) and anion−amide nitrogen distances (A−N) are close to those previously reported in the literature.[10,11] Provided in Table 3 is a comparison of the distance between the cation and anion when they are bound in the receptor and when they are in a crystalline lattice. Except for KI, the M−A distance is shorter when the salt is bound to the receptor.

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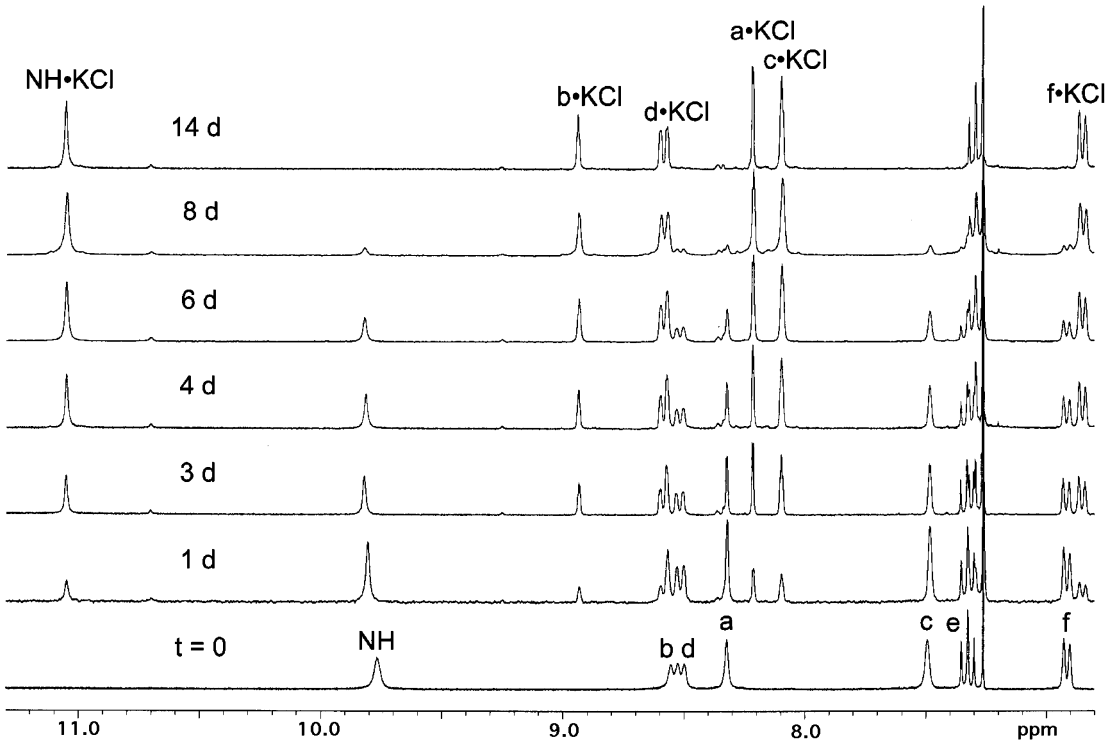

Figure 1. Partial ^{1}H NMR spectrum of **1** extracting KCl into $CDCl_3$.

Table 1. Changes in ^{1}H NMR Chemical Shifts (parts per million) for Receptor **1** upon Salt Extraction into $CDCl_3$[a]

proton	NaCl	KCl	NaBr	KBr	NaI	KI
NH	+0.94	+1.32	+0.83	+0.97	+0.39	+0.44
H_a	+0.02	−0.11	+0.17	−0.10	+0.11	+0.00
H_b	+0.66	+0.44	+0.55	+0.23	−0.01	+0.07
H_c	+0.87	+0.61	+0.81	+0.69	+0.72	+0.72
H_d	+0.07	+0.05	−0.02	+0.02	−0.15	+0.00
H_e	−0.05	+0.00	−0.02	−0.01	−0.02	+0.00
H_f	−0.06	−0.01	−0.06	−0.05	−0.05	−0.04

[a] T = 295 K. See Scheme 1 for hydrogen labeling scheme. Negative values indicate upfield movement toward zero parts per million. All spectra are referenced to tetramethylsilane (0.00 ppm).

Table 2. Average Supramolecular Distances (Å) for **1**·MA Complexes

	A−N[a]	M−O[b]
1·NaCl[c]	3.35	2.45
1·NaBr	3.51	2.49
1·NaI	3.67	2.46
1·KCl[c,d]	3.30	2.77
1·KBr[d]	3.55	2.75
1·KI	3.71	2.91

[a] Average distance from receptor amide nitrogens to bound anion. [b] Average distance from receptor crown oxygens to bound cation. [c] From ref 8a. [d] Average of the two complexes in the unit cell.

Membrane Transport. We have previously reported on the ability of **1** to transport KCl across a phospholipid bilayer membrane.[8b] Here, we evaluate its ability to transport various alkali halide salts through a supported liquid membrane (SLM). The transport apparatus has been described previously.[13] In short, the receptor is dissolved in 2-nitrophenyl octylether (NPOE) and the organic liquid immobilized in a thin, flat sheet of porous polypropylene. Initially, the source phase consisted of 1 M aqueous salt solution, and the membrane contained the receptor at 50 mM. The data in Table 4 are the initial fluxes that were observed for the noncompetitive transport of salts mediated by **1** and by *cis*-dicyclohexano-18-crown-6, **2**. Inspection of Table 4 shows that transport fluxes with ditopic **1** are up to 10-fold higher than those with monotopic **2**. Both transport systems exhibit the same qualitative order of ion selectivity; that is, for a constant anion, the cation selectivity order is $K^+ > Na^+ > Li^+$, and for a constant cation, the anion transport selectivity order is $I^- > Br^- > Cl^-$. A competitive transport experiment was conducted with a membrane containing **1** (50 mM) and a source phase containing a mixture of KCl, NaCl, and LiCl (1 M each). After 3 h of transport, the ratio of metal cations

Table 3. Alkali Halide Distances (Å) for Crystalline Salt and Salt Bound to **1**

	crystalline[a]	[**1**·MA]
NaCl	2.76	2.702(2)[b]
NaBr	2.98	2.793(2)
NaI	3.23	2.975(2)
KCl	3.14	3.04[b,c]
KBr	3.29	3.17[c]
KI	3.53	3.798(2)

[a] From ref 12. [b] From ref 8a. [c] Average of the two complexes in the unit cell.

(11) A−N distances for hydrogen-bonded halide−amide complexes follow. (a) Cl−N, 3.33 Å: Deetz, M. J.; Shang, M.; Smith, B. D. *J. Am. Chem. Soc.* **2000**, *122*, 6201−6207. (b) Br−N, 3.54 Å: Kavallieratos, K.; Bertao, C. M.; Crabtree, R. H. *J. Org. Chem.* **1999**, *64*, 1675−1683. (c) I−N, ∼3.75 Å: Jeffreys, J. A. D.; Ferguson, G. *J. Chem. Soc. B* **1970**, 826−829. Funato, N.; Takayanagi, H.; Konda, Y.; Toda, Y.; Harigaya, Y.; Iwai, Y.; Omura, S. *Tetrahedron Lett.* **1994**, *35*, 1251−1254.

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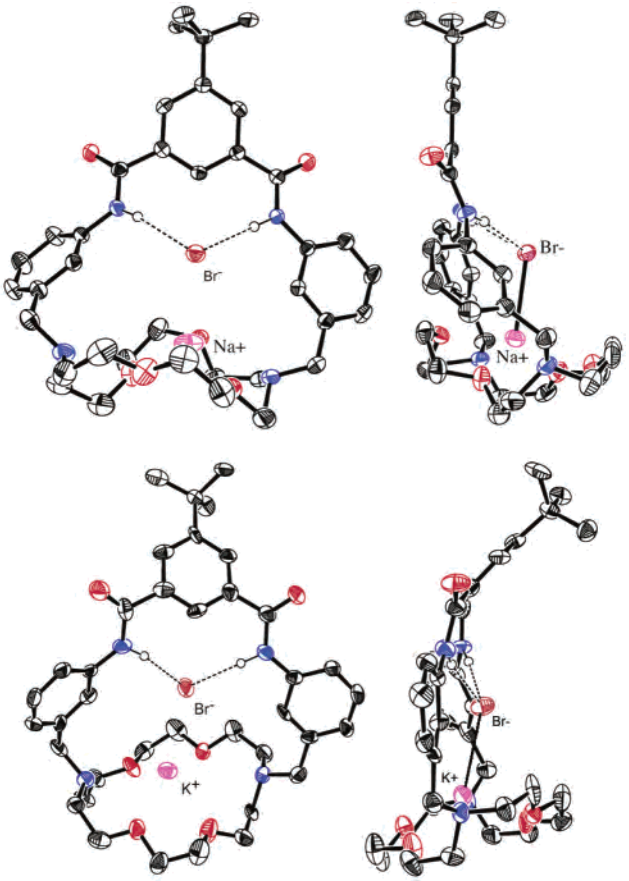


Figure 2. Front and side views of ORTEP structures showing 50% probability ellipsoids. Top: [**1**·NaBr]. Bottom: [**1**·KBr]. Only the relevant protons are shown. The ionic M−Br bond in the front view and lattice-included solvent have been omitted for clarity.

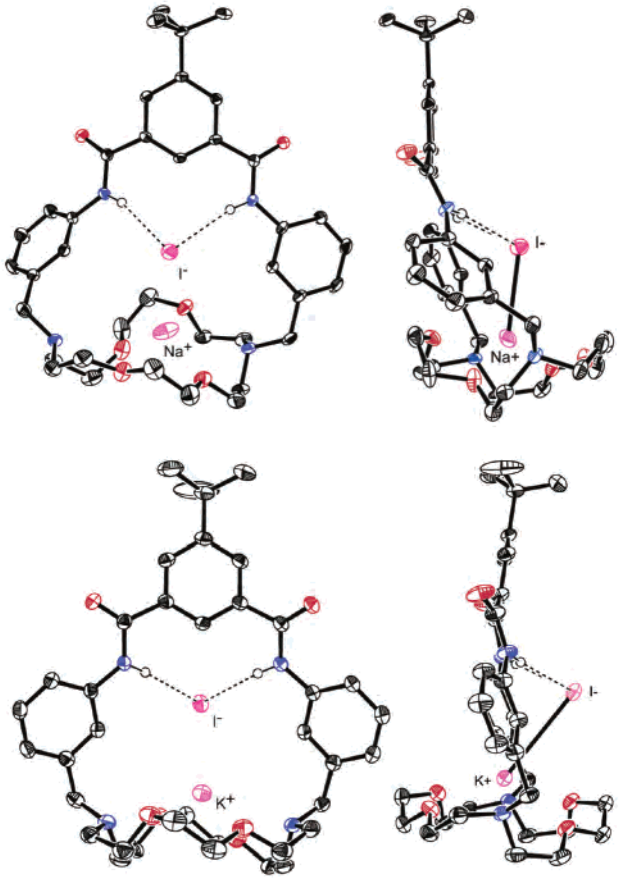


Figure 3. Front and side views of ORTEP structures showing 50% probability ellipsoids. Top: [**1**·NaI]. Bottom: [**1**·KI]. Only the relevant protons are shown. The ionic M−I bond in the front view and lattice-included solvent have been omitted for clarity.

in the receiving phase was found to be 81% K^+, 19% Na^+, and 0% Li^+, which matches the order of noncompetitive fluxes. These trends are in general agreement with the Hofmeister series, a solvation-based selectivity bias that is typically observed for liquid−liquid partitioning processes.[14] Transport fluxes decrease with the smaller, more charge-dense ions because they have a more unfavorable Gibbs free energy for aqueous to organic transfer.[15] It appears that the Hofmeister bias overwhelms any differences in the salt−receptor binding affinities.

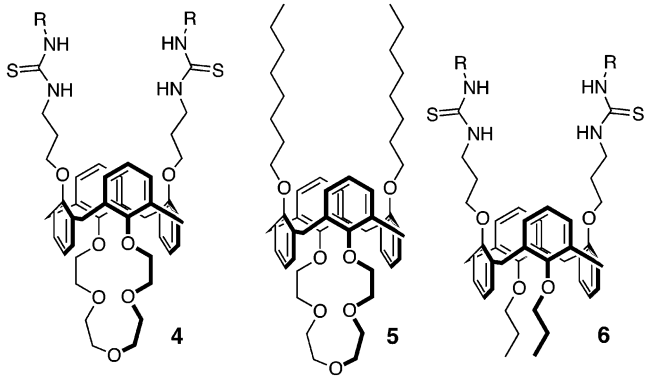
Comparison of the Ditopic Receptor with the Dual Carrier Receptor. Before the current transport system is discussed further, it is worth summarizing in more detail the Reinhoudt transport results mentioned briefly in the Introduction. In the case of KCl transport, Reinhoudt observed that when the salt concentration in the source phase was high enough (>0.5 M) to saturate the receptor, the KCl flux mediated by ditopic receptor **4** (Scheme 2) was about 2-fold slower than that achieved by a mixture of cation receptor **5** and anion receptor **6**.[7a] Since transport was proven to be diffusion-limited, a likely rationalization of the Reinhoudt data is that diffusion of the zwitterionic, **4**·KCl, complex

Table 4. Initial Transport Fluxes ($\times 10^{-8}$ mol m^{-2} s^{-1})[a]

carrier	1	2	carrier	1	2
LiCl	6 ± 1	6 ± 1	KBr	111 ± 3	20 ± 1
NaCl	37 ± 2	5 ± 1	LiI	7 ± 1	7 ± 1
KCl	90 ± 3	12 ± 1	NaI	43 ± 2	27 ± 2
LiBr	10 ± 1	6 ± 1	KI	160 ± 5	40 ± 2
NaBr	32 ± 2	3 ± 1			

[a] Source phase, 1 M salt; membrane, 50 mM receptor in NPOE; receiving phase, water. T = 25 °C.

Scheme 2. Ditopic Salt Receptor **4**, Monotopic Cation Receptor **5**, and Monotopic Anion Receptor **6**[7a]



through the membrane is slow due to either increased solute−solute or increased solvent−solute interactions. A molecular model of ditopic receptor **4** suggests that it does not bind

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Table 5. Initial Transport Fluxes for SLMs Containing Different Receptors[a]

	1	**2**	**3**	**2 + 3**
flux ($\times 10^{-8}$ mol m^{-2} s^{-1})	90 ± 3	12 ± 1	18 ± 1	50 ± 2

[a] Source phase, 1 M KCl; membrane, 50 mM receptor in NPOE; receiving phase, water. $T = 25$ °C.

KCl as an associated ion pair; instead, the ions are separated, which would make the **4**·KCl complex very polar. This rationalization leads to the hypothesis that a ditopic receptor that binds KCl as an associated ion pair may exhibit higher transport fluxes because it would be less polar and, therefore, able to diffuse more rapidly through the membrane. The fact that ditopic receptor **1** binds KCl as a contact ion pair allows this hypothesis to be tested.

KCl transport fluxes were measured for SLMs containing ditopic receptor **1**, cation receptor **2**, anion receptor **3**,[16] and the dual receptor mixture of **2** and **3** (Scheme 1).[17] The receptor concentration in the membrane was 50 mM (for the binary **2**/**3** mixture, it was 50 mM each**)**, and the source phase consisted of 1 M aqueous KCl, which ensured receptor saturation. As listed in Table 5, the flux observed with ditopic receptor **1** is almost 2-fold higher than that of the dual receptor mixture, which is opposite to the outcome observed by Reinhoudt.[7a] There are likely two factors that contribute to this result. First, the **1**·KCl complex is smaller than the binary mixtures of **2**·K^+ and **3**·Cl^-, and hence its diffusion constant is likely to be higher.[18] Second, the polarity of the **1**·KCl complex is minimized because the KCl is bound inside the receptor as an associated ion pair (most likely a contact ion pair).[19]

The ability of **1** to tightly bind monovalent salts as associated ion pairs is likely to be a major reason for its effectiveness at extracting solid salts into organic phases. In contrast, ditopic receptors that bind salts as separated ion pairs are expected to have diminished salt extraction abilities. Evidence for the latter conclusion is the fact that several ditopic, calixarene-based receptors with structures that are similar to **4** (i.e., they likely bind alkali halide salts as separated ion pairs) are known to be poor solubilizers of solid alkali chlorides.[6e,p,v]

Conclusion

The transport of hydrophilic salts through a liquid organic membrane can be improved by adding to the membrane either a binary mixture of monotopic anion and cation receptors or a single ditopic receptor. Transport effectiveness can be evaluated in terms of two independent properties, extraction constant and maximal flux (the flux that is observed when the receptor-transport system is saturated with salt). Both dual receptor and ditopic receptor transport systems lead to improvements in extraction; however, the maximal flux depends on the size and polarity of the receptor−salt complexes. In the case of a ditopic receptor, the polarity of the receptor−salt complex can be lowered if the salt is bound as an associated ion pair (a contact ion pair is the best case). This is likely to produce faster diffusion of the complex through the membrane (due to reduced intermolecular interactions) and a higher maximal flux.

Experimental Section

Receptors. The monotopic cation receptor **2** was purchased from Aldrich (as a mixture of syn-cis and anti-cis isomers), whereas the ditopic salt receptor **1**[8a] and the monotopic anion receptor **3**[16] were synthesized using previously described methods.

Solid−Liquid Extractions. Solutions of **1** in fresh $CDCl_3$ (~10 mM) were prepared in 5 mm NMR tubes. An initial ^{1}H NMR spectrum was acquired for each tube, and then excess powdered salt (oven-dried for 24 h prior to use) was added to the NMR tubes. A spectrum was acquired every 24 h until the signals for the free receptor disappeared. The changes in the receptor chemical shifts upon complexation were calculated using the formula $\Delta\delta = \delta_{final} - \delta_{initial}$.

X-ray Crystallography. X-ray crystal determinations were performed on a Bruker Apex diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 170 K. The

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(17) A reviewer suggests that the binary **2**/**3** mixture is not an appropriate dual receptor system for comparison with ditopic receptor **1**. At first glance, it may appear that a more appropriate dual receptor system is N,N′-dibenzyl(1,10-diaza-18-crown-6) and N,N′-diarylisophthalamide; however, as demonstrated in ref 8b, this system is a very poor salt transporter because N,N′-diphenylisophthalamide is a very poor anion binder. Presumably, this is because the amide groups in acyclic N,N′-diarylisophthalamide do not readily adopt the syn conformation that allows double hydrogen bonding to the anion (as seen in the crystal structures with cyclic **1**). In other words, a minimum requirement to be a dual receptor control is that both of the monotopic cation and anion receptors have strong affinities for their respective ions. The practical challenge is to find an uncharged, monotopic anion receptor with very high anion affinity and suitable organic solubility. From this perspective, the binary **2**/**3** mixture is an imperfect but, nonetheless, useful control system. As stated in the text, the **1**·KCl complex is smaller than the binary mixtures of **2**·K^+ and **3**·Cl^-, and hence, its diffusion constant is likely to be higher. However, this effect alone is not enough to fully account for the observed increase in flux.

(18) Smith, B. D.; Davis, J. P.; Draffin, S. P.; Duggan, P. J. *Supramol. Chem.* **2004**, *16*, 87−90.

(19) Although the X-ray structures consistently show that receptor **1** binds the salts as contact ion pairs in the solid state, the question of whether these structures are maintained in solution arises. The NMR evidence strongly suggests that the receptor−salt complexes in solution are primarily at a 1:1 stoichiometry, with the salts most likely bound as contact ion pairs. The case of KCl binding has already been described in ref 8a. To briefly summarize, when receptor **1** is titrated with tetrabutylammonium chloride in the highly competitive solvent DMSO, only the NMR signals of the receptor's anion binding region change in the chemical shift, whereas titration with potassium tetraphenylborate induces changes only in the receptor's cation binding region. When aliquots of tetrabutylammonium chloride are added to a mixture of **1** and 1 molar equiv of potassium tetraphenylborate, only changes in the NMR signals of the receptor's anion binding region are induced. The resulting titration isotherm fits nicely to a 1:1 binding model, which produces a chloride affinity constant that is more than 10-fold higher than that obtained with **1** alone. In other words, receptor **1** strongly prefers to bind KCl in a polar organic solvent as the ion pair rather than **1**·K^+ and **1**·Cl^-. This salt-binding preference is magnified in less polar solvents such as $CDCl_3$ or the liquid membrane, NPOE. The X-ray structure of **1**·KCl shows that the salt is bound inside the receptor as a contact ion pair with many ideal noncovalent interactions. It seems unlikely that KCl would bind strongly to the receptor if it were a solvent-separated ion pair. Even if this were the case, the fundamental conclusion of the study would be unchanged; for example, the polarity of a receptor−salt complex will be lowered if the salt is bound to the receptor as an associated ion pair (a contact ion pair is the best case). A complex with lowered polarity is more likely to diffuse faster through the liquid membrane.

structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97 (G. M. Sheldrick, University of Göttingen, Göttingen, Germany).

[1·NaBr]. X-ray quality crystals were obtained from the slow evaporation of a solution of [**1**·NaBr] in ethyl acetate. Crystallographic summary: monoclinic, $P2(1)/c$; $Z = 4$ in a unit cell with the dimensions $a = 8.4819(8)$ Å, $b = 29.976(3)$ Å, $c = 15.3807(14)$ Å, $\alpha = 90°$, $\beta = 99.346(2)°$, $\gamma = 90°$, $V = 3858.7(6)$ Å^3, μ(Mo Kα) = 1.126 mm^{-1}, $D_{calcd} = 1.311$ Mg/m^3, R1 ($I > 2\sigma(I)$) = 3.87%, wR2 ($I > 2\sigma(I)$) = 7.65% for 6779 observed independent reflections. Hydrogen atom positions were placed at idealized positions, except for the amide hydrogen atoms, which were located on the difference map, and a riding model with variable thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements. The X-ray data can be retrieved from the Cambridge Crystallographic Data Center using deposition number CCDC 215471.

[1·KBr]. X-ray quality crystals were obtained from the slow evaporation of a solution of [**1**·KBr] in ethyl acetate. Crystallographic summary: monoclinic, $P2(1)/c$; $Z = 8$ in a unit cell with the dimensions $a = 22.685(6)$ Å, $b = 13.290(4)$ Å, $c = 27.755(7)$ Å, $\alpha = 90°$, $\beta = 103.992(5)°$, $\gamma = 90°$, $V = 8120(4)$ Å^3, μ(Mo Kα) = 1.167 mm^{-1}, $D_{calcd} = 1.333$ Mg/m^3, R1 ($I > 2\sigma(I)$) = 7.35%, wR2 ($I > 2\sigma(I)$) = 15.83% for 10 991 observed independent reflections. Non-hydrogen atoms were found by the successive full-matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters, except for the disordered carbon atoms, which were isotropically refined. Hydrogen atom positions were placed at idealized positions, and a riding model with variable thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements. The asymmetric unit contains two macrocycles with associated K−Br pairs and a disordered ethyl acetate molecule that was determined by NMR to be present at a ratio of 1:3.4 (solvent/macrocycle); therefore, it has 60% occupancy in the asymmetric unit. The position and thermal parameters of the atoms comprising ethyl acetate were not refined. One macrocycle also exhibited a 2-fold disorder involving atoms C43−C45/C43A−C45A, C53−C57/C53A−C57A, and C59/C59A. The occupancies were determined to be 50% for each position, and the hydrogen atoms for the disordered portion were not included in the refinement. The X-ray data can be retrieved from the Cambridge Crystallographic Data Center using deposition number CCDC 215472.

[1·NaI]. X-ray quality crystals were obtained from the slow evaporation of a solution of [**1**·NaI] in ethyl acetate. Crystallographic summary: monoclinic, $P2(1)/c$; $Z = 4$ in a unit cell with the dimensions $a = 8.6649(6)$ Å, $b = 29.681(2)$ Å, $c = 15.4372(10)$ Å, $\alpha = 90°$, $\beta = 100.2490(10)°$, $\gamma = 90°$, $V = 8120(4)$ Å^3, μ(Mo Kα) = 1.167 mm^{-1}, $D_{calcd} = 1.333$ Mg/m^3, R1 ($I > 2\sigma(I)$) = 7.35%, wR2 ($I > 2\sigma(I)$) = 15.83% for 10 991 observed independent reflections. Hydrogen atom positions were placed at idealized positions, and a riding model with variable thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements. The X-ray data can be retrieved from the Cambridge Crystallographic Data Center using deposition number CCDC 215639.

[1·KI]. X-ray quality crystals were obtained from the slow evaporation of a solution of [**1**·KI] in ethyl acetate. Crystallographic summary: monoclinic, $P2(1)/n$, $Z = 4$ in a unit cell with the dimensions $a = 13.4663(6)$ Å, $b = 24.6790(11)$ Å, $c = 13.5514(6)$ Å, $\alpha = 90°$, $\beta = 100.6750(10)°$, $\gamma = 90°$, $V = 4425.7(3)$ Å^3, μ(Mo Kα) = 0.871 mm^{-1}, $D_{calcd} = 1.370$ Mg/m^3, R1 ($I > 2\sigma(I)$) = 3.95%, wR2 ($I > 2\sigma(I)$) = 11.48% for 10 513 observed independent reflections. Hydrogen atom positions were placed at idealized positions, and a riding model with variable thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements. The X-ray data can be retrieved from the Cambridge Crystallographic Data Center using deposition number CCDC 215473.

Transport Studies. The transport apparatus consisted of two water-jacketed half-cells (~34 mL of each) clamped together and separated by the SLM.[13] Each half-cell was stirred at a constant speed with an internally mounted, magnetically driven paddle, and the cells were maintained at 25 °C. The polymer support was a flat sheet of Accurel 1E polypropylene (thickness of 0.1 mm, pore size of 0.1 μm). Membranes were prepared individually by dissolving 1.2×10^{-5} mol of the carrier(s) in 5 mL of chloroform followed by the addition of 240 μL of 2-nitrophenyl octylether. The volatile solvent was removed in vacuo to give an oil, which was used to coat the polymer support. The membrane was then exposed overnight to high vacuum (~2 mmHg). Blank membranes were prepared using the same method but with no carrier. The noncompetitive transport experiments began with a source phase containing a freshly prepared salt solution (1 M) and a receiving phase consisting of distilled water. Samples were taken from the receiving phase at ~30 min intervals, and their salt concentrations were quickly determined by conductivity using a Crison instrument (model 0-522). The samples were then immediately returned to the source phase. All transport experiments were conducted in duplicate. The same fluxes were obtained when the source phase contained 0.5 M salt, indicating that the receptor is saturated with salt under the transport conditions (i.e., source phase containing 1 M salt). Repeated experiments with the same membrane indicated that the loss of carrier **1** or **2** from the membrane was insignificant over the 5 h time frame of the transport experiments. No transport was observed with blank membranes. The competitive transport experiments began with a source phase containing KCl, NaCl, and LiCl (1 M each) and a receiving phase consisting of distilled water. After 3 h, the receiving phase was removed and analyzed for metal cation content by atomic absorption spectroscopy using a Perkin-Elmer instrument (model 3110).

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Supporting Information Available: X-ray data files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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