Facilitated Transport of Hydrophilic Salts by Mixtures of Anion and Cation Carriers and by Ditopic Carriers

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Received May 12, 1999

Abstract: Anion transfer to the membrane phase affects the extraction efficiency of salt transport by cation carriers **1** and **3**. Addition of anion receptors **5** or **6** to cation carriers **1**, **3**, or **4** in the membrane phase enhances the transport of salts under conditions in which the cation carriers alone do not transport salt. The extraction of salt by the carrier mixtures is larger than by cation or anion carrier only, but the rate of diffusion is lower. Ditopic receptors **8** and **9** transport CsCl or KCl much faster than monotopic anion receptor **7** or cation receptors **1** and **2**. The faster transport is due to a higher extraction constant K_{ex} despite a lower diffusion constant of the ditopic salt complex.

Introduction

Facilitated salt transport by neutral cation carriers is greatly affected by the hydrophobicity of the cotransported anion.[1] The distribution of salt between an organic and aqueous phase is inversely related to the dehydration energy[2] or the lyotropic number of the anion.[3] In practice, only salts with lipophilic anions, such as NO_3^-, I^-, or ClO_4^-, are transported in cation-facilitated transport.[4] Transport of hydrophilic salts requires increased complex stability of the cation complex. However, we have previously shown that this leads to a higher kinetic stability of the complexes.[5] Consequently, the rate-limiting step in the transport is no longer the rate of diffusion but the rate of decomplexation. This reduces both the rate of transport and the selectivity.

In the literature, several systems have been reported that circumvent anion transfer in membrane transport. In the case of charged lipophilic carriers, a cation is transported in the opposite direction.[6] Proton-ionizable macrocyclic carriers such as crown ethers with pendant carboxylic acid or ammonium groups,[7,8] diaza- and tetraazamacrocycles,[9,10] and oxime carriers[11] allow counter transport of protons. Also mixtures of neutral cation carriers and lipophilic anions have been used.[12] Redox-driven transport of cations is possible by cotransport of electrons with nickel bis(dithiolene) or anthraquinone.[13] These systems form a lipophilic anion by reversible reduction and oxidation of the carrier. We study the transport of hydrophilic salts by mixtures of anion[14] and cation[15] receptors.

The obvious extension of this work is to combine the anion and cation recognition site in a neutral *ditopic or bifunctional*

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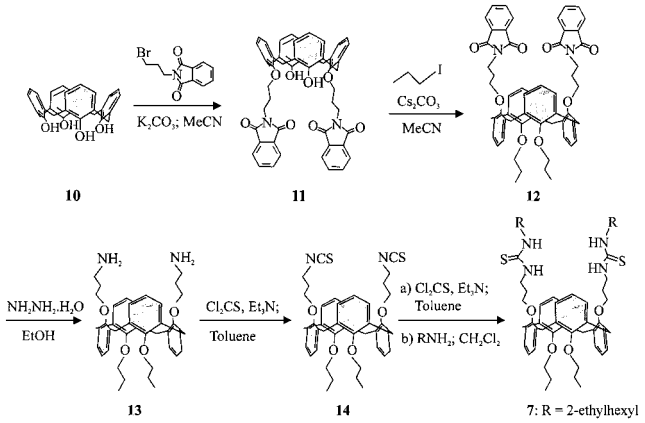
10.1021/ja991588g CCC: $18.00
Published on Web 11/03/1999

receptor.[16] Our group and others have reported the complexation of salts in organic media by bifunctional receptors.[16,17] In this paper, we describe the transport of *hydrophilic* salts when both the anion and cation are complexed either by two separate carriers or by one bifunctional receptor. First, the effect of anion transfer on cation-facilitated transport of potassium salts by carrier **1** and sodium salts by carrier **3** is described. In the second part salt transport by mixtures of cation carriers **1**, **3**, or **4** and anion carriers **5** or **6** is reported. Carriers **5** and **6** are uranyl salene receptors in which Lewis and Brønsted acidic sites are combined.[18] We have successfully applied these as neutral anion carriers for the transport of lipophilic Cl^- and $H_2PO_4^-$ salts.[19] The mechanism of salt transport by the carrier mixtures has been compared with cation-facilitated transport of salt. Finally, the transport of CsCl and KCl by ditopic carriers **8** and **9** is described.

Results and Discussion[20]

Synthesis of Anion Receptors, Cation Receptors, and Bifunctional Receptors. From the literature, it is known that (thio)ureas complex halides.[21] Our group has reported the complexation of halides by (thio)urea functionalized calix[4]-arenes.[21d] We have also demonstrated that K^+ or Cs^+ can be bound by calix[4]crown-5[22] and calix[4]crown-6[23] receptors, respectively. Combination of these binding sites on a calix[4]-arene platform in the 1,3-alternate conformation (receptors **8** and **9**) results in a bifunctional salt receptor.

Scheme 1



The synthesis of cation carriers **1**,[22] **2**,[23] and **3**[24] was carried out according to literature procedures. The 15-crown-5 derivative (**4**) was prepared by alkylation of 2-hydroxymethyl-15-crown-5 with 8(-bromooctyl)-2-nitrophenyl ether[25] in the presence of 1.1 equiv of NaH in acetonitrile. The syntheses of lipophilic uranyl salene carriers **5** and **6** will be published elsewhere.[19] The preparation of dipropoxy-bis(2-ethylhexylthioureidopropoxy) calix[4]arene receptor **7** is depicted in Scheme 1. First, calix-[4]arene **10** was reacted with 3-bromopropyl phthalimide in the presence of 2.5 equiv of K_2CO_3 to give bis(3-phthalimidopro-poxy)-calix[4]arene **11** in 80% yield. Subsequently, calix[4]arene **11** was reacted with propyl iodide using Cs_2CO_3 as a base to give dipropoxy-bis(3-phthalimidopropoxy) calix[4]arene **12** in 52% yield. The *1,3-alternate* conformation of calix[4]arene **12** was confirmed by the carbon absorption of the bridging methylene groups ($ArCH_2Ar$) of the calix[4]arene present at 37.3 ppm in the ^{13}C NMR spectrum and the singlet around 3.68 ppm in the ^1H NMR spectrum for the corresponding methylene hydrogens.[26] The phthalimido groups were removed with hydrazine hydrate in EtOH to give bis(3-aminopropoxy)calix-[4]arene **13** in 96% yield. Bis(2-ethylhexylthioureido)calix[4]-arene receptor **7** was obtained by conversion of calix[4]arene **13** to the corresponding bis(isothiocyanatopropoxy) calix[4]-arene **14** and subsequent reaction with 2-ethylhexylamine.

The synthesis of bis(thioureido)calix[4]crown-5 **8** and bis-(thioureido)calix[4]crown-5 **9** is depicted in Scheme 2. Calix-[4]crown-5 **15** and calix[4]crown-6 **16**, both having the *1,3-alternate* conformation, were synthesized by reacting calix[4]arene **11** with tetra- or pentaethylene glycol di-*p*-toluene sulfonate, respectively, and 2.5 equiv of Cs_2CO_3 as a base in refluxing MeCN. The *1,3-alternate* conformation was confirmed by ^{13}C NMR spectroscopy as the carbon absorption of the bridge CH_2 of the calix[4]arene is present at 38 ppm.[26] The phthalimido groups of **15** and **16** were removed with hydrazine monohydrate in refluxing ethanol to give the bis(3-aminopropoxy)calix[4]-crown derivatives **17** and **18**, respectively. For the synthesis of the ditopic receptors **8** and **9**, first bis(3-aminopropoxy)calix-[4]crown-5 **17** and bis(3-aminopropoxy)calix[4]crown-6 **18** were converted with thiophosgene in the presence of triethylamine in toluene to the corresponding bis(3-isothiocyanatopropoxy)-calix[4]crown derivatives **19** and **20**. Subsequently, these were

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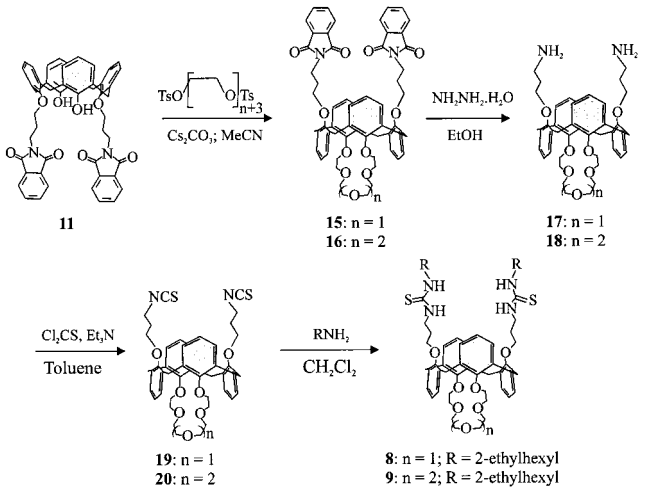
Table 1. Transport Parameters D_m, K_{ex}, and $\Delta G_{ex,NPOE}$ for the Transport of KX Salts by Carrier **1** and of NaX Salts by Carrier **3**; $[\mathbf{1}]_m$ or $[\mathbf{3}]_m = 10$ mM

	transport of KX by carrier **1**			transport of NaX by carrier **3**			
anion X^-	D_m (10^{-12} $m^2\,s^{-1}$)	K_{ex} (M^{-1})	$\Delta G_{ex,NPOE}$(KX) (kJ mol^{-1})[a]	D_m (10^{-12} $m^2\,s^{-1}$)	K_{ex} (M^{-1})	$\Delta G_{ex,NPOE}$(NaX) (kJ mol^{-1})[a]	$\Delta G_{tr,NPOE}(X^-)$ (kJ mol^{-1})[b]
ClO_4^-	7.7	3.7×10^4	−26.0	8.0	14	−6.5	10.6
SCN^-	10.8	1.3×10^3	−17.8	8.9	4.0×10^{-1}	2.3	19.2
I^-	8.2	9.0×10^2	−16.8	8.5	1.2×10^{-1}	5.3	21.1
NO_3^-	8.8	1.8×10^2	−12.9				21.8
Br^-	8.4	3.4	−3.0				33.8
CN^-	10	2.8×10^{-1}	3.2				37.1
Cl^-	10.4	3.5×10^{-2}	8.3				43.1

[a] $\Delta G_{ex,NPOE}$(MX) calculated from K_{ex} (M^{-1}). [b] Taken from ref 19.

Scheme 2



reacted with 2-ethylhexylamine in chloroform to give the ditopic carriers **8** and **9**.[27]

Effect of Cotransported Anions on Cation-Facilitated Transport. The transport of salts by potassium carrier **1** and sodium carrier **3** was measured as a function of the salt activity a_s to determine the extraction coefficient K_{ex} (see eq 2) and diffusion constant D_m of the carrier complexes from eq 1 (Table 1). The model has recently been developed in our group[24] and applied to describe the facilitated transport of alkali[24] and earth-alkaline[22,23] metal salts and silver salts.[28]

$$J_0 = \frac{D_m}{2d_m}\left[-K_{ex}a_s^2 + \sqrt{(K_{ex}a_s^2)^2 + 4L_0K_{ex}a_s^2}\right] \qquad (1)$$

The diffusion coefficients are all in the same range; 8×10^{-12} to 11×10^{-12} $m^2\ s^{-1}$.[29] Apparently, the cotransported anion only slightly affects the rate of diffusion in the membrane phase.[30,31] The extraction constant (K_{ex}), however, is strongly anion-dependent; it decreases by a factor of 10^6 when ClO_4^- is replaced by Cl^-. The transport of KH_2PO_4 was too low for an accurate determination of D_m and K_{ex}; hence K_{ex} of **1**·KH_2PO_4 is much smaller than that of **1**·KCl. For carrier **3**, accurate values of D_m and K_{ex} were only obtained for $NaClO_4$, NaI, and NaSCN. The corresponding Gibbs free energies of extraction ($\Delta G_{ex,NPOE}$(MX)) were calculated from K_{ex} according to eq 2 (Table 1).

$$\Delta G_{ex,NPOE}(MX) = -RT\ln(K_{ex}) \quad \text{with} \quad K_{ex} = \frac{[ML^+]_m[X^-]_m}{[M^+]_s[L]_m[X^-]_s} \qquad (2)$$

The cation complex and anion are solvent-separated ions in the membrane phase.[19] In this case $\Delta G_{ex,NPOE}$(MX) is the sum of the Gibbs free energy of cation transfer $\Delta G_{tr,NPOE}(M^+)$, the Gibbs free energy of anion transfer $\Delta G_{tr,NPOE}(X^-)$, and the Gibbs free energy of cation complexation $\Delta G_{a,NPOE}(M^+)$.

$$\Delta G_{ex,NPOE}(MX) = \Delta G_{tr,NPOE}(M^+) + \Delta G_{tr,NPOE}(X^-) + \Delta G_{a,NPOE}(M^+) \qquad (3)$$

For carrier **1**, $\Delta G_{ex,NPOE}$(KX) is indeed related linearly to the Gibbs free energies of anion transfer to NPOE ($\Delta G_{ex,NPOE}(X^-)$)[19] with the expected slope of 1 ($y = 1.072x - 37.9$, $R^2 = 0.990$). A similar relation is observed for the transport of NaX by carrier **3** ($y = 1.093x - 18.2$, $R^2 = 0.994$). Equation 3 illustrates the limitations of the application of neutral cation carriers. Salt transport is not efficient in practice when $\Delta G_{ex,NPOE}$(MX) is too large (>10 kJ mol^{-1}). This situation occurs when the relative contribution of $\Delta G_{a,NPOE}(M^+)$ is not sufficient to compensate for the unfavorable Gibbs free energy of salt transfer. In this case, both an anion receptor *and* a cation receptor should be used in the membrane. The complexation in the membrane solvent is described by eq 4.

$$[L_M]_m + [M^+]_m \rightleftarrows [L_MM^+]_m \quad \text{with} \quad K_{a,M} = \frac{[L_MM^+]_m}{[L_M]_m[M^+]_m}$$

$$[L_X]_m + [X^+]_m \rightleftarrows [L_XX^-]_m \quad \text{with} \quad K_{a,X} = \frac{[L_XX^-]_m}{[L_X]_m[X^-]_m} \qquad (4)$$

When $[L_MM^+]_m \gg [M^+]_m$ and $[L_XX^-]_m \gg [X^-]_m$, the cooperative extraction of salt K_{ex}^{coop} is defined by eq 5 and 6 in which K_p, $K_{a,X}$, and $K_{a,M}$ are the equilibrium constants for salt partitioning, anion complexation, and cation complexation, respectively. $\Delta G_{ex,NPOE}^{coop}$(MX) was derived from K_{ex}^{coop} (eq 7), from which it is clear that salt extraction can be enhanced, because of the additional term for anion complexation, $\Delta G_{a,NPOE}(X^-)$.

(27) Lipophilic, branched alkyl chains were attached to provide sufficient lipophilicity and to increase the solubility of the carriers in organic solutions.

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(29) D_m is the membrane diffusion coefficient. D_m is affected by the membrane characteristics, tortuosity Θ, and porosity τ. A diffusion coefficient D_b in the bulk solvent can be calculated from D_m according to $D_b = (\tau/\Theta)D_m$.

(30) The diffusion coefficient D_{MX} of an electrolyte MX in dilute solution can be calculated from the individual diffusion coefficients (D_M and D_X): $D_{MX} = (2D_MD_X)/(D_M + D_X)$. As the diffusion coefficients of the cation D_M and the anion D_X are inversely related to the radius of the diffusing species, D_X will be much larger than D_M.

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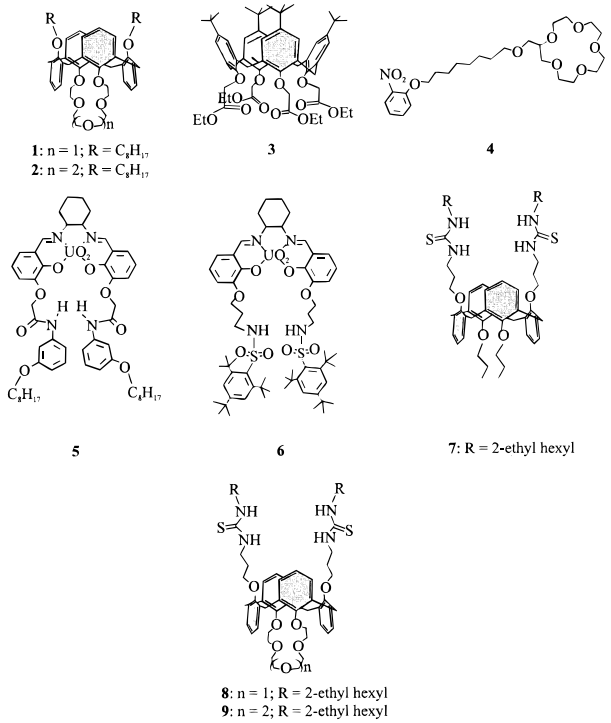
Chart 1



$$[L_X]_m + [L_M]_m + [M^+]_{aq} + [X^-]_{aq} \rightleftarrows [L_X X^-]_m + [L_M M^+]_m \quad (5)$$

$$K_{ex}^{coop} = K_p K_{a,X} K_{a,M} = \frac{[L_X X^-]_m [L_M M^+]_m}{[L_X]_m [L_M]_m [M^+]_{aq} [X^-]_{aq}} \quad (6)$$

$$\Delta G_{ex,NPOE}^{coop}(MX) = \Delta G_{tr,NPOE}(X^-) + \Delta G_{tr,NPOE}(M^+) + \Delta G_{a,NPOE}(M^+) + \Delta G_{a,NPOE}(X^-) \quad (7)$$

Cooperative Salt Transport with Carrier Mixtures. Transport of KCl, NaCl, and KH_2PO_4 with mixtures of cation carriers **1**, **3**, and **4** and anion carriers **5** and **6** (Chart 1) was measured as a function of the ratio of anion and cation carrier in the membrane phase keeping the total carrier concentration constant ($[L_X + L_M]_m = 15$ mM). First, KCl was transported from a low initial source phase concentration with mixtures of calix-[4]crown-5 **1** and uranyl salene **5**. NaCl was transported from a high source phase concentration by mixtures of calix[4]arene tetraester **3** and uranyl salene **5** to promote salt extraction to the membrane phase (Figure 1). Neither the cation carrier nor anion carrier alone transports salt, but the carrier mixtures do. For the mixtures of carriers of both **1** and **5** and **3** and **5**, the transport-rate reaches a maximum at equal concentration of anion carrier and cation carrier (Figure 1).

The ratio of anion carrier vs cation carrier for which the flux is maximal is directly related to the stoichiometry of the carrier complexes in the membrane phase. A maximum flux at 1:1 ratio of anion carrier and cation carrier indicates that cooperative salt extraction occurs by complexes that have a 1:1 stoichiometry. We further studied the influence of complex stoichiometries on the transport of KCl with mixtures of 15-crown-5 derivative **4** and uranyl salene **5** (Figure 2). It is known from complexation studies and crystallography data that 15-crown-5 derivatives form 2:1 sandwich complexes with K^+.[32] Transport of KCl by

(32) Cox, B. G., Schneider, H., Eds. *Studies in Physical and Theoretical Chemistry*; Elsevier Science: Amsterdam, The Netherlands, Vol. 76, 1992.

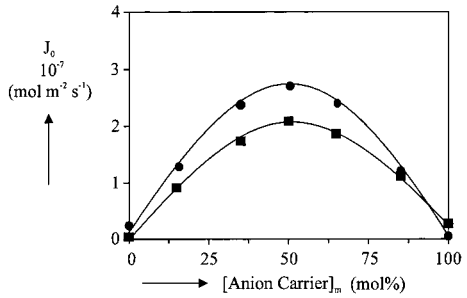


Figure 1. Transport of NaCl by mixtures of carriers **3** and **5** and of KCl by mixtures of carriers **1** and **5**; $[\mathbf{3} + \mathbf{5}]_m = [\mathbf{1} + \mathbf{5}]_m = 15$ mM, $[NaCl]_s = 1.0$ M (■) and $[KCl]_s = 25$ mM (●).

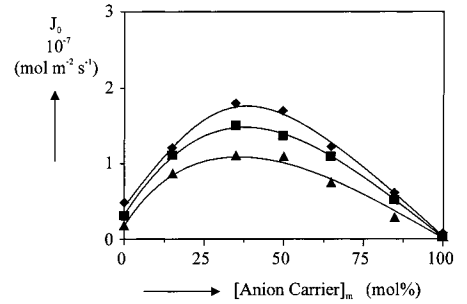


Figure 2. Transport of KCl by carrier mixtures of **4** and **5**; $[\mathbf{4} + \mathbf{5}]_m = 15$ mM, $[KCl]_s = 0.5$ M (▲), 1.0 M (■), and 1.5 M (◆).

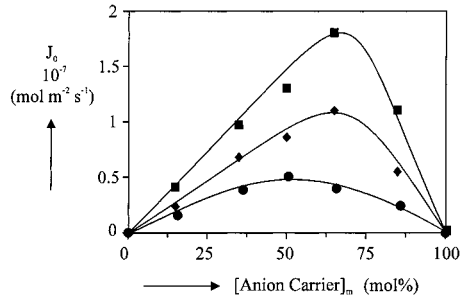


Figure 3. Transport of KH_2PO_4 by mixtures of carriers **1** and **5** (◆), carriers **1** and **6** (■), and carriers **4** and **5** (●); $[\mathbf{1} + \mathbf{5}]_m = [\mathbf{1} + \mathbf{6}]_m = [\mathbf{4} + \mathbf{5}]_m = 15$ mM, $[K_2HPO_4 + KH_2PO_4]_s = 0.05$ M, $pH_s = 6.7$.

15-crown-5 **4** or uranyl salene **5** individually is low, but for mixtures of carriers **4** and **5**, transport does occur. A maximum transport rate is now observed for a 2:1 ratio of cation carrier vs anion carrier.

We also found that mixtures of cation carrier **1** and anion carriers **5** and **6** cooperatively transport KH_2PO_4.[33] Fluxes were measured at pH = 6.7 with mixtures of carriers **1** and **5** and carriers **1** and **6** as a function of the carrier composition in the membrane phase (Figure 3). Salt is not transported by the cation carrier or the anion carrier alone. Only carrier mixtures transport KH_2PO_4 with a maximum transport rate at a ratio of anion versus cation carrier of 2:1. Apparently, uranyl salenes form 2:1 complexes with $H_2PO_4^-$ in the membrane phase. Complexation studies with uranyl salene receptors studied by ^{1}H NMR

(33) The experiments have been carried out from a source phase at $pH_s = 6.7$ at which both HPO_4^{2-} and $H_2PO_4^-$ are present at equal concentration. The type of anion transported was determined by salt transport ($[KH_2PO_4 + K_2HPO_4]_s = 0.045$ M) from an acidic (pH = 4.5; $J_0 = 14 \times 10^{-8}$ mol m^{-2} s^{-1}), neutral (pH = 7.1; $J_0 = 9.5 \times 10^{-8}$ mol m^{-2} s^{-1}), and basic (pH = 9.2; $J_0 = 0.8 \times 10^{-8}$ mol m^{-2} s^{-1}) source phase with a mixture of calix[4]crown-5 **1** and uranyl salene **6** ($[\mathbf{1}]_m = [\mathbf{6}]_m = 0.01$ M). At low pH_s, phosphate ($H_2PO_4^-$) transport occurs. Moreover, the ratio of K^+ versus total phosphate (PO_4^{3-}) in the receiving phase was determined after transport from a neutral source phase: $(K^+)/(PO_4^{3-}) = 1.07$. This strongly indicates that almost exclusive KH_2PO_4 transport takes place.

Table 2. Diffusion Coefficients D_m, D_{lag}, and α for the Transport of KI, KCl, and KH_2PO_4 by Mixtures of Carriers **1** and **5**

carrier mixture	transported salt[a]	D_m[b] (10^{-12} m^2 s^{-1})	α[b]	t_{lag} (s)	D_{lag} (10^{-12} m^2 s^{-1})	D_m[c] (10^{-12} m^2 s^{-1})
1[d]	KI	7.6	0	800	19	12
1 + **5**[e]	KCl	5.0	0	501	13	5.8
1 + **5**[f]	KH_2PO_4	3.7	0.17	1484	4.5	3

[a] $[KX]_s = 0.4$ M. [b] Determined from eq 8. [c] Determined from D_{lag}. [d] $[\mathbf{1}]_m = 0.01$ M. [e] $[\mathbf{1}]_m = [\mathbf{5}]_m = 0.01$ M. [f] $[\mathbf{1}]_m = 0.01$ M and $[\mathbf{5}]_m = 0.02$ M.

spectroscopy confirm the 2:1 stoichiometry with $H_2PO_4^-$ in organic media.[34]

When salene **5** is mixed with 15-crown-5 **4**, the flux reaches a maximum at 1:1 carrier ratio. Because both 15-crown-5 **4** and salene **5** form a dimeric complex with K^+ and with H_2PO_4-, respectively, the 1:1 carrier ratio indicates a 2:2 complex stoichiometry.

The Mechanism of Facilitated Salt Transport. The rate-limiting step of transport was determined from a measurement of the transport rate as a function of the membrane thickness d_m.[5] When $L_0J_0^{-1}$ is plotted as a function of d_m, the slope of the fitted line gives the mean diffusion coefficient of the complex and the intercept is indicative for a chemical resistance (eq 8).

$$\frac{L_0}{J_0} = (1 + \alpha)\frac{d_m}{D_m} \tag{8}$$

The transport of KI, KCl, and KH_2PO_4 by mixtures of carriers **1** and **5** was measured as a function of the membrane thickness from a source phase concentration of 0.4 M to ensure that all carrier at the source phase interface is present as complex.[5] The mean diffusion coefficients D_m and α are given in Table 2. The intercept of the fitted lines is very small ($\alpha \ll 1$). Thus the transport is diffusion-limited for all systems. With more than one carrier involved in transport, the apparent diffusion coefficient D_m decreases (Table 2) in agreement with the Stokes−Einstein equation.

Lag-time experiments yield independent values for D_m.[35] From the experimental lag time t_{lag}, $D_{lag} = d_m/6t_{lag}$ was calculated (Table 2). The value for D_m was calculated from D_{lag} by $D_m = \Theta D_{lag}$, Θ being the porosity of the membrane. The values for D_m obtained from lag times are in reasonable agreement with those obtained from flux measurements.

The influence of the salt concentration on transport is shown in Figure 4. The transport rate increases with the salt concentration but reaches a maximum ($J_{0,max}$), indicating that all carrier at the interface becomes complexed at high salt concentrations. Because the transport is diffusion-limited, D_m can be calculated from $J_{0,max}$ according to eq 9 (Table 3).[24]

$$J_{0,max} = \frac{D_m L_0}{d_m} \tag{9}$$

The diffusion coefficients determined by different methods (Tables 2 and 3) are the same within experimental error and the relative order is $D_m(\mathbf{1}\cdot KCl) > D_m((\mathbf{1} + \mathbf{5})\cdot KCl) > D_m((\mathbf{1} + \mathbf{5})\cdot KH_2PO_4)$.

The efficiency of selective uphill transport was determined for calix[4]crown-5 **1** alone and for a mixture of calix[4]crown-5 **1** and uranyl salene **5** (1:1 stoichiometry). Experiments were performed with 2.5×10^{-4} M KCl/0.25 M NaCl as source phase (Table 4). With the carrier mixture, more than 50% of all K^+ was transported in 1 day with a very high selectivity of about 10^4. After 2 days, more than 95% of all potassium was transported. The selective uptake of K^+ by the calix[4]crown-5 in the membrane remains responsible for the high selectivities.

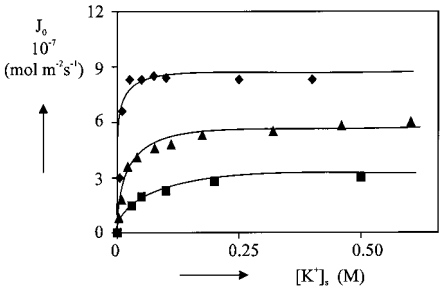


Figure 4. The initial flux J_0 as a function of the salt concentration for the transport of KI by carrier **1** (0.01 M) (◆), KCl by a mixture of carriers **1** (0.01 M) and **5** (0.01 M) (▲), and KH_2PO_4 by a mixture of carriers **1** (0.01 M) and **5** (0.02 M) (■).

Table 3. Maximum Flux $J_{0,max}$ and Diffusion Coefficient D_m for the Transport of KI, KCl and KH_2PO_4 by Mixtures of Carriers **1** and **5**

carrier mixture	transported salt	$J_{0,max}$ (10^{-7} mol m^{-2} s^{-1})	D_m[a] (10^{-12} m^{-2} s^{-1})	D_m[b] (10^{-12} m^2 s^{-1})
1	KI	8.1	8.1	7.7
1 + **5**	KCl	5.7	5.7	5.7
1 + **5**	KH_2PO_4	3.0	3.0	3.4

[a] D_m value from $J_{0,max}$ (Figure 4). [b] D_m value from the transport as a function of the carrier concentration ($[salt]_s = 0.4$ M).

Table 4. Selective and Uphill Transport of KCl in the Presence of NaCl by Carrier **1** and by a Mixture of Carriers **1** and **5**; $[KCl]_s = 2.5 \times 10^{-4}$ M and $[NaCl]_s = 0.25$ M

time (10^3 s)	carrier **1**	carrier **5**	%Na^+ transported	%K^+ transported	selectivity S[a] (10^3)
67	0.01		0.0018	7.8	4.3
67	0.01	0.01	0.0064	60.1	9.4
137	0.01		0.0020	14.8	7.4
137	0.01	0.01	0.0040	95	23.8

[a] $S = (\%K^+/\%Na^+)$.

Transport Efficiency by a Cation Carrier and by a Carrier Mixture. Although salt extraction into the membrane phase is clearly enhanced by addition of an anion carrier to a cation carrier, the mean diffusion coefficient of the carrier mixtures is lower than that of the cation carrier alone. These two counteracting factors may lead to a situation in which salt transport by carrier mixtures is not always most efficient. This is illustrated by the transport of KCl by calix[4]crown-5 **1** alone in comparison with the transport by a (1:1) mixture of calix[4]crown-5 **1** and uranyl salene **5** as a function of the source phase activity of KCl (Figure 5). At low salt activity, the extraction of salt by the mixture of **1** and **5** is higher; thus transport of KCl is most efficient. At high salt activity when the flux approaches a plateau, $J_{0,max}$, salt transport by carrier **1** alone becomes more efficient due to a higher diffusion coefficient. The mean diffusion coefficient of **1**·KCl is 10.4×10^{-12} m^2 s^{-1}, whereas $D_m = 5.7 \times 10^{-12}$ m^2 s^{-1} for the transport of KCl by the mixture of **1** and **5**.

The limitations of carrier mixtures to transport salt are also reflected in the influence of the salt concentration on the facilitated transport of KCl by mixtures of calix[4]crown-5 **1** and uranyl salene **5** at different carrier compositions (Figure 6).

(34) Antonisse, M. A. Ph.D. Thesis, University of Twente, Enschede, The Netherlands, 1998.

(35) Bromberg L.; Levin, G.; Kedem, O. *J. Membr. Sci.* **1992**, *72*, 41.

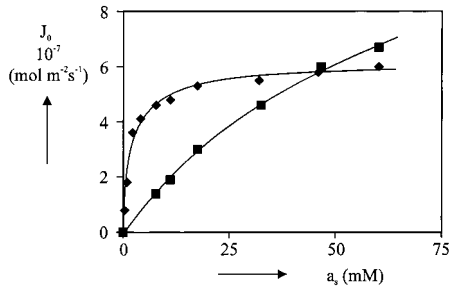


Figure 5. The flux J_0 as a function of the salt activity a_s for the transport of KCl by carrier **1** ($[\mathbf{1}]_m = 0.01$ M, ■) and by the carrier mixture of **1** and **5** ($[\mathbf{1}]_m = [\mathbf{5}]_m = 0.01$ M, ◆).

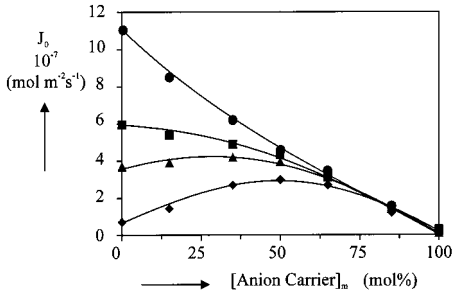


Figure 6. Transport of KCl by carrier mixtures of **1** and **5**; $[\mathbf{1} + \mathbf{5}]_m = 15$ mM, $[KCl]_s = 0.05$ (◆), 0.25 (▲), 0.5 (■), and 1.0 (●) M.

Table 5. Transport Parameters D_m and K_{ex} for the Transport of $CsClO_4$ and CsCl by Calix[4]crown-6 Derivatives **2** and **9**

carrier	transported salt MX	D_m (10^{-12} m^2 s^{-1})	K_{ex} (M^{-1})[a]	$G_{ex,NPOE}$(MX) (kJ mol^{-1})
2	$CsClO_4$	11	3130	−19.9
2	CsCl	11	0.0037	13.9
9	$CsClO_4$	6.2	1970	−18.8
9	CsCl	4.2	472[a]	−15.2

[a] K'_{ex} (M^{-2}) defined according to eq 12.

At low salt concentration ($[KCl]_s = 0.025$ M) the curve is a bell-shaped. With increasing salt concentration, facilitated transport of KCl by calix[4]crown-5 **1** increases and exceeds the transport of KCl by the mixture of carriers **1** and **5**. Ultimately, at high salt concentration substitution of part of calix[4]crown-5 **1** by uranyl salene **5** results in less efficient transport![36] The observed trends can be rationalized by an extraction model based on salt partitioning and independent complexation of the anion and cation. (for further detail: see Supporting Information).

Transport of CsCl with a Bifunctional Receptor. We have applied carriers **8** and **9** in SLMs to describe the mechanistic aspects of transport with bifunctional receptors.[17] First, carriers **2** and **9** were used for the transport of CsCl and $CsClO_4$.[37] Since the transport of these salts is cation facilitated, eq 1 can be applied to describe the fluxes and determine values for K_{ex} and D_m.[24]

The transport of $CsClO_4$ by *monotopic* carrier **2** is most efficient (Table 5). The maximum flux $J_{0,max}$ of ditopic carrier **9** transporting $CsClO_4$ is much lower than that of carrier **2**, due to a lower diffusion coefficient D_m. This is attributed to the presence of the thiourea groups in the ditopic carrier. Small amounts of (thio)urea derivatives can serve as gelating agents for organic solvents, due to intermolecular hydrogen bonding of the (thio)urea moieties.[38] This effect increases the viscosity of the membrane solvent and therefore retards the rate of diffusion. $\Delta G_{ex,NPOE}(\mathbf{2}\cdot CsClO_4)$ is slightly higher than $\Delta G_{ex,NPOE}(\mathbf{9}\cdot CsClO_4)$, indicating that the binding strength for Cs^+ is not much affected by the thiourea moieties in carrier **9**.

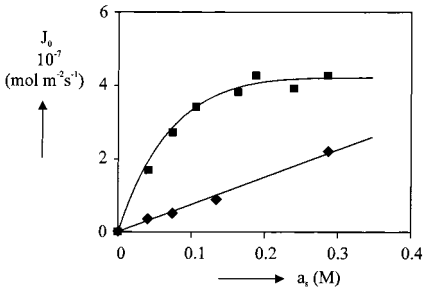


Figure 7. Transport of CsCl by ditopic carrier **9** (■) and monotopic carrier **2** (◆) as a function of the source phase salt activity; $[carrier]_m = 0.01$ M.

The transport of CsCl by carriers **2** and **9** is totally different from the previous case (Figure 7). Although carrier **2** is the most efficient carrier for $CsClO_4$, carrier **9** transports CsCl more efficiently. At $[CsCl]_s = 0.1$ M, the transport by **9** ($J_0 = 23 \times 10^{-8}$ mol m^{-2} s^{-1}) is about 5 times higher than that by **2** ($J_0 = 4.5 \times 10^{-8}$ mol m^{-2} s^{-1}), which clearly demonstrates that both binding sites are involved in the complexation of CsCl.

The transport of CsCl by the *monotopic* 1,3-dioctyloxycalix-[4]crown-6 carrier **2** is described by eq 1 (Table 5). When we assume that the D_m values of complexes **2**·CsCl and **2**·$CsClO_4$ are about the same, the value for K_{ex} of carrier **2** for CsCl can be determined from eq 1 ($K_{ex} = 3.7 \times 10^{-3}$ M^{-1}) with a corresponding Gibbs free energy of $\Delta G_{ex,NPOE}(CsCl) = 13.9$ kJ mol^{-1}. Transport of CsCl by ditopic carrier **9** can no longer be described by the model for cation-facilitated transport but by the diffusion of a ditopic complex in which the Cs^+ and Cl^- are simultaneously bound as a ligand-separated ion pair. Therefore eq 11 holds for the flux as a function of the experimental parameters and D_m and K'_{ex}.[4b]

$$M_s^+ + L_{ms} + X_s^- \leftrightarrows MLX_{ms}; \quad K'_{ex} = \frac{[MLX]_{ms}}{[M^+]_s[X^-]_s[L]_{ms}} \tag{10}$$

$$J_0 = \frac{D_m K'_{ex} L_0}{d_m}\left[\frac{a_s^2}{(1 + K_{ex}a_s^2)}\right] \tag{11}$$

The diffusion coefficient D_m and extraction constant K'_{ex} of carrier **9**·CsCl were determined by fitting eq 11 to the data in Figure 7 (Table 5). The diffusion coefficient of carrier **9**·CsCl ($D_m = 4.2 \times 10^{-12}$ m^2 s^{-1}) is low. Diffusion coefficients of macrocyclic complexes in SLMs are generally in the range of 10×10^{-12} m^2 s^{-1}.[4] The relative order of the diffusion coefficients was confirmed with lag-time experiments; $D_m(\mathbf{2}\cdot CsClO_4) > D_m(\mathbf{9}\cdot CsClO_4) > D_m(\mathbf{9}\cdot CsCl)$.

The extraction constants for the transport of CsCl by **2** ($K_{ex} = 3.7 \times 10^{-3}$ M^{-1}) and **9** ($K_{ex}' = 472$ M^{-2}) cannot be compared directly. However, when we calculate[39] the percentage of complex **2**·CsCl and **9**·CsCl in the membrane phase after

(36) This demonstrates that extraction of KCl by anion carrier **5** individually is much less effective than the extraction of KCl by cation carrier **1**.

(37) The transport of KCl, CsCl, and $CsClO_4$ facilitated by anion carrier **7** was too low to be determined ($J_0 < 0.5 \times 10^{-8}$ mol m^{-2} s^{-1}).

(38) Van Esch, J.; Kellogg, R. M.; Feringa, B. L. *Tetrahedron Lett.* **1997**, *38*, 281.

(39) For the monotopic cation complex, the percentage of complex in the membrane phase is defined as % complex = 100% × ($[ML^+]_m$/$[L]_{m,0}$) and follows from eq 2. For the ditopic complex, it is defined as % complex = 100% × ($[MLX]_m$/$[L]_{m,0}$) and follows from eq 11.

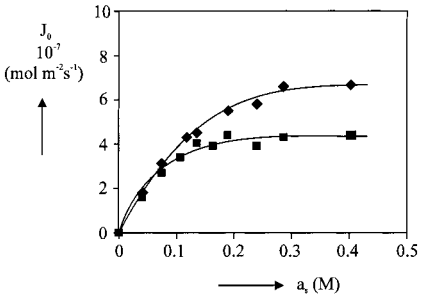


Figure 8. Transport of CsCl by ditopic carrier **9** (■) and the mixture of carriers **2** and **7** (◆) as a function of the source phase salt activity; $[\mathbf{9}]_m = 0.01$ M and $[\mathbf{2}]_m = [\mathbf{7}]_m = 0.01$ M.

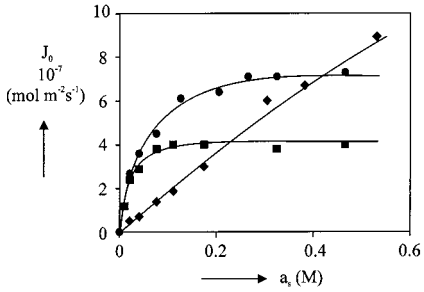


Figure 9. Transport of KCl by cation carrier **1** (◆), the mixture of carriers **1** and **7** (●), and ditopic carrier **8** (■) as a function of the source phase salt activity; $[\mathbf{8}]_m = [\mathbf{1}]_m = [\mathbf{7}]_m = 0.01$ M.

extraction from CsCl ($a_{s,CsCl} = 0.1$ M) with 0.01 M carrier, 83% of the receptor **9** is present as complex, whereas only 6% of the monotopic carrier **2** is complexed.

From the extraction constants K_{ex}, K'_{ex} (Table 5), and the ratio of the partition constants $K_p(CsClO_4)/K_p(CsCl) = 8.5 \times 10^5$, the binding constant $K_{a,Cl}$ for the complexation of Cl^- by carrier **9** was calculated (eq 12); $K_{a,Cl} = 1 \times 10^5$ M^{-1} or $\Delta G_a(\mathbf{9}\cdot Cl^-) = -28.5$ kJ mol^{-1}.

$$K_{a,Cl} = \frac{K_p(CsClO_4)}{K_p(CsCl)} \times \frac{K'_{ex}(CsCl)}{K_{ex}(CsClO_4)} \qquad (12)$$

As $K_{a,Cl} \gg 1$ M^{-1}, we can conclude that the complexation of Cl^- in the bifunctional receptor clearly contributes to the extraction of CsCl by ditopic carrier **9**. $K_{a,Cl}$ is about 1 order of magnitude higher than those reported for the complexation of Cl^- by the urea-based anion receptors in $CDCl_3$ by Scheerder et al. ($K_{a,Cl} = 10^3 - 10^4$ M^{-1}).[21d] The enhanced binding affinity must be due to additional attractive electrostatic forces of Cs^+ bound in the bifunctional receptor.

We found that CsCl is transported selectively in the presence of a large excess of NaCl by ditopic carrier **9** ($[CsCl]_s = 2.5 \times 10^{-4}$ M and $[NaCl]_s = 0.25$ M), as about 87% of all CsCl was transported within 2 days. For monotopic carrier **2** the transport of CsCl was much lower, as only 3% of all Cs^+ was transported after 2 days. Both for carrier **2** and for carrrier **9**, Na^+ could not be detected in the receiving phase even after 2 days.

CsCl Transport Facilitated by a Ditopic Carrier and a Carrier Mixture. To evaluate the effect of covalent linkage of the two recognition sites on salt transport, we compared the transport of CsCl by *ditopic* bis(thioureido)calix[4]crown-6 **9** and the mixture of bis(thioureido)calix[4]arene **7** and di-(1-octyloxy)calix[4]crown-6 **2**. The transport of CsCl by the 1:1 carrier mixture of **2** and **7** (10 mM in NPOE) and by carrier **9** was studied as a function of the CsCl concentration (Figure 8). For both systems, a maximum flux $J_{0,max}$ is reached at higher salt concentration ($[CsCl]_s > 0.3$ M). In contrast to what was expected on the basis of the size of the diffusing complexes, the carrier mixture of **2** and **7** transports CsCl more efficiently than ditopic carrier **9**. There is a substantial difference in the maximum flux $J_{0,max}$, namely, $J_{0,max}(\mathbf{9}) = 4.1 \times 10^{-7}$ mol m^{-2} s^{-1} and $J_{0,max}(\mathbf{2} + \mathbf{7}) = 6.3 \times 10^{-7}$ mol m^{-2} s^{-1}.

The diffusion of the complex through the membrane phase is the rate-limiting step of transport of CsCl by both ditopic carrier **9** and the mixture of carriers **2** and **7**.[5] The diffusion coefficient of the carrier mixture is higher than of the ditopic carrier, which was confirmed by lag-time measurements. On the basis of the Stokes−Einstein, this result was unexpected. The lower diffusion velocity might be explained from the zwitterionic character of the complex. This has also been observed for the diffusion of amino acids as cationic species and as zwitterions.[40]

Facilitated Transport of KCl by a Cation Carrier, a Carrier Mixture, and a Bifunctional Carrier. Ultimately, we compared the transport of KCl for three different systems; (i) ditopic calix[4]crown-5 **8**, (ii) monotopic calix[4]crown-5 **1**, and (iii) the mixture of calix[4]crown-5 **1** and calix[4]arene **7**.[37] The transport of KCl was measured as a function of the KCl activity (Figure 9). At low salt activity ($a_s < 0.1$ M), ditopic carrier **8** and the mixture of the monotopic cation carrier **1** and anion carrier **7** exhibit the highest flux. This is due to the enhanced extraction of KCl because of the additional binding site for chloride as anion carrier or in the bifunctional receptor.

At high salt activity ($a_s > 0.4$ M), the transport rate of KCl by the carrier mixture of **1** and **7** as well as by ditopic carrier **8** reaches a maximum. The maximum flux $J_{0,max}$ of ditopic calix-[4]crown-5 carrier **8** is much lower than that of the carrier mixture of calix[4]crown-5 **1** and calix[4]arene **7**. This difference is also observed for the transport of CsCl by the calix[4]crown-6 carriers. Since the transport is diffusion-limited, the low maximum flux $J_{0,max}$ is attributed to the lower diffusion velocity of bifunctional carrier **8** compared to the mixture of anion carrier **7** and cation carrier **1**. This hypothesis is supported by the diffusion coefficients D_m determined from the transport of KCl as a function of the membrane thickness. The diffusion coefficients decrease in the order $D_m(\mathbf{1}\cdot KCl) = 10.4 \times 10^{-12}$ m^2 s^{-1} > $D_m((\mathbf{1} + \mathbf{7})\cdot KCl) = 6.8 \times 10^{-12}$ m^2 s^{-1} > $D_m(\mathbf{8}\cdot KCl) = 3.9 \times 10^{-12}$ m^2 s^{-1}. For diffusion-limited transport, $J_{0,max}$ at higher salt concentration is determined by the diffusion coefficient D_m. Therefore, when $[KCl]_s > 0.5$ M, the transport rates decrease in the order $J_0(\mathbf{1}) > J_0(\mathbf{1} + \mathbf{7}) > J_0(\mathbf{8})$. The monotopic calix[4]crown-5 carrier **1** becomes the most efficient carrier as it reaches the highest plateau $J_{0,max}$, whereas under these conditions the lowest transport efficiency is obtained for ditopic carrier **8**!

Conclusions

The cotransported anion largely influences the extraction efficiency in cation-facilitated transport, due to the unfavorable contribution of $\Delta G_{ex,NPOE}(X^-)$ to $\Delta G_{ex,NPOE}(MX)$. Mixtures of cation carriers **1**, **3**, or **4** and anion carriers **5** or **6** cooperatively transport hydrophilic salts, such as KCl and KH_2PO_4. The transport is limited by the rate of diffusion, and the mean diffusion coefficient decreases with increasing number of carriers involved in transport. Addition of anion carrier **5** to cation carrier **1** does not always improve salt transport. At high salt concentration a single carrier system of carrier **1** is advantageous, whereas at low salt concentration the carrier

(40) Cohn, E. J., Edstall, J. T., Eds. *Proteins, Amino Acids and Peptides as Ions and Dipolar Ions*; Hafner Publishing Company: New York, 1965.

mixture of **1** and **5** is a more efficient system. KCl and CsCl were transported by ditopic receptors **8** and **9**, respectively, by simultaneous complexation of both the cation and anion. Ditopic receptor **9** transports CsCl much more efficiently than cation carrier **2** or anion carrier **7**. However, at high salt concentration, the transport of KCl by bifunctional carrier **8** is less effective than by cation carrier **1**, due to the surprisingly low rate of diffusion of the bifunctional carrier complex.

Experimental Section

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AC 250 spectrometer in $CDCl_3$. The presence of solvent in the analytical samples was confirmed by ^{1}H NMR spectroscopy. Fast atom bombardment (FAB) mass spectra were obtained with a Finnigan MAT 90 spectrometer. The spectra were obtained with use of *m*-nitrobenzyl alcohol as a matrix.

CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves (4 Å) prior to use. CH_3CN and DMSO were dried over molecular sieves (4 Å) prior to use. Petroleum ether refers to the fraction with bp 40−60 °C. Other chemicals were of reagent grade and were used without purification. Column chromatography was performed with silica gel (Merck; 0.015−0.040 mm) unless stated otherwise. All reactions were carried out under an argon atmosphere.

Carriers **1**,[22] **2**,[23] **3**,[41] and **10**[42] were synthesized according to literature procedures. The synthesis of carriers **5** and **6** is described elsewhere.[19]

2-[[8-(2-Nitrophenoxy)-1-octyloxy]methyl]-15-crown-5 (4). NaH (60%) as suspension in mineral oil (76 mg, 1.9 mmol) was washed twice with petroleum ether. Then THF (50 mL) was added followed by 2-hydroxymethyl-15-crown-5 (400 mg, 1.6 mmol). The mixture was stirred for 1 h. Subsequently, 8(-bromooctyl)-2-nitrophenyl ether (690 mg, 2.1 mmol) was added and the mixture was refluxed for 24 h. Water was added slowly, and the aqueous solution was extracted with CH_2Cl_2 (2 × 100 mL). The organic layer was washed with water (2 × 100 mL) and dried over $MgSO_4$. The crude residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 95:5) to obtain **4** as a yellow oil. Yield 46%; N_D^{20} 1.5425; ^{1}H NMR δ 7.76 (dd, 1 H, J_o = 8.1 Hz, J_m = 1.7 Hz, ArH), 7.5−7.35 (m, 1 H, ArH), 7.0−6.85 (m, 2H, ArH), 4.04 (t, 2H, J = 6.4 Hz, ArOCH_2), 3.8−3.4 (m, 19H, OCH_2CH_2), 3.4−3.25 (m, 4H, OCHCH_2O and OCH_2CH$_2$CH$_2$), 1.85−1.65 (m, 2H, ArOCH$_2$CH_2), 1.6−1.4 (m, 4H, CH$_2$OCH$_2$CH_2 and ArOCH$_2$CH$_2$CH_2), 1.35−1.1 (s, 6H, CH_2); ^{13}C NMR δ 152.5 (s, Ar*C*O), 139.9 (s, Ar*C*NO$_2$), 134.0−114.5 (d, Ar*C*H), 78.6 (d, O*C*H), 71.6−69.5 (t, *C*H$_2$O), 29.6−25.8 (t, CH$_2$*C*H$_2$CH$_2$); MS−FAB *m*/*z* 523.0 [(M + Na)$^+$, calcd 523.0].

25,27-Dipropoxy-26,28-bis[(3-(*N*′-(2-ethylhexyl)thioureido)propyl)oxy] calix[4]arene (7), *1,3-Alternate*. A solution of calix[4]arene **14** (0.50 g, 0.71 mmol) and 2-ethylhexylamine (0.58 mL, 3.5 mmol) in dry CH_2Cl_2 (100 mL) was stirred in a closed tube at room temperature for 10 h. Then CH_2Cl_2 was removed under reduced pressure. The solid was purified by column chromatography (CH_2Cl_2) and preparative TLC (hexane/EtOAc = 4:1) to afford **7** as a white solid. Yield 59%; mp 118−120 °C; ^{1}H NMR(400 MHz) δ 7.05 (d, 4 H, J = 7.2 Hz, ArH-*m*), 7.01 (d, 4 H, J = 7.2 Hz, ArH-*m*), 6.87 (t, 2 H, J = 7.4 Hz, ArH-*p*), 6.80 (t, 2 H, J = 7.6 Hz, ArH-*p*), 6.07 (bs, 4 H, N*H*), 3.81 (s, 8 H, ArCH$_2$Ar), 3.47 (bs, 8 H, CH$_2$CH_2N and NCH_2CH), 3.4−3.3 (m, 8 H, J = 7.6 Hz, OCH_2C$_2$H$_5$ and OCH_2(CH$_2$)$_2$N), 1.7−1.55 (m, 2 H, NCH$_2$C*H*), 1.55−1.45 (m, 4 H, CH_2CH$_2$N), 1.45−1.2 (m, 16 H, CH$_3$(CH_2)$_3$CH(CH_2CH$_3$)), 1.15−1.0 (m, 4 H, CH_2CH$_3$), 0.95−0.8 (m, 12 H, CH_3(CH$_2$)$_3$CH(CH$_2$CH_3)), 0.65 (t, 6 H, J = 7.6 Hz, CH_3); ^{13}C NMR-(400 MHz) δ 181.7 (s, C═S), 157.1, 156.2 (s, ArC−O), 134.3, 133.2 (s, ArC-*o*), 129.2, 128.9 (d, ArC-*m*), 122.2, 121.4 (d, ArC-*p*), 71.6, 67.0 (t, OCH$_2$C$_2$H$_4$N and OCH$_2$C$_2$H$_5$), 47.7, 40.6 (t, *C*H$_2$N), 38.9 (d, *C*HCH$_2$N), 38.0 (t, Ar*C*H$_2$Ar), 30.8, 29.4, 28.6, 24.0, 22.8, 21.9 (t, CH$_3$(*C*H$_2$)$_3$CH(*C*H$_2$CH$_3$) and *C*H$_2$CH$_2$N and *C*H$_2$CH$_3$), 13.8, 10.6, 9.6 (q, *C*H$_3$); IR (KBr) 3266 cm^{-1} (NH); MS−FAB *m*/*z* 963.5 [(M−H)$^-$, calcd 963.6]. Anal. calcd for $C_{58}H_{84}N_4O_4S_2$: C, 72.16; H, 8.77; N, 5.80. Found: C, 72.53; H, 8.71; N, 5.70.

General Procedure for the Synthesis of 25,27-Bis[(3-(*N*′-(2-ethylhexyl) thioureido)propyl)oxy]calix[4]arene-crown-*n* (*n* = 5, 6), *1,3-Alternate*. A solution of calix[4]arene-crown-*n* (*n* = 5, 6) **20** or **19** (0.64 mmol) and 2-ethylhexylamine (0.25 g, 1.92 mmol) in dry CH_2Cl_2 (50 mL) was stirred in a closed tube at room temperature for 10 h. Then CH_2Cl_2 was removed under reduced pressure. The pure compound were obtained after preparative TLC as a viscous oil (CH_2Cl_2/EtOAc = 19:1 and subsequently increasing the polarity with EtOAc).

25,27-Bis[(3-(*N*′-(2-ethylhexyl)thioureido)propyl)oxy]calix[4]arene-crown-5 (8). Yield 77%; ^{1}H NMR δ 7.09 (d, 4 H, J = 7.5 Hz, ArH-*m*), 7.06 (d, 4 H, J = 7.5 Hz, ArH-*m*), 7.0−6.8 (m, 4 H, ArH-*p*), 6.12 (bs, 4 H, NH), 3.85 (s, 8 H, ArCH$_2$Ar), 3.7−3.4 (m, 20 H, ArOCH_2-CH$_2$OCH_2CH_2 and OCH_2CH$_2$CH_2N), 3.2−3.0 (m, 8 H, ArOCH$_2$CH_2O and NCH_2CH), 1.65−1.55 (m, 2 H, NCH$_2$C*H*), 1.5−1.2 (m, 20 H, CH$_3$-(CH_2)$_3$CH(CH_2CH$_3$) and OCH$_2$CH_2CH$_2$N), 1.0−0.8 (m, 12 H, CH$_3$); ^{13}C NMR δ 182.4 (s, CS), 156.9 (s, ArC−O), 134.8, 133.8 (s, ArC-*o*), 129.5 (d, ArC-*m*), 123.2, 122.6 (d, ArC-*p*), 73.3, 71.1, 69.7, 68.1, 67.6 (t, OCH$_2$CH$_2$O and ArOCH$_2$), 48.3, 41.0 (t, *C*H$_2$N), 39.5 (d, CH$_3$-(CH$_2$)$_3$*C*H(C$_2$H$_5$)), 38.5 (t, ArCH$_2$Ar), 31.5, 30.0, 29.2, 24.7, 23.3 (t, CH$_3$(*C*H$_2$)$_3$CH(*C*H$_2$CH$_3$)CH$_2$N and OCH$_2$*C*H$_2$CH$_2$N), 14.3, 11.2 (q, CH$_3$); MS−FAB *m*/*z* 1037.3 [(M − H)$^-$, calcd 1037.6].

25,27-Bis[(3-(*N*′-(2-ethylhexyl)thioureido)propyl)oxy]calix[4]arene-crown-6 (9). Yield 95%; ^{1}H NMR δ 7.1−7.0 (m, 8 H, ArH-*m*), 6.95−6.85 (m, 4 H, ArH-*p*), 3.84 (s, 8 H, ArCH$_2$Ar), 3.69 (s, 4 H, ArO(CH$_2$CH$_2$O)$_2$CH_2), 3.65−3.45 (m, 20 H, ArOCH_2CH$_2$O(CH_2)$_2$O and OCH_2CH$_2$CH_2N), 3.2−3.0 (m, 8 H, ArOCH$_2$CH_2OC$_2$H$_4$ and NCH_2-CH), 1.62 (bs, 2 H, NCH$_2$C*H*), 1.5−1.2 (m, 20 H, CH$_3$(CH_2)$_3$CH(CH_2-CH$_3$) and OCH$_2$CH_2CH$_2$N), 1.0−0.8 (m, 12 H, CH$_3$); ^{13}C NMR δ 182.4 (s, CS), 157.2, 157.0 (s, ArC−O), 134.5, 133.9 (s, ArC-*o*), 129.8 (d, ArC-*m*), 123.0, 122.6 (d, ArC-*p*), 71.3, 71.2, 71.0, 69.5, 69.2, 67.6 (t, OCH$_2$CH$_2$O and ArOCH$_2$), 48.3, 41.1 (t, *C*H$_2$N), 39.5 (d, *C*HCH$_2$N), 38.5 (t, ArCH$_2$Ar), 31.4, 30.6, 29.2, 24.7, 23.3 (t, CH$_3$(*C*H$_2$)$_3$CH(*C*H$_2$-CH$_3$) and OCH$_2$*C*H$_2$CH$_2$N), 14.3, 11.1 (q, CH$_3$); MS−FAB *m*/*z* 1081.1 [(M − H)$^-$, calcd 1081.6].

25,27-Bis[(3-phthalimidopropyl)oxy]calix[4]arene (11). A mixture of 25,26,27,28-tetrahydroxycalix[4]arene **10** (1.00 g, 2.35 mmol), *N*-(3-bromopropyl)phthalimide (1.32 g, 4.94 mmol), K_2CO_3 (0.39 g, 2.82 mmol), and a catalytic amount of KI in dry CH_3CN (30 mL) was refluxed for 60 h. Then the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with 1 N NH_4Cl (2 × 25 mL). The organic phase was separated, dried with $MgSO_4$, and evaporated to dryness to afford a white solid that was triturated with CH_3CN. Yield 80%; mp 302−304 °C; ^{1}H NMR δ 7.95 (s, 2 H, OH), 7.85−7.70 (m, 8 H, Ph-H pht), 7.09 (d, 4 H, J = 9.5 Hz, ArH-*m*), 6.88 (d, 4 H, J = 10.7 Hz, ArH-*m*), 6.69 (t, 2 H, J = 9.5 Hz, ArH-*p*), 6.63 (t, 2 H, J = 10.7 Hz, ArH-*p*), 4.35 (d, 4 H, J = 13.0 Hz, ArCH$_{ax}$Ar), 4.18 (t, 8 H, J = 5.9 Hz, OCH_2CH$_2$CH_2N), 3.45 (d, 4 H, J = 11.9 Hz, ArCH$_{eq}$Ar), 2.51 (q, 4 H, J = 5.9 Hz, OCH$_2$CH_2-CH$_2$N); ^{13}C NMR δ 168.2 (s, C═O), 153.3, 151.9 (2s, ArC−O), 133.7 (d, PhCH, pht), 133.2, 132.1 (s, ArC-*o*), 128.9, 128.4 (d, ArC-*m*), 128.0 (s, PhC, pht), 125.3, 123.1 (d, PhCH, pht), 119.0 (d, ArC-*p*), 74.6 (t, OCH$_2$), 35.7 (t, NCH$_2$), 31.4 (t, ArCH$_2$Ar), 29.4 (t, OCH$_2$*C*H$_2$CH$_2$N); MS−FAB *m*/*z* 798.3 (M$^+$, calcd 798.9). Anal. calcd for $C_{50}H_{42}N_2O_8$·2CH$_3$CN: C, 73.62; H, 5.49; N, 6.36. Found: C, 73.77; H, 5.54; N, 6.28.

25,27-Dipropoxy-26,28-bis[(3-phthalimidopropyl)oxy]calix[4]-arene (12), *1,3-Alternate*. A solution of calix[4]arene **11** (1.0 g, 1.25 mmol), Cs_2CO_3 (1.6 g, 4.9 mmol), and PrI (1.3 g, 7.5 mmol) in dry MeCN (100 mL) was refluxed for 3 days. Then the solvent was removed under reduced pressure. Subsequently, the residue was dissolved in CH_2Cl_2 (70 mL) and washed with 1 N NH_4Cl (3 × 50 mL) and water (2 × 50 mL). The organic phase was separated, dried with $MgSO_4$, and evaporated to afford a solid, which was crystallized from MeOH to give **27** as a pure white powder. Yield 52%; mp 208−211 °C; ^{1}H NMR δ 7.9−7.6 (m, 8 H, PhH pht), 7.1−6.9 (m, 8 H, ArH-*m*), 6.81 (t, 2 H, J = 7.3 Hz, ArH-*p*), 6.72 (t, 2 H, J = 7.5 Hz, ArH-*p*), 3.68 (s, 8 H, ArCH$_2$Ar), 3.62 (t, 4 H, J = 3.2 Hz, OCH_2(CH$_2$)$_2$N), 3.51, 3.43 (2 × t, 8 H, J = 3.0 Hz and J = 3.0 Hz, CH_2N and OCH_2C$_2$H$_5$), 1.9−

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(42) Gutsche, C. D.; Lin, L.-G. *Tetrahedron* **1986**, *51*, 742.

1.6 (m, 4 H, CH_2CH$_2$N), 1.5−1.4 (m, 4 H, CH_2CH$_3$), 0.78 (t, 6 H, J = 7.5 Hz, OCH$_2$CH$_2$CH_3); ^{13}C NMR δ 168.3 (s, C═O), 156.7, 156.3 (s, ArC−O), 133.9, 133.8 (s, ArC-*o*), 133.8 (d, PhCH, pht), 132.2 (s, PhC, pht), 129.8, 129.6 (d, ArC-*m*), 123.3, 123.2 (d, ArC-*p*), 122.3, 122.0 (d, PhCH, pht), 72.8, 68.7 (t, OCH$_2$CH$_2$CH$_3$ and OCH$_2$CH$_2$CH$_2$N), 37.3 (t, ArCH$_2$Ar), 35.3 (t, CH$_2$N), 29.1 (t, CH$_2$CH$_2$N), 23.1 (t, CH$_2$CH$_3$), 10.3 (q, OCH$_2$CH$_2$CH$_3$); IR (KBr) 1714 cm^{-1} (C═O); MS−FAB *m*/*z* 905.5 [(M + Na)$^+$, calcd 905.4]. Anal. calcd for $C_{56}H_{54}N_2O_8\cdot0.5H_2O$: C, 75.40; H, 6.21; N, 3.14. Found: C, 75.17; H, 6.05; N, 3.16.

25,27-Dipropoxy-26,28-bis[(3-aminopropyl)oxy]calix[4]arene (13), *1,3-Alternate*. A solution of calix[4]arene **27** (0.20 g, 0.23 mmol) and $NH_2NH_2\cdot H_2O$ (0.22 g, 4.5 mmol) in ethanol (30 mL) was stirred in a closed tube at 110−120 °C for 8 h. Then the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with a solution of NH_4OH (pH ≈ 9) (3 × 15 mL). The organic phase was separated, dried with $MgSO_4$, and evaporated to afford **13** as a pure solid. Yield 96%; mp 195−198 °C; ^{1}H NMR δ 7.0−6.9 (m, 8 H, ArH-*m*), 6.8−6.6 (m, 4 H, ArH-*p*), 3.61 (s, 8 H, ArCH$_2$Ar), 3.56, 3.39 (2 × t, 8 H, J = 6.6 Hz and J = 7.5 Hz, OCH_2-CH$_2$CH$_2$N and OCH_2CH$_2$CH$_3$), 2.62 (t, 4 H, J = 6.8 Hz, CH$_2$N), 1.7−1.55 (m, 4 H, CH$_2$CH$_2$N), 1.45−1.3 (m, 4 H, CH$_2$CH$_3$), 0.76 (t, 6 H, J = 7.5 Hz, CH_3); ^{13}C NMR δ 156.7 (s, ArC−O), 134.0, 133.7 (s, ArC-*o*), 129.9, 129.7 (d, ArC-*m*), 121.9, 121.7 (d, ArC-*p*), 72.9, 70.2 (t, OCH$_2$), 39.9 (t, NCH$_2$), 37.1 (t, ArCH$_2$Ar), 34.1 (t, CH$_2$CH$_2$N), 23.0 (t, CH$_2$CH$_3$), 10.3 (q, CH$_3$); IR (KBr) 3369 cm^{-1} (NH$_2$); MS−FAB *m*/*z* 623.3 [(M + H)$^+$, calcd 623.4]. Anal. calcd for $C_{40}H_{50}N_2O_4$: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.68; H, 8.14; N, 4.48.

25,27-Dipropoxy-26,28-bis[(3-isothiocyanatopropyl)oxy]calix[4]-arene (14), *1,3-Alternate*. A solution of calix[4]arene **13** (0.50 g, 0.80 mmol), thiophosgene (0.50 g, 3.2 mmol), and NEt$_3$ (0.80 g, 8.0 mmol) in dry toluene (160 mL) was heated to 60 °C for 6 h. The solvent was removed under reduced pressure, after which the crude product was dissolved in CH_2Cl_2 (20 mL) and washed with water (3 × 10 mL). The organic phase was dried with $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc = 1:1) and crystallization from MeOH. Yield 62%; mp 177−179 °C; ^{1}H NMR(400 MHz) δ 7.1−7.0 (m, 8 H, ArH-*m*), 6.88 (t, 2 H, J = 7.6 Hz, ArH-*p*), 6.82 (t, 2 H, J = 7.4 Hz, ArH-*p*), 3.81, 3.79 (2 × d, 8 H, J = 6.8 Hz, J = 10.4 Hz, ArCH$_2$Ar), 3.64, 3.36 (2 × t, 8 H, J = 6.4 Hz, J = 7.8 Hz, OCH_2C$_2$H$_5$ and OCH_2(CH$_2$)$_2$N), 3.11 (t, 4 H, J = 6.6 Hz, CH$_2$N), 1.8−1.6 (m, 4 H, CH$_2$CH$_2$N), 1.2−1.0 (m, 4 H, CH$_2$CH$_3$), 0.68 (t, 6 H, J = 7.2 Hz, CH_3); ^{13}C NMR(400 MHz) δ 157.0, 156.2 (s, ArC−O), 134.2, 133.5 (s, ArC-*o*), 129.5, 129.1 (d, ArC-*m*), 122.6, 122.0 (d, ArC-*p*), 71.8, 66.2 (t, OCH$_2$(CH$_2$)$_2$N and OCH$_2$C$_2$H$_5$), 41.8 (t, CH$_2$N), 38.1 (t, ArCH$_2$Ar), 30.4 (t, CH$_2$CH$_2$N), 22.3 (t, CH$_2$-CH$_3$), 9.9 (q, CH$_3$); IR (KBr) 2094 cm^{-1} (N═C═S); MS−FAB *m*/*z* 707.7 [(M + H)$^+$, calcd 707.3]. Anal. calcd for $C_{42}H_{46}N_2O_4S_2$: C, 71.36; H, 6.56; N, 3.96. Found: C, 71.04; H, 6.51; N, 3.92.

General Procedure for the Synthesis of 25,27-Bis[(3-phthalimidopropyl)oxy] calix[4]arene-crown-*n* (*n* = 5, 6), *1,3-Alternate*. A solution of calix[4]arene **11** (2.00 g, 2.5 mmol), Cs_2CO_3 (4.00 g, 12.3 mmol), and tetra- or pentaethylene glycol di-*p*-toluenesulfonate (2.58 mmol) in dry MeCN (500 mL) was refluxed for 5 days. Subsequently, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (40 mL) and washed with 1 N NH_4Cl (3 × 20 mL). The organic phase was separated, dried with $MgSO_4$, and evaporated to afford a brown solid, which was purified by column chromatography (CH_2Cl_2/MeOH = 95:5).

25,27-Bis[(3-phthalimidopropyl)oxy]calix[4]arene-crown-5 (15). Yield 40%; mp 106−108 °C; ^{1}H NMR δ 7.9−7.7 (2 × m, 2 × 4 H, PhH pht), 7.10 (d, 4 H, J = 8.7 Hz, ArH-*m*), 7.02 (d, 4 H, J = 8.0 Hz, ArH-*m*), 6.87 (t, 4 H, J = 8.0 Hz, ArH-*p*), 3.82 (s, 8 H, ArCH$_2$Ar), 3.60 (s, 8 H, ArO(CH$_2$)$_2$OCH_2CH_2), 3.55−3.35 (m, 12 H, ArOCH_2-CH$_2$O and OCH_2CH$_2$CH_2N), 3.15 (t, 4 H, J = 7.0 Hz, ArOCH$_2$CH_2O), 1.6−1.4 (m, 4 H, CH_2CH$_2$N); ^{13}C NMR δ 168.2 (s, C═O), 156.5, 156.1 (s, ArC−O), 134.1, 134.0 (s, ArC-*o*), 133.7 (d, PhCH, pht), 132.1 (s, PhC, pht), 129.2, 129.1 (d, ArC-*m*), 123.1, 123.0 (d, ArC-*p*), 122.6 (d, PhCH, pht), 72.6, 70.6, 69.9, 68.3, 67.8 (t, OCH$_2$CH$_2$O and ArOCH$_2$), 38.1 (t, ArCH$_2$Ar), 35.0 (t, CH$_2$N), 28.5 (t, CH$_2$CH$_2$N); MS−FAB *m*/*z* 979.6 [(M + Na)$^+$, calcd 979.4]. Anal. calcd for $C_{58}H_{56}N_2O_{11}$: C, 72.79; H, 5.90; N, 2.93. Found: C, 73.04; H, 5.68; N, 3.03.

25,27-Bis[(3-phthalimidopropyl)oxy]calix[4]arene-crown-6 (16). Yield 78%; mp 180−181 °C; ^{1}H NMR δ 7.85−7.70 (m, 8 H, PhH pht), 7.07 (d, 4 H, J = 8.0 Hz, ArH-*m*), 7.00 (d, 4 H, J = 8.0 Hz, ArH-*m*), 6.80 (t, 4 H, J = 8.0 Hz, ArH-*p*), 3.78 (s, 8 H, ArCH$_2$Ar), 3.68 (s, 4 H, ArO(CH$_2$CH$_2$O)$_2$CH_2), 3.65−3.40 (m, 20 H, OCH_2CH$_2$-OCH_2CH_2OCH$_2$ and CH_2CH$_2$CH_2N), 3.16 (t, 4 H, J = 7.1 Hz, ArOCH$_2$CH_2O), 1.6−1.4 (m, 4 H, CH_2CH$_2$N); ^{13}C NMR δ 168.2 (s, C═O), 156.5 (s, ArC−O), 134.0, 133.8 (s, ArC-*o*), 133.7 (d, PhCH, pht), 132.1 (s, PhC, pht), 129.6, 129.5 (d, ArC-*m*), 123.1, 122.9 (d, ArC-*p*), 122.5 (d, PhCH, pht), 71.1, 70.9, 69.7, 67.9 (t, OCH$_2$CH$_2$O and ArOCH$_2$), 38.0 (t, ArCH$_2$Ar), 35.0 (t, CH$_2$N), 28.5 (t, CH$_2$CH$_2$N); MS−FAB *m*/*z* 1023.9 [(M + Na)$^+$, calcd 1024.1]. Anal. calcd for $C_{60}H_{60}N_2O_{12}\cdot2H_2O$: C, 69.48; H, 6.22; N, 2.70. Found: C, 69.38; H, 5.79; N, 2.67.

General Procedure for the Synthesis of 25,27-Bis[(3-aminopropyl)-oxy]calix[4]arene-crown-*n* (*n* = 5, 6), *1,3-alternate*. To a solution of calix[4]crown-*n* (*n* = 5, 6) **16** or **15** (0.62 mmol) in ethanol (30 mL) was added $NH_2NH_2\cdot H_2O$ (0.63 g, 12.6 mmol). The reaction mixture was stirred in a closed tube at 110 °C for 10 h. Then the solvent was evaporated, and the remaining solid was dissolved in CH_2Cl_2 (25 mL) and washed with a 1 mM solution of NaOH (3 × 15 mL) and water (2 × 15 mL). The organic phase was dried with $MgSO_4$. Removal of the solvent under reduced pressure gave the desired bis[(3-aminopropyl)-oxy]calix[4]crown-*n* (*n* = 5, 6) derivatives **18** and **17**.

25,27-Bis[(3-aminopropyl)oxy]calix[4]arene-crown-5 (17). Yield 87%; mp 146−148 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.12 (d, 4 H, J = 7.4 Hz, ArH-*m*), 7.05 (d, 4 H, J = 7.5 Hz, ArH-*m*), 6.88 (t, 4 H, J = 7.3 Hz, ArH-*p*), 3.84 (s, 8 H, ArCH$_2$Ar), 3.7−3.6 (m, 8 H, OCH$_2$-CH$_2$O), 3.57 (t, 4 H, J = 6.25 Hz, ArOCH_2CH$_2$O), 3.44 (t, 4 H, J = 6.80 Hz, OCH_2(CH$_2$)$_2$N), 3.10 (t, 4 H, J = 6.8 Hz, ArOCH$_2$CH_2O), 2.48 (t, 4 H, J = 6.6 Hz, CH$_2$N), 1.57 (bs, 4 H, NH$_2$), 1.55−1.4 (m, 4 H, CH$_2$CH$_2$N); ^{13}C NMR δ 161.0 (s, ArC−O), 134.5, 134.3 (s, ArC-*o*), 129.7 (d, ArC-*m*), 122.8 (d, ArC-*p*), 73.1, 71.0, 69.9, 69.6, 68.2 (t, OCH$_2$), 39.6 (t, ArCH$_2$Ar), 38.5 (t, CH$_2$CH$_2$N), 29.9 (t, CH$_2$CH$_2$N); IR (KBr) 3404 cm^{-1} (NH$_2$); MS-DCI *m*/*z*, 697.5 [(M + H)$^+$, calcd 697.4].

25,27-Bis[(3-aminopropyl)oxy]calix[4]arene-crown-6 (18). Yield 88%; mp 159−160 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.07 (d, 4 H, J = 6.1 Hz, ArH-*m*), 7.05 (d, 4 H, J = 6.1 Hz, ArH-*m*), 6.9−6.8 (m, 4 H, ArH-*p*), 3.80 (s, 8 H, ArCH$_2$Ar), 3.7−3.5 (m, 20 H, OCH$_2$ and ArOCH$_2$(CH$_2$)N), 3.29 (t, 4 H, J = 6.2 Hz, ArOCH$_2$CH_2O), 2.90 (bs, 4 H, CH_2NH$_2$), 2.16 (bs, 4 H, NH$_2$), 1.55−1.4 (m, 4 H, CH_2CH$_2$N); ^{13}C NMR δ 156.3, 155.3 (s, ArC−O), 134.5, 133.3 (s, ArC-*o*), 129.9, 129.7 (d, ArC-*m*), 123.4, 122.7 (d, ArC-*p*), 70.7, 70.6, 70.5, 69.3, 69.0, 68.9 (t, OCH$_2$), 38.3 (t, ArCH$_2$Ar), 37.5 (t, CH$_2$N), 29.2 (t, CH$_2$CH$_2$N); IR (KBr) 3380 cm^{-1} (NH$_2$); MS-DCI *m*/*z*, 741.4 [(M + H)$^+$, calcd 741.4].

General Procedure for the Synthesis of 25,27-Bis[(3-isothiocyanatopropyl)oxy] calix[4]arene-crown-*n* (*n* = 5, 6), *1,3-Alternate*. Thiophosgene (0.33 g, 2.9 mmol) and NEt$_3$ (0.73 g, 7.2 mmol) were added to a solution of calix[4]arene-crown-*n* (*n* = 5−6) **18** or **17** (0.72 mmol) in dry toluene (100 mL). The solution was stirred and heated at 60 °C for 6 h, after which the solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 (20 mL) and washed with water (3 × 10 mL). The organic phase was dried with $MgSO_4$ and evaporated under reduced pressure. The residual solid was purified by column chromatography (CH_2Cl_2/EtOAc = 4:1).

25,27-Bis[(3-isothiocyanatopropyl)oxy]calix[4]arene-crown-5 (19). Yield 67%; mp 184−186 °C; ^{1}H NMR δ 7.12 (d, 4 H, J = 7.4 Hz, ArH-*m*), 7.07 (d, 4 H, J = 7.4 Hz, ArH-*m*), 6.95−6.85 (m, 4 H, ArH-*p*), 3.87 (s, 8 H, ArCH$_2$Ar), 3.7−3.5 (m, 12 H, ArOCH_2CH$_2$-OCH_2CH_2O), 3.46 (t, 4 H, J = 6.7 Hz, OCH_2CH$_2$CH$_2$N), 3.03 (t, 4 H, J = 6.5 Hz, OCH$_2$CH$_2$CH_2N), 3.02 (t, 4 H, ArOCH$_2$CH_2O), 1.7−1.5 (m, 4 H, OCH$_2$CH_2CH$_2$N); ^{13}C NMR δ 157.0 (s, ArC−O), 134.5, 133.9 (s, ArC-*o*), 129.6, 129.3 (d, ArC-*m*), 125.9 (s, NCS), 123.4, 122.9 (d, Ar-*p*), 73.3, 71.1, 70.2, 69.8, 68.1, 66.4 (t, OCH$_2$CH$_2$O and ArOCH$_2$), 42.0 (t, CH$_2$NCS), 38.4 (t, ArCH$_2$Ar), 30.6 (t, CH$_2$CH$_2$NCS); MS-DCI *m*/*z* 780.0 [M$^+$, calcd 780.5].

25,27-Bis[(3-isothiocyanatopropyl)oxy]calix[4]arene-crown-6 (20). Yield 63%; mp 179−180 °C; ^{1}H NMR δ 7.11 (d, 4 H, J = 7.6 Hz, ArH-*m*), 7.07 (d, 4 H, J = 7.7 Hz, ArH-*m*), 6.95−6.85 (m, 4 H, ArH-*p*), 3.85 (s, 8 H, ArCH$_2$Ar), 3.70 (s, 4 H, ArO(CH$_2$CH$_2$O)$_2$CH_2), 3.7−

3.4 (m, 16 H, ArOCH_2CH$_2$OCH_2CH_2O and OCH_2(CH$_2$)$_2$N), 3.14 (t, 4 H, J = 6.7 Hz, CH_2N), 3.08 (t, 4 H, J = 6.8 Hz, ArOCH$_2$CH_2O), 1.6−1.4 (m, 4 H, CH_2CH$_2$N); ^{13}C NMR ($CDCl_3$) δ 157.0, 156.7 (s, ArC−O), 134.3, 134.0 (s, ArC-*o*), 129.9, 129.6 (d, ArC-*m*), 125.9 (s, NCS), 123.3, 122.8 (d, ArC-*p*), 71.4, 71.3, 71.1, 70.2, 69.5, 69.1, 66.5 (t, OCH$_2$-CH$_2$O and ArOCH$_2$), 42.1 (t, *C*H$_2$NCS), 38.4 (t, ArCH$_2$Ar), 30.6 (t, *C*H$_2$CH$_2$NCS); MS-DCI *m*/*z* 824.6 [M$^+$, calcd 824.4].

Transport Measurements. The polymeric film Accurel 1E-PP was obtained from Enka Membrana (thickness d_m = 100 μm, porosity τ = 64%). *o*-Nitrophenyl *n*-octyl ether (NPOE) was purchased from Fluka and was used without further purification. All salts were of analytical grade and were obtained from Across. The transport experiments were performed at 298 K in an apparatus of which the details are described elsewhere.[43] The carrier was dissolved in *o*-nitrophenyl *n*-octyl ether (NPOE) and immobilized in the solid support according to a standard procedure previously described by our group.[43] The aqueous solutions were prepared with doubly distilled and deionized water. The transport of single salts was monitored by a measurement of the conductivity with time (Radiometer CDM 83). The concentration was calculated using a constant that correlates the conductivity to the concentration. The activity was determined by calculation of the activity coefficient using the Debye−Hückel equation.[44] The transport rates of KH_2PO_4 and NaH_2PO_4 were determined by phosphate analysis of the receiving phase after 14 h of transport. From the receiving phase, several aliquots of 100 μL were taken. To each sample was added 1 mL of commercial phosphorus reagent (Sigma chemicals). The reaction of the inorganic phosphorus with ammonium molybdate in the presence of sulfuric acid produces an unreduced phosphomolybdate complex, of which the absorbance at 320 nm is proportional to the phosphorus concentration. In the case of competitive transport, the transport was monitored by atomic absorption measurements of samples from the receiving phase. The lag-time experiments and the transport at different membrane thickness have been carried out according to literature procedures.[5]

Caution: *Care should be taken when handling uranyl-containing compounds because of their toxicity and radioactivity.*[45]

Supporting Information Available: Equations to calculate the Extraction efficiency of salts by a mixture of anion and cation carrier via a 1:1 complex or via a 1:1 cation complex and a 2:1 anion complex; transport model for facilitated transport of salt by a mixture of anion and cation receptor; two figures with calculated extraction efficiencies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA991588G

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