JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

Controlling Cesium Cation Recognition via Cation Metathesis within an Ion Pair Receptor

Sung Kuk Kim,[†] Gabriela I. Vargas-Zúñiga,[†] Benjamin P. Hay,*[,∥] Neil J. Young,[∥] Lætitia H. Delmau,[∥] Charles Masselin,[∥] Chang-Hee Lee,*[,‡] Jong Seung Kim,*[,§] Vincent M. Lynch,[†] Bruce A. Moyer,*[,∥] and Jonathan L. Sessler*[,†,⊥]

[†]Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station, A5300, Austin, Texas 78712-0165, United States

[‡]Department of Chemistry, Kangwon National University, Chun-Chon 200-701, Korea

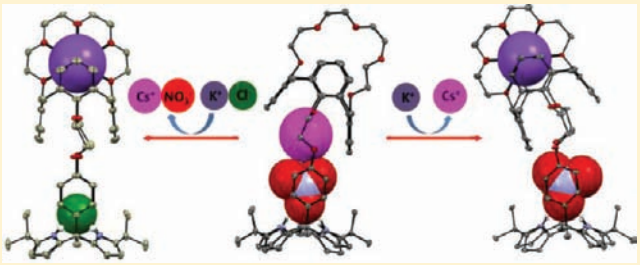
[§]Department of Chemistry, Korea University, Seoul 136-701, Korea

[∥]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830-6119, United States

[⊥]Department of Chemistry, Yonsei University, Seoul 120-749, Korea

Supporting Information

ABSTRACT: Ion pair receptor **3** bearing an anion binding site and multiple cation binding sites has been synthesized and shown to function in a novel binding−release cycle that does not necessarily require displacement to effect release. The receptor forms stable complexes with the test cesium salts, CsCl and $CsNO_3$, in solution (10% methanol-d_4 in chloroform-d) as inferred from ^{1}H NMR spectroscopic analyses. The addition of $KClO_4$ to these cesium salt complexes leads to a novel type of cation metathesis in which the "exchanged" cations occupy different binding sites. Specifically, K^+ becomes bound at the expense of the Cs^+ cation initially present in the complex. Under liquid−liquid conditions, receptor **3** is able to extract $CsNO_3$ and CsCl from an aqueous D_2O layer into nitrobenzene-d_5 as inferred from ^{1}H NMR spectroscopic analyses and radiotracer measurements. The Cs^+ cation of the $CsNO_3$ extracted into the nitrobenzene phase by receptor **3** may be released into the aqueous phase by contacting the loaded nitrobenzene phase with an aqueous $KClO_4$ solution. Additional exposure of the nitrobenzene layer to chloroform and water gives **3** in its uncomplexed, ion-free form. This allows receptor **3** to be recovered for subsequent use. Support for the underlying complexation chemistry came from single-crystal X-ray diffraction analyses and gas-phase energy-minimization studies.



INTRODUCTION

The March 2011 Tohoku earthquake and tsunami and subsequent release of radioactive material, including ^{137}Cs (half-life 30.2 y), from the Fukushima Daiichi Nuclear Power Plant has added new urgency to the long-standing need to develop synthetic receptors for Cs^+. Precedent for use of metal ion receptors in nuclear applications has been growing rapidly in the past 10 years, with first simple crown ethers and more recently more powerful calixarenes being applied to the problem of Cs^+ recognition.[1] To be effective, these receptors must recognize the cesium cation selectively under a variety of conditions and in the presence of various potentially competing cations, including notably Na^+ (as found in seawater and so-called tank waste). However, selective binding is only the first part of recognition as defined by Lehn.[2] Specifically, recognition in a supramolecular sense implies control of function. For most applications involving the cesium cation (e.g., sensor development, solid-phase separations, liquid−liquid extraction), this translates, at a minimum, into an ability to control both initial Cs^+ binding and subsequent release. In actual practice, the latter part of the recognition event often constitutes the greater challenge. Traditionally, release strategies have centered around simple mass-action equilibrium shifts driven by concentration differences and simple displacement reactions. However, the accessible range of gradients is usually modest. This has the consequence that many stripping stages are generally required, as is the case for the caustic-side solvent extraction (CSSX) process currently operating at the pilot scale for the removal of ^{137}Cs from tank waste.[1,3] By contrast, a binding−release cycle effected by an on−off switching mechanism could in principle reduce the separation process to just two ideal stages, namely, initial binding and subsequent controlled release. Examples of synthetic recognition systems displaying such efficiency remain elusive. Among the concepts explored, albeit not in the context of Cs^+ complexation, are photochemical,[4] electrochemical,[5] and binding-induced conformational switching mechanisms.[6] Here we

Received: October 25, 2011
Published: December 19, 2011

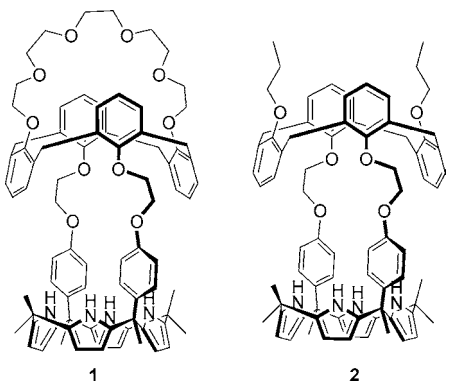
   dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782−1792

report a new approach involving cation metathesis within an ion pair receptor. As detailed below, it permits the complexation and controlled release of various cesium salts (including the nitrate and chloride anion forms relevant to studies involving tank waste and seawater, respectively) both in organic media (10% methanol-d_4/chloroform-d) and under conditions of liquid–liquid (aqueous–nitrobenzene) extraction. The receptor itself can be regenerated in its ion-free form through a simple sequence of liquid–liquid contacts with chloroform and neutral aqueous phases. To the best of our knowledge, a binding–release cycle employing release stimulated by remote binding has not been previously observed using either ion pair receptors or combinations of simple anion or cation receptors.

We consider the use of an ion-pairing strategy appealing as a means of controlling the binding and subsequent release of the cesium cation. Broadly speaking, ion pair receptors are species that have two or more different ion recognition sites and which are able to bind both cations and anions.[7,8] In early pioneering work Smith and Beer reported ditopic systems that displayed enhanced affinities for targeted ion pairs as compared to appropriately chosen monotopic or single site receptor controls.[7,8] More broadly, the putative improvements in affinity and selectivity that can be achieved relative to single-site receptors has made ion pair receptors attractive for use in salt solublization, ion extraction, transmembrane ion transport, and ion sensing and as logic gates.[8−17] However, in spite of their potential advantages in functional recognition, to our knowledge no ion pair receptor has been successfully applied to the problem of controlled cesium cation binding, extraction, and release.

It was our thought that ion pair receptors could function as on–off switches if they contain two binding sites, each selective for a different metal cation, within the same molecule. A fundamental problem with displacement-type release mechanisms is that they require a binding site that is able to accommodate different cations, which paradoxically tends to defeat the goal of high binding selectivity. However, if two separate binding sites are present, each with high selectivity for different cations and whose binding affinities are codependent, then a switched binding–release cycle would become possible via a novel process in which the exchange takes place at remote sites. As detailed below, we have now demonstrated the viability of this approach.

Recently, we reported the ion pair receptor **1** bearing two strong ion binding sites (a calix[4]arene crown-6 for the Cs^+ cation and a calix[4]pyrrole for anions) and demonstrated its ability to stabilize a solvent-separated cobound CsF ion pair complex.[18] Subsequently, we found that the crown-free ion pair receptor **2** formed ion pair complexes with CsF, CsCl, CsBr, and $CsNO_3$.[14] Depending on the salt in question, the Cs^+ cations were found to bind to the ethylene glycol moieties between the calix[4]pyrrole subunit and the calix[4]arene "cap". In all cases, however, preference for Cs^+ relative to other alkali-metal cations was seen. Thus, neither **1** nor **2** acts as a switchable functional receptor, wherein release of the bound cation can be achieved by means other than mass action or displacement. With the goal of obtaining an ion pair receptor that might allow for the controlled recognition and release of the cesium cation, we have now prepared receptor **3** (cf. Scheme 1). While retaining the calix[4]pyrrole anion binding site, receptor **3** differs from **1** in that it has one fewer oxygen atom in the calix[4]arene crown ring (i.e., a crown-5, rather than crown-6, strapping moiety). This change was expected to provide a system with a dedicated K^+ binding site and thus an inherent preference for K^+ relative to Cs^+ at that site.[19,20] To the extent this proved true, it was expected to give rise to a system that would allow for the initial complexation of the cesium cation (in any of several possible ion pair binding modes[14,18,21]) in the absence of K^+ and then its subsequent release by exposure to the K^+ cation. In the limit, these thermodynamic differences could be exploited to achieve cesium cation extraction and stripping under conditions of liquid–liquid extraction. The validity of this strategy, shown schematically in Figure 1, has now been demonstrated in the case of both cesium nitrate and cesium chloride salts (as present in tank waste and seawater, respectively). Furthermore, under conditions of aqueous nitrobenzene liquid–liquid extraction, interference from the sodium cation was found to to be nil. Finally, a simple sequential liquid–liquid contacting strategy has been discovered that demonstrates the principle of regeneration of the metal-free form of the receptor.



1 2

RESULTS AND DISCUSSION

The synthesis of ion pair receptor **3** is summarized in Scheme 1. Briefly, the hydroxyl group of 1-[4-(2-hydroxyethoxy)-phenyl]ethanone (**4**) was tosylated using NaOH and TsCl in THF to give tolsylate **5** in high yield. This intermediate was subsequently condensed with pyrrole in the presence of 20 equiv of trifluoroacetic acid (TFA) at 65 °C to produce dipyrromethane **6** in 62% yield. The dipyrromethane tosylate **6** was reacted with the calix[4]arene monocrown-5 (**7**)[22] in the presence of 3.0 equiv of Cs_2CO_3 in acetonitrile under reflux to afford the calix[4]arene crown-5 dipyrromethane **8** in the 1,3-alternate conformation in 61% yield. Further condensation of compound **8** with acetone in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ gave ion pair receptor **3** in 18% yield.[14,18] Compound **3** was fully characterized by standard spectroscopic means, as well as by single-crystal X-ray diffraction analysis (Figure S1, Supporting Information). The resulting crystal structure revealed that the calix[4]arene subunit adopts the expected 1,3-alternate conformation.

Theoretical support for the suggestion that receptor **3** would prove selective for K^+ over Cs^+ came from molecular mechanics calculations carried out for the gas phase in the absence of solvent (cf. Supporting Information). Figure 2 shows four limiting binding modes for the complexation of cesium salts. These distinct modes, which are also seen for the corresponding potassium salts, are designated crown/crown, crown/pyrrole, glycol/pyrrole, and pyrrole/pyrrole. Here, the first part of the name indicates the location of the cation and the latter part of the name indicates the location of the anion. The relative stabilities of these binding modes with several

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782−1792

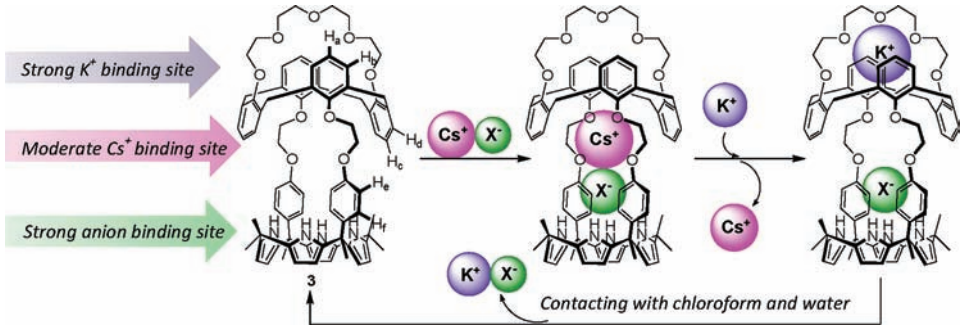
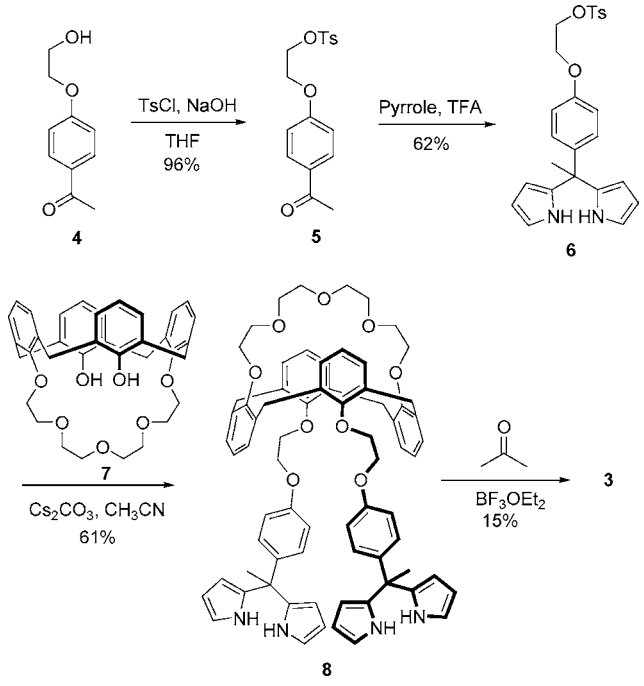


Figure 1. Design concept underlying ion pair receptor **3**.

Scheme 1. Synthesis of Ion Pair Receptor 3



cation−anion pairs are summarized in Table 1. These values are consistent with the design expectation that, irrespective of the binding mode, there is a strong preference for binding K^+ over Cs^+. They also reveal decisively that, in the absence of solvation,

Table 1. Calculated Gas-Phase Binding Energy for Ion Pairs in Different Binding Modes of 3

	ΔE^a (kcal/mol)			
ion pair	crown/crown	crown/pyrrole	glycol/pyrrole	pyrrole/pyrrole
KCl	−152.4	−130.1	−144.8	−130.0
CsCl	−132.4	−115.8	−135.5	−117.6
KNO_3	−149.7	−132.7	−149.9	−114.6
$CsNO_3$	−129.6	−116.7	−135.8	−103.5
$KClO_4$	−143.9	−119.1	−138.1	−103.1
$CsClO_4$	−126.8	−104.1	−121.3	−91.7

$^a\Delta E = E(\text{complex}) - E(\text{ligand}) - E(\text{cation}) - E(\text{anion})$.

the preferred gas-phase binding modes are those that minimize the distance between the two ions. Crown/crown and glycol/pyrrole pairs are thus preferred, but they are not greatly different in energy nor is one mode consistently more stable than the other. As a consequence, the $KClO_4$ and $CsClO_4$ salts exhibit a modest preference for the crown/crown mode, whereas CsCl and $CsNO_3$ exhibit a slight preference for the glycol/pyrrole mode. In contrast to what is true for simple calix[4]pyrroles,[21] complexation via the pyrrole/pyrrole mode is not favored.

Experimental support for the notion that receptor **3** can complex the cesium cation came from a single-crystal X-ray diffraction analysis of the 1:1 complex with CsCl. The resulting structure revealed that the Cs^+ and Cl^- ions are bound to calix[4]arene crown-5 and the calix[4]pyrrole moieties, respectively (Figure 3). The N···Cl^- and Cs^+···O distances

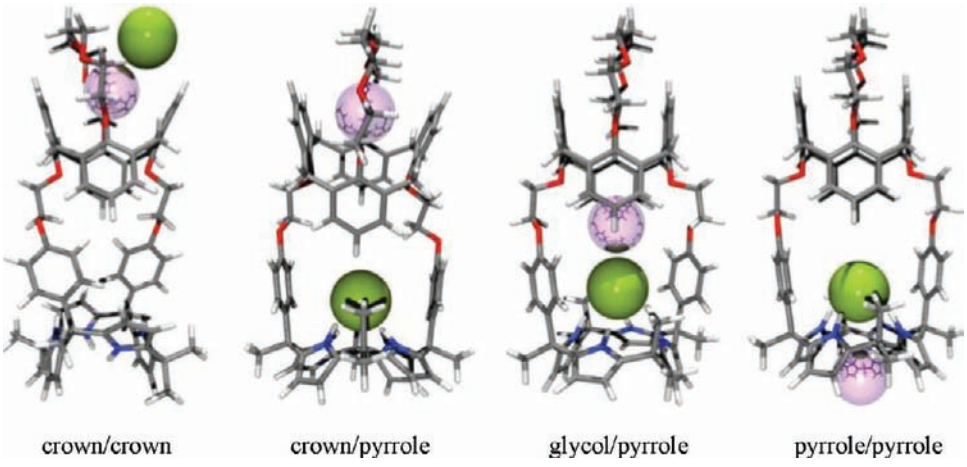


Figure 2. Views of the four limiting binding modes proposed for the interaction of receptor **3** with CsCl. Similar modes are considered in the case of other salts; cf. Table 1.

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782−1792

and the π–metal separation between the Cs^+ ion and the aromatic carbon atoms of the calix[4]arene core were found to

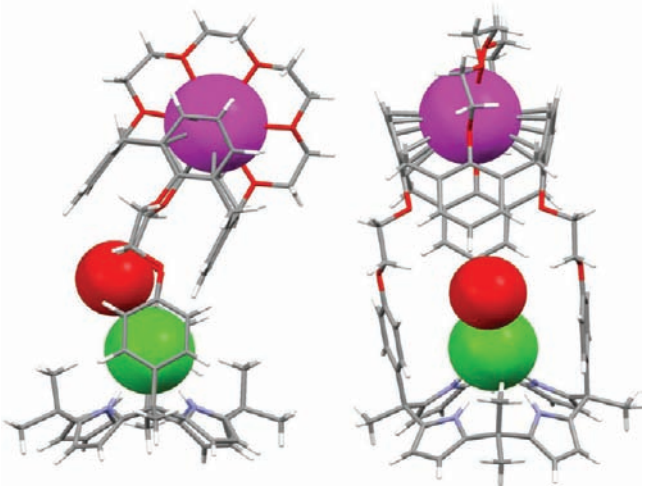


Figure 3. Two different views of the single-crystal X-ray diffraction structure of **3**·$CsCl·H_2O$. Solvent molecules not involved in the ion pair complex have been removed for clarity.

be 3.23–3.31, 2.84–3.10, and 3.29–3.40 Å, respectively. One water molecule also interacts with the bound Cl^- anion through what is assumed to be a hydrogen-bonding interaction. The relevant O···Cl^- distance is 3.22 Å. Although it may seem that the X-ray structure "disobeys" the gas-phase prediction of a crown–crown structure, the disparity presumably reflects the proximity of neighboring ions in the solid state. This, in turn, permits the apparent cation–anion separation within the ion pair receptor in the X-ray structure.

The structure of the $CsNO_3$ complex in the solid state was also determined by X-ray diffraction analysis of single crystals obtained via the slow evaporation of an ethanol/chloroform solution of **3** in the presence of excess $CsNO_3$. The resulting crystal structure revealed that, in contrast to what was seen for the CsCl complex, the Cs^+ cation is coordinated by the oxygen atoms of the ethylene glycol spacers but not by the crown-5 ring (Figure 4). Such anion-dependent structural differences in complexation mode stands in contrast to what was seen in the case of **1** and **2**.[14,18] The distances between the Cs^+ cation and the oxygen atoms of the ethylene glycolic spacers were found to be 3.01–3.63 Å in the $CsNO_3$ complex. In addition, the bound Cs^+ ion interacts closely with two oxygen atoms of the cobound nitrate anion with Cs^+···O distances of 3.19 and 3.50 Å, as well as with an ethanol molecule. Interactions between the Cs^+ cation and the aromatic carbon atoms of the inverted phenoxy groups of the calix[4]arene moiety were also inferred from the structural parameters (e.g., Cs^+···C contacts of 3.50–3.66 Å). One oxygen atom of the NO_3^- ion is also hydrogen-bonded to the calix[4]pyrrole NH protons, with the relevant N···O distances being 2.92–3.00 Å.

Initial evidence that the potassium cation would be bound in preference to Cs^+ came from an X-ray diffraction analysis of single crystals of the KNO_3 complex of **3** obtained by allowing a chloroform/ethanol solution of the preformed **3**·$CsNO_3$ complex to undergo slow evaporation in the presence of 1 molar equivalent of $KClO_4$ relative to the added $CsNO_3$ (Figure 5). That a new complex, containing K^+ instead of Cs^+, is formed leads us to suggest that the formation of the

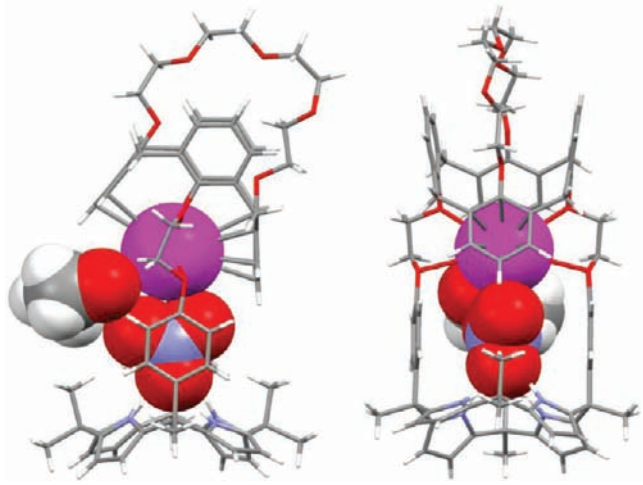


Figure 4. Two different views of the single-crystal X-ray structure of **3**·$CsNO_3·CH_3CH_2OH$. Solvent molecules not involved in the ion pair complex have been removed for clarity.

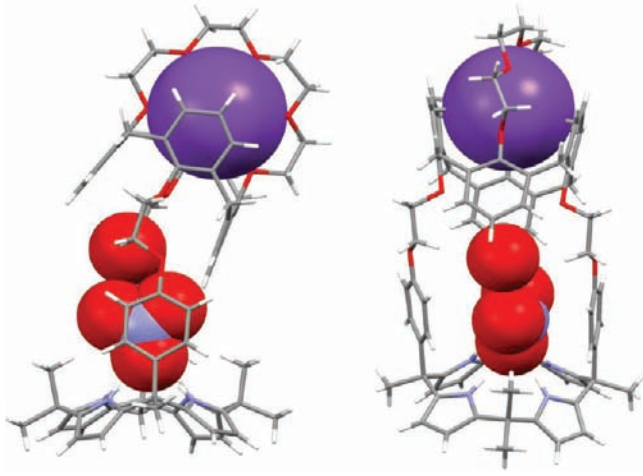


Figure 5. Two different views of the single-crystal X-ray diffraction structure of **3**·$KNO_3·H_2O$. Solvent molecules not involved in the ion pair complex have been removed for clarity.

KNO_3 complex occurs via cation metathesis involving displacement of Cs^+ by a K^+ ion in what is a thermodynamically driven process. The resulting crystal structure revealed that the K^+ cation is bound to the crown-5 ring rather than to the ethylene glycol moieties (crown/pyrrole vs glycol/pyrrole mode). The relevant distances are 2.73–2.84 Å for the Cs^+···O and 3.07–3.31 Å for the π–metal interactions, respectively (Figure S18, Supporting Information). As expected, the NO_3^- anion is hydrogen-bonded to the calix[4]pyrrole moiety at a N···O^- distance of 2.93–3.01 Å. The anion is separated from the cobound K^+ cation by a distance of 8.32 Å.

The solution-phase anion and cation binding behavior of **3** was investigated via ^1H NMR spectroscopy using a mixed solvent system consisting of $CDCl_3$ and CD_3OD (9:1, v/v). This particular choice of solvents was dictated by the solubility of the salts under study. In analogy to what was seen with receptors **1** and **2** (which were also studied in this same solvent system),[14,18] no appreciable change in the ^1H NMR spectrum of **3** was seen upon treatment with 5 equiv of $TBAClO_4$, TBACl, or $TBANO_3$ (Figure S2, Supporting Information). On this basis, we conclude that the TBA^+ cation is not bound and

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782–1792

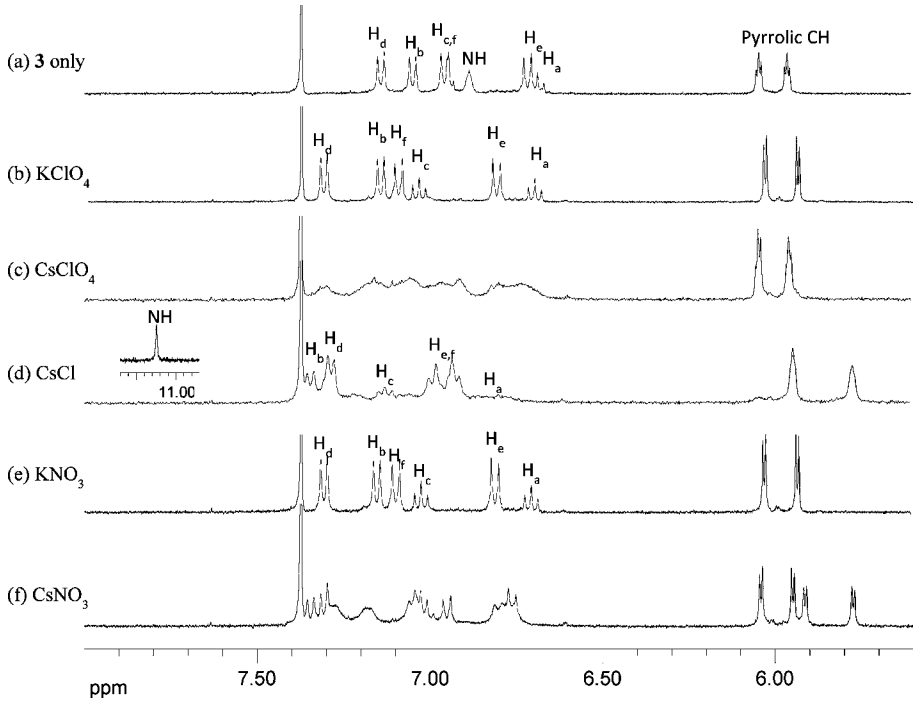


Figure 6. Partial ^{1}H NMR spectra of (a) **3** (4 mM) only, (b) **3** with 4.0 equiv of $KClO_4$, (c) **3** with 4.0 equiv of $CsClO_4$, (d) **3** with 4.0 equiv of CsCl, (e) **3** with 4.0 equiv of KNO_3, and (f) **3** with 4.0 equiv of $CsNO_3$ in $CD_3OD/CDCl_3$ (1:9, v/v).

that neither the chloride nor nitrate anion is complexed by receptor **3** as a TBA^+ salt in this mixed solvent system.

Remarkably different spectral behavior was observed when receptor **3** was treated with $KClO_4$ and $CsClO_4$. As shown in Figure 6, the addition of either of these salts to solutions of **3** in $CDCl_3$ and CD_3OD (9:1, v/v) led to a significant chemical shift change in the signals for both the aromatic protons of the calix[4]arene core and the aliphatic protons of the crown ether ring (Figure 6; Figure S3, Supporting Information). These changes are consistent with the cations being encapsulated by the crown ether ring with the aid of the aromatic rings of the calix[4]arene, perhaps via π–metal interactions. Notably, the addition of these salts did not induce a substantial change in the proton signals of the calix[4]pyrrole moiety. This lack of change provides support for the notion that the perchlorate anion is bound either very weakly or not at all by the calix[4]pyrrole moiety. Therefore, taken in concert, these findings are consistent with the expectation that the addition of $KClO_4$ and $CsClO_4$ leads to the formation of the cation-bound complexes ($[\mathbf{3}\cdot K^+]ClO_4^-$ and $[\mathbf{3}\cdot Cs^+]ClO_4^-$), where the ClO_4^- counteranion is not cobound (i.e., crown/crown mode; cf. Figure 2). This finding is fully in line with the results of the calculations, which revealed that both $KClO_4$ and $CsClO_4$ prefer this binding mode in the gas phase (see Table 1).

Analyzing the spectra in greater detail reveals that the peaks of both the aromatic protons of the calix[4]arene moiety and the crown ring are broadened in the presence of $CsClO_4$, while they remain sharp in the presence of $KClO_4$ (Figure 6; Figure S3, Supporting Information). Such findings are consistent with the expectation that receptor **3** binds the K^+ cation more strongly than the Cs^+ cation. This stronger affinity for the K^+ cation was further evidenced by a ^{1}H NMR spectrum measured in the presence of 1.0 equiv of $KClO_4$, where two sets of distinguishable proton signals were seen corresponding to the free receptor and its K^+ complex, respectively (Figure S4, Supporting Information). This observation is consistent with slow exchange and strong K^+ complexation. Indeed, the binding constant of receptor **3** for the K^+ cation measured by isothermal titration calorimetry (ITC) in acetonitrile using KTPB (potassium tetraphenylborate) was found to be much higher than that for the Cs^+ cation ($K_a = 6.5 \times 10^6$ M^{-1} for K^+ vs $K_a = 3.3 \times 10^4$ M^{-1} for Cs^+) (Table S1 and Figures S5 and S6, Supporting Information). These observations are consistent with calculation results showing that receptor **3** exhibits an intrinsic preference for the K^+ cation over the Cs^+ cation. They also provide support for the suggestion that treatment with K^+ could be used to induce the thermodynamically driven, chemically induced release of a Cs^+ cation prebound in receptor **3**.

In accord with design expectations, receptor **3** was found to form a 1:1 ion pair complex with KNO_3 in 10% CD_3OD in $CDCl_3$. As inferred from the ^{1}H NMR spectroscopic analyses, it does so in a sequential manner. Specifically, upon addition of KNO_3 to a solution of receptor **3** in 10% CD_3OD in $CDCl_3$, the proton signals of the calix[4]arene crown-5 were seen to undergo a shift while those of the calix[4]pyrrole moiety were largely unchanged (Figure 6e). Such observations are consistent with receptor **3** coordinating the K^+ cation first through the calix[4]arene crown-5 ring without the NO_3^- anion being bound to the calix[4]pyrrole moiety (crown/crown mode). Once the K^+ is bound to receptor **3** (to produce the potassium complex $[\mathbf{3}\cdot K^+]$), the binding of the NO_3^- counteranion becomes thermodynamically favorable under these solution-phase conditions (cf. Figures 6 and 7 and Figure S7 in the Supporting Information). As the ion pair complex of receptor **3** with KNO_3 ($[\mathbf{3}\cdot KNO_3]$; crown/pyrrole mode) forms, it starts to precipitate from solution (Figures 6–8; Figures S7 and S8, Supporting Information). As a consequence, complexation of these potassium salts by **3** becomes irreversible under these experimental conditions.

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782–1792

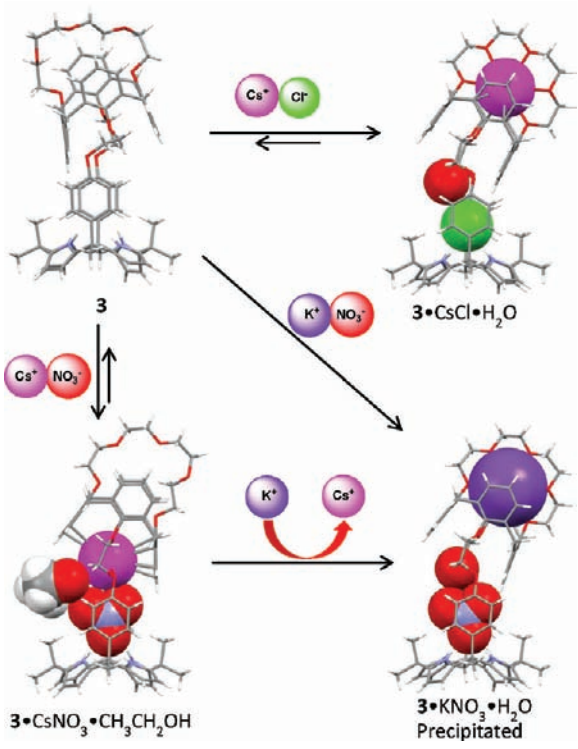


Figure 7. Proposed binding interactions involving receptor **3** and various K^+ and Cs^+ ion pairs in 10% methanol in chloroform (10% CD_3OD in $CDCl_3$ for ^1H NMR spectral studies). Also shown are the crystal structures of the various ion pair complexes in question grown from mixtures of chloroform and methanol or ethanol.

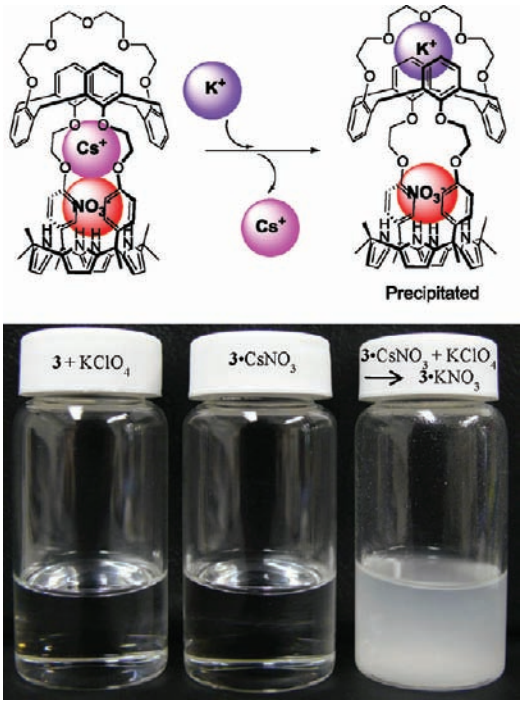


Figure 8. Precipitation induced via cation metathesis observed upon addition of the K^+ cation (as $KClO_4$) to the preformed $CsNO_3$ complex of **3** in $CD_3OD/CDCl_3$ (1:9, v/v).

Spectral changes corresponding to different binding modes are also seen in the ^1H NMR spectrum when receptor **3** is exposed to $CsNO_3$ in 10% CD_3OD in $CDCl_3$ (cf. Figures 6 and 7 and Figures S8 and S9 in the Supporting Information). However, they differ from what was observed in the case of **3** and KNO_3. For instance, in the presence of 4.0 equiv of $CsNO_3$ in $CD_3OD/CDCl_3$ (1:9, v/v), a new set of sharp peaks in the ^1H NMR spectrum corresponding to the β-pyrrolic protons are seen while other peaks corresponding to the aromatic protons of the calix[4]arene moiety become broadened (Figure 6f). This is consistent with two different kinds of binding interactions involving receptor **3** and the $CsNO_3$ ion pair. In one set, only the Cs^+ cation but not the NO_3^- anion is weakly bound to the crown-5 ring to form a cesium complex ($[\mathbf{3}\cdot Cs^+]NO_3^-$) where the NO_3^- counteranion is not cobound (crown/crown binding mode). This complex exists in fast equilibrium with the free receptor, as evidenced by peak broadening seen for the aromatic protons of the calix[4]arene moiety. By contrast, in the other binding mode, the Cs^+ cation and the NO_3^- anion are concurrently and strongly bound to the receptor **3** being stabilized by the ethylene glycol spacers and the calix[4]pyrrole moiety, respectively (i.e., $[\mathbf{3}\cdot CsNO_3]$; glycol/pyrrole mode; cf. Figures 2 and 7 and Figures S7 and S8 in the Supporting Information). This latter complexation mode is similar to what was seen in the case of the $CsNO_3$ complex of compound **2**.[14] These two species exist in equilibrium, and over time, the ion pair complex $[\mathbf{3}\cdot CsNO_3]$ is formed in preference, leading us to suggest that it represents the thermodynamically favored species in this solvent system.

In contrast to what is seen with $KClO_4$ and $CsClO_4$, in the presence of cesium chloride and potassium chloride, receptor **3** forms strong ion pair complexes wherein the cation is bound to the calix[4]arene crown-5 moiety and the anion to the calix[4]pyrrole cavity (crown/pyrrole mode; cf. Figures 3, 6, and 7 and Figures S8 and S9 in the Supporting Information). Support for this conclusion comes from NMR spectral studies carried out in $CD_3OD/CDCl_3$ (1:9, v/v). For instance, upon addition of CsCl to a solution of receptor **3** in 10% CD_3OD in $CDCl_3$, the proton signals of the calix[4]arene crown-5 underwent a significant downfield shift (an observation consistent with Cs^+ complexation), while those of the calix[4]pyrrole moiety were shifted upfield, presumably as the result of chloride anion binding (Figure 6d; Figure S3d, Supporting Information). A remarkable downfield shift ($\Delta\delta \approx$ 4.5 ppm) in the NH peak is also observed (Figure 6d). In contrast, addition of KCl to a solution of receptor **3** in 10% CD_3OD in $CDCl_3$ leads to precipitation of the KCl ion pair complex, $[\mathbf{3}\cdot KCl]$.

To provide support for the inferences drawn from the ^1H NMR spectral measurements, namely, that receptor **3** binds both cesium salts and potassium salts but displays high selectivity for potassium salts over the cesium salts, we investigated whether cation metathesis would occur when a precomplexed Cs^+ cation ion pair complex was exposed to K^+. These studies were carried out by adding $KClO_4$ to a solution of the $[\mathbf{3}\cdot CsNO_3]$ complex in 10% $CD_3OD/CDCl_3$ (Figures 7 and 8; Figure S7, Supporting Information). Under these conditions, precipitation was observed. This is interpreted in terms of the $CsNO_3$ complex (glycol/pyrrole mode) being converted into the KNO_3 complex (crown/pyrrole mode) via cation exchange as summarized in eqs 1 and 2. As noted above, the latter complex is insoluble and precipitates from solution. Presumably, this helps drive the initial removal of the cesium cation from the $CsNO_3$ complex.

$$[\mathbf{3}\cdot CsNO_3] + KClO_4 \rightarrow [\mathbf{3}\cdot KNO_3] + CsClO_4 \qquad (2)$$

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782–1792

$$[\mathbf{3}] + CsNO_3 \rightarrow [\mathbf{3}\cdot CsNO_3] \quad (1)$$

The fact that receptor **3** binds K^+ selectively over Cs^+ but complexes the cesium cation in the absence of the potassium salts led us to consider that this receptor could have use as an extractant. In particular, it was thought that it could be used to extract the Cs^+ cation from aqueous media while permitting its subsequent release by exposure to K^+ as shown schematically in Figure 9.

To test this possibility, ^{1}H NMR spectroscopy was used in conjunction with a two-phase system consisting of D_2O and nitrobenzene-d_5. Upon exposure of receptor **3** in $C_6D_5NO_2$ to aqueous (D_2O) solutions of $NaNO_3$, KNO_3, and $CsNO_3$, respectively, significant changes in the ^{1}H NMR spectra were observed in the case of KNO_3 and $CsNO_3$ but not $NaNO_3$ (Figures 10 and 11; Figure S10, Supporting Information). This is taken as evidence that receptor **3** is capable of extracting both KNO_3 and $CsNO_3$ from an aqueous environment into a nitrobenzene organic phase. Independent support for the suggestion that receptor **3** was capable of effecting $CsNO_3$ extraction came from radiotracer studies involving $^{137}CsNO_3$. Experiments were conducted with varying initial concentrations of $CsNO_3$ in the aqueous phase and **3** in the nitrobenzene phase (Figure 12). The mass-action behavior was analyzed to show the predominance of three species with stoichiometries $[\mathbf{3}\cdot Cs^+]$, $[\mathbf{3}\cdot CsNO_3]$, and $[\mathbf{3}_2\cdot CsNO_3]$ (see the Supporting Information). At concentrations of **3** less than approximately 3 mM, the ion pair complex $[\mathbf{3}\cdot CsNO_3]$ is the major species, but at low loading, it dissociates to $[\mathbf{3}\cdot Cs^+]$ and free NO_3^- in the nitrobenzene phase, with the apparent association constant for this latter equilibrium being 1.2×10^5 M^{-1}. This is a relatively strong ion pair association for nitrobenzene and is in accord with the previous finding that *meso*-octamethylcalix[4]pyrrole itself can function as an ion pair receptor.[21] The slope of approximately 0.5 observed at the left side of the curve in Figure 12b is consistent with the dissociated regime. No evidence for the bound nitrate as the complex anion $[\mathbf{3}\cdot NO_3^-]$ was obtained, and neither was this species expected to be significant.[23]

An interesting feature of the system is the tendency for the complex $[\mathbf{3}_2\cdot CsNO_3]$ to form at high concentrations of **3**, involving the participation of two molecules of **3** to accommodate one ion pair. This complex becomes predominant above 3 mM **3** at intermediate loading, as reflected in the slope of 2 observed in the right side of the curve in Figure 12b. As the loading is increased, the relative concentration of $[\mathbf{3}_2\cdot CsNO_3]$ diminishes as $[\mathbf{3}\cdot CsNO_3]$ becomes the sole complex at saturation.

To examine the spectrum of only the ion pair complex $[\mathbf{3}\cdot CsNO_3]$, we equilibrated 4 mM **3** in nitrobenzene-d_5 with 0.5 M $CsNO_3$ in D_2O. Under these conditions, we obtained exactly the same spectrum as the one shown in Figure 11d, a finding that we interpret as confirming that the glycol/pyrrole form of bound $CsNO_3$ is the dominant species under these conditions.

Differences between KNO_3 and $CsNO_3$ were inferred from the ^{1}H NMR spectroscopic analyses of the nitrobenzene-d_5 layer. For instance, in the case of KNO_3, the proton signals of both the aromatic ring of the calix[4]arene moiety and the crown-5 ring were seen to shift toward lower field whereas the peaks of the β-pyrrolic protons did not shift appreciably (Figure 10b). On this basis we propose that only the K^+ cation of the KNO_3 ion pair is bound appreciably by receptor **3** to generate $[\mathbf{3}\cdot K^+]NO_3^-$ in the organic phase (Figure S10, Supporting Information). This crown/crown binding mode stands in marked contrast with what is seen in the case of $CsNO_3$. Here, recording the ^{1}H NMR spectrum after an analogous extraction process reveals a significant downfield shift in the proton signals of the calix[4]arene crown-5 protons relative to those of free receptor **3**. Upfield shifts in the signal of the β-pyrrolic protons of the calix[4]pyrrole moiety were also observed (Figure 10c). Such changes are attributable to the formation of an ion pair complex between $CsNO_3$ and receptor **3** to give $[\mathbf{3}\cdot CsNO_3]$ (Figure 9). The conclusion that the NO_3^- anion is bound to the calix[4]pyrrole cavity with the Cs^+ cation bound to the ethylene glycol moieties (i.e., glycol/pyrrole binding mode) was further

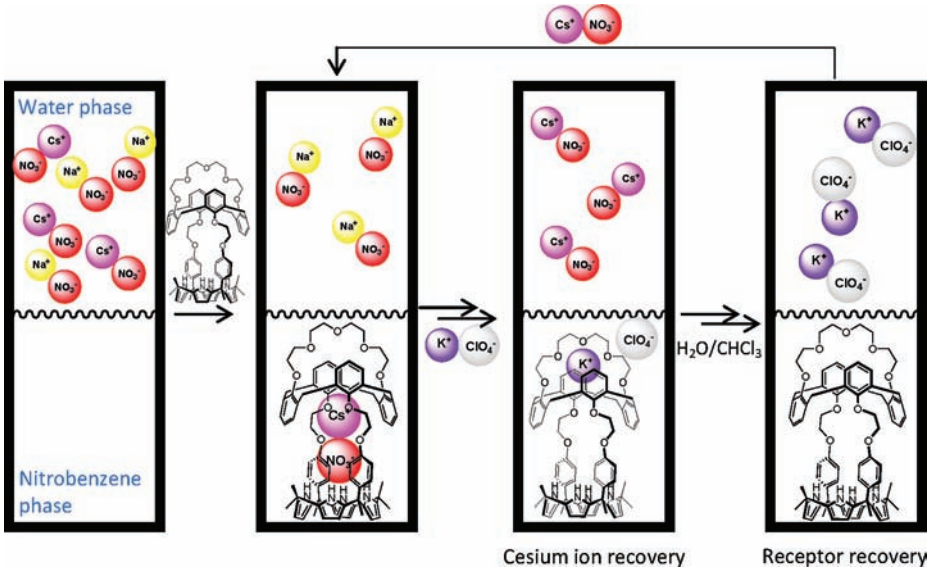


Figure 9. Schematic representation of the two-phase extraction and recovery of $CsNO_3$ achieved using the ion pair receptor **3**. The stages involved include initial Cs^+ complexation and K^+-for-Cs^+ cation exchange, followed by regeneration of the free receptor by contact with chloroform and water.

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782–1792

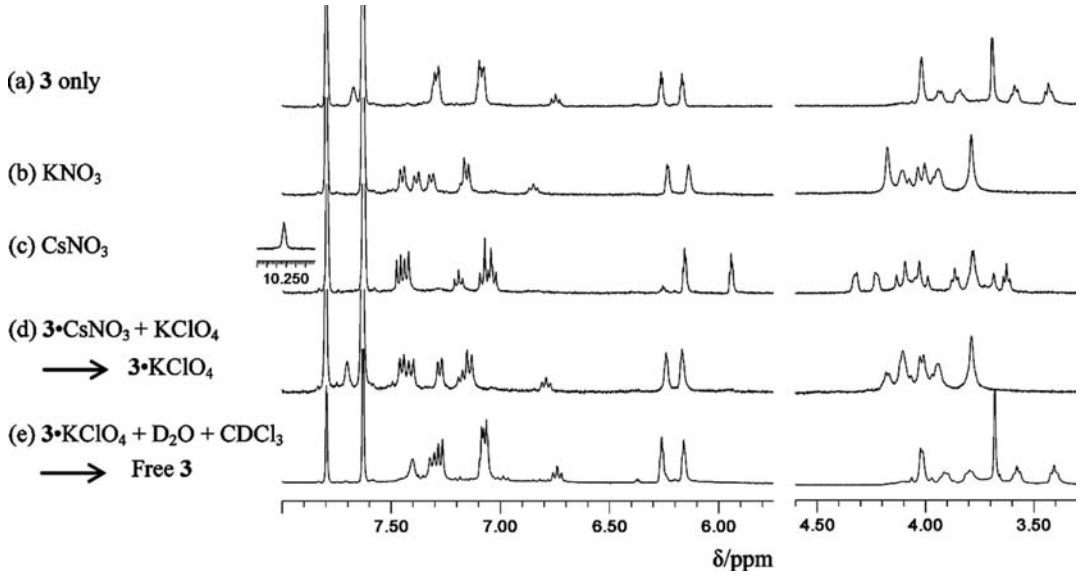


Figure 10. Partial ^{1}H NMR spectra of nitrobenzene-d_5 solutions of **3** (4 mM) (a) after being contacted with D_2O, (b) after being contacted with an aqueous D_2O/KNO_3 solution (5 equiv), (c) after being contacted with an aqueous $D_2O/CsNO_3$ solution (5 equiv), (d) after the nitrobenzene phase obtained from (c) was contacted with D_2O and then with an aqueous $D_2O/KClO_4$ solution (5 equiv), and (e) after the organic phase obtained from (d) was contacted with D_2O and chloroform-*d*.

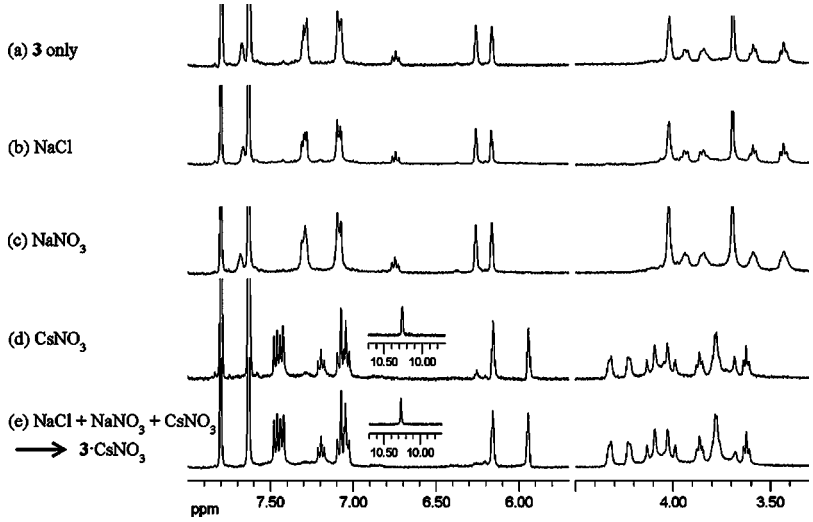


Figure 11. Partial ^{1}H NMR spectra of nitrobenzene-d_5 solutions of **3** (4 mM) (a) after being contacted with D_2O, (b) after being contacted with an aqueous D_2O/NaCl solution (5 equiv), (c) after being contacted with an aqueous $D_2O/NaNO_3$ solution (5 equiv), (d) after being contacted with an aqueous $D_2O/CsNO_3$ solution (5 equiv), and (e) after being contacted with an aqueous D_2O solution consisting of a mixture of NaCl (5 equiv), $NaNO_3$ (5 equiv), and $CsNO_3$ (5 equiv).

supported by the finding that the NH signal of the calix[4]pyrrole moiety undergoes a downfield shift ($\Delta\delta \approx 2.5$ ppm) when receptor **3** is exposed to $CsNO_3$ under these two phase conditions (Figure 10c).

When the nitrobenzene-d_5 phase containing complex [**3**·$CsNO_3$] formed via extraction is contacted with an aqueous D_2O solution of $KClO_4$, the binding of the K^+ cation causes the expulsion of the Cs^+ cation originally cobound within **3**. This apparent exchange, which we propose involves an ion-stimulated release, is ascribed to the destabilizing effect of the incipient electrostatic repulsion between the two cations in question, namely, the prebound Cs^+ cation and the entering K^+ cation.[19] As a result of this metathesis, a new complex, [**3**·K^+]ClO_4^-, is produced in the organic phase (Figures 9 and 10) and $CsNO_3$ is released into the aqueous phase. The efficacy of this exchange process is evidenced by the emergence of a ^{1}H NMR spectrum for the nitrobenzene-d_5 phase that is similar to that recorded for the KNO_3 complex (Figure 10d). In accord with expectations, the ^{133}Cs NMR spectrum of the water phase measured after extraction of [**3**·$CsNO_3$] with the aqueous $KClO_4$ solution revealed the presence of the Cs^+ cation, presumably reflecting the existence of a solubilized $CsNO_3$ ion pair in the water phase (Figure S11, Supporting Information). While not established directly, the decomplexation of the nitrate anion (and its transfer to the aqueous phase) was inferred from the fact that, after contact with an aqueous $KClO_4$ solution, the ^{1}H NMR spectrum of **3** (recorded in the nitrobenzene-d_5 layer) matches that of complexes where an anion is not cobound (i.e., the NH proton and β-pyrrolic proton signals appear significantly upfield and downfield

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782–1792

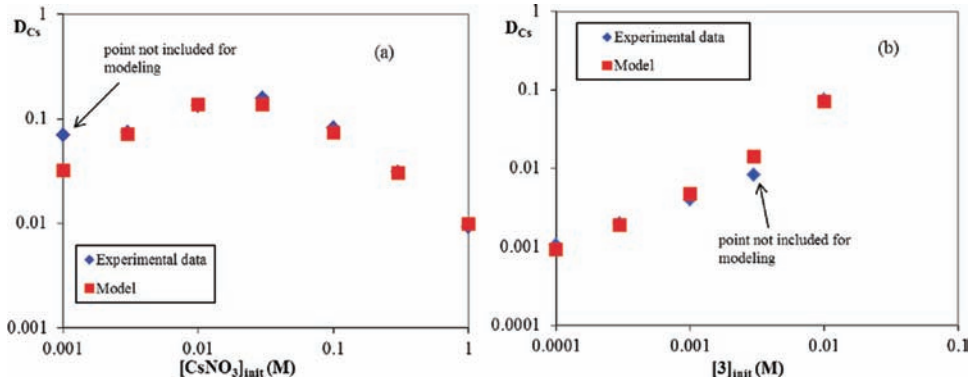


Figure 12. Cesium distribution ratio (D_{Cs}) at 25 °C as a function of (a) increasing initial aqueous $CsNO_3$ concentration with 10 mM **3** in nitrobenzene and (b) increasing concentration of **3** in nitrobenzene with 3 mM initial aqueous $CsNO_3$. The organic:aqueous volume ratio was 1:1. The red squares represent a fit to the best mass-action equilibrium model (see the Supporting Information).

shifted, respectively, as compared to those of the initial [**3**·$CsNO_3$] complex).

These findings are in line with the standard molar Gibbs free energies for hydration of the K^+ cation ($\Delta_{hyd}G° = -295$ kJ/mol) and ClO_4^- ($\Delta_{hyd}G° = -214$ kJ/mol) and those of the Cs^+ cation ($\Delta_{hyd}G° = -250$ kJ/mol) and NO_3^- ($\Delta_{hyd}G° = -300$ kJ/mol).[24] In accord with its design features, receptor **3** extracts $KClO_4$ better than it does $CsNO_3$, which is rationalized on the basis of the stronger binding of K^+ vs Cs^+ and the lower hydration of ClO_4^- vs NO_3^-. Stronger binding of K^+ thus serves to overcome the hydration energy bias that would otherwise favor extraction of Cs^+.[24] As important, the lower hydration of ClO_4^- drives the exchange for NO_3^-. Overall, the fact that $KClO_4$ is extracted well under these interfacial conditions allows it to be used to effect Cs^+ release from **3** using the simple biphasic contacting procedure described above.

In a further step of note, it was found that contacting the nitrobenzene layer containing [**3**·K^+]ClO_4^- with chloroform-*d* and D_2O (twice) leaves receptor **3** in its free form in the organic phase (Figures 8 and 9e). After separation of the organic phase followed by removal of chloroform in vacuo, receptor **3** can be recycled for further use.

The above experiments introduce a new paradigm for devising a binding−release cycle in a separation system by showing how a binding event in a remote part of the molecule (that of K^+ binding by the crown in the present instance) can stimulate the release of prebound cation in a different location (Cs^+ in the glycol site in the case of receptor **3**). Given this proof of principle, it is worth considering the pathway to more practical systems. Not only would one move to more acceptable process diluents such as paraffinic hydrocarbons, as opposed to toxic, volatile solvents such as nitrobenzene or chloroform, but one would also design for an alternative to K^+ as a metathesis agent that would not be itself a waste constituent. If this competing ion was also a preferred constituent of a final waste form suitable for disposal, the strip solution could be routed directly to waste-form production without concerns regarding secondary waste production. This may be actually preferable to stripping with pure water, which Figure 12 leads us to suggest could be used directly to strip the loaded cesium, owing to the low distribution ratios (D_{Cs}). An advantage of a metathesis strategy for stripping over water stripping is that it is potentially more efficient, and additionally, organic phases often do not disengage from pure water cleanly. Thus, our system serves as a first prototype of a novel type of binding−release cycle from which new examples, perhaps more practical, can be designed.

The ability of receptor **3** to extract $CsNO_3$ selectively over sodium salts, such as NaCl and $NaNO_3$, was also tested by ^1H NMR spectroscopy (Figure 11). No appreciable change was observed in the ^1H NMR spectrum of the nitrobenzene-d_5 layer after this layer (containing receptor **3**) was contacted with an aqueous D_2O layer containing 5 equiv of NaCl or $NaNO_3$ (relative to **3**), leading us to suggest that such sodium salts are not extracted efficiently (if at all) by receptor **3**. In contrast, contacting the nitrobenzene-d_5 layer containing receptor **3** with a mixture of NaCl, $NaNO_3$, and $CsNO_3$ (5 equiv of each) gave rise to a ^1H NMR spectrum identical to that obtained when the same experiment was carried out using just 5 equiv of $CsNO_3$. This finding is consistent with the suggestion that receptor **3** is capable of extracting $CsNO_3$ selectively in the presence of excess NaCl and $NaNO_3$ (Figure 11).

Chloride, rather than nitrate, is the dominant counteranion in the case of $^{137}Cs^+$ present in seawater. The chloride anion is more highly hydrated than the nitrate anion ($\Delta_{hyd}G° = -340$ kJ/mol for Cl^-; $\Delta_{hyd}G° = -300$ kJ/mol for NO_3^-). It thus represents a greater challenge in terms of binding and extraction. Gratifyingly, receptor **3** proved capable of extracting CsCl from D_2O into nitrobenzene-d_5 (Figure S12, Supporting Information). The ^1H NMR spectrum shown in Figure S12b is fully consistent with CsCl (20 mM in D_2O) being extracted by receptor **3** (4 mM in nitrobenzene-d_5) in the form of an ion pair complex, wherein the Cs^+ cation and the Cl^- anion are cobound to **3** via the calix[4]arene crown-5 ring and calix[4]pyrrole subunits, respectively (crown/pyrrole binding mode; cf. Figure 2). As in the case of the extractions carried out with the nitrate salt, further exposure to $KClO_4$ led to spectral changes consistent with decomplexation of the Cs^+ cation (Figure S12c). For example, after contact of the nitrobenzene phase ($C_6D_5NO_2$) obtained after the initial CsCl extraction receptor **3** with an aqueous D_2O solution containing 5 equiv of $KClO_4$, a ^1H NMR spectrum was produced that was identical to the one obtained when receptor **3** (in $C_6H_5NO_2$) was washed with an aqueous D_2O solution of KCl (5 equiv). Thus, as in the case of the nitrate salts, we conclude that Cs^+ cation release is being induced as the result of cation metathesis.

■ CONCLUSIONS

A new ion pair receptor, **3**, that contains a dedicated calix[4]pyrrole anion binding subunit and various sites suitable

dx.doi.org/10.1021/ja209706x | J. Am. Chem.Soc. 2012, 134, 1782−1792

for K^+ and Cs^+ complexation has been synthesized and characterized by standard spectroscopic means as well as by single X-ray crystal diffraction analysis. The ^1H NMR spectroscopic analyses and the X-ray crystal structural data reveal that both in the solid states and in mixed methanol/chloroform solution, receptor **3** forms 1:1 ion pair complexes with potassium and cesium salts. As evidenced by ^1H NMR spectroscopic analyses, receptor **3** displays a higher affinity for the K^+ cation relative to the Cs^+ cation. However, in the absence of potassium salts, receptor **3** binds cesium salts. The addition of potassium salts containing a noncoordinating anion, such as perchlorate, to preformed cesium ion pair complexes of **3** induces an effective release of Cs^+ by the binding of K^+. This produces new ion pair complexes containing the potassium cation. This key feature enables receptor **3** to extract $CsNO_3$ from an aqueous phase to an organic layer consisting of nitrobenzene. By exploiting the dual cation binding features of receptor **3**, it is thus possible to stimulate the release of the Cs^+ cation without displacement. Specifically, contacting a nitrobenzene phase containing the **3**·$CsNO_3$ complex (produced by extraction) with an aqueous $KClO_4$ solution serves to release $CsNO_3$ into the aqueous phase. Further contacting the nitrobenzene phase containing the newly formed $KClO_4$ complex with chloroform and water serves to strip out the $KClO_4$ and regenerate the free form of receptor **3** in the organic phase. This stepwise control of the thermodynamics appears very efficient in terms of (i) the initial complexation of the Cs^+ cation and (ii) its controlled release and (iii) subsequent regeneration of the receptor. It is important to note, however, that the present study was carried out under idealized laboratory conditions using solvents and concentrations selected to facilitate analysis. Thus, direct comparisons with existing extraction-based methods for radioactive cesium recovery are not realistic or useful. Nevertheless, we believe that ion pair receptors such as the one described here could serve as a useful model for liquid−liquid separations. Furthermore, we think the new principle of cation metathesis described here can be applied broadly, including to other situations where functional recognition requires the careful control of both initial substrate binding and subsequent release.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic details, NMR spectroscopic data, ITC analyses, equilibrium analysis of liquid-liquid extraction data, and X-ray structural data (CIF) for **3**·CH_3CN (CCDC 826576), **3**·KNO_3·$(C_5H_{12})_{1/2}$·CH_3Cl·H_2O (CCDC 826575), **3**·$CsCl$·$CHCl_3$·$(CH_3CH_2OH)_{1/2}$·$(H_2O)_{11/2}$ (CCDC 826574), and **3**·$CsNO_3$·C_2H_5OH·C_6H_{14} (CCDC 826577). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

chhlee@kangwon.ac.kr; jongskim@korea.ac.kr; moyerba@ornl.gov; sessler@mail.utexas.edu

■ ACKNOWLEDGMENTS

This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy (DOE) (Grant DE-FG02-01ER15186 to J.L.S.), a Korea National Research Foundation (NRF) grant (MEST 2009-0087013 to C.-H.L.), the Creative Research Initiatives (CRI) project of the Korea Research Foundation (KRF) (2011-0000420 to J.S.K), and the Korean World Class University (WCU) program (Grant R32-2010-000-10217-0) administered through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (MEST). B.P.H., B.A.M., L.H.D., and N.J.Y. acknowledge support from the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. DOE.

■ REFERENCES

(1) (a) Moyer, B. A.; Birdwell, J. F., Jr.; Bonnesen, P. V.; Delmau, L. H. Use of Macrocycles in Nuclear-Waste Cleanup: A Real-World Application of a Calixcrown in Technology for the Separation of Cesium. In *Macrocyclic Chemistry—Current Trends and Future*; Gloe, K., Ed.; Springer: Dordrecht, The Netherlands, 2005; pp 383−405. (b) Wilmarth, W. R.; Lumetta, G. J.; Johnson, M. E.; Poirier, M. R.; Thompson, M. C.; Suggs, P. C.; Machara, N. P. *Solvent Extr. Ion Exch.* **2011**, *29*, 1−48. (c) Collins, E. D.; Del Cul, G. D.; Moyer, B. A. Fission Product Separation/Extraction Techniques. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Nash, K. L., Lumetta, G. J., Eds.; Woodhead Publishing: Cambridge, U.K., 2011.

(2) (a) Lehn, J.-M. In *Alkali Metal Complexes with Organic Ligands*; Dunitz, J. D., Ed.; Springer-Verlag: New York, 1973; Vol. *16*, pp 1−69. (b) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.

(3) (a) Delmau, L. H.; Birdwell, J. F. Jr.; McFarlane, J.; Moyer, B. A. *Solvent Extr. Ion Exch.* **2010**, *28*, 19−48. (b) Delmau, L. H.; Haverlock, T. J.; Bazelaire, E.; Bonnesen, P. V.; Ditto, M. E.; Moyer, B. A. *Solvent Extr. Ion Exch.* **2009**, *27*, 172−198.

(4) (a) Shinkai, S.; Nakaji, T.; Nishida, Y.; Ogawa, T.; Manabe, O. *J. Am. Chem. Soc.* **1980**, *102*, 5860−5865. (b) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111−115. (c) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161−5165. (d) Shinkai, S.; Ogawa, T.; Kusano, Y.; Manabe, O.; Kikukawa, K.; Goto, T.; Matsuda, T. *J. Am. Chem. Soc.* **1982**, *104*, 1960−1967. (e) Shinkai, S.; Minami, T.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1982**, *104*, 1967−1972. (f) Shinkai, S.; Kinda, H.; Manabe, O. *J. Am. Chem. Soc.* **1982**, *104*, 2933−2934. (g) Shinkai, S.; Minami, T.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1983**, *105*, 1851−1856.

(5) (a) Webber, P. R. A.; Beer, P. D.; Chen, G. Z.; Felix, V.; Drew, M. G. B. *J. Am. Chem. Soc.* **2003**, *125*, 5774−5785. (b) Lyskawa, J.; Le Derf, F.; Levillain, E.; Mazari, M.; Sallé, M.; Dubois, L.; Viel, P.; Bureau, C.; Palacin, S. *J. Am. Chem. Soc.* **2004**, *126*, 12194−112195. (c) Caballero, A.; Lloveras, V.; Tárraga, A.; Espinosa, A.; Velasco, M. D.; Vidal-Gancedo, J.; Rovira, C.; Wurst, K.; Molina, P.; Veciana, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 1977−1981.

(6) (a) Nielsen, K. A.; Cho, W.-S.; Jeppesen, J. O.; Lynch, V. M.; Becher, J.; Sessler, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 16296−16297. (b) Nielsen, K. A.; Sarova, G. H.; Martín-Gomis, L.; Fernández-Lázaro, F.; Stein, P. C.; Sanguit, L.; Levillain, E.; Sessler, J. L.; Guldi, D. M.; Sastre-Santos, A.; Jeppesen, J. O. *J. Am. Chem. Soc.* **2008**, *130*, 460−462. (c) Park, J. S.; Karnas, E.; Ohkubo, K.; Chen, P.; Kadish, K. M.; Fukuzumi, S.; Bielawski, C. W.; Hudnall, R. W.; Lynch, V. M.; Sessler, J. L. *Science* **2010**, *329*, 1324−1326. (d) Fukuzumi, S.; Ohkubo, K.; Kawashima, Y.; Kim., D. S.; Park, J. S.; Jana, A.; Lynch, V. M.; Kim, D.; Sessler, J. L. *J. Am. Chem. Soc.* **2011**, *133*, 15938−15941.

(7) (a) Smith, B. D. In *Ion-Pair Recognition by Ditopic Receptors, Macrocyclic Chemistry: Current Trends and Future Prospectives*; Gloe, K., Antonioli, B., Eds.; Kluwer: London, 2005; pp 137−152. (b) Kirkovits, G. J.; Shriver, J. A.; Gale, P. A.; Sessler, J. L. *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *41*, 69−75.

(8) Kim, S. K.; Sessler, J. L. *Chem. Soc. Rev.* **2010**, *39*, 3784−3809 and references cited therein.

(9) (a) Pfeifer, J. R.; Rei*β*, P.; Koert, U. *Angew. Chem., Int. Ed.* **2006**, *45*, 501−504. (b) Sisson, A. L.; Shah, M. R.; Bhosale, S.; Matile, S. *Chem. Soc. Rev.* **2006**, *35*, 1269−1286. (c) Nakamura, T.; Akutagawa,

T.; Honda, K.; Underhill, A. E.; Coomber, A. T.; Friend, R. H. *Nature* **1998**, *394*, 159−162. (d) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, *104*, 2723−2750. (e) Davis, A. P.; Sheppard, D. N.; Smith, B. D. *Chem. Soc. Rev.* **2007**, *36*, 348−357.
(10) (a) Chrisstoffels, L. A. J.; De Jong, F.; Reinhoudt, D. N.; Sivelli, S.; Gazzola, L.; Casnati, A.; Ungaro, R. *J. Am. Chem. Soc.* **1999**, *121*, 10142−10151. (b) Rudkevich, D. M.; Mercer-Chalmers, J. D.; Verboom, W.; Ungaro, R.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 6124−6125. (c) Tong, C. C.; Quesada, R.; Sessler, J. L.; Gale, P. A. *Chem. Commun.* **2008**, 6321−6323.
(11) (a) Mahoney, J. M.; Stucker, K. A.; Jiang, H.; Carmichael, I.; Brinkmann, N. R.; Beatty, A. M.; Noll, B. C.; Smith, B. D. *J. Am. Chem. Soc.* **2005**, *127*, 2922−2928. (b) Deetz, M. J.; Shang, M.; Smith, B. D. *J. Am. Chem. Soc.* **2000**, *122*, 6201−6207. (c) Mahoney, J. M.; Beatty, A. M.; Smith, B. D. *Inorg. Chem.* **2004**, *43*, 7617−7621. (d) Mahoney, J. M.; Davis, J. P.; Smith, B. D. *J. Org. Chem.* **2003**, *68*, 9819−6820. (e) Mahoney, J. M.; Beatty, A. M.; Smith, B. D. *J. Am. Chem. Soc.* **2001**, *123*, 5847−5858. (f) Mahoney, J. M.; Nawaratna, G. U.; Beatty, A. M.; Duggan, P. J.; Smith, B. D. *Inorg. Chem.* **2004**, *43*, 5902−5907. (g) Mahoney, J. M.; Marshall, R. A.; Beatty, A. M.; Smith, B. D.; Camiolo, S.; Gale, P. A. *J. Supramol. Chem.* **2003**, *1*, 289−292.
(12) Reeske, G.; Bradtmöller, G.; Schürmann, M.; Jurkschat, K. *Chem.—Eur. J.* **2007**, *13*, 10239−10245.
(13) Scheerder, J.; van Duynhoven, J. P. M; Engbersen, J. F. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1090−1093.
(14) Kim, S. K.; Sessler, J. L.; Gross, D. E.; Lee, C.-H.; Kim, J. S.; Lynch, V. M.; Delmau, L. H.; Hay, B. P. *J. Am. Chem. Soc.* **2010**, *132*, 5827−5836.
(15) Lankshear, M. D.; Cowley, A. R.; Beer, P. D. *Chem. Commun.* **2006**, 612−614.
(16) Lankshear, M. D.; Dudley, I. M.; Chan, K.-M.; Cowley, A. R.; Santos, S. M.; Felix, V.; Beer, P. D. *Chem.—Eur. J* **2008**, *14*, 2248−2263.
(17) de Silva, P.; McClean, G. D.; Pagliari, S. *Chem. Commun.* **2003**, 2010−2011.
(18) Sessler, J. L.; Kim, S. K.; Gross, D. E.; Lee, C.-H; Kim, J. S.; Lynch, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 13162−13166.
(19) Kim, S. K.; Lee, S. H.; Lee, J. Y.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 16499−16506.
(20) (a) Kim, S. K.; Lee, J. K.; Lee, S. H.; Lim, M. S.; Lee, S. W.; Sim, W.; Kim, J. S. *J. Org. Chem.* **2004**, *69*, 2877−2880. (b) Kim, S. K.; Sim, W.; Vicens, J.; Kim, J. S. *Tetrahedron Lett.* **2003**, *44*, 805−809. (c) Kim, S. K.; Vicens, J.; Park, K.-M.; Lee, S. S.; Kim, J. S. *Tetrahedron Lett.* **2003**, *44*, 993−997. (d) Lee, J. K.; Kim, S. K.; Bartsch, R. A; Vicens, J.; Miyano, S.; Kim, J. S. *J. Org. Chem.* **2003**, *68*, 6720−6725. (e) Kim, J. S.; Lee, W. K.; Suh, I.-H.; Kim, J.-G.; Yoon, J.; Lee, J. H. *J. Org. Chem.* **2000**, *65*, 7512−7517.
(21) Custelcean, R.; Delmau, L. H.; Moyer, B. A.; Sessler, J. L.; Cho, W. -S.; Gross, D.; Bates, G. W.; Brooks, S. J.; Light, M. E.; Gale, P. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2537−2542.
(22) Kim, J. S.; Lee, W. K.; Sim, W.; Ko, J. W.; Cho, M. H.; Ra, D. Y.; Kim, J. W. *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *37*, 359−370.
(23) Wintergerst, M. P.; Levitskaia, T. G.; Moyer, B. A.; Sessler, J. L.; Delmau, L. H. *J. Am. Chem. Soc.* **2008**, *130*, 4129−4139.
(24) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.