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Selective Separation of Lithium Chloride by Organogels Containing Strapped Calix[4]pyrroles

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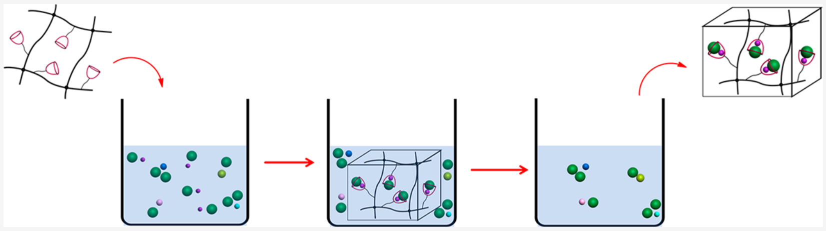

ABSTRACT: Reported herein are two functionalized crown ether strapped calix[4]pyrroles, **H1** and **H2**. As inferred from competitive salt binding experiments carried out in nitrobenzene-d_5 and acetonitrile-d_3, these hosts capture LiCl selectively over four other test salts, *viz*. NaCl, KCl, $MgCl_2$, and $CaCl_2$. Support for the selectivity came from density functional theory (DFT) calculations carried out in a solvent continuum. These theoretical analyses revealed a higher innate affinity for LiCl in the case of **H1**, but a greater selectivity relative to NaCl in the case of **H2**, recapitulating that observed experimentally. Receptors **H1** and **H2** were outfitted with methacrylate handles and subject to copolymerization with acrylate monomers and cross-linkers to yield gels, **G1** and **G2**, respectively. These two gels were found to adsorb lithium chloride preferentially from an acetonitrile solution containing a mixture of LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ and then release the lithium chloride in methanol. The gels could then be recycled for reuse in the selective adsorption of LiCl. As such, the present study highlights the use of solvent polarity switching to drive separations with potential applications in lithium purification and recycling.

INTRODUCTION

Lithium and its compounds play critical roles in high-energy batteries, nuclear fusion power generation and ultralight and high-strength lithium alloys. Not surprisingly, therefore, lithium occupies an increasingly important position in modern industry.[1−7] The rapid development of the new energy industry, in particular, has led to a sharp increase in the market demand for lithium, which makes the development and recovery of lithium resources particularly important. Currently, lithium is obtained primarily from minerals and brines, as well as to a much lesser extent the recycling of lithium-containing waste.[8−10] In these sources, lithium typically coexists with various metal salts (such as those of sodium, potassium, magnesium, and calcium). The similarity between the associated salts (e.g., NaCl vs LiCl) makes the selective extraction of lithium a challenge. Moreover, other potentially competitive metal cations, such as Mg^{2+} and Ca^{2+}, are characterized by higher inherent charge densities, which often hampers Li^+ binding selectivity. Methods that have been examined in the context of isolating lithium from minerals include sulfuric acid extraction, lime sintering, chlorination roasting, and soda ash pressure cooking, among others.[12] Lithium is typically isolated from brine by means of precipitation, solvent extraction, or adsorption.[13] Acidification−precipitation processes are often used for the recycling of lithium-containing wastes. However, all these approaches suffer from limitations. For instance, large amounts of water are used to isolate lithium (as the carbonate salt) from salt deposits, which adds stress to the surrounding ecosystem. Therefore, the development of new methods for purifying lithium constitutes an important research direction. Here we report a new approach to lithium chloride separation from simple salt mixtures that operates entirely in organic solvents, thus circumventing the need to overcome the high hydration energy of the Li^+ cation. It relies on the use of crown ether-calix[4]pyrrole hosts tethered to a polymer backbone. As detailed below, this provides easy-to-manipulate gels that can be recycled through several rounds of solid−liquid LiCl

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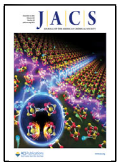

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extraction and release. A key feature of the present approach is the reliance on changes in solvent polarity to drive separations.

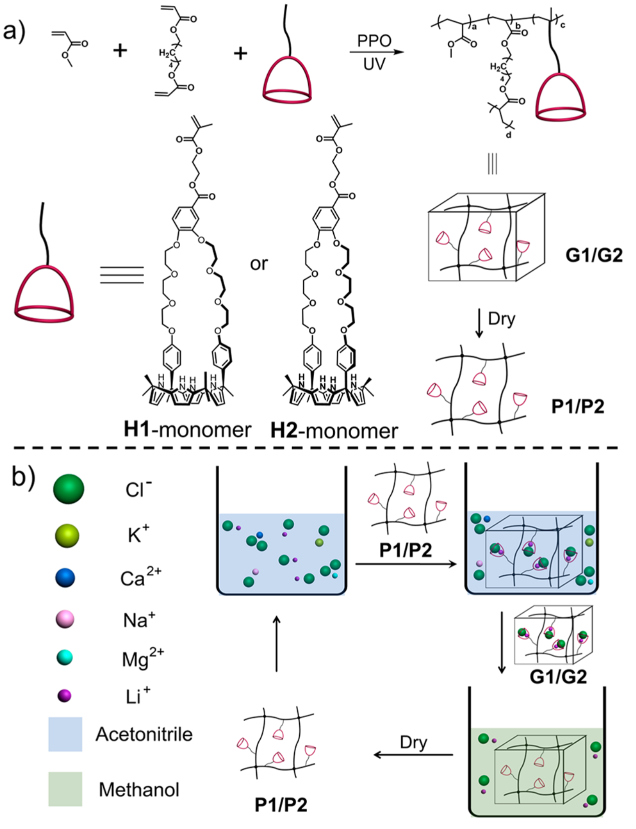
Calix[4]pyrroles, nonaromatic tetrapyrrolic macrocycles, have attracted attention for their ability to selectively interact with neutral molecules, anions, and ion pairs.[14−16] In recent years, calix[4]pyrroles have been explored as potential sensors,[17] catalysts,[18] extractants,[19] ion transporters,[20,21] and drug carriers.[22] Compared to simple calix[4]pyrroles, so-called strapped calix[4]pyrroles, systems wherein the macrocyclic core is bridged by one or more tethers, typically display enhanced affinities and greater selectivities toward certain anionic and ion-pair guests.[23−29] For instance, in 2016 Sessler and co-workers reported a hemispherand-strapped calix[4]-pyrrole that exhibits selectivity for lithium salts.[30] This receptor was found to form 1:1 ion-pair complexes with LiCl, LiBr, LiI, LiNO$_2$, and LiNO$_3$ in preference over the corresponding sodium and potassium salts under both model solid−liquid and liquid−liquid extraction conditions (SLE and LLE, respectively). Subsequently, we reported a hemispherand-strapped calix[4]pyrrole that could selectively capture LiCl under SLE conditions (involving nitrobenzene as the liquid phase).[31] Also reported was a phenanthroline-strapped calix[4]pyrrole that adsorbs LiCl under both model SLE (nitrobenzene) and LLE (CHCl$_3$/water) conditions. Jang and co-workers synthesized a triazole-bearing strapped calix[4]-pyrrole as a lithium selective ion-pair receptor.[32] This receptor proved effective at bringing lithium salts into an organic phase under LLE (CH$_2$Cl$_2$/water) conditions. In seminal early work, Smith and co-workers reported non-calix[4]pyrrole lithium ion-pair receptors.[33]

This prior work has served to underscore the potential utility of small molecule receptors for lithium separations via SLE and LLE. Unfortunately, when functioning as extractants, small molecules can be difficult to remove from solution; this can provide limitations to reuse and recycle. To circumvent these hurdles, we have examined the use of receptor-functionalized polymers to target specific guests. In the context of lithium separations such putative polymeric materials are attractive for separation by physical means (by, e.g., lifting out from the medium) and washing with a different solvent to promote cation release, thereby facilitating initial use and subsequent reuse (Scheme 1). The present study was designed to test this possibility. We note that during this work, Oral and Abetz reported a crown ether functionalized polymer that shows considerable promise as a lithium cation extractant;[34] this system was not, however, designed to allow separations based on physical removal of the polymeric material from a source phase or release of bound salts by modulating the solvent polarity.

■ RESULTS AND DISCUSSION

Given the study objectives, an effort was made to functionalize our previously reported lithium salt receptors such that they could be converted to a polymerizable monomer (e.g., acrylate). However, carboxylate-bearing versions of our first-generation systems proved relatively ineffective as lithium cation receptors. Therefore, we designed a strapped calix[4]-pyrrole containing a relatively large crown ether host moiety (**H**) that was designed to wrap around a bound lithium cation while the calix[4]pyrrole NH protons were expected to bind to the counteranion (e.g., chloride). The synthesis of this targeted host is shown in Scheme 2. In the last step of the ring-forming reaction, we obtained two crown ether strapped calix[4]-pyrroles (**H1** and **H2**) characterized by different substitution patterns. The first of these, **H1**, is linked through the 15α and 20α positions of the calix[4]pyrrole ring, whereas **H2** is substituted at the 10α and 20α positions. The isolation of these two isomers, obtained in 15% and 20% yield, respectively, reflect presumed scrambling of the dipyrrolic precursors under the Lewis acidic condensation conditions. **H1**-monomer and **H2**-monomer were synthesized from **H1** and **H2** by reacting with 2-hydroxyethyl methacrylate.

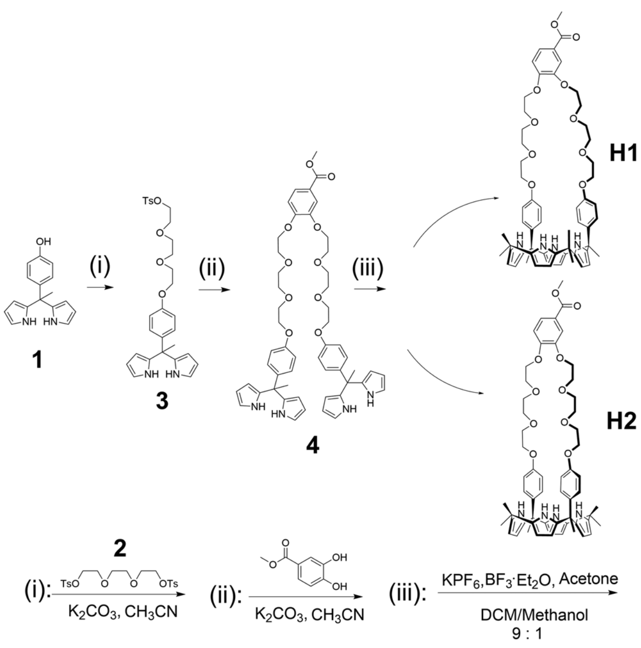
Scheme 1. (a) Chemical Structures and Artistic Representations of the Polymeric Materials P1 and P2 Used in This Study;[a] (b) LiCl Removal from Acetonitrile by Use of a Polymeric Network, P1 or P2, Containing a Salt Receptor, H1 or H2, and the Associated Regeneration Process Yielding the Starting Polymer, P1 or P2



[a]Note: **H1**-monomer is linked through the 15α and 20α positions of the calix[4]pyrrole ring, whereas **H2**-monomer is substituted at the 10α and 20α positions.

The configurations of **H1** and **H2** were confirmed *via* single crystal X-ray diffraction analyses of the respective LiCl host−guest complexes (Figure 1). Single crystals of **H1**-LiCl and **H2**-LiCl were obtained by allowing isopropyl ether to diffuse slowly into a mixed solution of **H1** + LiCl or **H2** + LiCl in acetonitrile. The resulting structures served to establish not only the connectivity patterns for **H1** and **H2** but also their ability to complex lithium chloride as a cobound ion pair in the solid state. In the case of **H1**-LiCl, the Li$^+$ cation forms six coordination bonds with five oxygen atoms and an acetonitrile molecule. As a result, the crown ether strap is twisted. As typical for calix[4]anion complexes, the Cl$^-$ anion in **H1**-LiCl is stabilized *via* four hydrogen bonding interactions with the pyrrolic NH protons. The Li$^+$ cation and Cl$^-$ anion are completely separated, and the Li$^+$⋯Cl$^-$ distance is 6.505 Å. In

Scheme 2. Synthesis of H1, H2, H1-Monomer, and H2-Monomer



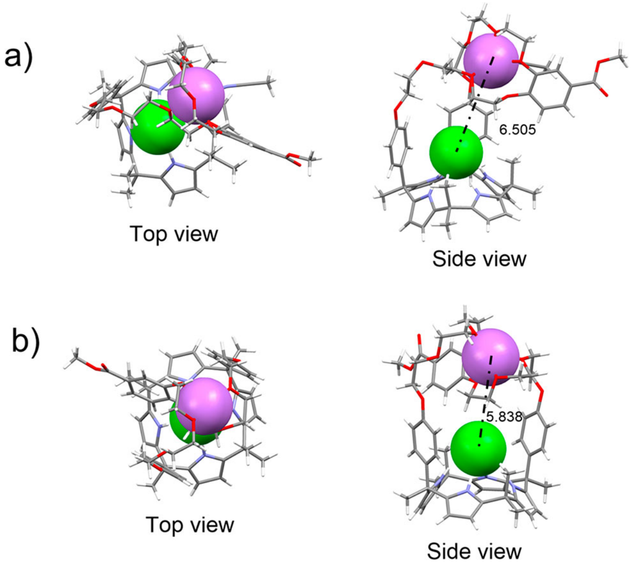


Figure 1. Single-crystal structures of the complexes (a) **H1**-LiCl and (b) **H2**-LiCl. The LiCl is shown in space-filling representations. Other species (*e.g.*, solvent molecules) have been omitted for clarity. Li, light purple; Cl, light green.

H2-LiCl the Li$^+$ cation is bound to five oxygen atoms with no participation of solvent. The crown ether strap is again twisted, and the Li$^+$ cation is complexed within the upper region of the receptor, while the Cl$^-$ anion forms four hydrogen bonds with the calix[4]pyrrole NH protons. The Li$^+$···Cl$^-$ distance is 5.838 Å. In both complexes the two oxygen atoms closest to the pyrrole ring do not participate in the coordination of the bound Li$^+$ cation. This may reflect the fact that the benzene ring connected to the pyrrole ring cannot adopt a conformation suitable for phenolic ether-based cation complexation. To the extent this supposition is correct, the maximum number of oxygen atoms available for cation recognition would be only 6, leading us to infer that **H1** and **H2** would be selective for LiCl over other common halide salts.

Support for the contention that **H1** and **H2** would prove selective for LiCl came from DFT-based comparisons of the continuum-phase binding energies of **H1**-LiCl and **H2**-LiCl relative to their closest anticipated congeners, namely **H1**-NaCl and **H2**-NaCl. Four different low energy conformational isomers of **H1** and **H2** (see Figures S99−S104) were considered in these studies. The binding energies are shown in Figure 2 and are all strongly negative in terms of ΔE_b for the binding of both LiCl and NaCl to each receptor. The raw data are presented in Tables S5−S11. Figure 2 shows that both **H1** and **H2** preferentially bind to LiCl over NaCl, as the binding energies for LiCl-bound receptors are more negative, on average.

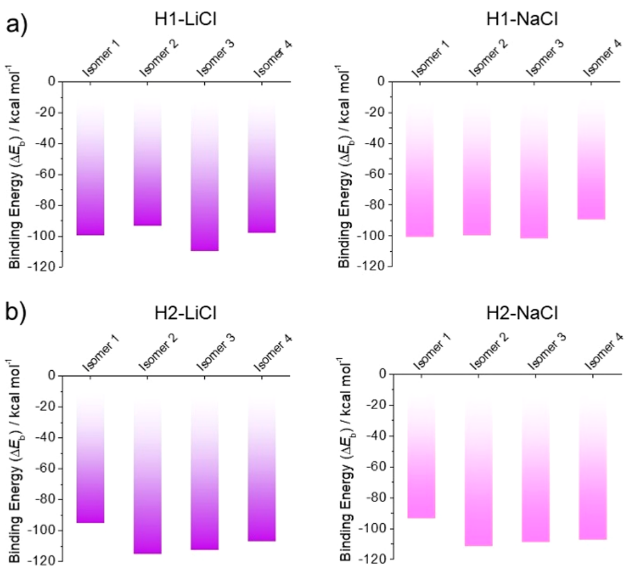


Figure 2. DFT-calculated binding energies of LiCl and NaCl to four different conformational isomers of receptors (a) **H1** and (b) **H2** in an acetonitrile continuum.

Differences in binding energies between the bound LiCl and NaCl to the **H1** receptor are presented in Figure 3a, left, and for **H2**, right. Here, the negative values of $\Delta\Delta E_b$ represent favorable LiCl-bound structures, while positive values represent favorable NaCl-bound structures. We can see that the largest peaks in Figure 3a (left and right) are mostly negative, and thus both receptors **H1** and **H2** have on average a stronger affinity for LiCl than NaCl. Figure 3b shows differences in receptor energies for each salt. We see that, on average, **H1** binds LiCl and NaCl less well than **H2**; in other words, **H2** has a higher affinity (positive bars) for these salts than **H1**. Isomer 2 displays a positive difference in binding (Figure 3a) and thus prefers NaCl. One possible reason among many, for this preference is the relative orientation of the ester group appendage; the arm is raised up compared to isomer 3 and 4 wherein it is down. This has an effect on the overall backbone conformation of the monomer and presumably the stability of each isomer. The ester arms in the "down" configuration may impart van der Waals interactions with the rest of the calix[4]pyrrole (isomer 4) or stabilize $\pi-\pi$ interactions between the phenyl subunits (isomer 3), and therefore help to stabilize the overall structure. Other factors that may influence the binding specifics include the distance

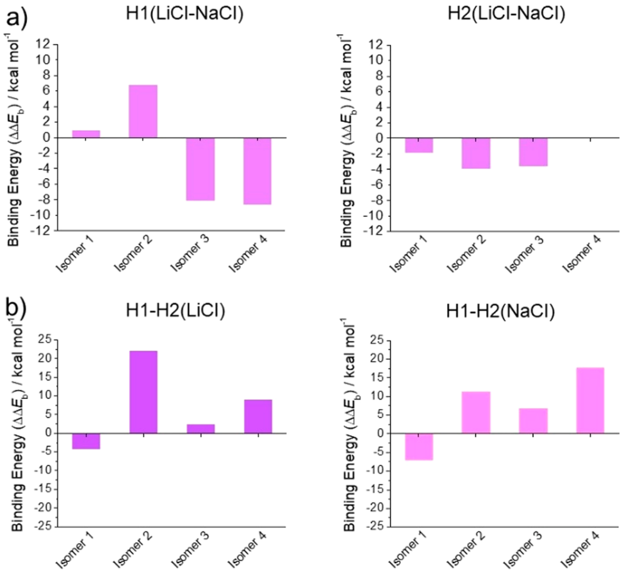


Figure 3. Differences between the DFT-calculated binding energies between (a) the two salts, LiCl and NaCl, for each receptor **H1** (left) and **H2** (right); (b) differences in the binding energies between the two receptors **H2** and **H1** for each salt, LiCl (left) and NaCl (right).

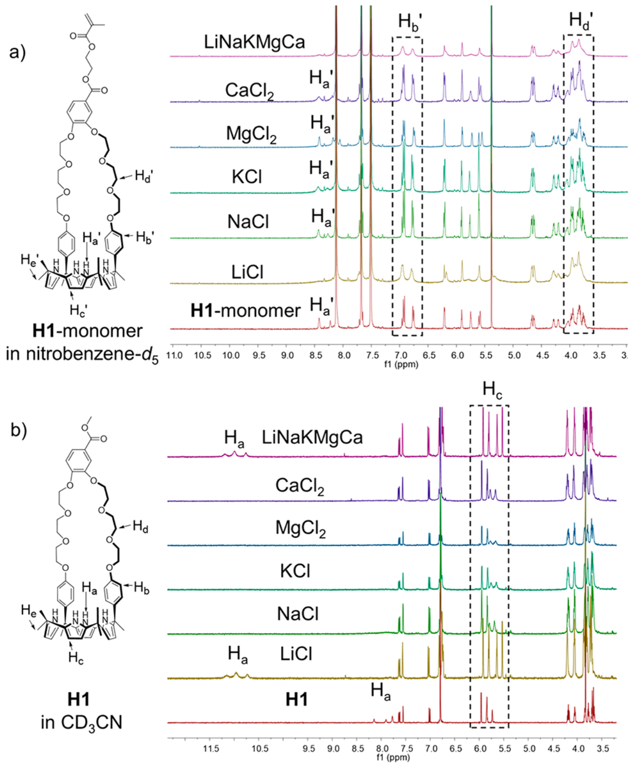


Figure 4. (a) ^{1}H NMR spectra (400 MHz, nitrobenzene-d_5, 298 K) of 5.00 mM solutions of **H1**-monomer made up in nitrobenzene-d_5 and contacted with excess solid LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ alone and in combination for 1 week; (b) ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of 5.00 mM solutions of **H1** made up in CD_3CN and contacted with solid LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ in excess alone and in combination for 1 week.

between the cation and anion, the number of cation-oxygen interactions, the strength of those interactions, and the ability of the solvent to stabilize them.

Given these computational results, our experimental efforts were thus directed to test the ability of **H1** and **H2** to recognize selectively LiCl under conditions relevant to their proposed use as solid−liquid extractants.

In previous work, it was confirmed that LiCl is considerably less soluble in nitrobenzene than either NaCl or KCl (See Table S5 in ref 31). Nitrobenzene was thus selected as an initial solvent with which to test whether **H1**-monomer or **H2**-monomer would function as an extractant under SLE conditions. Toward this end, 5.00 mM solutions of **H1**-monomer and **H2**-monomer were made up in nitrobenzene-d_5 and contacted with solid LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ in excess (to produce a saturated solution) alone and in combination for 1 week. In the case of **H1**-monomer (Figure 4a), the pyrrole NH signals H_a' disappeared and the peak ascribed to protons H_d' on the crown ether broadened after adding LiCl. On the other hand, no discernible change in the H_a' and H_d' resonances was seen in the presence of the other test metal salts, *viz.* NaCl, KCl, $MgCl_2$, and $CaCl_2$. Moderate changes in the H_c' signals were seen in the presence of $MgCl_2$ and $CaCl_2$. In the case of the mixed, five metal salt study, the ^{1}H NMR spectrum was to all extents and purposes identical to that recorded in the presence of just LiCl. On this basis we conclude that **H1**-monomer complexes LiCl well under these conditions and has little, if any, affinity for $MgCl_2$, $CaCl_2$, NaCl, or KCl. Similarly, in the case of **H2**-monomer (Figure S27a), the pyrrole NH signals H_α' disappeared and an appreciable downfield shift in the pyrrole NH signals (by ca. 3.25 ppm) was seen after adding LiCl. A similar disappearance of the pyrrole NH signals H_α' and an appreciable, but more moderate, downfield shift in the pyrrole NH signals (by *ca.* 2.02 ppm) was seen after adding $MgCl_2$. The peak ascribed to protons H_d' on the crown ether broadened after adding LiCl. However, no change in these signals was seen after adding NaCl, KCl, or $CaCl_2$. These findings were rationalized in terms of **H2**-monomer possessing a relatively high affinity for LiCl, a weaker affinity, for $MgCl_2$, and little if any affinity for NaCl, KCl, or $CaCl_2$ in nitrobenzene-d_5 (Figure S27a).

Support for the above conclusions came from inductively coupled plasma mass spectrometry (ICP-MS) studies. It was found that in the absence of a receptor the inherent solubility of NaCl in nitrobenzene exceeded that of LiCl by ≥250× in a 0.1 mL saturated solution of all five test salts considered in this study (Figure S28). In absolute terms the values were 653 and 2.48 ppb for sodium and lithium, respectively. The corresponding normalized values for KCl, $MgCl_2$, and $CaCl_2$ were 33.36, 0.84, and 53.1, respectively (where [LiCl] is set to 1.0) (cf. Figure S28a for absolute values). After adding 2 mg of **H1**-monomer into the 0.1 mL nitrobenzene mixture of the solid five salts (LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$), the normalized ratios were 3.65, 0.48, 0.23, and 0.33 for NaCl, KCl, $MgCl_2$, and $CaCl_2$. In other words, the relative percent lithium went from 0.25% to 17.6% of the total mixture or a ca. 70× increase. The corresponding normalized values were 3.62, 0.50, 0.24, and 0.48 in the case of **H2**-monomer tested under otherwise identical conditions (Figure S28b). In this case the lithium percentage was 17.1% of the total. The error estimates in these values are ≤5%. We thus conclude that both **H1**-monomer and **H2**-monomer act as selective receptors for LiCl in nitrobenzene.

The greater volatility of acetonitrile (bp 82 °C) compared to nitrobenzene (bp 210.9 °C) led us to consider that it would be a more practical polar aprotic medium for use in studies, such as those involving polymers based on **H1** and **H2**, where removal of solvent is important. We thus tested the ability of **H1** and **H2** to function as complexants in acetonitrile. To carry out ^{1}H NMR spectroscopic measurements analogous to those performed above, 5.00 mM solutions of **H1** and **H2** were made up in CD_3CN and contacted with solid LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ in excess (to give a saturated solution) alone and in combination for 1 week. In the case of **H1**, the pyrrole NH signals H_a disappeared and appreciable downfield shifts in the pyrrole NH signals (by *ca.* 3.11 ppm) were seen after adding LiCl (Figure 4b). As true in nitrobenzene-d_5, in CD_3CN the signal assigned to H_d on the crown ether part broadened. However, in contrast to what was found in nitrobenzene-d_5, in CD_3CN a reduced intensity was seen for the H_a resonance but no new peak appeared after adding the other test metal salts, namely NaCl, KCl, $MgCl_2$, and $CaCl_2$. As a consequence, the ^{1}H NMR spectrum for the mixture proved identical to that recorded in the presence of just LiCl.

In the case of **H2** (Figure S27b), the pyrrole NH signals H_a disappeared and appreciable downfield shifts in the pyrrole NH signals (by *ca.* 2.95 ppm) were seen after adding LiCl. The H_a signal was also reduced in intensity, and an appreciable downfield shift in the pyrrole NH signals was seen after adding NaCl, KCl, $MgCl_2$, and $CaCl_2$. In the study involving a mixture of five metal salts, the ^{1}H NMR spectrum was essentially the same as that recorded with just LiCl. These results are taken as evidence that **H2** displays a preference for LiCl over NaCl, KCl, $MgCl_2$, and $CaCl_2$ in CD_3CN.

The above conclusions were supported by ICP-MS studies. Specifically, these analyses revealed a normalized Li/Na:K/Mg/Ca ratio of 1.0:0.85:0.14:1.78:0.64 in a saturated acetonitrile solution of LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$. The corresponding ratios were 1.0:0.59:0.10:1.1:0.50 and 1.0:0.61:0.10:1.11:0.51 after treating with 2 mg of **H1**/**H2** in 0.1 mL of acetonitrile with a mixture of excess solid five salts (LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$), respectively (Figure S29). In other words, the relative percent lithium went from 22.7% to 30.5% of the total mixture after adding **H1** and from 22.7% to 30.1% after adding **H2**. The specific experimental steps are described after Figure S29.

To probe further the putative selectivity of **H1** for lithium chloride, a competitive study involving NaCl and LiCl was carried out (Figure S72). Here, **H1** and NaCl were mixed in a 1:1 ratio (5.00 mM **H1** and 1 molar equiv of NaCl (0.30 mg) in 1.00 mL of CD_3CN), and subject to mixing for 5 days. A ^{1}H NMR spectral analysis revealed that the three peaks corresponding to H_a on **H1** had broadened. In addition, the number of integrated protons in this spectral region decreased from 4 to 2.46. These changes are ascribed to the partial complexation of NaCl by **H1**, which causes the chemical shift of the H_a signal corresponding to the complex to move to lower field under conditions of apparent slow exchange. When 1 equiv of LiCl (0.22 mg) was then added to this mixture, the proton signals of H_a were seen to shift to 11.06 ppm with three distinct peaks, integrating to 4 protons, being observed. The resulting spectrum proved concordant with the ^{1}H NMR spectrum of a 1:1 mixture of **H1** and LiCl. On this basis, we infer that **H1** has a higher affinity for LiCl than for NaCl. The results of other competition studies involving **H1** and **H2** and the five test metal salts considered in this study (i.e., LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$) are provided in Figures S30–S79. Throughout these studies the complexation of LiCl with **H1** or **H2** was found to be fast, whereas slow complexation on the NMR time scale was seen for the other four metal salts (viz. NaCl, KCl, $MgCl_2$, and $CaCl_2$).

Based on the peak integrations, the relative affinity of **H1** and **H2** for LiCl could be ascertained, at least qualitatively, and the ratio of **H1** or **H2** involved in the complexation with various metal salts could be calculated as a function of time (Figure S80). After reaching equilibrium, the normalized ratio of **H1** bound to LiCl vs NaCl, KCl, $MgCl_2$, and $CaCl_2$ was found to be 1.0:0.385:0.812:0.675:0.803 (Table S1); the corresponding values in the case of **H2** were 1.0:0.475:0.820:0.745:0.843.

An effort was also made to assess the relative affinities of **H1** and **H2**. For this study, a mixed CD_3CN solution consisting of **H1** (5.00 mM), **H2** (5.00 mM), and 1 equiv of LiCl (0.22 mg) in 1.00 mL of acetonitrile was made up. In this case, a ^{1}H NMR spectral analysis revealed that the chemical shift of H_α in **H2** moved to lower field (Figure S81). In contrast, the chemical shift of the signal corresponding to H_a of **H1** remained unchanged. On this basis, we conclude that **H2** has a higher affinity for LiCl than its congener **H1**. This qualitative assessment matches what was predicted on the basis of theory (Figure 2).

In contrast to what was inferred in the case of the chloride anion salts, when corresponding qualitative analyses were carried out using $LiPF_6$ and $NaPF_6$ in conjunction with **H1**-monomer, selectivity for the sodium salt was observed (Figures S82 and S83). Specifically, an analysis of the relevant ^{1}H NMR spectra revealed that **H1**-monomer has no appreciable affinity for $LiPF_6$, but interacts with $NaPF_6$. Thus, both crown ether-driven cation recognition and calix[4]pyrrole-based anion binding contribute to the ion pair selectivity of **H1** and **H2**.

The complexation of anions by calix[4]pyrrole is driven by NH-anion hydrogen bonding interactions. It was thus expected that in polar protic solvents the interaction between **H1** or **H2** and various chloride anion salts would be reduced. In fact, no evidence of LiCl (or any other test salt) complexation was seen in methanol-d_4 (Figure S89). It was thus considered likely that methanol could be used to release LiCl from polymers containing **H1** or **H2**. This, in turn, led us to consider that it would be possible to use changes in solvent polarity to drive the recognition, purification, and release of lithium chloride from a mixture of potentially competitive salts.

This strategy is summarized in Scheme 2. Briefly, the acrylate functionalized form of receptors **H1** or **H2**, namely **H1**-monomer and **H2**-monomer, were prepared. They were then used to generate two organic gels (**G1** and **G2**) by copolymerizing (5 mol % **H1-monomer** or **H2-monomer**) with methyl acrylate (94.7 mol %) and cross-linking with 1,6-hexanediol diacrylate (0.3 mol %). Gels **G1** and **G2** provided a stable and solvent swellable macroscopic framework for good solvent exchange capacity. Removal of internal solvents present in **G1** and **G2** in vacuo gave the solid cross-linked networks **P1** and **P2**. **P**-control, a polymer that does not contain either host, **H1** nor **H2**, was also prepared (Figure 5a). Mechanical characterization and microstructural analyses for the macromolecular materials are given in Figures S87 and S88 and serve to confirm that all three structures are porous. In terms of design, it was then expected that following (presumed) selective uptake of LiCl from acetonitrile solutions containing LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$, gels **G1** and **G2** containing LiCl could be lifted out of the acetonitrile solution and put into methanol to release the bound lithium ion salt. Drying of gels **G1** and **G2** would then regenerate **P1** and **P2**,

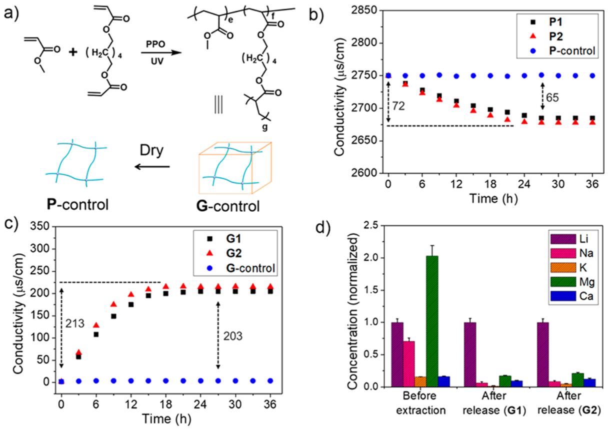


Figure 5. (a) Preparation of **G**-control and **P**-control; (b) conductivities of saturated acetonitrile (10 mL) solutions of the five metal salts considered in this study (LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$) recorded as a function of time after contacting with **P1**, **P2**, and **P**-control (330 mg) for the indicated times; (c) time course of the conductivities of methanol solutions used to treat **G1**, **G2**, and **G**-control after completion of the studies in (b). Results of ICP-MS analyses: (d) Normalized concentrations of Li, Na, K, Mg, and Ca as determined by ICP-MS for a saturated acetonitrile solution (10 mL) of LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ before extraction and after methanol release experiments involving polymers **P1**, **P2**, and **P**-control (330 mg in all cases). For ease of comparison, the raw values (Table S2) have been normalized to the lithium concentration (set to 1.0). The error estimates in the underlying conductivity values are ≤0.5% and ICP-MS values are ≤5%.

which could be recycled to allow a second round of lithium chloride adsorption. Since the entire separation process is carried out in organic solvents, there is no need to overcome the very high hydration energy of lithium chloride.

Conductivity measurements were accomplished in an effort to test the ability of **P1**, **P2**, and **P**-control to extract metal salts. Following construction of conductivity vs concentration calibrations curves in both acetonitrile and methanol (Figure S90), single salt adsorption studies were carried out. In the case of LiCl and $MgCl_2$, conductivities of 495 and 233 μs/cm were recorded for saturated acetonitrile solutions (10 mL), respectively. These values dropped to 439 and 188 μs/cm, respectively, after 24 h in the presence of 330 mg of **P1**. According to the conductivity vs concentration calibrations curves in acetonitrile, the concentration of LiCl dropped from 0.0259 M^{-1} to 0.0207 M^{-1}. Similarly, the concentration of $MgCl_2$ decreased from 0.0023 M^{-1} to 0.0018 M^{-1}. Little appreciable change in conductivity was seen in the case of NaCl, KCl, and $CaCl_2$ (Figure S92a). After soaking for 8 h in acetonitrile 3× using fresh acetonitrile to remove surface adsorbed salts, the resulting gels, **G1**, were physically removed and placed in methanol. After 20 h, the conductivity of the methanolic solutions containing **G1** from the LiCl solution increased from ca. 2 to 211 μs/cm, whereas that for $MgCl_2$ increased to 45 μs/cm (Figure S92b). According to the conductivity vs concentration calibrations curves in methanol, the concentration of LiCl increased from 0 M^{-1} to 0.005 M^{-1} (96% of LiCl is released). Similarly, the concentration of $MgCl_2$ increased from 0 M^{-1} to 0.00049 M^{-1} (98% of $MgCl_2$ is released). Little change was seen in the conductivity of the methanolic solutions of the polymers **G1** soaked initially with NaCl, KCl, and $CaCl_2$. Analogous results were seen for **P2** (Figures S92c and S92d).

Next, a two-salt adsorption experiment involving LiCl and NaCl was carried out. Again, the conductivity of a saturated LiCl + NaCl acetonitrile solution (10 mL) was followed as a function of time in the presence of 330 mg of **P1** or **P2** (Figure S93a). The initial conductivity was 398 μs/cm. After 24 h, at which point saturation was seen, the conductivity of the solution containing **P1** had dopped to 348 μs/cm, whereas that for **P2** was 342 μs/cm. Treating gels **G1** and **G2** as above gave conductivities of 157 and 168 μs/cm for the respective methanol wash solutions after 20 h (Figure S93b). The errors in these measurements are ≤5%.

Analogous studies involving all five test metal salts LiCl, NaCl, KCl, $MgCl_2$ and $CaCl_2$ revealed that both polymer networks **P1** and **P2** had excellent adsorption capacities (Figure 5b). The resulting gels, **G1** and **G2**, were again found to release the adsorbed metal salts in methanol (Figure 5c). In marked contrast, **P**-control, the polymer network lacking a receptor, produced little-to-no appreciable change in conductivity, during either the initial acetonitrile adsorption or subsequent methanol release stages. The lack of efficacy seen for **P**-control serves to underscore the important role that receptors **H1** and **H2** play in driving the metal salt binding seen for **P1** and **P2**.

Next, ICP-MS was used to assess the lithium selectivity of gels **G1** and **G2** under conditions of capture in acetonitrile and release in methanol. To mirror the conductivity studies for the free receptors discussed above, an initial LiCl vs NaCl competition was carried out. The results are summarized in Table S2. A Li/Na ratio of 1.0:0.25 was found for a saturated LiCl + NaCl acetonitrile solution. After the adsorption and release experiments, normalized Li/Na ratios of 1.0:0.06 and 1.0:0.07 were found for the methanolic solutions based on **G1** and **G2**, respectively (Table S2 and Figure S93c).

The ICP-MS study was then extended to a mixed saturated acetonitrile solution of LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ (Figure 5d and Table S2). Again, as compared with the solution before extraction, the normalized concentrations of Na, K, Mg, and Ca in the methanol release phase were significantly reduced (initial normalized Li/Na/K/Mg/Ca ratios of 1.0:0.71:0.15:2.03:0.16 vs 1.0:0.06:0.01:0.17:0.09 and 1.0:0.08:0.05:0.23:0.13 after extraction and release with **G1** and **G2**, respectively). In other words, the relative percent lithium went from 24.6% to 75.2% of the total mixture after **G1** extraction and from 24.6% to 67.1% after **G2** extraction. Considered in concert, these results are taken as evidence that **P1** and **P2** are selective for LiCl over NaCl, KCl, $MgCl_2$, and $CaCl_2$.

After methanol-triggered salt release, the resulting gel could be dried in vacuum at room temperature overnight. The resulting dry polymers, **P1**-regenerated and **P2**-regenerated, could then be used to extract LiCl from a saturated mixture of LiCl and NaCl in 10 mL of acetonitrile (Figure S94). In this case, the initial conductivity value of 398 μs/cm dropped to 349 μs/cm and 343 μs/cm when treated with 330 mg of **P1**-regenerated and **P2**-regenerated, respectively. Compared to the first cycle from 398 μs/cm to 348 μs/cm and 342 μs/cm, the adsorption capacity was essentially unchanged. On this basis, we propose that the materials of this study can be readily recycled for repeated use.

In summary, we have synthesized two new functionalized crown-ether strapped calix[4]pyrroles **H1** and **H2**. The structures of these two strapped calix[4]pyrroles were confirmed by single crystal X-ray diffraction analyses.

Receptors **H1** and **H2** differ from one another by the position of the strap, being linked through the 15α,20α and 10α,20α positions of the calix[4]pyrrole ring, respectively. Among the five metal chloride salts considered in the present study, LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$, both **H1** and **H2** displayed high selectivity for LiCl, as inferred from ^{1}H NMR spectroscopic analyses and supporting ICP-MS studies. Postsynthetic functionalization of **H1** and **H2** allowed for the preparation of two organic gels, **G1** and **G2**. These two gels were designed to possess network structures so as to maintain their integrity in organic media and facilitate their applicability in metal sequestration and recycling. Both gels were used to extract LiCl from saturated acetonitrile solutions in the presence of potentially competing salts. After physical removal of the gels from the initial medium, salt release was affected by treating with methanol. On the basis of conductivity and ICP-MS analyses, it was concluded that both gels are selective for LiCl. The present approach to lithium capture and release, involving the use of soft materials that function entirely in organic solvents, obviates the need to overcome the high hydration energies of lithium ion salts and serves to underscore the potential benefits of solvent polarity switching as an approach to metal salt separations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c10255.

Additional experimental details, materials, and methods, including photographs of organogels (PDF)

Accession Codes

CCDC 2107218 and 2107227 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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