A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201805127
Angew. Chem. 10.1002/ange.201805127

Link to VoR: http://dx.doi.org/10.1002/anie.201805127
http://dx.doi.org/10.1002/ange.201805127

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10.1002/anie.201805127

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Selective Solid–liquid Extraction and Liquid–liquid Extraction of Lithium Chloride using Strapped Calix[4]pyrroles

Qing He, Neil J. Williams, Ju Hyun Oh, Vincent M. Lynch, Sung Kuk Kim,* Bruce A. Moyer,* and Jonathan L. Sessler*

Abstract: LiCl is a classic "hard" ion salt that is present in lithium–rich brines and a key component in end–of–life materials (i.e., used lithium–ion batteries). Its isolation and purification from like salts is a recognized challenge with potential strategic and economic implications. Here, we describe two ditopic calix[4]pyrrole-based ion pair receptors (**2** and **3**), that are capable of selectively capturing LiCl. Under solid–liquid extraction conditions, using **2** as the extractant, LiCl could be separated from a NaCl–KCl salt mixture containing as little as 1% LiCl with ~100% selectivity, while receptor **3** achieved similar separations when the LiCl level was as low as 200 ppm. Under liquid–liquid extraction conditions using nitrobenzene as the non–aqueous phase, the extraction preference displayed by **2** is KCl > NaCl > LiCl. In contrast, **3** exhibits high selectivity towards LiCl over NaCl and KCl, with no appreciable extraction being observed for the latter two salts.

Over the past two decades, the worldwide demand for lithium has increased substantially. This rise is consumption driven by the critical role of lithium in areas as diverse as modern materials, pharmaceuticals, and lithium–ion batteries (LIBs). However, the global lithium reserve is finite. Some estimates have supply from readily accessible lithium resources not being able to meet demand by 2023.[1] Compounding the problem is that the global rate of lithium recycling is <1%.[2] This provides an incentive to develop new strategies that might allow lithium salts to be isolated from non–traditional supply sources, such as brackish brines, where LiCl is expected to define the dominant lithium form. Both so–called solid–liquid extraction (SLE) and liquid–liquid extraction (LLE) strategies are appealing in this regard. However, such approaches are made challenging by the high lattice (–834 kJ·mol^{-1}) and hydration energies (–475 kJ·mol^{-1} for Li^+, –340 kJ·mol^{-1} for Cl^-) of LiCl.[3] Here, we detail the synthesis and study of two calix[4]pyrrole-based ion pair receptors (**2** and **3**) that allow LiCl to be captured selectively under SLE conditions. System **3** also permits the selective LLE extraction of LiCl into chloroform from an aqueous source phase. To the best of our knowledge, systems **2** and **3** are also the first receptors capable of stabilizing a LiCl complex in the solid state without an intervening water molecule between the Li^+ cation and Cl^- anion.

The design and synthesis of Li^+ ionophores dated back to the 1980s, when Cram and his colleagues reported a spherand for recognition of Li^+.[4] Since then, considerable progress has been made in this area. However, most reported systems are cation receptors and require a lipophilic anion (e.g., picrate and perchlorate) to achieve effective Li^+ recognition.[5] Therefore, with few exceptions,[6] unwanted counter anionic components are needed when these systems are applied as extractants for separation of lithium from mixtures.[7] The use of ion pair receptors,[8] small molecules that are capable of binding anions and cations concurrently, may obviate this need. However, the chemistry of ion pair receptors, especially for lithium salt recognition, is not well developed. In 2004, Smith and coworkers reported the SLE extraction of $LiCl_{(s)}$ into $CDCl_3$ with selectivity ratios of 94:4:2 (LiCl : NaCl : KCl) by means of a ditopic ion pair receptor.[9] Impressive as these early results were, further advances are needed. For instance, the Salar de Uyuni in Bolivia, the largest salt flat on earth, contains a large amount of alkali metal salts mainly in their respective chloride forms (i.e., NaCl, KCl and LiCl). However, the lithium content is low (between 80 and 1500 ppm) relative to the high concentrations of competing cations.[10]

Direct separation of LiCl from such mixtures, either in brine form or after evaporation to a solid salt mixture, remains an unmet challenge. Recently, our group reported an ion pair receptor (**1**) that permitted the extraction of $LiNO_2$(aq) into an organic phase.[11] However, neither our system nor Smith's proved effective for LiCl under LLE conditions. This failure may reflect an inability to stabilize LiCl complexes that are free of a bridging water molecule between the co-bound charge dense Cl^- anion and Li^+ cation. We envisioned that the effectiveness and selectivity of ion pair binding might be enhanced if direct contact between co-bound ions could be enforced by use of receptors containing smaller internal cavities since it might maximize the Coulombic attraction within the complex. To test this hypothesis within the context of LLE and SLE, we prepared the ditopic ion-pair receptors **2** and **3**. These new systems were fully characterized by standard spectroscopic means, as well as by X–ray diffraction analysis (Schemes S1–S2, Figures S1–S2).

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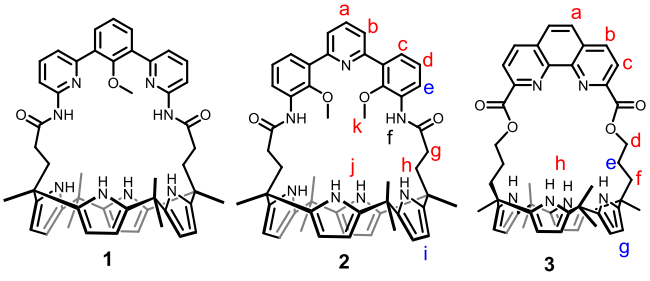

Figure 1. Chemical structures of receptors **1**–**3**.

10.1002/anie.201805127

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As a first step toward testing whether **2** and **3** would act as ion pair receptors, their ability to bind LiCl salts was probed via ^{1}H NMR spectroscopy in a mixture of $CDCl_3/CD_3OD$ (9:1, v/v). As is shown in Figure S3, significant chemical shift changes were observed when these two receptors were treated with excess $LiCl_{(s)}$ and allowed to equilibrate for 60 minutes. Specifically, upon exposure to excess LiCl in this way, all aromatic hydrogen atoms signals (***a***, ***b***, ***c***, and ***d***), along with the aliphatic proton signals denoted ***k***, ***g***, and ***h*** of receptor **2** underwent downfield shifts. Similarly, in the case of receptor **3**, the phenanthroline protons ***a***, ***b***, and ***c*** and the aliphatic protons ***d*** and ***f*** shifted to lower field in the presence of excess LiCl. Such observations are consistent with the Li^+ cations being bound to the hemispherand and phenanthroline subunits in the case of **2** and **3**, respectively. Evidence for interactions between the calix[4]pyrrole subunits present in **2** and **3** and the chloride anions of LiCl came from the large downfield shifts observed for the pyrrolic NH protons (***j*** for **2** and ***h*** for **3**) and the slight upfield shifts seen for the pyrrolic CH protons (***i*** for **2** and ***g*** for **3**).

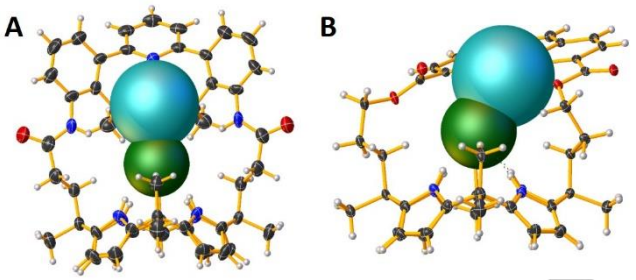

Figure 2. Single–crystal structures of (A) **2**·LiCl and (B) **3**·LiCl. The Li^+ and Cl^- ions are shown in space–filling form. Displacement ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.

Further support for the fact that **2** and **3** are capable of capturing LiCl came from single crystal X–ray diffraction analyses. Suitable crystals of the LiCl complexes of **2** (**2**·LiCl) and **3** (**3**·LiCl) were obtained by subjecting a $CH_2Cl_2/CH_3OH/CH_3CN$ solution of **2** or a CH_3CN/CH_3OH solution of receptor **3** to slow evaporation in the presence of excess LiCl, respectively. In contrast to what was seen in the case of **1**·LiCl, where a water molecule was observed to bridge the Li^+ cation and the Cl^- anion,[11] receptors **2** and **3**, as anticipated, entrap the LiCl ion pair directly within their cavities. This gives rise to close $Li^+\cdots Cl^-$ distances of 2.67 Å and 2.38 Å, respectively (Figure 2). In the case of **2**·LiCl, both the Li^+ and Cl^- ions were found entirely embedded within the cavity of receptor **2**, while in the case of **3**·LiCl, the cation was forced to extrude from the cavity leading to distortion of the receptor framework. The solid-state structures of **2**·NaCl, **2**·KCl, and **2**·CsCl were also obtained (Figure S4). Although the Na^+, K^+, and Cs^+ are all complexed by the hemispherand portion of receptor **2**, as the ionic radius increases from Li^+ to Cs^+, the cations extrude further and further from the receptor cavity. Such findings led us to consider that both **2** and **3** might prove selective for LiCl over other alkaline metal chloride salts. Since **3** possesses the smallest cavity within the series **1**-**3** we further imagined it might prove to be an even more effective extractant than **2**.

To obtain more direct experimental insights into the binding selectivities of **2**, ^{1}H NMR spectroscopic titrations were performed in THF–d_8/D_2O (9:1, v/v) (Figure S13–S20). The resulting data could be fit to a 1:1 binding model giving calculated affinity constants of (8.3 ±0.3) $\times10^2$ M^{-1}, (1.2 ± 0.3) $\times10^4$ M^{-1}, (6.7 ± 2.5) $\times10^3$ M^{-1}, and (2.5 ± 0.6) $\times10^3$ M^{-1} for LiCl, NaCl, KCl and CsCl, respectively. This resulting binding selectivity, namely NaCl > KCl > CsCl > LiCl, differs from what was inferred from the gas phase DFT calculations (LiCl > NaCl > KCl > CsCl) (Figure S5-S12, Table S1-S3). The strong reduction in the relatively LiCl affinity is ascribed to the presence of water in the solvent mixture and the particularly "hard" nature of the lithium cation (ΔG_{hyd} = –475 kJ·mol^{-1} for Li^+ vs. ΔG_{hyd} = –365 kJ·mol^{-1}, –295 kJ·mol^{-1}, and –250 kJ·mol^{-1} for Na^+, K^+, and Cs^+, respectively).[3b] When **3** was subject to analogous titrations, no appreciable changes in any of the proton signals for **3** were observed after 30 equivalents of MCl (M = Li, Na, K, Cs) were added (Figures S21–S24). This latter finding is rationalized in terms of the interactions between **3** and these alkali metal salts being insufficient to compete effectively with hydration in this mixed aqueous medium. However, the treatment of receptor **3** in a water-free mixture of $CDCl_3/CD_3OD$ (9:1, v/v) with excess LiCl to leads to chemical shift changes consistent with the concurrent complexation of both the Li^+ and Cl^-. No appreciable changes in any of the receptor–based proton signals were seen when receptor **3** was treated with excess NaCl, KCl, or CsCl (Figure S25).

The above findings led us to consider that **2** and **3** might prove effective as extractants for LiCl under both SLE and LLE conditions in the presence of excess NaCl and KCl, as would be present in common lithium–containing salt flats. In a first study, solutions of **2** in $C_6D_5NO_2$ were layered over solid samples consisting of excess powdered LiCl, NaCl, and KCl, respectively. Control experiments revealed that exchange between the different receptor/salt complexes is slow on the NMR time scale (Figures S26 and S27). Thus, each extracted complex (i.e., **2**·LiCl, **2**·NaCl, and **2**·KCl) in the organic phase could be recognized directly by ^{1}H NMR spectroscopy and the relative concentrations of the free and bound forms of the receptor measured by integrating the respective signals. On this basis, it was found that receptor **2** was capable of extracting efficiently LiCl, NaCl and KCl into nitrobenzene over the course of 48 h (Figure S28). After this equilibration time, receptor **2** was almost 100% loaded in the case of each salt. As inferred from ^{1}H NMR spectral studies, high selectivity (~100%) was seen for LiCl over NaCl and KCl in the case of a competitive solid/liquid salt extraction study wherein a solution of **2** in $C_6D_5NO_2$ was layered over a mixture of LiCl, NaCl and KCl (100:100:100, molar ratio relative to **2**) and allowed to stand for 1 h. Little change in the ^{1}H NMR spectrum is seen over time (up to 7 days), indicating that the selectivity for LiCl under these conditions of receptor saturation is likely thermodynamic in origin (Figure S29). More striking, strapped calix[4]pyrrole **2** was found capable of selectively extracting LiCl from mixtures of salts (NaCl and KCl; 1:1, m/m) containing either 10% or only 1% of LiCl by mass (Figure S30–S31).

Further support for the fact that receptor **2** can act as an ion-pair extractant for LiCl with selectivity towards LiCl over NaCl and KCl came from the qualitative flame tests. Control experiments confirmed the expected colors, namely red, yellow and purple (Figure 3A-3C) when a loop was dipped into 1 M aqueous

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solutions of LiCl, NaCl, and KCl, respectively, and held within a flame. The red flame characteristic of lithium was seen when clean loops were dipped into solutions of **2** in nitrobenzene after treatment with a mixture of LiCl, NaCl and KCl (in a 100:100:100, molar ratio) (Figure S32). Similar color features characteristic of lithium were also seen when mixtures of NaCl and KCl containing either 10% or 1% LiCl (by mass) were subject to the same qualitative analysis (Figure 3D-3E).

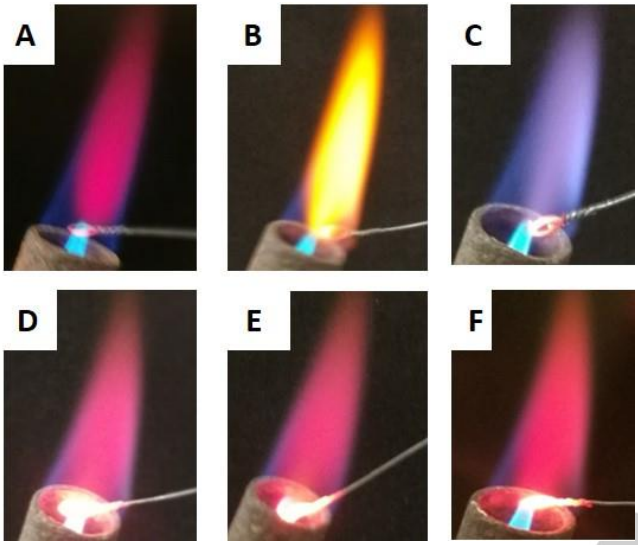

Figure 3. Flame test experiments involving control aqueous solutions consisting of (A) LiCl; (B) NaCl; (C) KCl; (D) extracted nitrobenzene solutions of **2** after contacting with a mixture of NaCl and KCl containing 10% of LiCl (mass content); (E) analogous experiments where the LiCl content was 1% by mass; (F) The extracted solution obtained using receptor **3** as the extractant and a mixture of NaCl and KCl containing 200 ppm of LiCl (mass content) as the source phase.

More quantitative support for the suggestion that **2** is selective for LiCl came from inductively coupled mass spectrometric (ICP-MS) analyses. These experiments were performed by layering nitrobenzene solutions of **2** over the above-mentioned salt mixtures for 48 h. In each case, the organic phase was then separated off and back extracted with 0.2 M sulfuric acid. The resulting aqueous phase was then diluted with 2% aqueous HNO_3 and subject to ICP-MS analysis. After accounting for uptake of salts by the solvent alone, the loading of each ion pair was calculated and reported in terms of the percentage of total receptor sites bound (Figure 4A-4C, Tables S4 and S5).

In the case of the mixture consisting of LiCl, NaCl and KCl in a 100:100:100 molar ratio, the loading of LiCl was estimated to be ca. 62%, while in the case of the solid-liquid extraction experiments involving lower relative LiCl concentrations (i.e., 10% and 1% by mass), the loading levels were estimated to be ca. 55% and 45 %, respectively. In contrast, the loading of NaCl and KCl was found to be < 7% and < 2%, respectively. This was found to be true for all three LiCl ratios. It is noted that the absolute loading levels inferred from the ICP-MS studies are lower than the ~100% loading levels calculated from the ^{1}H NMR spectroscopic studies, even if the selectivity ratios were similar. We account for the relatively low total loading levels seen in the ICP-MS studies to continual dilution before the final elemental analysis.

Much to our surprise, receptor **3** proved even more selective for LiCl relative to NaCl and KCl than **2** when tested as an extractant under conditions of SLE. After a 3.0 mM solution of **3** in $CDCl_3$ was allowed to stand over excess quantities of solid LiCl, NaCl and KCl, respectively, a new set of signals corresponding to the complex **3**·LiCl was observed in the sample involving solid LiCl (Figure S33). In contrast, no appreciable change in the proton signals of **3** was seen after contacting with solid NaCl or KCl, even if the putative equilibration time was extended to two weeks (Figure S34–S35). Such observations are taken as an indication that receptor **3** acts as a selective extractant for LiCl under SLE conditions where chloroform serves as the organic phase.

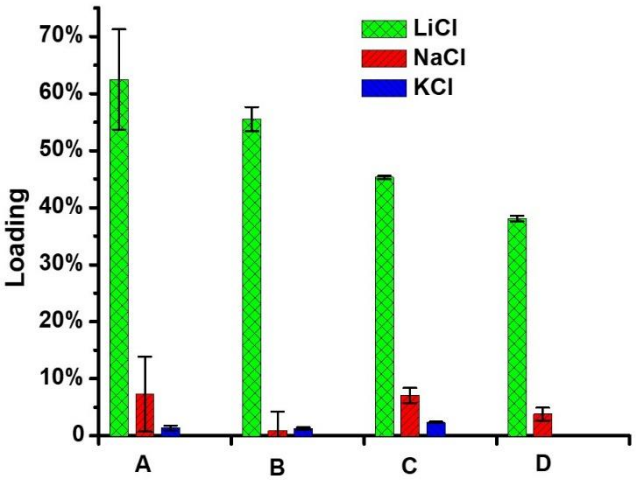

Figure 4. Results of ICP-MS analyses showing the percent receptor loading of the indicated alkaline chloride salt after extraction from solid mixtures of (A) LiCl, NaCl and KCl (100:100:100, molar ratio), (B) NaCl and KCl containing 10% of LiCl (mass content), and C) analogous experiments where the LiCl content was 1% by mass, the concentration of receptor **2** was 4 mM in nitrobenzene in all three studies. (D) Analogous studies involving a solid mixture of NaCl and KCl containing 200 ppm of LiCl (by mass) using receptor **3** (3 mM in chloroform).

To test this concept further, receptor **3** was tested as an extractant in SLE studies involving solid samples with extremely high Na(K)/Li ratios. Specifically, a solution of **3** in $CDCl_3$ was layered over a solid NaCl-KCl (1:1, by mass) mixture containing 200 ppm LiCl and subject to sonication for 1 h. A new set of peaks was seen in the ^{1}H NMR spectrum that was readily assigned to **3**·LiCl, along with signals corresponding to free **3**. Expanding the exposure time to 48 h led to essentially complete conversion to the complex form (Figure S36). Even under these long contact times, no new peaks corresponding to either **3**·NaCl or **3**·KCl were observed. The fact that, under this extreme condition, LiCl was selectively extracted to the chloroform phase was qualitatively supported by flame test experiments (Figure 3F) and quantitative ICP-MS studies analogous to those described above (Figure 4D, Tables S4 and S5). In the case of the latter one, the loading of LiCl was estimated to be ca. 38%, while that of NaCl and KCl were too low to be assessed with confidence in light of the relatively high background levels. To our knowledge, this is

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the first example for an ion pair receptor to complex effectively small quantities of LiCl under SLE conditions in the presence of large quantities of NaCl and KCl, two common salts that are likely to be in excess under possible real-world application scenarios.

Efforts were then made to assess whether **2** or **3** was capable of extracting LiCl under LLE conditions. When a solution of **2** in $C_6D_5NO_2$ (4.0 mM) is exposed to solutions of LiCl in D_2O at concentrations varying from 1 M to 4 M, two sets of readily distinguishable proton signals, assigned to the free host **2** and the **2**·LiCl complex, respectively, were observed. Slow exchange predominates, meaning the relative concentrations of the species in question could be measured via signal integration. Thus, the loading (of **2**), which is defined as the molar percentage of extractant containing LiCl after exposure to the concentrated aqueous LiCl solution, was estimated to be ca. 12 %, 20%, 27%, and 40% when solutions of **2** in $C_6D_5NO_2$ were exposed to 1 M, 2 M, 3 M, and 4 M LiCl solutions in D_2O, respectively (Figure S37, black curve). As expected, the loading increases as the source phase LiCl concentrations increase. For instance, nearly 100% loading was seen at a LiCl concentration of 10 M (Figure S38). The analogous liquid–liquid extraction loading was also tested in the case of NaCl and KCl (Figures S37, S39–S40). The selectivity proved inversely correlated with the cation hydration energies, i.e., KCl > NaCl > LiCl. However, in the case of **3**, when a 3.0 mM solution of **3** in $CDCl_3$ was exposed to a saturated D_2O solution of LiCl, all proton signals known to be diagnostic of Cl^- binding and Li^+ complexation shifted downfield or upfield shifts in the expected manner relative to the ^{1} H NMR spectrum of free **3** in D_2O saturated $CDCl_3$ (Table S6 and Figure S41). These spectral changes were taken as evidence that LiCl was being extracted effectively (~100% receptor loading) from the D_2O phase into chloroform. In contrast, exposure of **3** to saturated D_2O solutions of NaCl or KCl under otherwise identical conditions produced no appreciable changes in the ^{1}H NMR spectrum. Unfortunately, the extent of LiCl receptor loading dropped to ~15% when the concentration of LiCl in D_2O was lowered to 10 M (Figure S42). Thus, the overall efficacy is lower for **3** than for **2**. However, the selectivity of **3** is far greater than it is for **2**.

In summary, the ion pair binding properties of a new hemispherand–strapped calix[4]pyrrole **2** and a phenanthroline–strapped calix[4]pyrrole **3** have been studied in detail. Receptor **2** proved capable of capturing LiCl, NaCl, KCl and CsC, while its congener **3** proved capable of complexing LiCl as confirmed by ^{1}H NMR spectroscopy, single–crystal structures, and DFT calculations. Interestingly, **2** could be used to separate LiCl from a solid NaCl–KCl mixture containing only 1% of LiCl. In contrast, receptor **3** was able to strip LiCl from a solid NaCl–KCl mixture containing only 200 ppm of LiCl with ~100% selectivity. When used as a extractant for LLE, **2** proved capable of extracting LiCl, NaCl and KCl into a bulk nitrobenzene phase at relatively low salt concentrations (< 1 M), with the selectivity being KCl > NaCl > LiCl. In contrast, **3** proved capable of extracting LiCl from an aqueous source phase into a chloroform receiving phase with ~100% selectivity under conditions of near–saturation. Overall, these studies are expected to advance our understanding of the design criteria needed to produce ion pair receptors targeted for the recognition and extraction of a given anion-cation salt combination.

Acknowledgements

The work in Austin was supported by the Office of Basic Energy Sciences, U.S. Department of Energy (DOE) (grant DE–FG02–01ER15186 to J.L.S.). S.K.K. acknowledges the Basic Science Research Program of the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2017R1A4A1014595). Support from the Robert A. Welch Foundation (F–0018 to J.L.S.) is also acknowledged. B.A.M. (advice on binding and extractions) and N.J.W. (supporting extraction measurements) acknowledge support by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

Conflict of interest

The authors declare no conflict of interest.

Keywords: Ion-pair receptor • solid-liquid extraction • lithium chloride • calix[4]pyrrole • liquid-liquid extraction

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10.1002/anie.201805127

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Selective Solid–liquid Extraction and Liquid–liquid Extraction of Lithium Chloride using Strapped Calix[4]pyrroles

Organically extracting LiCl at ppm level: How can ion-pair receptors be made selective for inorganic ion pairs? Here, we show that well-designed ion-pair extractants are capable of extracting LiCl from a solid mixture containing LiCl at the ppm level with ~100% selectivity under solid-liquid extraction conditions. Selective liquid-liquid extraction can also be achieved.