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Strapped calix[4]pyrrole as a lithium salts selective receptor through separated ion-pair binding†

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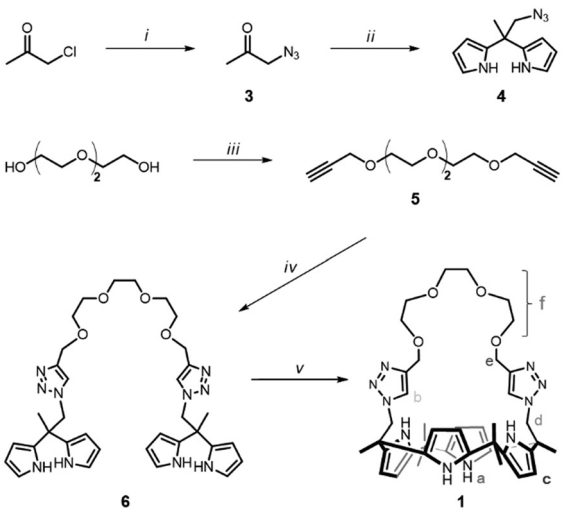
A triazole-bearing strapped calix[4]pyrrole (1) was synthesized as a lithium salt selective ion pair receptor. ^{1}H NMR spectral studies and X-ray crystallography showed that the capture of LiCl by 1 occurs *via* separated ion pair binding. Furthermore, lithium salts extracted by 1 could be solidified in the form of Li_2CO_3 through CO_2 or K_2CO_3 treatment.

Lithium is an important element in industrial applications, including lithium-ion batteries, lubricants, and ceramics.[1] Currently, most of the available lithium reserves are concentrated in the form of salt flats in a few countries.[2] Owing to increasing industrial demand, as well as the limited amount of lithium deposited in salt flats, the price of lithium has greatly increased in recent years. Therefore, finding an alternative lithium source would be of great value. The total amount of Li^+ present in seawater is much higher than that in terrestrial reserves. However, the selective extraction of Li^+ from seawater is extremely difficult due to the abundance of other cations, such as Na^+, K^+, and Mg^{2+}.[3,4] Recently, ditopic receptors have attracted attention owing to their various applications, including salt solubilization, membrane transport, and as logic gates.[4–6] Several types of ion-pair receptors have been designed using calix[4]pyrrole,[7–11] calix[4]arene,[12,13] and carbazole derivatives[14] to capture CsF, KF, $LiNO_2$, and other salts.[15] Until now, very few examples of extraction of lithium salts by ion-pair receptors in organic solvents have been reported.[16] Most reports of the extraction of lithium salts from aqueous solutions were achieved from aqueous $LiNO_2$ solution.[17,18] For the extraction of Li^+ from seawater, it would be essential to develop an ion-pair receptor that can extract LiCl, LiBr, and Li_2SO_4 due to the natural abundance of Cl^- (19.35 g L^{-1}), SO_4^{2-} (2.71 g L^{-1}), and Br^- (67 mg L^{-1}).[19] However, the development of ion-pair receptors able to extract LiCl or LiBr from aqueous solutions has been challenging. For this reason, Sessler's group reported phenanthroline strapped calix[4]pyrrole as a contact ion-pair receptor for LiCl.[20] Recently, we developed triazole-bearing calix[4]pyrroles that showed strong affinities towards halide anions.[21] Based on the strong binding affinity of the triazole-bearing calix[4]pyrroles towards halide ions, we designed a new type of ion-pair receptor (**1**; Scheme 1) with an oligoethylene glycol strap to facilitate the binding of Li^+. Through ^{1}H NMR spectral studies, we confirmed the successful binding of LiCl and LiBr to **1** in organic solvent. Although it is unfavorable for LiCl or LiBr extraction through a separated ion-pair binding process due to the high hydration energy of halide ions, we have successfully extracted lithium halide through liquid–liquid extraction using **1**. Moreover, lithium salts extracted by



Scheme 1 Synthesis procedure of **1**. (i) NaN_3, acetone; (ii) TFA, pyrrole; (iii) propargyl bromide, NaH, KI, THF; (iv) **4**, $CuSO_4$, Na ascorbate, THF/H_2O; and (v) BF_3·OET_2, acetone.

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of all compounds, ^{1}H NMR spectral titration for **1**·LiCl, **1**·LiBr, and **1**·$LiClO_4$, ^{1}H NMR spectral experiments for testifying anion selectivity, and computational data. Detailed information for X-ray crystallographic data, and other supporting figures. CCDC of **1**·LiCl is 1990576. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc04809g

1 could be solidified in the form of Li_2CO_3 through CO_2 or K_2CO_3 treatment.

The synthesis of a triazole-bearing oligoether strapped calix[4]pyrrole, **1**, is outlined in Scheme 1. ^{1}H NMR observation of **1** in 10% CD_3OD/CD_2Cl_2 was performed upon addition of several salts, such as LiCl, NaCl, and KCl (Fig. 1).

The ^{1}H NMR spectrum of **1** exhibited large spectral shifts by addition of LiCl, whereas the addition of NaCl or KCl did not cause any spectral changes, indicating the selective binding of LiCl to **1**. The pyrrolic N–H (H_a) signal was dramatically downfield shifted from 8.64 to 10.61 ($\Delta\delta$ = −1.97 ppm), indicating the formation of hydrogen bonding with Cl^-. The signals of the methylene bridge (H_d) and triazole C–H (H_b) were also downfield shifted from 4.71 and 6.68 to 5.22 and 7.00, respectively ($\Delta\delta$ = −0.51 and −0.32 ppm, respectively). Alternatively, the signals of the pyrrolic beta proton (H_c) were upfield shifted from 6.07–5.93 to 5.73–5.72 due to the structural changes of calix[4]pyrrole to a cone shape.

As **1** exhibited selective binding to LiCl rather than NaCl and KCl, various lithium salts, including LiF, LiCl, LiBr, LiI and $LiClO_4$, were added to **1** to examine the anion binding selectivity (Fig. S1, ESI†). As a result, relatively large ^{1}H NMR spectral changes were observed upon the addition of LiCl and LiBr, indicating that **1** can accommodate both LiCl and LiBr. Therefore, Cl^- and Li^+ were sequentially added to **1** in the form of tetrabutylammonium (TBA) and ClO_4^- salts, respectively, and the spectral changes of **1** were monitored to confirm whether they were induced by the binding of LiCl or not. When excess Cl^- was added to a solution of **1** in 10% CD_3OD/CD_2Cl_2, the ^{1}H NMR spectral change of **1** differed from the result of LiCl addition (Fig. S2b and d, ESI†). Because Cl^- can be tightly bound to calix[4]pyrrole, pyrrolic N–H protons were strongly shifted to 10.94 ppm ($\Delta\delta$ = −2.3 ppm). In the case of the pyrrolic beta protons, the peak appeared as a singlet at 5.67 ppm, indicating the transformation to the cone shaped geometry of the calix[4]pyrrole unit. Subsequently, excess Li^+ was added to the solution of **1** with excess Cl^-. As a result, the ^{1}H NMR spectrum of **1** with excess Cl^- was changed to that with LiCl (Fig. S2c and d, ESI†). Similarly, the sequential addition of Br^- and Li^+ in the form of tetrabutylammonium (TBA) and ClO_4^- salts, respectively, to **1**, resulted in the same ^{1}H NMR spectrum of **1** with LiBr(s) (Fig. S3, ESI†). These observations again indicated the selective ion-pair binding of **1** for LiCl and LiBr. The association constants of **1** for LiCl and LiBr binding were determined by ^{1}H NMR spectral titrations. From the spectral shift of the ^{1}H NMR signals upon successive addition of LiCl and LiBr, the association constants were estimated to be 60.5 and 19.5 M^{-1}, respectively, as calculated by commercial software HypNMR 2008 (Fig. S4 and S5, ESI†). Although the proton signals of the calix[4]pyrrole unit showed large shifts following addition of LiCl or LiBr, the chemical shifts of the protons in the triethylene glycol units (H_e and H_f) maintained their initial position while forming **1**·LiCl and **1**·LiBr complexes. Alternatively, the chemical shifts of H_e and H_f were relatively large following the addition of Li^+ in the form of ClO_4^- salt, indicating the binding of Li^+ to a triethylene glycol unit. From the ^{1}H NMR spectral titration of Li^+ to **1** in 10% CD_3OD/CD_2Cl_2, the association constant was estimated to be 4.4 M^{-1} (Fig. S6, ESI†). As the chemical shifts of H_e and H_f were not changed by the binding of LiCl or LiBr to **1**, we can expect that the binding mode of the ion pairs differs from that of Li^+ binding alone. The binding constants of halide ions such as Cl^- and Br^- were also obtained as 377 and 61 M^{-1}, respectively, through ^{1}H NMR spectral titration (Table S2, ESI†). The binding constants of the anions were greater than that of Li^+. Therefore, the binding of Li^+ to **1** was enhanced by the participation of halides through conformational changes of **1**.

To clarify the binding mode of ion pairs, single crystal X-ray crystallography of **1**·LiCl was performed. As shown in Fig. 2, **1** formed a 2 : 2 complex with LiCl. Cl^- was bound to calix[4]pyrrole units through multiple hydrogen bonds, producing a cone shaped geometry. The C–H proton in the triazole groups also stabilized Cl^- binding to the calix[4]pyrrole unit (the distance of C–H···Cl was 3.96 Å and 4.01 Å). Interestingly, the crystal structure exhibited binding of Li^+ to triazole nitrogen (the distance of Li···N was 2.0 Å). Furthermore, three water molecules were coordinated between **1** and LiCl. Within these three water molecules, one was in contact with Li^+, another was bound to the triethylene glycol strap (the O···H_2O distance was 2.4 Å) and the other was bound to Cl^- (the Cl···H distance was 2.39 Å). The distance between Li^+ and Cl^- in **1**·LiCl was 4.58 Å, which is much larger than the 2.02 Å in LiCl(s). Based on the single crystal structure, computational aided density functional theory (DFT) calculations with Beck's three-parameter hybrid

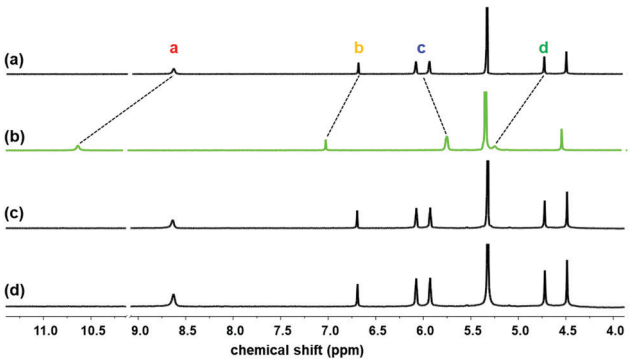

Fig. 1 Partial ^{1}H NMR spectra of (a) **1** (2 mM) and **1** with (b) excess LiCl(s), (c) excess NaCl(s), and (d) excess KCl(s) recorded in 10% CD_3OD/CD_2Cl_2.

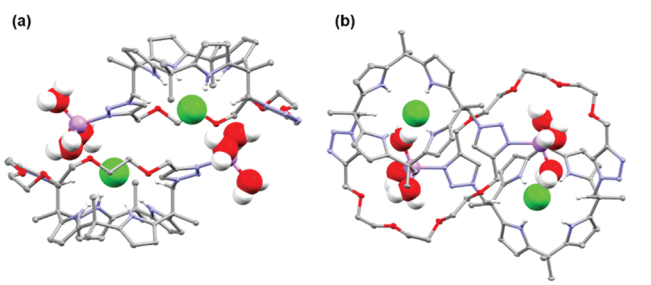

Fig. 2 (a) Side view and (b) top view of the crystal structure of the 2 : 2 : 6 complex (**1** : LiCl : H_2O). Minor hydrogen atoms and solvent are omitted for clarity (green: Cl, pink: Li, red: O, grey: C and blue: N).

exchange functional and the Lee–Yang–Parr correlation functional (B3LYP), employing the 6-31G(d) basis set in the gas phase were performed for three types of possible binding modes including contact-, separated-, and solvent bridged ion-pairs (Fig. S7, ESI†). The minimized binding energies have been estimated to be −911.06, −815.62, and −1166.70 kJ mol^{-1} for the three contact-, separated-, and solvent bridged ion-pair models, respectively.

These theoretical calculations also supported the formation of a water-separated dimeric complex corresponding to the single crystal structure. The result of 2-D NOESY experiments also supported the formation of a dimeric complex (Fig. S8–S10, ESI†). A cross peak between H_d and H_g appeared by the formation of a dimeric complex.

Some ion pair receptors have been explored for the liquid–liquid extraction of lithium salts such as $LiNO_2$ and $LiNO_3$. From a practical perspective, the extraction of halide salts would have great value. To confirm whether the extraction of LiCl is possible or not using **1** from an aqueous to an organic phase through liquid–liquid extraction, ^{1}H NMR spectral studies were conducted with 5.0 mM of **1** diluted in CD_2Cl_2.

LiCl solution in D_2O was added to the solution of **1** and stirred for 1 h. Subsequently, the ^{1}H NMR spectrum of the organic phase was recorded to observe whether spectral changes appeared. The ^{1}H NMR spectrum of **1** exhibited spectral shifts by formation of a **1**·LiCl complex, possibly indicating the successful extraction of LiCl from the aqueous phase (Fig. 3b). Several experiments were also performed using 25%, 50%, 80%, and 95% saturated LiCl solutions to determine the minimum amount of LiCl in the aqueous phase for liquid–liquid extraction (Fig. S11, ESI†). **1** succeeded in extracting LiCl with 80% or more saturated LiCl solution. Additionally, the ^{1}H NMR spectra rarely changed when the solution of **1** was exposed to NaCl(aq) and KCl(aq) (Fig. S12b and c, ESI†), indicating the high selectivity of **1** to lithium salt.

When LiCl(s) was added to the solution of **1** in CD_2Cl_2 and stirred for 1 h for solid–liquid extraction, the ^{1}H NMR spectrum was consistent with that of **1**·LiCl from liquid–liquid extraction (Fig. 3c). For the competition experiments, a mixture of alkali halide(s) containing LiCl(s), NaCl(s), and KCl(s) was added to a solution of **1**. As a result, **1** exhibited selective extraction of LiCl(s) (Fig. 3d). The ^{1}H NMR spectra obtained after solid–liquid extraction with NaCl(s) or KCl(s) (Fig. 3e and f, respectively) were identical with those of **1**. The extraction experiments with LiBr were also examined in a similar way to the LiCl extraction experiments.

All spectral changes exhibited the successful liquid–liquid and solid–liquid extraction of LiBr (Fig. S13, ESI†). Competition experiments using mixtures of LiBr(s), NaBr(s), and KBr(s) also resulted in the selective formation of host–guest complexes between **1** and LiBr (Fig. S13, ESI†).

For practical applications, the precipitation of lithium salt was attempted after extraction of LiCl by **1**. As Li_2CO_3 has relatively poor solubility in both organic solvents and water, CO_3^{2-} was added to the host–guest complexes between **1** and LiCl to obtain a Li_2CO_3 precipitate. For example, the organic phase was collected after the extraction of LiCl, and a small amount of deionized water was added to the solution. Then, CO_2(g) was bubbled through the solution to obtain a carbonate solution. As a result, the organic layer became turbid due to the formation of Li_2CO_3 (Fig. 4). Through modification of the Warder titration method which is known to be a way to calculate the amount of sodium carbonate in a NaOH solution, the amount of Li_2CO_3 precipitated by **1** was measured through acid–base titration using methyl orange as a pH indicator (Fig. S14 and S15, ESI†). Compared with deionized water, the volume of 0.05 M HCl needed more than deionized water. The formation of Li_2CO_3 was also confirmed by direct addition of K_2CO_3. After the liquid–liquid extraction of LiCl(aq) using 100 mg mL^{-1} of **1** diluted in CH_2Cl_2, the organic layer was separated from the aqueous layer. Upon addition of K_2CO_3, the organic layer containing the **1**·LiCl complex, became turbid (Fig. S16, ESI†). The extracted Li_2CO_3 was also confirmed by scanning electron microscopy energy dispersive X-ray spectroscopy (SEM/EDXS) mapping experiments (Fig. S17, ESI†).

In summary, we synthesized a triazole-bearing oligoether strapped calix[4]pyrrole **1** as a lithium selective ion pair receptor. Through ^{1}H NMR spectral studies, **1** demonstrated selective binding of both LiCl and LiBr in 10% MeOD/CD_2Cl_2. The binding mode between **1** and LiCl was confirmed by using

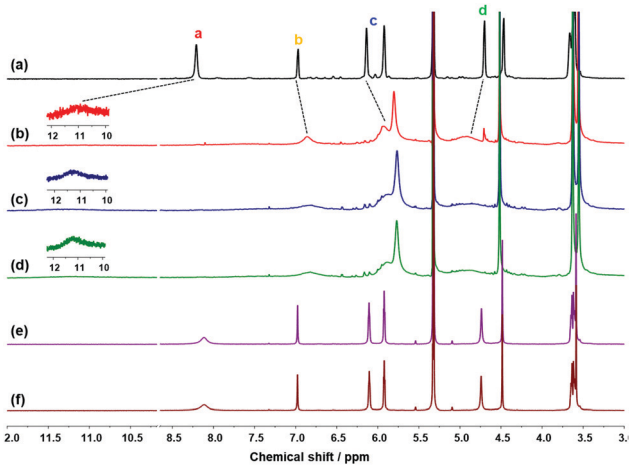

Fig. 3 ^{1}H NMR spectra of (a) **1** (5 mM) and **1** after extraction with (b) LiCl(aq), (c) LiCl(s), (d) a mixture of LiCl(s), NaCl(s) and KCl(s), (e) excess NaCl(s), and (f) excess KCl(s).

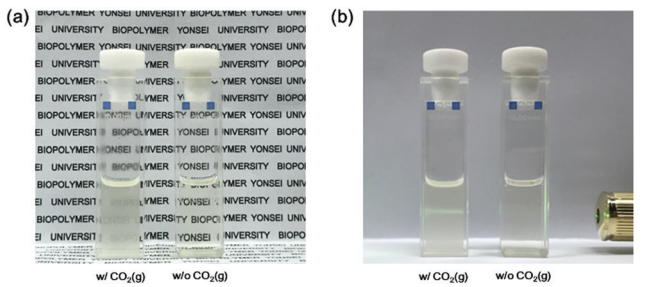

Fig. 4 (a) Turbidity and (b) the Tyndall effect of a solution containing the **1**·LiCl complex after CO_2(g) bubbling with deionized water.

single crystal X-ray crystallography, which was further supported by theoretical calculations. LiCl was captured by **1** through separated ion-pair binding assisted by three water molecules. Furthermore, we performed liquid–liquid extraction of LiCl and LiBr using **1** to bring the lithium salts into the organic phase. The ^{1}H NMR study indicated successful extraction of LiCl and LiBr into the organic phase through ion pair binding to **1**. Moreover, lithium salts extracted by **1** could be isolated in the form of Li_2CO_3. From a practical point of view, the precipitation of Li_2CO_3 using K_2CO_3 and $CO_2(g)$ could be very important.

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Conflicts of interest

There are no conflicts to declare.

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