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Desing and Synthesis of Selective Solvent Extractant for Lithium Halides

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Summary

Demand for lithium-ion batteries has increased in the direction of carbon neutrality. Methods for extracting and purifying lithium salts from natural sources have been widely developed. Recently, we found that a flexible ditopic receptor **1**, prepared from commercially available starting materials in a single step, can solubilize LiCl in high concentration in organic solvents. However, the selectivity of receptor **1** for Li/Mg is not sufficient. In this study, the solid-liquid extraction of lithium salt, especially lithium chloride, by ditopic receptors has been investigated. In addition, phosphorus is completely dependent on imports, and the recent strong demand for lithium ferro-phosphate (LFP) in lithium-ion batteries requires a recovery technology for both lithium and phosphorus from LFP. A ditopic receptor for lithium cation and dihydrogen phosphate anion is also being designed and prepared.

In this study, we prepared and elucidated the recognition properties of a tripodal receptor, which is a three-dimensional extended version of receptor **1**, to enable selective solvent extraction of lithium halides. Using trimethylolethane as a starting material, we prepared receptors **4** and **5** with aliphatic and aromatic ether linkers, respectively. Receptor **4** was not obtained as the final product, however, receptor **5** was successfully prepared in four steps. The synthesis of **6** and **7** with ester linkers was also achieved. The UV-visible absorption spectral titrations of receptors **5b** and **6a**, which had relatively high solubility in organic solvents, were examined for their ability to associate with anions. Receptor **5b** showed high association ability, while **6a** showed relatively low recognition ability due to the aliphatic urea NH groups. The flexible structure of receptor **6a** was found to be capable of solid-liquid extraction of LiCl in organic solvents such as chloroform.

Ditopic receptor **8** was also prepared with an ether linker as the cation recognition site and a leucine-aminopyridine linkage site as the anion recognition site, and NMR titration confirmed the strong recognition of the $H_2PO_4^-$. The solid-liquid extraction of LiH_2PO_4 with chloroform was also demonstrated.