Chasing lithium: direct lithium salt extraction and purification from mixtures using stimuli-responsive "smart" molecular extractants

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Motivation: The rapid development of the electrotechnical industry has contributed to a dramatic growth in demand for lithium, which is used primarily in Li-ion batteries. This element is crucial for shifting our society from burning fossil fuels to clean energy generated from renewable sources. Considering the strategic interest in this most valuable resource of the 21st century, identifying and developing the practical and most sustainable lithium supply and recycling strategy is crucial for a successful transition to a low-carbon economy. Lithium is extracted primarily from minerals and brines and, to a lesser extent, from spent Li-ion batteries. In these resources, lithium typically co-occurs with various metal salts (*e.g.*, sodium, potassium, magnesium, and calcium). The similarity between the associated salts (*e.g.*, NaCl vs. LiCl) renders selective extraction of lithium a challenging and resource-consuming task. In addition, alternative potentially competing metal cations, such as magnesium and calcium, featuring higher specific charge densities often make selective lithium binding even more challenging. However, the current methods have significant limitations, such as tremendous energy requirements or the need to use large amounts of water and toxic reactants, resulting in a massive environmental impact. Thus, developing sustainable lithium extraction and purification technologies is one of the key research directions. Studies toward using synthetic molecular receptors containing cation and anion binding sites in their structure is an appealing solution to achieve direct lithium extraction (DLE) from the mixtures. However, the current molecular extractants have some limitations, such as inefficient synthesis, poor lithium selectivity, and slow kinetics of lithium salt release due to the high stability of the formed complex. In other words, lithium extraction using these systems can take from hours to days. Consequently, these systems are not suitable for practical use.

The aim of the research: In this project, we will evaluate the feasibility of employing photoswitchable receptors as direct extractants and transporters of lithium salts (Li-salts) of industrial importance, such as lithium chloride (LiCl). In principle, these "smart" systems exhibit capability for directly extracting Li-salts from the mixtures of various competing solid salts and their aqueous solutions to organic solvents, from which Li-salt can be recovered in pure form. The proposed azobenzene-based electroneutral extractants are equipped with lithium-cation-selective binding groups and anion binding groups selected for particular anions such as chloride.

We expect that the native *trans*-form of the extractant will demonstrate a weak affinity for Li-salts due to the spatial separation of cation and anion binding domains. In contrast, the light-generated metastable cis-form of the extractant will show superior binding, extraction, and transport of Li-salt due to the proximity and advantageous arrangement of ion-binding domains, shielding the guest from the environment. The efficient bidirectional *trans*/*cis* isomerization of the robust azobenzene linker allows control of the complex's thermodynamic stability and the rate of catching and releasing Li-salt from the host binding cavity. All these features will enable efficient and energy-efficient management of the Li-salt binding and release process, allowing the development of the continuous extraction of Li-salt from the mixtures for the first time.

The project is divided into sections. Firstly, we will initiate the theoretical studies to predict the molecular properties of the proposed *trans*/*cis*-extractants and their putative complexes with various salts, such as chlorides of alkali metal cations. We aim to synthesize only the compounds predicted to display selectivity for lithium over competing cations. Then, for chosen systems, we will examine in detail their solution-binding properties and extraction efficiency with more time-consuming $^{1}H/^{7}Li$ NMR titration techniques and solid-liquid- (SLE) and liquid-liquid extraction (LLE) studies. The theoretical model will be tuned due the course of the project by comparison with the experimental data from the binding and extraction studies. Finally, selected hosts will be tested continuously as the first stimuli-responsive lithium salt extractants using a custom-made testing apparatus.

Expected impact of the research project: The results of this project are essential for developing novel efficient, sustainable technologies for extracting and purifying Li-salts. The proposed research covers the objectives of sustainable management and saving energy in agreement with the "*New circular economy action plan for a cleaner and more competitive Europe*" released in 2020 by the European Commission. Also that year, the European Commission classified lithium as a critical raw material. It announced actions to increase the security and sustainability of raw material supply in Europe to meet the expected 18- and 60-fold increase in lithium demand in 2030 and 2050, respectively.