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2-in-1: Octafluoroazobenzenes as ON-OFF photoswitches and anion-binding sites in macrocyclic lithium-halide receptors

Currently, the most common kind of rechargeable battery used for electronics, motorization, energy storage, and other areas relying on rechargeable accumulators is the lithium-ion battery. The development of Li-ion batteries was even honored with a Nobel Prize, awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino in 2019. Lithium salts are necessary for manufacturing any kind of Li-ion battery, making lithium mining and recycling critical for the energy transition from a fossil fuels-based economy to a green, electricity-based economy. Due to the low lithium abundance on Earth, the low concentration of lithium salts in natural sources, and the high chemical similarity of lithium to typically co-existing sodium salts, lithium extraction poses a serious challenge. At this moment, lithium mining is conducted *via* energy-exhausting and environmentally harmful processes.

For those reasons, there is a need for the development of new, greener lithium-extraction techniques. Ideally, to extract lithium salts, always consisting of a lithium cation and some anion, often chloride, one should use a compound with the ability to strongly bind both the cation and anion. Such compounds are called ion-pair receptors. However, lithium salt bound by a receptor is useless – it needs to be subsequently freed. This is not a problem when the receptor doesn't bind too strongly, but such a receptor won't extract lithium salts from typical natural sources. A possible solution to this puzzle is to design a so-called photoswitchable ion-pair receptor. It's a receptor whose affinity to ion-pairs can be modulated by irradiation with UV light or, preferably, visible light of the proper color. Molecules with the ability to change their geometry in response to light are called photoswitches. The most commonly used photoswitch is an azobenzene unit, also present in many commercial dyes. A very limited number of photoswitchable ion-pair receptors are known in the literature, with none of them being particularly lithium selective.

In this research project, an unprecedented approach to this problem is proposed, based on a novel hypothesis that electron-deficient azobenzenes, commonly used in modern chemistry as photoswitches, can simultaneously act as anion-binding domains, active only in the V-shaped state. This 2-in-1 philosophy will be accompanied by the implementation of a state-of-the-art lithium-selective binding domain, able to fold and unfold in response to the contraction or elongation of the azobenzene domain during photoswitching (see **Fig. 1**).

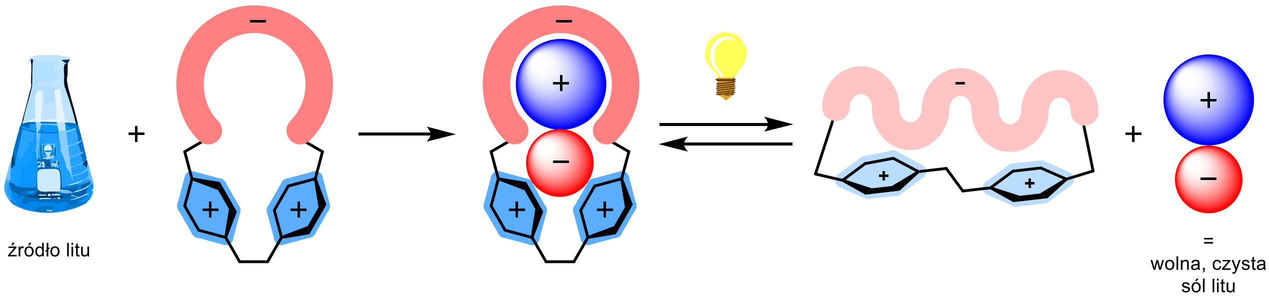

Fig. 1 Schematic representation of operation mode of proposed ion pair receptors. Anion-binding domains are marked in light blue, cation-binding domains are marked in pink, anions are marked in red, and cations are marked in bright blue.

This project, if successfully completed, would establish electron-poor azobenzenes as viable anion-binding sites in supramolecular chemistry, improving our knowledge of these important photoswitches and adding a new asset to the supramolecular chemistry toolbelt. The methodology of the synthesis of macrocyclic compounds with an azobenzene backbone will be advanced as well. Nonetheless, arguably the most important result of this project would be the development of photoresponsive lithium-selective ion-pair receptors with a novel operating mode, excellent lithium affinity and selectivity, as well as an extremely high ON/OFF binding strength ratio, paving the way to greener, more sustainable lithium production in the future.