"Development of novel light-controllable azobenzene switches as molecular receptors for selective sensing and transport of biologically relevant salts"

The pivotal role of ions in various fields of science, such as biology, catalysis, environmental protection or medicine, has created a demand for developing new synthetic molecular receptors capable of binding ions strongly and selectively.

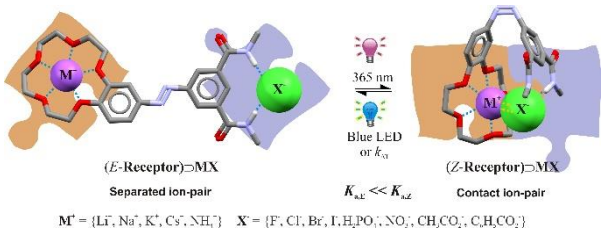
In spite of numerous studies, receptors of this type perform well only under laboratory conditions, when strong electrostatic interactions within the ion-pair are reduced by using a suitable soft and noncompeting counterion. In real-life situations, however, the counterion of the target salt is usually hard and strongly solvated, and hence strongly compete (and often win) with the receptor.

One way to counter this problem is to develop ditopic receptors that can simultaneously bind both the cation and the anion. However, the design of convergent ion-pair receptors is quite challenging since the ion binding sites have to be incorporate into a suitably preorganized scaffold that holds them in close proximity, but not so close that the sites interact with each other. Most salt receptors in the literature are ineffective since they bind ion-pair as spatially separated ions which implies that prior to salt binding the so-called "Columbic penalty" must be paid to enforce charge separation. To avoid this problem one can design the putative receptor that can bind the salt as an associated ion pair, in particular contact ion-pair. To date, there are only few examples in which this approach was successfully achieved.

lower stability **higher stability**

Apart from this, it is commonly recognized that change in the geometry of a given chemical entity may strongly affects its physicochemical properties. The intriguing possibility to control this process by using an external and non-invasive stimulus is for many reasons, highly desirable. Contrary to other external stimuli, light is especially attractive in this context since it possesses an electrically neutral character and ensures that the resulting transformation is rapid, strictly localized in space, and generally reversible.

In this research project I evaluate if light-triggered changes of the receptor conformation will allow for binding of the contact ion pair. In order to evaluate this assumption, I plan to synthetize and evaluate the photochemical and binding properties of series of new hybrid molecular receptors for ion-pairs.



These receptors utilize simple and well-known benzo-crown ethers and amide or urea groups to recognize cationic and anionic guest species respectively, while an azobenzene chromophore enables light-controllable switching of the receptor geometry. The obtained derivatives undergo fast and reversible light-induced *E*/*Z* isomerisation, which is accompanied by a large-amplitude structural changes between extended (*E*) and folded (*Z*) isomers. It is postulated here, that by bringing of the ion binding domains considerably closer together in the metastable *Z*-isomer, the phenomenon of binding of contact ion-pair could be accomplished.

The project is composed of several stages. The first stage comprises the synthesis of a series of hybrid receptors and the determination of their photochemical properties. Simultaneously, theoretical studies at sufficiently high level of theory will also be initiated with the aim of evaluating the binding properties of these azobenzene derivatives. Afterwards, the relatively fast liquid–solid extraction method will be employed for the solubilization of the library of *ca.* forty commercially available salts by both *E*- and *Z*-isomers of synthetized receptors. This allows for the identification of strong receptor/salt complexes which exact binding properties will be further evaluated by the more sophisticated, yet more time- and resources consuming methods (^{1}H NMR, UV-Vis, ITC titrations). At the last stage, the best receptors will be subjected to further investigations as innovative dynamic transporters of highly hydrophilic ion pairs, which ion-pair binding affinities can be activated and deactivated "on demand", thus providing the dynamic control over their transport through the membrane.

To date, there are no precedents to utilize this approach for a dynamic control of the binding properties of a putative ion-pair receptor. The results of my research might find broad applications in the processes of solubilization, extraction, detection, and membrane-transport of biologically relevant ion-pairs, separation and disposal of toxic and radioactive salts and also in the synthesis of new nanomaterials with desirable optical and electrochemical properties.