

Photoresponsive ditopic receptor for dynamic binding of ion pairs

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The majority of molecular receptors developed so far perform well only under laboratory conditions, when the strong electrostatic interactions within the ion-pair are greatly 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, hence strongly compete with the receptor.¹

One way to counter this problem is to develop ditopic receptors which can simultaneously bind cation and anion. However, most of the reported salt receptors are still not effective since they bind ion-pair as spatially separated ions which implies that prior to salt binding event the so-called "Coulombic energy penalty" must be paid to enforce charge separation. One strategy to circumvent this problem is to design the putative receptor that could bind salt as an associated, preferably contact ion pair. To date, there are only few examples in which this approach was successfully implemented.²

We envisioned that reversible switching between these two different binding modes should allow for construction of new type of receptor, in which one geometrical isomer can tightly bind close ion-pair while the second isomer cannot bind it so efficiently due to spatial separations of the ions (Fig. 1)

a) Separated vs contact ion-pair



b) Light-triggered E/Z isomerisation

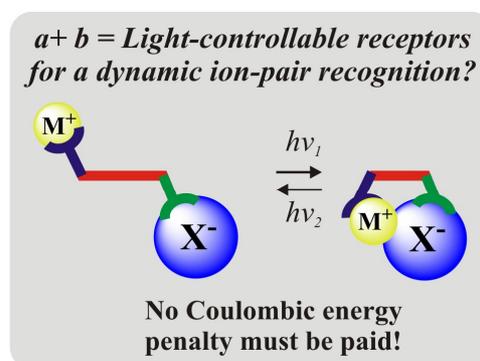
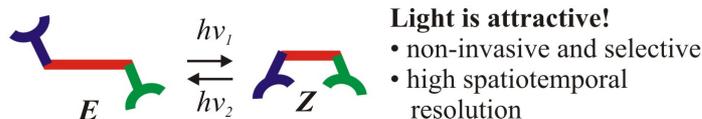


Figure 1

We selected azobenzene chromophore as photoswitch owing to its synthetic availability, robustness, and ability to undergo fast and reversible light-induced E/Z isomerization, which is accompanied by a large-amplitude structural changes between extended (E) and folded (Z) isomers. Structure analysis of photoswitchable ion receptors developed by us and others suggest that attachment of ion binding groups in meta positions relative to the N=N bond should facilitate binding of contact ion-pair by the metastable Z- over the E-isomer since no Coulombic energy penalty must be paid during binding.³

Here, we will present the design, synthesis, and binding properties of a series of new hybrid molecular ion-pair receptors based on azobenzene scaffold equipped with cation (benzo-crown ethers) and anion (amide or urea groups) binding groups.

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