A Photoswitchable Heteroditopic Ion Pair Receptor

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Supporting Information Placeholder

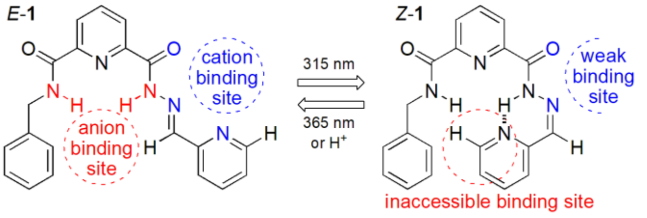
ABSTRACT: Designing light-switchable heteroditopic receptors is challenging because it necessitates simultaneous (de)activation of two separate binding sites. Herein, we present the first photoswitchable heteroditopic ion pair receptor in which both cation and anion binding sites are simultaneously and reversibly switched OFF and ON by a single photoswitch. Our receptor is simple, low molecular weight, and readily synthesized from commercially available precursors. Single-crystal X-ray structures and NMR spectroscopic titrations support ion pair binding to the receptor both in the solid state and in solution, with strong positive cooperativity between the cation and anion binding. The receptor can be completely switched OFF by UV light-triggered photoisomerization of an acylhydrazone C=N double bond and remains kinetically stable in the deactivated form due to an intramolecular hydrogen bond. Its re-activation could be achieved by light irradiation or, more effectively, by fast acid-catalyzed back-isomerization. Our simple photoswitchable ion pair receptor may serve as a blueprint for the design of new generations of switchable receptors, transporters, soft materials, and self-assembled systems, where incorporation of a functional heteroditopic ON/OFF photoswitch has been challenging up to now.

Irradiation by light is one of the most attractive ways to control the properties of a chemical system. It has been utilized in a number of photoresponsive host-guest systems,[1] supramolecular assemblies[2,3] and molecular devices,[4,5] with applications in catalysis,[6–8] materials chemistry[9,10] and cargo delivery,[11,12] just to name a few. Photoswitchable receptors[13,14] are an important class of the investigated systems because they facilitate the photo-controlled catch and release of chemical species. Due to the biological, environmental and industrial importance of charged species, receptors for cations,[15–17] anions,[18–24] and ion pairs[25–31] have been actively investigated. In particular, the ion pair receptors offer distinct advantages over single ion receptors in terms of affinity and selectivity due to cooperative effects.[32–34] However, while photo-switching functions have been frequently utilized in cation recognition,[13,17] studies on photoswitchable anion recognition are far less common[14,35–41] and photoswitchable ion pair receptors have not been reported yet. This may be due to the heteroditopic nature of ion pair receptors, which makes simultaneous (de)activation of two different binding sites challenging. Nevertheless, various binding/release strategies have been already successfully implemented in ion pair receptors, including ion metathesis, pH, and redox control.[42–44]

To address the challenge of photoswitching in ion pair receptors, we have considered a recently recognized, widely tunable, yet underexploited class of photoswitches – acylhydrazones.[45] Acylhydrazones are versatile dynamic systems that operate under light,[45] thermal,[46] pH[47,48] and even redox[49] control. In particular, acylhydrazones derived from pyridine 2-aldehyde possess potential anion and cation binding sites (i.e. hydrogen bond donors and electron lone pairs) that form an intramolecular hydrogen bond upon light-induced *E*/*Z* photoisomerisation of a C=N double bond.[47,50,51] Thus, in the *Z* form the two recognition elements effectively cancel out each other from interactions with other species. This feature of 2-pyridyl acylhydrazones has already been exploited in photoswitchable molecular shuttles,[52] enantioselective catalysts[7] and supramolecular assemblies.[46] This led us to the idea that incorporating a 2-pyridyl acylhydrazone switch into the ion pair receptor could enable the simultaneous photo-induced disruption of both cation and anion binding. Furthermore, acylhydrazones have often been used in cation and anion recognition,[47,50,53,54] although their light triggered catch/release functionality has rarely been exploited.[46]

Herein, we present the first example of a photoswitchable heteroditopic ion pair receptor, *E*-**1** (Scheme 1). *E*-**1** is composed of the 2-pyridyl acylhydrazone photoswitch and 2,6-pyridine bis- amide – a privileged anion recognition motif.[18–23,55] In contrast to the majority of ion pair receptors,[25,26] *E*-**1** is a simple, low molecular weight receptor and could be prepared in three simple steps from commercially available precursors (Scheme S1). Upon UV light irradiation *E*-**1** readily transforms into the *Z*-**1** isomer, which is remarkably stable and can be easily isolated by column chromatography.

Scheme 1. The design and working principle of *E*-1



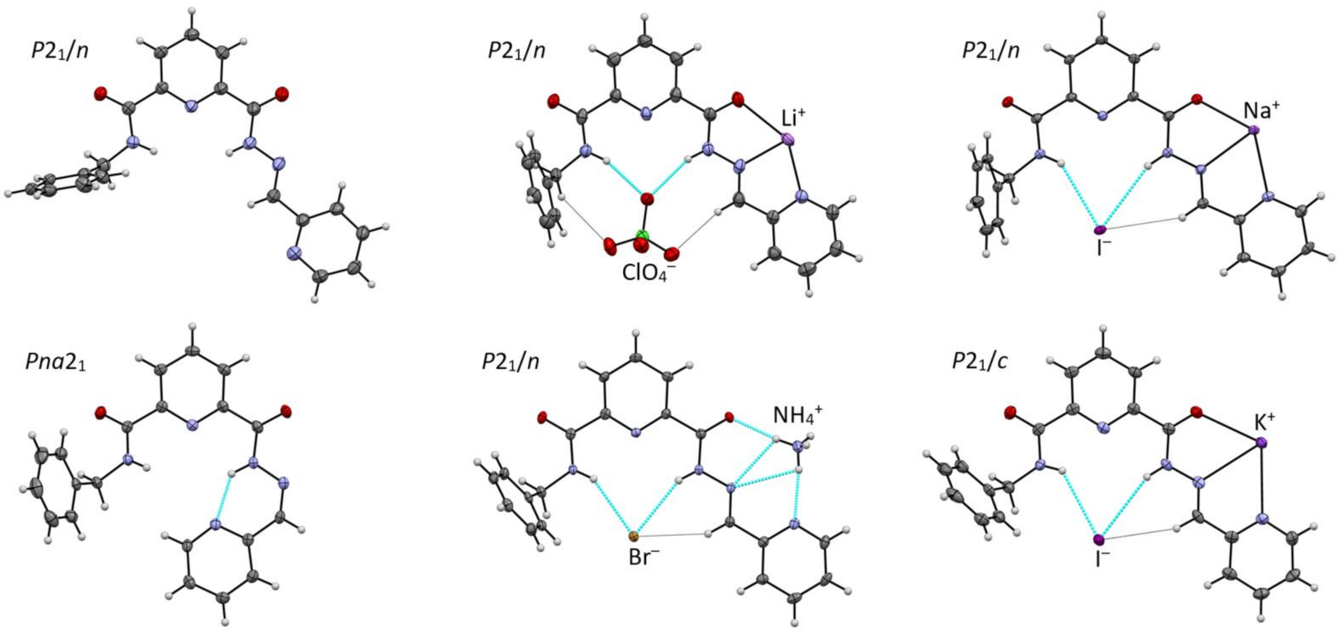


Figure 1. Single crystal X-ray structures of *E*-**1**, *Z*-**1**, and complexes of *E*-**1** with $LiClO_4$, NaI, KI, and NH_4Br.

The X-ray crystal structure of *E*-**1** shows a pre-organized anion binding site with two amide groups adopting a *syn*-*syn* conformation (Figure 1). On the other hand, the 2-pyridyl nitrogen atom points away from the cation binding site, possibly due to lone pairs repulsion. Five X-ray crystal structures of ion pair complexes of *E*-**1** were also obtained (Figure 1, see SI). All of them support the proposed general binding mode and show cations and anions in their respective binding sites depicted in Scheme 1. Anions are bound to *E*-**1** by two N–H···A$^-$ hydrogen bonds and exhibit also short C–H···A$^-$ contacts. On the other hand, the cation binding site shows two binding modes; *O*,*N*,*N* coordination of the 2-pyridyl acylhydrazone moiety to alkali metal cations[54] and, in a similar fashion, hydrogen bonding to the ammonium cation. The ability of *E*-**1** to bind anions and cations of various geometries is of general interest because of potential incorporation in a broader range of supramolecular systems. Finally, the X-ray structure of *Z*-**1** shows the receptor in the ‘closed’ form, in which the 2-pyridine side arm occupies the anion binding site.

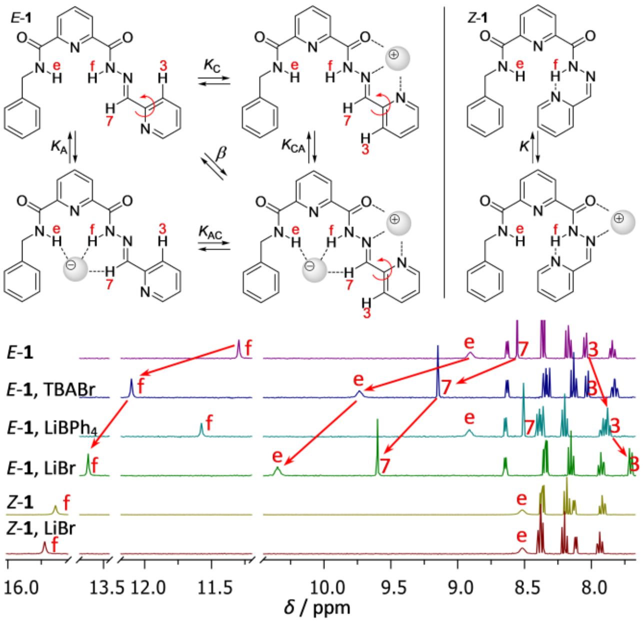


Figure 2. Equilibria included in the ion pair binding model used for fitting titration data and ^{1}H NMR spectra of *E*-**1** and *Z*-**1** in the absence and in the presence of various salts (2 mM, acetonitrile-d_3, 5 equiv. of each salt). The chemical shift changes suggest strong cooperative binding of LiBr to *E*-**1** and only very weak interaction with *Z*-**1** (see SI for details).

Initial evidence of ion pair binding to *E*-**1** in solution was obtained from ^{1}H NMR spectra in acetonitrile-d_3 (Figure 2). In the presence of TBABr (5 equiv.), significant downfield shifts were observed for both NH and imine CH protons ($\Delta\delta \approx +1$ ppm) due to anion binding, as could be anticipated from X-ray crystal structures. On the contrary, with $LiBPh_4$ these protons moved only slightly, while significant change was observed for the 2-pyridyl 3-H proton ($\Delta\delta \approx -0.2$ ppm). This was attributed to the rotation of the 2-pyridyl ring, as evident from the crystal structures and further supported by 2D ROESY measurements (Figures S14, S15). In the presence of LiBr, however, much more pronounced shifts were observed for all signals sensitive to both anion and cation binding ($\Delta\delta \leq 2.3$ ppm and $\Delta\delta \approx 0.3$ ppm, respectively), as compared to TBABr and $LiBPh_4$. This is highly indicative of LiBr ion pair binding to *E*-**1**. In striking contrast, the *Z*-**1** isomer exhibits only very small chemical shifts changes in the presence of LiBr ($\Delta\delta \leq 0.08$ ppm), suggesting very weak interactions with the salt.

To investigate the ion pair binding to *E*-**1** in more detail, we performed ^{1}H NMR spectroscopic titrations with model alkali metal halide salts (LiCl, LiBr, LiI, NaBr, NaI, KI), as permitted by their solubility in acetonitrile-d_3. Due to the irreducible complexity of ion pair binding equilibria,[22,23] all individual cation, anion, and ion pair binding equilibria as well as the competing ion pairing equilibria were included in the ion pair binding model (Figure 2, see also SI).[56]

Titrations of *E*-**1** with individual anions and cations (as TBA$^+$ and BPh_4^- salts, respectively) in acetonitrile-d_3 show excellent fits to the simple 1:1 binding model (Figure S20). The equilibrium constants obtained for anion binding follow the order of decreasing charge densities: Cl$^-$ > Br$^-$ > I (Table 1). Similarly, the observed trend of Li$^+$ > Na$^+$ > K$^+$ comes from stronger coordination of *E*-**1** to smaller cations with higher charge densities. This agrees also

Table 1. The equilibrium constants[a] (log*K* or log*β*) and cooperativity factors (*α*)[b] for anion, cation and ion pair binding to *E*-1 in acetonitrile-d_3.

	log*K* or log*β* (*α*)			
	Ph_4B^-	Cl^-	Br^-	I^-
TBA^+	-	2.80	1.96	< 1
Li^+	2.08	6.24 (23)	5.50 (29)	4.24 (15)
Na^+	1.54	/[c]	4.86 (26)	3.43 (8)
K^+	1.28	/[c]	/[c]	3.20 (9)

[a] average values from two experiments. Estimated errors ≤ 10 %. [b] $\alpha = \beta_{tot}/(K_A \times K_C)$. For iodide, K_A was set as 10 M^{-1}, even though experiments suggest it to be lower. Therefore, the values of cooperativity factors *α* for iodide salts are lower estimates only. [c] solubility issues did not permit titration studies.

with the solid state structures (Figure 1), where the bond lengths between cations and *E*-**1** follow the order $Li^+ < Na^+ < K^+$.

The titration experiments performed in the presence of both halide anions and alkali metal cations revealed strong and highly cooperative[32–34] binding of ion pairs to *E*-**1** (Table 1, Figure 3) The observed cooperativity is unusually high for halide salts binding to receptors in acetonitrile solution.[27,57–60] Larger cooperativity factors were obtained in less competitive, chlorinated solvent systems.[33,34] Given the rigid, fairly planar structure of *E*-**1**, the observed cooperativity is more likely due to electrostatic, rather than allosteric[16,61] interactions.

In contrast to *E*-**1**, the titration of *Z*-**1** with LiBr, LiI and NaI revealed extremely weak interactions, presumably with the cation, which could not be properly fit to any model due to a very small range of chemical shifts changes (Figures S94–99). These observations show that indeed the *E*-**1** and *Z*-**1** represent the binding and non-binding forms, respectively, in accord with the working principle proposed in Scheme 1.

UV-Vis spectra also indicated the ion pair interactions with *E*-**1** (Figure S105). The *E*-**1** and *Z*-**1** spectra in acetonitrile (1 mM) feature absorptions with maxima at 304 and 318 nm, respectively, in agreement with UV-Vis spectra for similar acylhydrazones.[45] In the presence of TBABr (20 equiv.), only a small blue shift from 304 to 300 nm was observed for the *E*-**1** due to anion binding, as supported by NMR spectroscopic titrations. In the presence of an excess of LiBr (20 equiv.), a fully bound *E*-**1**·LiBr is expected to dominate and, accordingly, the *E*-**1** absorption red shifted from 304 to 315 nm. No spectral changes were observed for *Z*-**1** in the presence of LiBr (20 equiv.), indicating negligible interactions (Figure S105).

Reversible switching between the ion pair binding (*E*-**1**) and non-binding (Z-**1**) forms was attempted both by irradiation with light of two different wavelengths and by light-triggered *E* to *Z* isomerization followed by acid catalyzed back-isomerization. An acetonitrile-d_3 solution of *E*-**1** (2 mM) containing an excess of LiBr (5 equiv.) provided photostationary states (PSS) of 58 % and 81 % *Z*-**1** after a few minutes of irradiation with 365 and 315 nm UV light, respectively (Figure S101). Once formed, the *Z*-**1** is very stable in this solution, as shown by the lack of any changes in the ^{1}H NMR spectra even after several days of standing in the dark (Figure S18).

Thus, thermal and ion-induced back-isomerization are negligible under these conditions.[38] Switching cycles obtained by alternating irradiation with the two wavelengths of UV light provided only modest changes in the PSS (Figure 4a), supporting nevertheless the possibility of light-induced switching in more carefully optimized systems.[45]

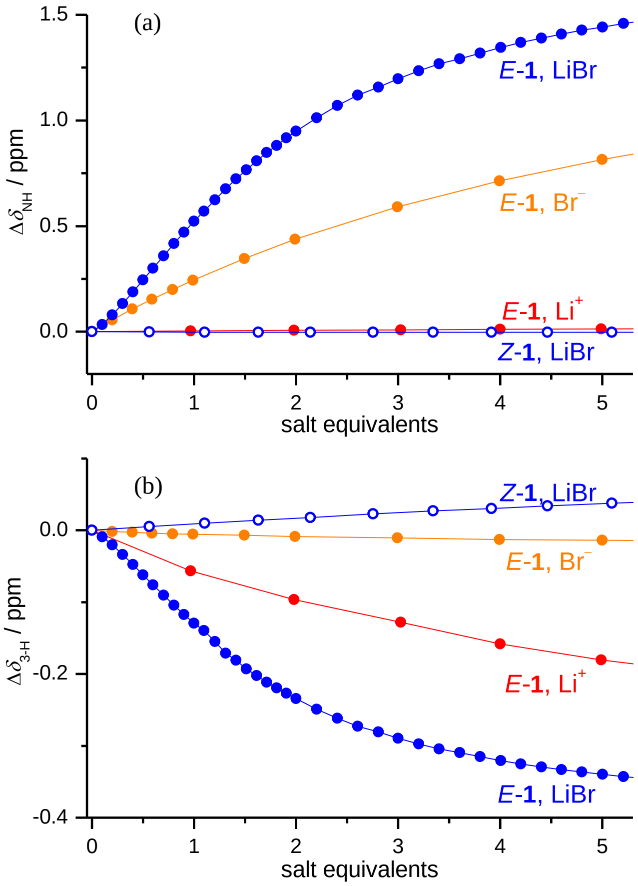


Figure 3. Chemical shift changes of (a) amide proton and (b) 3-H proton of the 2-pyridyl moiety during ^{1}H NMR spectroscopic titrations of *E*-**1** and *Z*-**1** (2 mM, acetonitrile-d_3) with LiBr, showing their sensitivity towards anion and cation binding, respectively. The data indicate cooperative binding of Li^+ and Br^- to *E*-**1** and very weak interactions with *Z*-**1**. Data for Br^- and Li^+ (as TBA^+ and Ph_4B^- salts, respectively) are shown for comparison.

The amplitude of switching cycles was greatly improved by alternating UV irradiation with an acid treatment followed by neutralization with a base[48,62] (Figure 4b). The back-isomerization of *Z*-**1** to *E*-**1** was nearly quantitative within a few minutes of triflic acid addition (1 equiv.). After neutralization with DIPEA, the binding of LiBr to *E*-**1** was restored (Scheme S21, Figure S103; DIPEA triflate is not appreciably bound to *E*-**1** in acetonitrile). This orthogonality of the external stimuli (i.e. photo and chemical) can be very useful in the design of functional supramolecular systems.[10,63–65] Nevertheless, using the orthogonal photo and chemical stimuli in flipping the configuration of hydrazone photoswitches is very

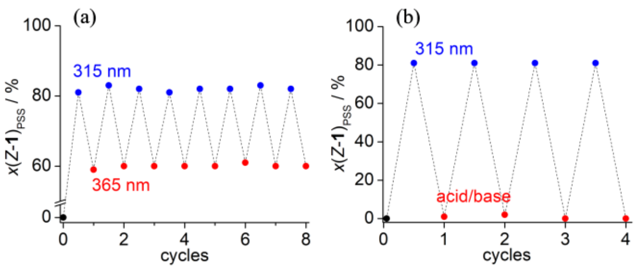


Figure 4. Switching between *E*-**1** and *Z*-**1** in acetonitrile-d_3 (2 mM) containing 5 equiv. of LiBr, using (a) different wavelengths of UV light; (b) UV irradiation and triflic acid/DIPEA addition (1 equiv.).

rare.[46,49,62] Moreover, such approach to the iterative catch and release of a guest molecule is, to the best of our knowledge, unprecedented.

In summary, this work presents the first ON/OFF photoswitchable heteroditopic ion pair receptor **1**, with a simple and modular design based on the acylhydrazone photoswitch. Despite its simple structure, *E*-**1** effectively binds various alkali metal salts in acetonitrile and shows strong cooperativity between the cation and anion binding. The receptor exhibits two very stable configurational isomers, *E*-**1** and *Z*-**1**, which represent binding and non-binding forms, respectively. The proposed modes of binding were unambiguously characterized by X-ray structures and NMR spectroscopic investigations. The *E*-**1** was found to bind anions, cations and ion pairs of different geometries. The photoswitching between the ON and OFF modes was successfully achieved through cycles of UV light irradiation with different wavelengths and, more effectively, by alternating UV light irradiation with acid/base treatment. Furthermore, the simple modular synthesis and versatile ion binding properties of *E*-**1** may allow its easy incorporation in a broad range of supramolecular systems. Potential applications may include ion transport,[22] soft materials,[66] or stimuli-responsive systems,[2,3] where the photo-induced catch and release of ions, or system (dis)assembly, are highly desirable. In such systems, the incorporation of a photoresponsive heteroditopic ON/OFF switch is still unprecedented.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxxxxx
General information, synthetic procedures, spectroscopic characterization, titration data, photoisomerization details (PDF)
X-ray structure of *E*-**1** (CIF)
X-ray structure of *E*-**1**·$LiClO_4$ (CIF)
X-ray structure of *E*-**1**·NaI (CIF)
X-ray structure of *E*-**1**·KI (CIF)
X-ray structure of *E*-**1**·NH_4Br (CIF)
X-ray structure of *E*-**1**·NH_4I (CIF)
X-ray structure of *Z*-**1** (CIF)

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Notes

The authors declare no competing financial interests.

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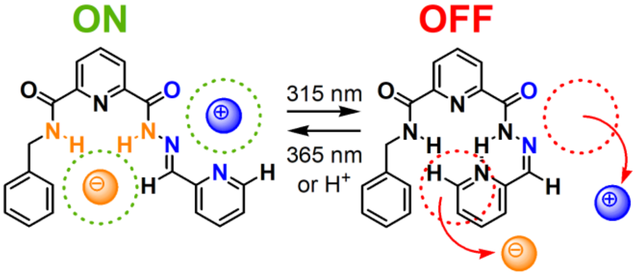
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