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## Review Article

# Anion recognition by simple chromogenic and chromo-fluorogenic salicylidene Schiff base or reduced-Schiff base receptors

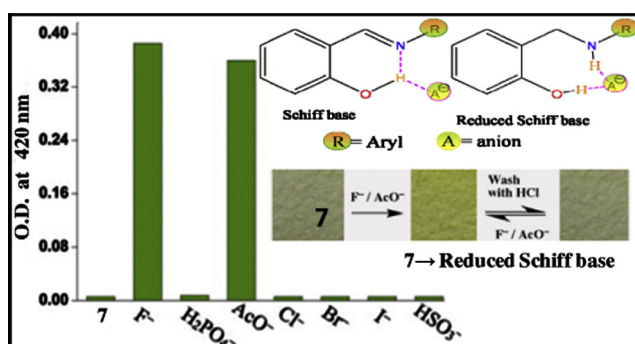
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## HIGHLIGHTS

- Structurally simple Schiff bases or reduced Schiff bases beneficial for selective anion recognition.
- Receptor and anions weak interaction studied by simple colorimetry and spectroscopy.
- Cheaper and user handling anion sensing test kits for useful practical applications.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This review contains extensive application of anion sensing ability of salicylidene type Schiff bases and their reduced forms having various substituents with respect to phenolic –OH group. Some of these molecular systems behave as receptor for recognition or sensing of various anions in organic or aqueous–organic binary solvent mixture as well as in the solid supported test kits. Development of Schiff base or reduced Schiff base receptors for anion recognition event is commonly based on the theory of hydrogen bonding interaction or deprotonation of phenolic –OH group. The process of charge transfer (CT) or inhibition of excited proton transfer (ESIPT) or followed by photo-induced electron transfer (PET) lead to naked-eye color change, UV–vis spectral change, chemical shift in the NMR spectra and fluorescence spectral modifications. In this review we have tried to discuss about the anion sensing properties of Schiff base or reduced Schiff base receptors.

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## Introduction

Design and synthesis of specific sensor for the recognition and sensing of anions is one of the most demanding areas of current chemical research because of their significant contribution in the field of chemical, biological, industrial, agricultural and environmental sciences [1–8]. Presently, designing of molecular sensors that can selectively recognize anions have great significance in supramolecular chemistry [9–12]. Over the past few years, a great deal of efforts have been dedicated for the development of fluorescent chemosensors for the detection of different anions such as  $F^-$ ,  $Cl^-$ ,  $I^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ ,  $HSO_3^-$ ,  $HCO_3^-$ ,  $ClO_4^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $HSO_4^-$  and  $SO_4^{2-}$  as fluorometric detection is cost-effective and highly sensitive. Regarding the development of fluorescent chemosensor quenching of fluorescence by interaction with anions is a rather commonly used technique. But, UV–vis absorption spectroscopy and colorimetric naked-eye detection techniques have gained comparatively faster attention than other techniques due to their simplicity, high sensitivity and cost effectiveness [12–15].

Currently, many excellent chemosensors have been reported for recognition and sensing of anions with high selectivity and sensitivity. But, there are disadvantages due to complicated structure of those chemosensors, required hard synthetic routes or troublesome purification process and poor yields. On the other hand, easy to synthesize with good yield are the most interesting and significant features of Schiff bases. Mainly, the Schiff bases derived from salicylaldehyde, i.e. salicylidene Schiff bases exist in a tautomerization equilibrium in solution due to the presence of  $-O-H \cdots N=C-$  (Scheme S1) type of hydrogen bonding network [1,16–21]. Therefore, action of base ( $OH^-$ ) or strongly basic anions (such as  $F^-$ ,  $AcO^-$  and  $Cl^-$ ) can easily deprotonate the  $-OH$  proton or promote the formation of keto-tautomer or inhibit the excited state proton transfer (ESIPT) phenomenon [2,22–25] and thereby modify the spectral characteristics and hence acts as an efficient sensor. Importantly, the acidity of the  $-OH$  proton also plays the key role for this H-bonding/acid–base type reaction. The acidity of  $-OH$  proton usually depends on the effect of substitution in the benzene ring, especially, with respect to the  $-OH$  group, in that case most electron withdrawing substituents (such as  $-NO_2$  and  $-Cl$ ) get preference. It is obvious that structurally reduced Schiff base loses the tautomerization equilibrium (as present in the Schiff base), but gain an extra function ( $-NH-$  proton, Scheme S2) which can help to form hydrogen bonded complex with anions, i.e. initially reduced Schiff base forms H-bonding complex with anions (with low conc.) and then produces a deprotonated species (at high conc. of anions) responsible for photophysical changes. The beneficial side of reduced Schiff bases is that these bases deserve to resist hydrolysis in water, but Schiff bases cannot.

In this review, we have primarily emphasized two types of anion sensing Schiff bases and reduced Schiff bases chemosensors: (1) Chromogenic anion receptor, (2) Chromo-fluorogenic anion receptor. Chromogenic anion receptors selectively recognize various anions and the phenomena are well rationalized on the basis of their naked-eye color change, UV–vis spectral change and chemical shift in the  $^1H$  NMR spectra. On the other hand, chromo-fluorogenic anion receptors selectively detect various anions by means of naked-eye color change, UV–vis and  $^1H$  NMR spectral shift as well as fluorescence spectral change. The color change or spectral modification is due to the formation of

hydrogen bonded complex (host–guest complex) between the receptor and the anion or may be due to the formation of deprotonated species. Host–guest interactions have been investigated by means of various spectral measurements and also with the assistance of simple theoretical model calculations. The summary of this review is compiled in Tables 1 and 2.

## Types of anion receptors

### Chromogenic anion receptors

There are various kinds of uniquely designed molecules which were reported to be as selective chromogenic anion receptors. Butcher et al. reported a simple but interesting Schiff base receptor **1** that exclusively exists in the solid state as keto–amine tautomeric form instead of phenol–imine tautomer due to the presence of highly acidic phenolic  $-OH$  proton and therefore enhances hydrogen bonding capability in presence of anions [26]. The receptor **1** shows yellow color in acetonitrile solvent and a broad absorption band was observed at 342 nm. After addition of considerable amount of  $F^-$ ,  $AcO^-$  and  $H_2PO_4^-$  anion (used their tetrabutylammonium ( $n-Bu_4N^+$ ) salts) in acetonitrile medium the naked-eye color of the solution turns to deep yellow from light yellow and a new absorption peak at 450 nm appears in the expense of decreasing the initial peak at 342 nm. Under the same experimental circumstances, addition of large amount  $Cl^-$ ,  $Br^-$ ,  $ClO_4^-$  and  $HSO_4^-$  anions results in neither naked-eye color change nor significant UV–vis spectral changes. The naked-eye color and UV–vis spectral change are attributed to the formation of strong hydrogen bonding complex between the receptor **1** and the anions with 1:1 stoichiometry. The selectivity and sensitivity of the receptor clearly depends on the basicity and shape of the anions and definitely on the acidity of hydroxyl group which depends on the nature of the substituents in the benzene ring with respect to the  $-OH$  group, i.e. more electron withdrawing substituents makes it more acidic. The selectivity of the receptor **1** towards Y-shaped  $AcO^-$  anion with strong doubly H-bonding capability has been further proved by using 10% water–acetonitrile solution of **1**, where only acetate anion is capable to change detectable naked-eye color as well as UV–vis spectral change, but there are hardly any changes that have been observed in case of fluoride and dihydrogenphosphate anions. Furthermore, the naked-eye color/UV–vis spectral change is reversible with respect to the addition of protic solvents, such as water and methanol. Because anions can exit in the highly solvated form in those solvents, which support the concept of host–guest H-bonding interactions.

Another simple symmetrical azine Schiff base receptor **2** exhibits strong and broad absorption bands at 288 nm and 345 nm, respectively [12] in aqueous–acetonitrile ( $CH_3CN:H_2O$ :  $DMSO = 94:4:1$ ) solvent. These bands are due to the transition between the localized  $\pi$ -orbitals on the azomethine group ( $-C=N-$ ) and due to the existence of charge transfer processes within the whole molecule. Upon addition of increasing amount of  $F^-/AcO^-$  ion to the receptor **2** in aqueous acetonitrile solvent, peaks at 288 nm and 345 nm gradually decrease their initial intensity and new absorption peaks gradually appear at 397 nm and 455 nm. The appearance of a distinct isosbestic point at 365 nm during the titration process indicates host–guest complexation equilibrium. The titration results were found to be well fitted with

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