Journal of Fluorine Chemistry 132 (2011) 536–540

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Naked-eye detection of F^- and AcO^- ions by Schiff base receptor

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ARTICLE INFO

Article history:
Received 28 April 2011
Received in revised form 20 May 2011
Accepted 26 May 2011
Available online 21 June 2011

Keywords:
Colorimetric sensing
Anion detection
Schiff-base
Hydrogen bonding
Density functional theory calculation

ABSTRACT

A Schiff base **2**, composed with *o*-phenylenediamine and 5-nitro-salicylaldehyde have been synthesized as an anion receptor. It consists with conjugated imine, phenolic –OH and electron withdrawing substituent nitro ($-NO_2$) group. Receptor **2** can recognize selectively biologically important F^- and AcO^- ions. The recognition properties have been investigated by naked-eye color change (colorless to yellow), followed by UV–vis spectral changes. Predicted stoichiometries of the complexes between receptor **2** and anions based on density functional theory (DFT) level calculations, corroborates well with experimental findings.

1. Introduction

For decades, Schiff bases were prepared mainly for complex formation with several metal ions [1,2], for their potential applications in catalysis [3], asymmetric synthesis [4], epoxidation [5], electrochemistry [6], magnetochemistry [7], molecular separation and biomedical applications [8]. On the other hand, Schiff bases as anion receptors are almost unexplored because interaction between metal and Schiff base are in general stronger than the hydrogen bond interactions between anion and Schiff base. Recently, only few examples are in the literature, where Schiff bases can also be used as anions receptor [9–12]. The reason behind utilizing Schiff bases includes (a) Schiff bases are easily obtained through one-step procedure *via* condensation of aldehydes with amines and (b) in particular, Schiff bases derived from salicylaldehyde derivatives having 2-hydroxy group are of interest mainly due to the existence of O–H···N and O···H–N type hydrogen bonds and tautomerization exist between phenol-imine and keto-amine forms. In contrast, many excellent chemosensors for anion detection have been reported. However, they need very complicated synthetic routes or troublesome purification procedures [13,14].

The recognition and sensing of anions by proper design of anion receptors is currently an expanding research area within the field of supramolecular chemistry [15–17]. Various kind of anions such as F^-, Cl^-, I^-, PO_4^{3-}, CH_3COO^-, etc. play a major role both in environmental and biological systems [18–20]. Among the above anions, fluoride ion received the most attention from chemists because of its unique properties. It is well known that a small quantity of fluoride ion is present in biological fluids, tissues and especially in bone and tooth. However, excess fluoride anions cause several serious diseases such as fluorosis, thyroid activity depression, bone disorders and immune system disruption [21,22]. Because of these significant importances, detection of anions with the help of easily synthesized receptor and minimal instrumental assistance is desirable towards practical applications.

Here, we report a Schiff-base receptor **2**, obtained by condensation of 5-nitro-salicylaldehyde with *o*-phenylenedianine, can recognize biologically important F^- and AcO^- anions exclusively, by visual observation without need of any spectroscopic instruments. Furthermore, the density functional theory (DFT) level calculations for the determination of stoichiometries of the complexes between receptor **2** and anions corroborates well with experimental results.

2. Results and discussion

Schiff base **1** (reference compound) was synthesized according to the literature procedure by mixing salicylaldehyde and *o*-phenylenediamine in methanol (Scheme 1) [23]. Schiff base **2** has been synthesized according to the literature method by heating 5-nitro salicylaldehyde and *o*-phenylenediamine in methanol

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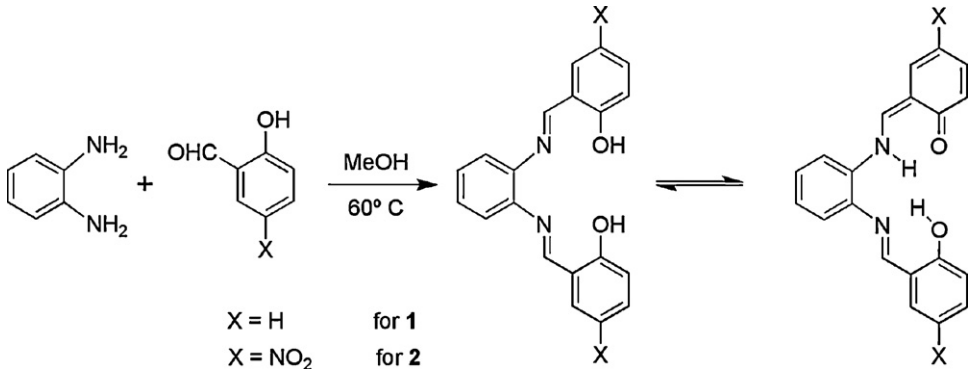
doi:10.1016/j.jfluchem.2011.05.025



Scheme 1. Syntheses of reference compound **1** and receptor **2**.

(Scheme 1) [24–26]. We have chosen nitro substituted Schiff-base receptor **2** mainly for two reasons: (a) the presence of *para* substituted $-NO_2$ group, having electron withdrawing effect is expected to enhance the acidity of the phenolic –OH and as a consequence, the hydrogen donor properties of the receptor **2** is also increase. (b) The UV–vis absorption properties of the chromogenic nitrophenyl moiety may be altered by receptor–anions interaction, thus providing colorimetric and spectral sensing recognition event [27,28]. Due to poor solubility of receptor **2** in CH_3CN, we used a mixture of DMSO and CH_3CN solvent (5:95, v/v ratio) for spectroscopic titration.

2.1. Visual sensing of anions

Visual color change of receptor **2** (1.0×10^{-5} M) was investigated in mixed solvent (CH_3CN and DMSO 95:5, v/v). Upon addition of F^- and CH_3COO^- ion to the solution of **2**, a detectable naked-eye color change was observed from colorless to intense yellow color (Fig. 1). Other ions such as Cl^-, Br^-, I^- and HSO_3^- did not exhibit any detectable color change. Under similar experimental condition, $H_2PO_4^-$ ion did not exhibit considerable color change, but at higher concentration of $H_2PO_4^-$ ion a faint yellow color was observed by naked-eye (Fig. 1).

Schiff-bases having 2-hydroxy group are generally undergoes phenol-imine and keto-amine tautomerization equilibrium. The keto-amine tautomerism in receptor **2** is facilitated by the electron withdrawing nitro ($-NO_2$) group, situated at the *para* position with respect to the phenolic –OH group, resulting in an increase in acidity of the phenolic –OH group and thereby enhance the hydrogen bonding interaction with the anions, as a result the increasing electron density on the "O" atom can resonate with $-NO_2$ group through the conjugated benzene ring (Scheme 2), resulting appearance of the yellow color [10]. It is noteworthy that the yellow color was disappeared and the original colorless solution came back on addition of protic solvent such as H_2O or CH_3OH, since the anions are no more bound with the receptor **2**, as they are highly solvated with the protic solvent.

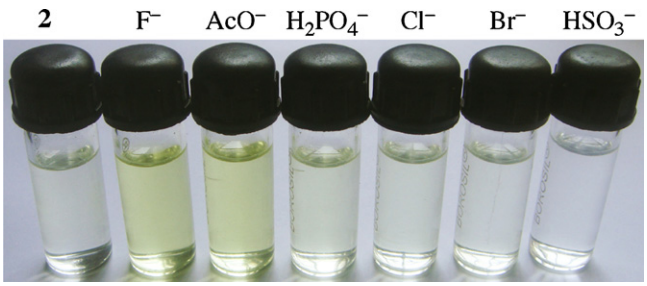


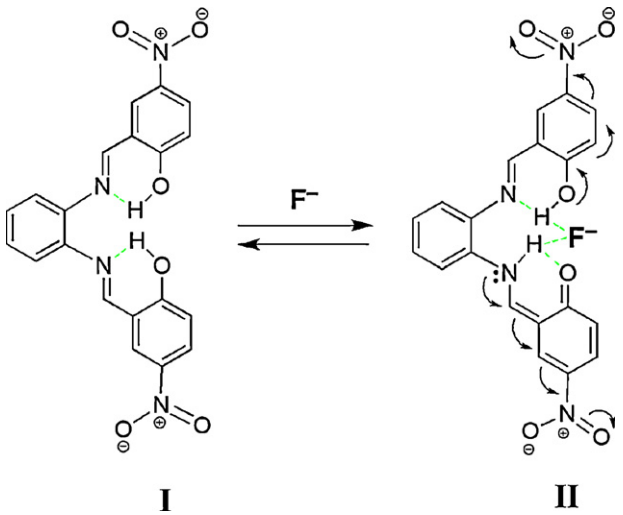
Fig. 1. Naked-eye color changes of receptor **2** (1.0×10^{-5} M) after addition of 2 equivalent of various anions in DMSO and CH_3CN solvent mixture (5:95, v/v).

2.2. UV–vis spectroscopic titration spectra

The anion recognition properties of receptor **2** have been investigated by monitoring UV–vis spectral change upon addition of different anions in a mixed solvent (CH_3CN and DMSO 95:5, v/v). Receptor **2** exhibited a strong and broad absorption band from 298 to 329 nm, peaked at 312 nm (Fig. 2). Fig. 2 shows the absorption spectral changes of **2** (1.0×10^{-5} M in CH_3CN and DMSO) in presence of F^- ion. Upon adding increasing amount of F^- ion to receptor **2** in CH_3CN solution, the peak at 312 nm gradually decreased its intensity and new absorption peaks at 360 nm and 422 nm gradually appeared. A distinct isosbestic point at 336 nm was observed during the titration process between the receptor **2** and F^- ion, which clearly indicated the formation of complex between **2** and F^- ion. During this titration the initial colorless solution gradually changed to yellow color. Similar type of UV–vis spectral changes were observed upon addition of acetate (AcO^-) ion into the solution of **2** (Fig. 3).

In contrast, under the similar experimental condition, $H_2PO_4^-$ ion exhibits only a tiny spectral change of **2**, which is difficult to detect by naked-eye. On addition of other anions such as Cl^-, Br^-, I^-, and HSO_3^- ions did not show any notable spectral or color change, indicating no interaction or complexation of these anions with receptor **2**. As shown in Fig. 4, compound **2** can selectively detect fluoride and acetate ion compared to the rest of the anions tested.

The selectivity and sensitivity of receptor **2** towards the F^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^-, I^-, and HSO_3^- ions can be rationalized on



Scheme 2. The plausible mechanism for keto-amine tautomerization and cause of color change upon complexation between **2** and anions.