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Chemosensor for fluoride ion based on chromone

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ABSTRACT

A novel visual chemosensor; receptor R, with high selectivity for fluoride ion based on chromone has been synthesized by simple condensation reaction between 3-formylchromone and 2,4-dinitrophenylhydrazine hydrochloride. The receptor R shows a dramatic color change from yellow to intense red upon the addition of fluoride ion with a large red shift of 118 nm in acetonitrile. No significant color change was observed upon the addition of other anions such as Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$ and AcO^-. Job's plot and Benesi–Hildebrand equation indicate that R associates with F^- in a 1:1 stoichiometry. Investigation of ^{1}H NMR spectrum titration indicates that creates a hydrogen bonding interaction between F^- and R. The receptor R proved to be an efficient naked eye detector for fluoride ion.

1. Introduction

Fluorine has unique biological and chemical properties, particularly because of its strong electro-negativity and small size. Low concentrations of fluoride have been considered beneficial to prevent dental carries. But researchers are now debating on the health benefits of fluoride even at low concentrations. It has long been known that chronic intake of fluoride even though below 1 mg/L can lead to severe dental and skeletal fluorosis. It not only affects teeth and skeleton, but its accumulation over a period can also lead to loss of mobility, lowering of IQ of children, change in the DNA structure and interference with liver and kidney functioning [1–3]. With the development of the industries, particularly food and food products and cosmetic goods of fluorine products, the contamination of fluorine becomes more serious. For these reasons, selective detection of fluoride ion assumes importance.

Anion recognition is an important and interesting area in supramolecular chemistry due to its vital role in a wide range of environmental, clinical, chemical, biological and industrial applications, and significant attention to the design of synthetic host for anion binding have become an essential area of research in chemistry [4–7]. In particular, synthesis of colorimetric anion sensors are of great importance because visual detection can propose qualitative and quantitative information even at low levels and widely used due to its low cost or no requirement of a specific equipment [8,9]. Chemosensors are created according to the receptor chromophore general binomial, which involves the binding of a specific anion substrate with receptor sites and a chromophore answerable for transforming the receptor–anion complex involvement into an optical signal. When anions interact with the sensor through electrostatic, hydrogen bonding, coordination to a metal center, hydrophobic interaction, or a combination of any two or more of these interactions, the sensor can yield binding information either by its altered absorption spectra, fluorescence or both behaviors [10–14]. This color variation can be related to either structural or conformational changes in the receptor structure when a complex is formed or to the formation of a charge transfer complex [5,7,15]. These schemes are mostly based on N–H proton transfer from the donor entity to anion, which induce π-electron delocalization, or N–H deprotonation [6,16]. Significant efforts have been made to develop hydrogen-bonding receptors containing imine [9,17], amine [18], phenol [19,20], urea [21,22], thiourea [23,24], imidazole ion [25] and pyrrole [26,27]. In the present study, design and synthesis of chemosensors based on chromone with Schiff base (–C=N–) as the bridge was attempted [6,28].

In search of a selective fluoride ion chemosensor, chromone based receptor R was synthesized by the condensation of 3-formyl chromone and 2,4-dinitrophenylhydrazine which is an organic colorimetric chemosensor. The sensing of the biologically important fluoride anion is attained in acetonitrile (CH_3CN) solution (Scheme 1). The result shows that fluoride ion could be detected by naked eyes without interference from other anions based on N–H

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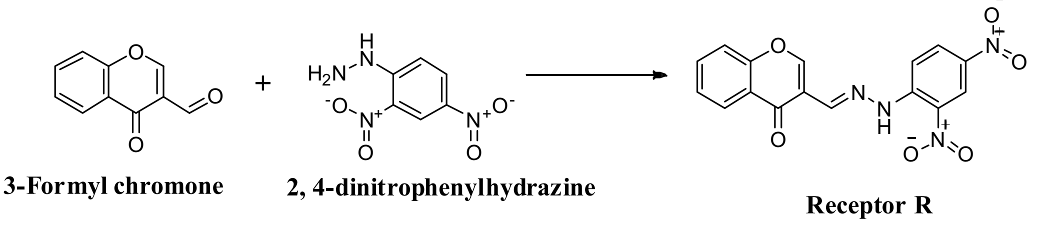

Scheme 1. Synthesis of receptor R.

proton transfer. The details of anion binding characteristics of the receptor R [((E)-3-((2-(2,4-dinitrophenyl)hydrazono) methyl)-4H-chromen-4-one)] have been investigated by UV–vis, fluorescence and ^{1}H NMR titrations. This receptor R shows high selectivity toward fluoride anions in both absorption and fluorescence modes.

2. Materials and methods

2.1. Chemicals and instruments

3-Formylchromone, 2,4-dinitrophenylhydrazine hydrochloride and all anions in the form of tetrabutylammonium salts were purchased from Sigma Aldrich, Mumbai, India and used without any further purification. All solvents used in the spectroscopic studies are spectroscopic grade and other reagents used were of analytical grade. All UV–vis spectra were recorded using Perkin Elmer Lambda 35; Luminescence spectra were performed on AV-500-Bruker 500 MHz high resolution multinuclear FT-NMR spectrometer-Germany.

2.2. Synthesis

3-Formylchromone (174 mg, 1 mmol) and 2,4-dinitrophenylhydrazine hydrochloride (DNP) (198 mg, 1 mmol) were added in ethanol (40 mL) (Scheme 1). The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the obtained yellow precipitate was filtered and washed several times with cold ethanol to yield the pure receptor R (280 mg, 79%).

δ_H (500 MHz; DMSO-d$_6$; Me$_4$Si): 7.55 (t, 1H, J = 2.5 Hz), 7.75 (d, 1H, J = 1.05 Hz), 7.90 (t, 1H, J = 2.5 Hz), 8.19–8.20 (m, 2H), 8.48–8.58 (m, 1H), 8.81–8.87 (m, 2H), 9.06 (s, 1H), 11.83 (s, 1H) (Figs. S1–S3). ^{13}C NMR was not recorded due to poor solubility of receptor R.

LCMS (ESI-APCI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{10}N_4O_6H$, 355.2, Found: 355.4 (Fig. S4).

Melting point: 258–260 °C.

IR (KBr, cm^{-1}): 3432, 3083, 1648, 1611, 1580, 1516, 1424, 1323, 1132, 1089, 767 (Fig, S5)

Anal. Calcd. for $C_{16}H_{10}N_4O_6$: C, 54.24; H, 2.85; N, 15.81. Found C, 54.18; H, 2.82; N, 15.76.

2.3. Spectroscopic procedures

Stock solution of receptor R (1.0×10^{-3} M in acetonitrile) was prepared and kept at room temperature. Then the stock solution was diluted with acetonitrile to a final concentration of 1.0×10^{-5} M for spectral analysis. All anion stock solutions were prepared by dissolving corresponding tetrabutylammonium salts into acetonitrile. Each time 2.5 mL of R solution was filled in a quartz cell of 1 cm optical path length, and different stock solutions of anions were added into the quartz cell gradually using a pipette. ^{1}H NMR titration experiments were carried out in the DMSO-d$_6$ solution. The receptor R prepared as 1×10^{-5} M solution was titrated by the shoot up amount of fluoride anion.

3. Results and discussion

The binding properties of fluoride and other anions with receptor R was investigated by UV–visible, fluorescence and ^{1}H NMR spectroscopy and density functional theory (DFT) studies.

3.1. Visual sensing of fluoride anion

Visual inspection of solutions of receptor R (1.0×10^{-5} M) in acetonitrile before and after addition of tetrabutylammonium fluoride showed dramatic changes in color from yellow to red (Fig. 1). The change could be detected by the naked eye. The color intensity gradually increased corresponding to the increase in the F^- concentration. The addition of Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$ and AcO^- did not show any significant color changes.

3.2. UV–visible spectral response of receptor R

The interactions between receptor R and anions were investigated through spectrophotometric titration with adding a standard solution of tetrabutylammonium salts of fluoride and other anions in acetonitrile by UV–vis spectroscopy. The maximum absorption of receptor R was at 380 nm and the molar absorption coefficient log ε was 4.76 in acetonitrile. On the addition of F^-, the color of receptor R turned from yellow to red (Fig. 1). A new peak appears at 498 nm resulting from complex between receptor R and F^- appeared and

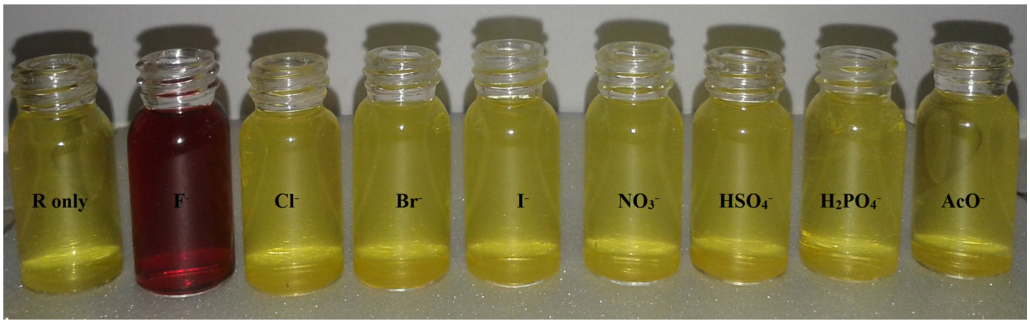

Fig. 1. Color changes upon addition of various anions to acetonitrile solution of receptor R (1×10^{-5} M).