

A Simple and Efficient Schiff Base Derived Chemosensor for Selective Detection of Fluoride Ion

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Abstract: A new thiazole substituted chemosensor **1** has been designed and synthesized for selective detection of fluoride ions. The chemosensor **1** was characterized by ¹H NMR and ¹³C NMR. The absorption studies of chemosensor in DMF exhibits two peaks at 283 nm and 327 nm. The anion sensing behaviour of chemosensor **1** for various anions (I⁻, Cl⁻, Br⁻, NO₃⁻, HSO₄⁻, PF₆⁻, ClO₄⁻) in DMF were investigated by UV-vis spectroscopy. Chemosensor **1** exhibited high degree of selectivity for fluoride ions over other anions. A good linearity in the range of 16-133 μM with 6.12 μM limit of detection value (LOD) was observed.

Key words: Chemosensor, Thiazole, Fluoride ions, Schiff base, UV-vis spectroscopy

1. Introduction

The sensing of anions has been a key research area in supramolecular chemistry due to their important role in biological, environmental and chemical sciences.¹⁻⁴ Particularly, of the different biological anions, fluoride is of special interest owing to its significance in preventing dental caries and in the treatment for osteoporosis.⁴ Fluoride is required for our body in optimum concentration however excess fluoride can cause several diseases like fluorosis, gastric and kidney problems.

Thus, the development of reliable sensing methods for fluoride is highly desired because of diversity of their functions. Chemosensors having different binding units have been employed for detection of fluoride anion with different mechanistic approach such as hydrogen-bonding, π - π interaction etc.⁵ Chemosensors with easy synthesis having high selectivity and sensitivity are of significant importance⁶⁻¹¹. We were interested to develop a low cost, thiazole-derived chemosensor for fluoride anion detection.

Thiazoles, a heterocyclic molecule has a very important place in synthetic chemistry due to its versatile applications.¹² Thiazole and their derivatives are found in many natural and synthetic products, display variety of applications and are mainly used pharmacology studies as well as for several sensing applications.¹³⁻²⁰

In the present work, we report the synthesis, photophysical and fluoride detection properties of the thiazole-derived chemosensor **1** ((*E*)-1-(1-(2-hydroxy-5-methylphenyl)ethylidene)-4-(4-phenylthiazol-2-yl)semicarbazide). The target chemosensor **1** was synthesized via condensation reaction of 4-(4-phenylthiazole-2-yl)semicarbazide with 1-(2-hydroxy-5-methylphenyl)ethenone. The chemosensor **1** upon interaction with fluoride anion exhibits high selectivity and sensitivity together with low limit of detection (LOD). These changes can easily be observed through UV-vis spectroscopy.

2. Experimental

2.1. General information

All chemicals were purchased from Sigma–Aldrich and used without further purification. All the HPLC grade solvents were purchased from Spectrochem, India and used without further distillation. The ¹H NMR and ¹³C spectra were recorded on Bruker, Avance II (400 MHz) spectrometer instrument using DMSO-*d*₆ as solvent. Resonance multiplicities are described as s (singlet), d (doublet), and m (multiplet). UV–Visible absorption spectra were recorded on Perkin Elmer UV–Vis spectrometer (Lambda 365).

2.2 Synthesis of target chemosensor **1** and characterization

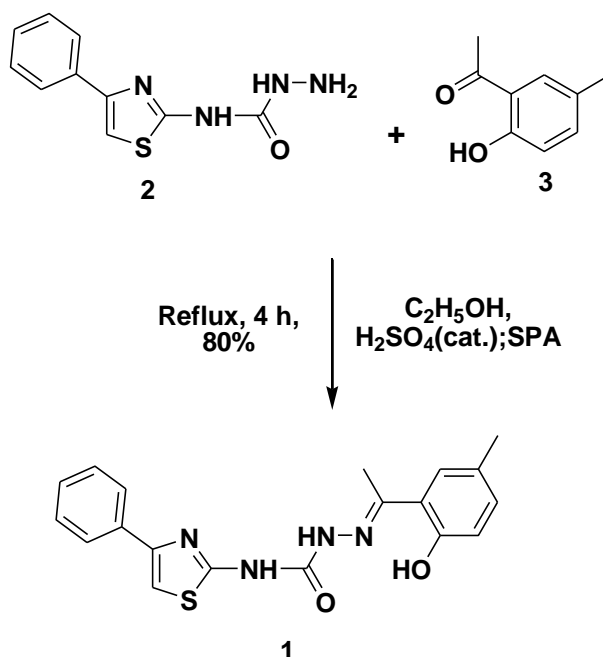
To a solution of 1-(2-hydroxy-5-methylphenyl)ethenone **3** (1.2 mmol) in ethanol (10 ml) was added a solution of 4-(4-phenylthiazole-2-yl)semicarbazide **2** (1.2 mmol) in ethanol followed by addition of sodium polyacrylate (SPA) and 2 drops of H₂SO₄. The solution was refluxed for 4 h. After the completion of reaction, the mixture was cooled to room temperature. (Scheme 1). Yield 80%; ¹H NMR (DMSO-d₆, 400 MHz) δ 10.15 (s, 1H), δ 7.88 (d, 2H), δ 7.58 (s, 1H), δ 7.44-7.30 (m, 5H), δ 7.09-7.07 (d, 1H, *J* = 7.04), δ 6.80-6.79 (d, 1H, *J* = 7.04), δ 4.11 (brs), δ 2.28 (s, 3H), δ 2.26 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 13.29, 20.25, 107.54, 116.96, 125.66, 127.15, 127.82, 128.33, 128.76, 131.40, 134.20, 148.83, 151.17, 152.85, 155.75, 158.83.

2.3 Preparation of sample solutions for titration

For sensing studies, a 10⁻² M stock solution of chemosensor **1** was prepared in 5 mL of DMF, and diluted to 66 μM during the titration for absorption studies. For interference studies a stock solutions (10⁻³ M) of different anions of tetrabutylammonium salts were prepared in DMF and utilized during titration with chemosensor **1**.

3. Results and Discussion

The thiazole-derived chemosensor **1** was synthesized using Schiff base condensation reaction (Scheme 1). Intermediate **2** was synthesized according to literature procedure.²¹⁻²² The reaction of compound **2** with 1-(2-hydroxy-5-methylphenyl)ethenone **3** using catalytic amount of sulfuric acid and sodium polyacrylate (SPA) in ethanol resulted chemosensor **1** in 80% yield. The chemosensor **1** was characterized by ¹H and ¹³C NMR (Figure 1 and 2). The chemosensor **1** showed good solubility in a variety of solvents (DMSO, DMF, acetone, dichloromethane, tetrahydrofuran etc).



Scheme 1. Synthesis of chemosensor **1**

The absorption studies of chemosensor **1** in DMF exhibits two peaks at 283 nm and 327 nm (Fig 3 (A)). The absorption behavior of chemosensor **1** in the presence of TBA salts of various anions (I^- , Cl^- , Br^- , NO_3^- , HSO_4^- , PF_6^- , ClO_4^-) was investigated as shown in Fig 3 (B). The results indicated significant change in the absorption upon titration with fluoride ions. The UV-Vis spectra does not show any significant change upon addition of TBA salts of I^- , Cl^- , Br^- , NO_3^- , HSO_4^- , PF_6^- , ClO_4^- . Thus chemosensor **1** shows strong selectivity for fluoride ions. The UV-Vis spectra of chemosensor **1** upon addition of different concentration of fluoride ions is shown in Fig 4a. The successive addition of fluoride ion into DMF solution of chemosensor **1** leads to decrease in peak intensity at 283 nm while peak at 327 nm undergoes a gradual red shift and appears at 357 nm upon addition of 132 μM solution of fluoride ions (Fig 4 (A)). Chemosensor **1** shows an isobestic point at 308 nm. From the absorption studies, the calibration curve was plotted (Fig 4 (B)) by using absorbance at 327 nm and 283 nm with respect to different concentration of fluoride ion. Good linearity is observed from 16 μM to 133 μM of fluoride ions with a limit of detection (LOD) value of 6.12 μM as calculated using the formula $\text{LOD} = 3\sigma/n$; where σ is the σ represents the standard deviation for blank response and n denotes the slope of the calibration curve. The complexation of fluoride ion with **chemosensor 1** follows 1:1 binding ratio as can be seen from Jobs plot (Fig

4(C)). The binding constant value was calculated as $4.73 \times 10^3 \text{ M}^{-1}$ from Benesi-Hildebrand plot as observed from Fig 4(D).²³⁻²⁴

Conclusion:

In summary we have designed and synthesized a thiazole based molecule which functions as fluoride ion sensor. The chemosensor **1** was characterized by ^1H NMR, ^{13}C NMR and UV-vis spectroscopy. The chemosensor **1** shows high selectivity towards fluoride ions. A systematic red shift is observed upon titration with fluoride ions leading to the appearance of a band at ca. 357 nm. Chemosensor **1** exhibits limit of detection (LOD) values in micromolar range with high selectivity towards fluoride over other anions. The study presented in this article will provide a platform to design and synthesize novel sensors based on heterocyclic compounds.

Conflicts of interest

There are no conflicts to declare.

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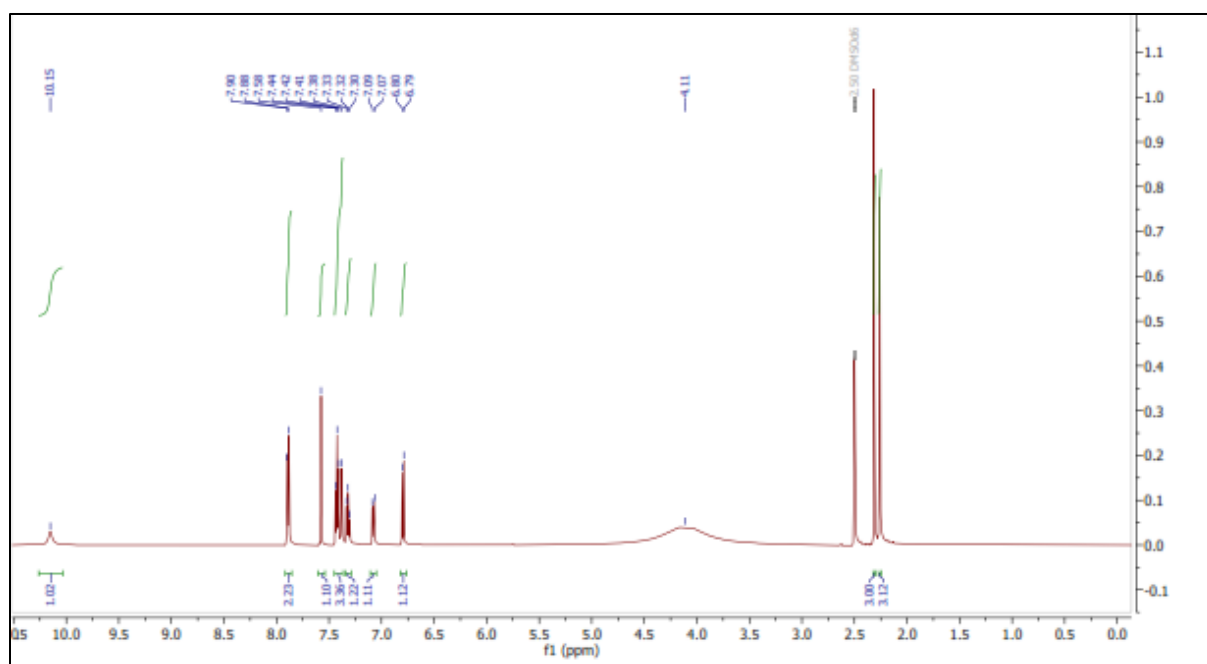


Fig 1: ^1H NMR Spectra of chemosensor 1

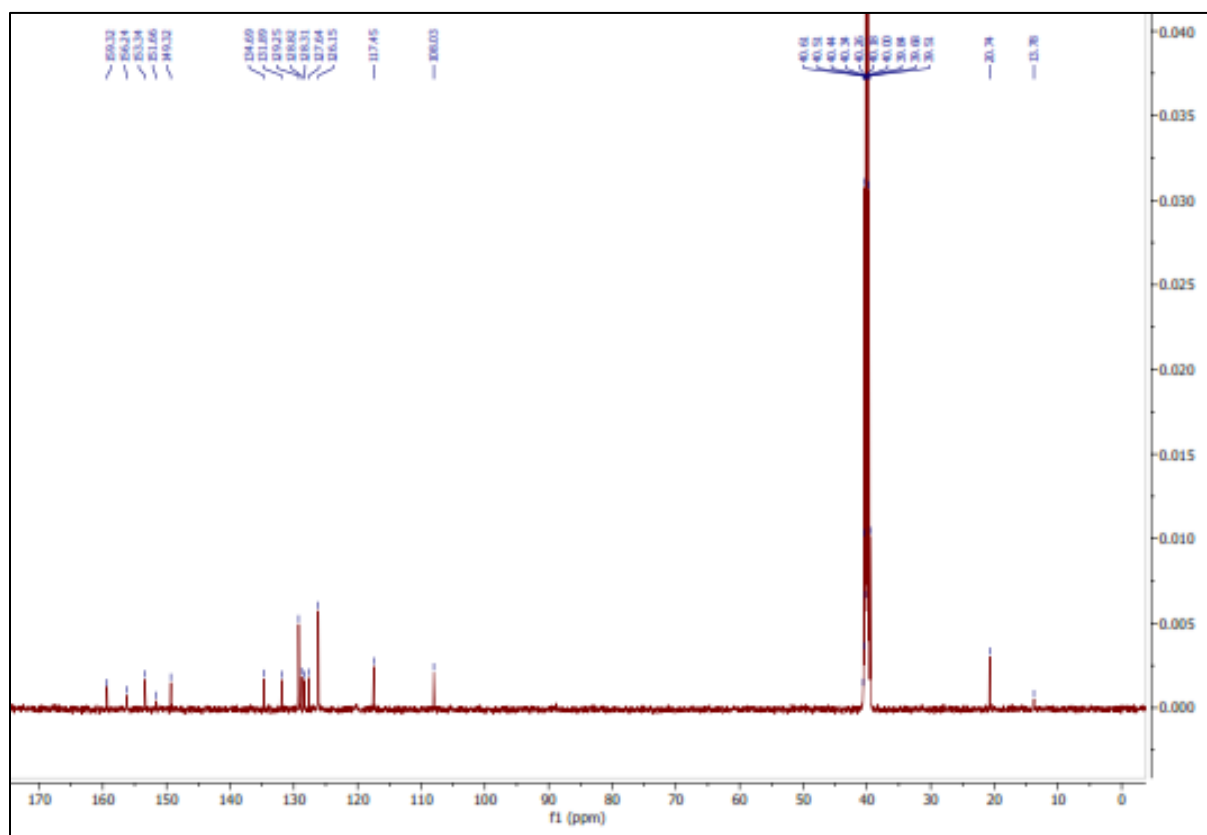


Fig 2: ^{13}C NMR Spectra of chemosensor 1

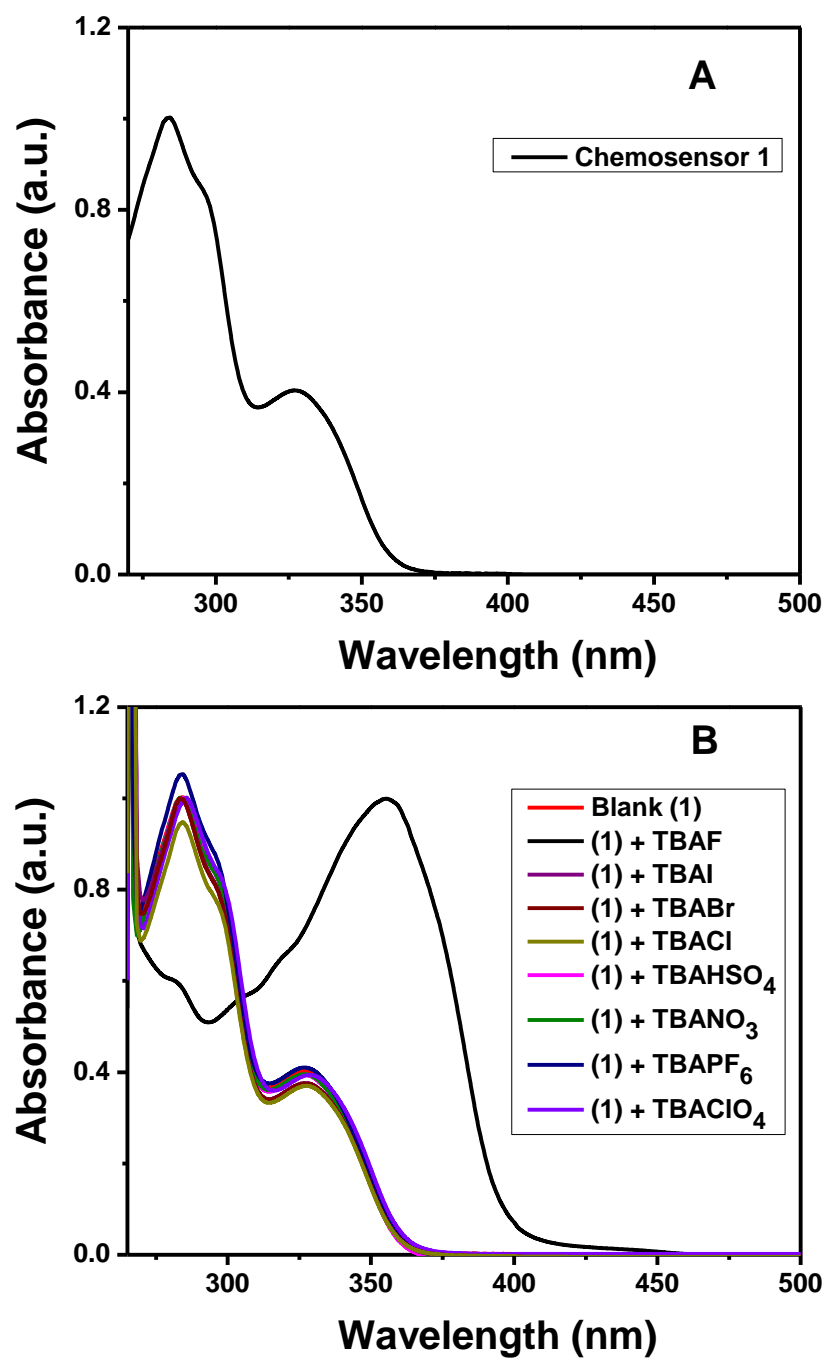


Fig 3: (A) UV-Vis spectra of Chemosensor **1** in DMF; (B) UV-Vis spectra of Chemosensor **1** in presence of 0.166 mM TBA salt different anions in DMF

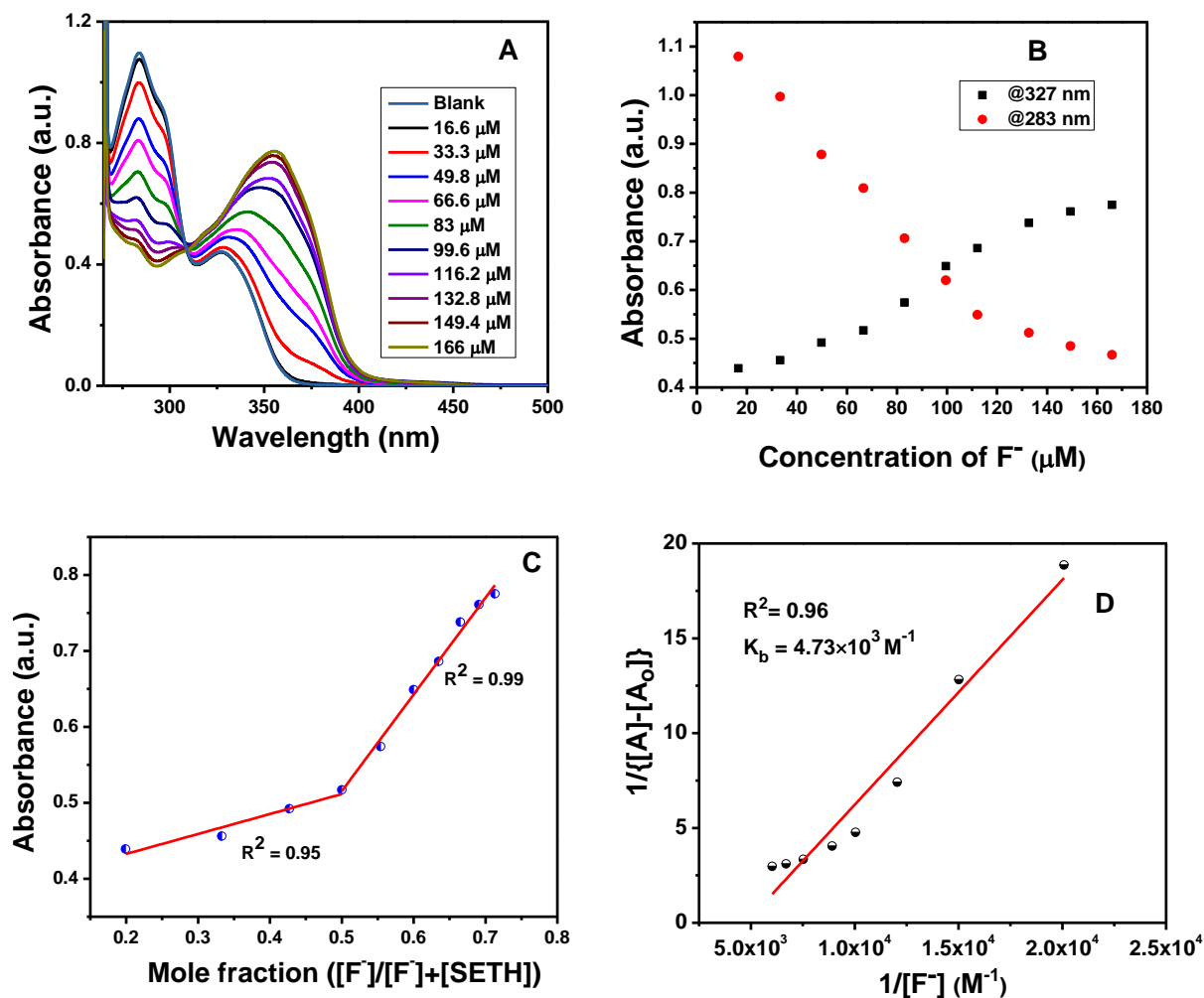


Fig 4: (A) UV-Vis spectra of chemosensor **1** in presence of various concentration of F^- ion; (B) Calibration curve as constructed from UV-Vis studies by plotting absorbance (at 283 and 327 nm) vs concentration of F^- ions; (C) Job's plot pertaining to 1:1 binding of chemosensor **1** with F^- at 327 nm; (D) Benesi-Hildebrand plots for evaluation of binding constant regarding the complexation of SETH with F^- obtained from UV-Vis.