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Novel thiophene based colorimetric and fluorescent receptor for selective recognition of fluoride ions

D. Renuga, D. Udhayakumari, S. Suganya, S. Velmathi *

Organic and Polymer Synthesis Laboratory, Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India

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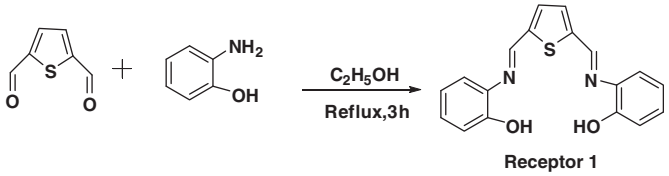
ABSTRACT

A colorimetric anion sensor 2,2′-(1*E*,1′*E*)-(thiophene-2,5-diylbis(methan-1-yl-1-ylidene)) was synthesized and characterized by various spectroscopic techniques. Anion binding studies were carried out using UV–visible spectrophotometric titrations and emission spectra studies, revealed that the receptor exhibits selective recognition toward F^-over other anions. The selectivity for F^-among the halides is attributed mainly to the hydrogen-bond interaction of the receptor with F^-. Receptor **1** showed color change from fluorescent green to orange in the presence of tetrabutylammonium fluoride with 1:1 stoichiometry. Receptor **1** exhibits remarkably enhanced fluorescence intensity.

Chemical sensors, especially optical sensors, are elegant alternative to the traditional analytical instruments. They have the advantages of size, cost-effectiveness, simplicity, no necessity of the reference solution, and fieldwork applicability.[1,2] Among the methods available for chemical sensors, a colorimetric technique has many advantages. It can be easily observed and determined by the naked eye, rather than by using large, sophisticated, and expensive analytical instruments (such as mass spectrometers).[3a–c,4a–e] Among the anion species, fluoride sensing has attracted considerable attention because of its crucial role in dental care and the treatment of osteoporosis.[5] On the other hand, it is highly advantageous to develop a high-effective sensor that can selectively detect fluoride ion with the naked eye 'no–yes' response.[6] The addition of fluoride in drinking water and toothpastes has become widespread due to the valuable effects in human health. However, high doses of fluoride are hazardous and can lead to dental or skeletal fluorosis.[7] Charge neutral receptors have been used for anion sensor and most of them contain pyrrole, amide, indolocarbazole, guanidium, imidazolium, and/or urea/thiourea moieties, and the anion is recognized via H bonding or deprotonation of protons on the receptor NH in organic solvents.[8–16] Although thiophene based compounds were reported for several studies it was not reported anywhere for sensing studies, so our interest was captured by thiophene based receptors for sensing studies. In continuation of our ongoing research in the chemo sensor field,[17a–c] herein we report the synthesis, characterization, and application of a simple thiophene based receptor as a colorimetric and fluorescent sensor for fluoride ion. The receptor reported in this Letter has only one previous report about its conformational analysis.[18] Other than that no information is available in the open literature. To the best of our knowledge this is the first report on the synthesis, characterization, and utilization of receptor **1** as a selective fluoride ion sensor. Upon the addition of 2 equivalents of F^- ion, receptor **1** turned from fluorescent green to orange color. Among the various anions, receptor **1** exhibits high selectivity, sensitivity toward fluoride ion and remarkably enhanced fluorescence intensity.

Receptor **1** was prepared by a simple condensation method according to Scheme 1.[19] A very strong absorption at 1598 cm^{-1} in the FTIR spectrum indicates the presence of C=N group. O-H stretching vibration of this compound was observed around 3376 cm^{-1}. C=C, C–O, and C–N stretching vibrations are seen at 1452 cm^{-1}, 1227 cm^{-1}, and 1368 cm^{-1} respectively. Receptor **1** gave a singlet at δ 8.9 ppm corresponding to CH=N proton indicating the formation of imine and the aromatic protons of receptor resonate in the δ 6.8–7.2 region and the thiophene ring protons



Scheme 1. Synthesis of 2,2′-(1*E*,1′*E*)-(thiophene-2,5-diylbis(methan-1-yl-1-ylidene))bis(azan-1-yl-1 ylidene)diphenol.

* Corresponding author. Tel.: +91 431 2503640; fax: +91 431 2500133.
E-mail address: velmathis@nitt.edu (S. Velmathi).

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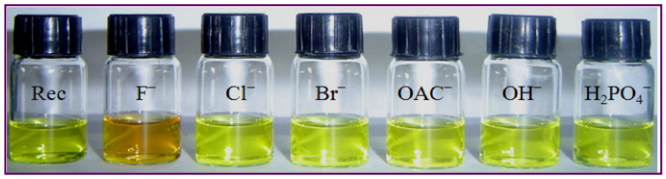


Figure 1. Color changes of receptor **1** (2.5×10^{-5} M solution in CH_3CN) before and after the addition of 100 μL (2 equiv) of F^-, Cl^-, Br^-, AcO^-, OH^-, and $H_2PO_4^-$ (1.5×10^{-3} M solution in CH_3CN) ions, respectively.

gave a singlet at δ 7.7. In addition, the –OH protons in the aromatic rings are shown as a singlet at δ 9.2 ppm. In ^{13}C spectrum, the aromatic carbons resonate in the δ 116–137 region. Thiophene ring carbons resonate around δ 133–146. Imine carbon resonates at δ 153 ppm. Thus the structure of the receptor was confirmed without any ambiguity by various spectroscopic methods.

The recognition properties of the receptor **1** toward different anions were studied by the naked-eye experiment, UV–visible, and fluorescence titration.

In the naked eye experiment, color changes were studied in acetonitrile (CH_3CN). Upon addition of 2 equivalents of fluoride ions in the form of TBAF salt solution (1.5×10^{-3} M in CH_3CN), fluorescent green solution of receptor **1** (2.5×10^{-5} M in CH_3CN) became orange. The color changes are shown in Figure 1. No color changes were observed for the addition of dihydrogen phosphate, chloride, bromide, and acetate ions even to the addition of large excess of Cl^-, Br^-, AcO^-, OH^-, and $H_2PO_4^-$ ions (up to 10 equiv) in the form of their tetrabutylammonium salts and the receptor was found to be insensitive. The appearance of the color change signifies the interaction of F^- with the OH groups of receptor through hydrogen bond. These H-bond interactions produced a new interaction between electron-rich F^- and receptor, resulting in a visible color change from fluorescent green to orange.

The sensing behavior of receptor **1** toward fluoride ion was determined by spectrophotometric methods in CH_3CN. Absorption titrations were carried out with receptor **1** (2.5×10^{-5} M) in CH_3CN and incremental addition of tetrabutylammonium fluoride (1.5×10^{-3} M) in CH_3CN up to 2 equivalents to the receptor **1** and the resulting spectra are shown in Fig. 2a. Receptor **1** in the absence of F^- ions showed three bands. The first band in the wavelength 270 nm was assigned to the excitation of the π electrons of the aromatic system. This band is sensitive to the substitution at the aromatic rings and their positions are little influenced by changing the solvent polarity confirming the local π–π^* nature of

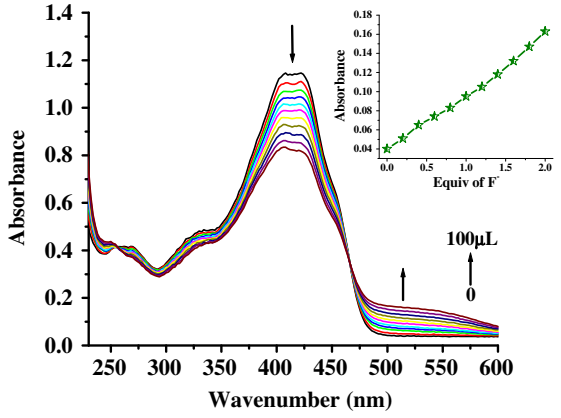


Figure 2a. UV–vis spectral changes of receptor **1** (2.5×10^{-5} M in CH_3CN) upon titration with F^- ion (1.5×10^{-3} M in CH_3CN). (Inset: changes of absorbance upon addition of F^- ion at 520 nm).

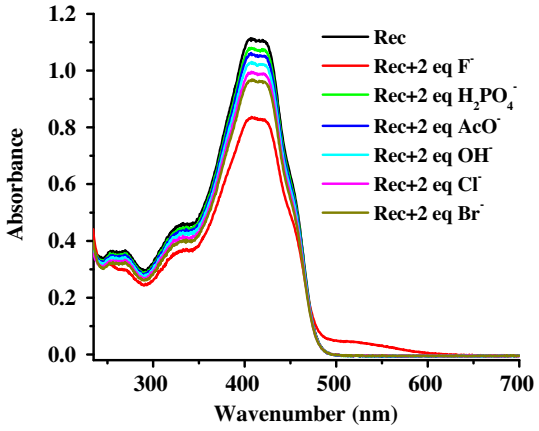


Figure 2b. UV–vis spectrum of receptor **1** (2.5×10^{-5} M) upon titration with anions in CH_3CN ($H_2PO_4^-$, AcO^-, OH^-, Cl^-, Br^-).

the electronic transition. The second band observed in the wavelength 320 nm could be due to the transition between the π-orbital localized on the central band of azomethine group (CH=N).[20] The third band obtained in the wavelength of 420 nm is may be due to an intra molecular charge transfer (CT) transition within the whole molecule. As a function of F^-, a new red-shifted absorption band centered at 520 nm increased with a concomitant decrease of the band at 420 nm with the isosbestic point. The band at 520 nm is attributable to the Internal Charge Transfer (ICT). The other anions did not give any response in acetonitrile medium, there was no extra band observed after the addition of 2 equivalents of anions as their tetrabutylammonium salts (Fig. 2b). Thus receptor **1** can sense F^- ions selectively in the presence of other competing anions.

The binding constant of the receptor for fluoride ion was calculated as 1.3×10^3 according to Benesi–Hildebrand (B–H) equation. Job's plot studies revealed that the stoichiometry between the receptor **1** and anion was 1:1.

The sensitivity of receptor was also investigated with the help of emission spectra. Titration experiments were carried out similar to UV–vis analysis with the same solutions, receptor **1** (2.5×10^{-5} M) and anion (1.5×10^{-3} M) both in CH_3CN. Upon excitation at 460 nm due to the strong fluorescent nature of the receptor **1** it gave a

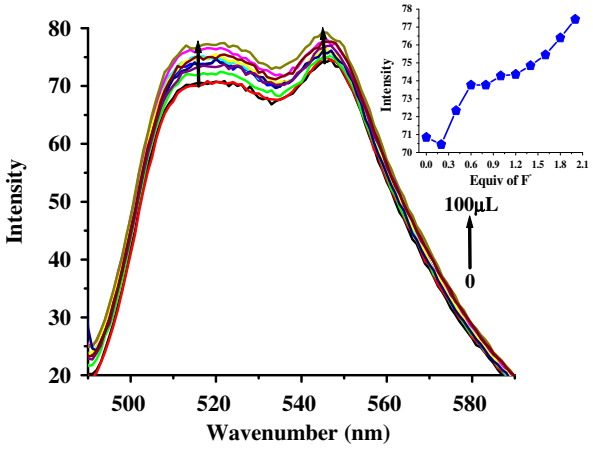
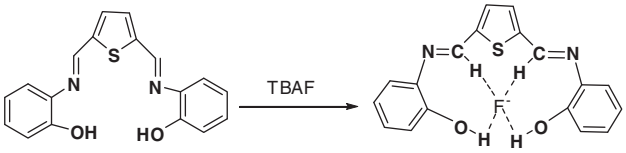


Figure 3a. Fluorescence titration spectrum of receptor **1** (2.5×10^{-5} M in CH_3CN) upon the gradual addition of (0–100 μL) TBAF (1.5×10^{-3} Min CH_3CN). (Inset: changes of fluorescence emission upon addition of F^- ion at 510 nm.) (Excited at 460 nm).



Scheme 2. Possible structure of complex formed between receptor **1** and F^-.

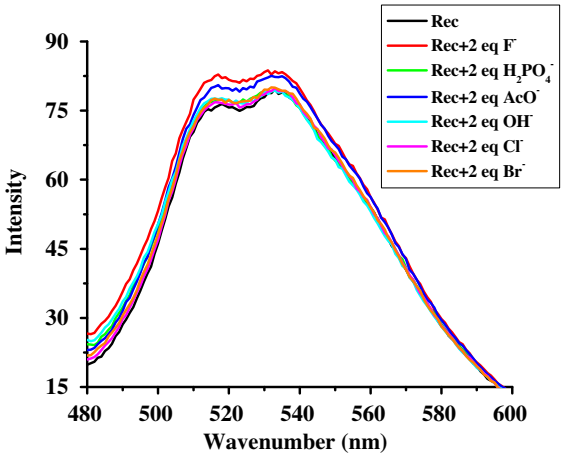


Figure 3b. Fluorescence titration spectrum of receptor **1** (2.5×10^{-5} M) upon titration with anions in CH_3CN ($H_2PO_4^-$, AcO^-, OH^-, Cl^-, Br^-).

strong emission band at 510 and 545 nm. Fig. 3a shows the spectral variation of the receptor upon gradual addition of TBAF.

Observed enhancement in fluorescent intensity upon the incremental addition (0–2 equiv) of F^- ions may be due to the efficient charge transfer between guest–host species. This highly indicates that there is a strong sensing action taking place between receptor **1** and F^- ion through hydrogen bonding formation as shown in Scheme 2. Emission spectrum of receptor **1** with other anions is shown in Figure 3b. Only in the case of acetate ions there was a marginal increase in the emission intensity and other anions did not show any change. Thus it can be concluded that the receptor **1** can be utilized as a selective chemosensor for F^- ions in the presence of other interfering ions.

In conclusion, we have designed and synthesized a highly sensitive thiophene based chemosensor for the detection of F^- ion selectively. The chemosensor can be utilized for the detection of F^- in the presence of competing anions such as Cl^-, Br^-, AcO^-, OH^-, and $H_2PO_4^-$ ions. The changes in absorption and fluorescence spectra were driven by the hydrogen bonding between receptor **1** and fluoride anions.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.06.147.

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19. *Synthesis of receptor* ***1***: To a hot solution of 2,5-thiophene dicarboxaldehyde (1 mmol, 0.139 g) in 10 mL of ethanol was added 2 mmol (0.218 g) of *o*-amino phenol in 20 mL of ethanol and the mixture was slowly refluxed for 3 h at 70 °C. On cooling, a yellow coloured solid separated out, it was filtered and washed with ethanol and then dried in vacuum. Yield was 0.255 g (79%). The structure of the ligand was confirmed by: IR (KBr ν cm^{-1}) 3376 (OH), 1598 (C=N), 1452 (C=C), 1227 (C–O), 1368 (C–N). ^{1}H NMR (δ ppm, 400 MHz, DMSO-d_6): 6.81 (1H, s), 6.83 (1H, dd), 6.95 (1H, s), 7.18 (1H, dd), 7.7 (1H, s), 8.9 (1H, s), 9.2 (1H, s); ^{13}C NMR (δ ppm, 100 MHz, DMSO-d_6): 116.22, 119.61, 122.44, 127.68, 137.19, 150.96, 133.11, 146.08, 152.87.
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