



# A multi writable thiophene-based selective and reversible chromogenic fluoride probe with dual –NH functionality



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## ABSTRACT

A chromogenic fluoride probe bearing bis imine groups having dual –NH functionality (**BSB**) has been designed, synthesised and structurally characterized by its single crystal X-ray diffraction studies. The **BSB** could visually and spectroscopically recognise  $F^-$  with high selectivity over other anions by exhibiting intense chromogenic response (from colourless to red) for  $F^-$  in acetonitrile solution. The UV–visible titration and  $^1H$  NMR titration experiments indicated that the observed changes occur via a combined process including hydrogen bonding and deprotonation between the **BSB** and  $F^-$ . Moreover theoretical calculations at the Density Functional Theory (DFT) level shed further light upon probe design strategy and the nature of interactions between **BSB** and  $F^-$ . The limit of detection and binding constant of **BSB** towards  $F^-$  were found to be  $6.9 \times 10^{-7}$  M and  $1.42 \pm 0.069 \times 10^8$  M<sup>-2</sup> respectively. Finally, by using  $F^-$  and  $H^+$  as chemical inputs and the absorbance as output, a IN-HIBIT logic gate was constructed, which exhibits “Multi-write” ability without obvious degradation in its optical output.

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## 1. Introduction

The fundamental role of anions in a wide range of biological and chemical processes [1] has given an impetus to the development of optical chemosensors. In most cases, the actions of these optical sensors towards anions were found to be a consequence of hydrogen bonding, electrostatic interactions or coordination with suitable metal complexes [2]. The hydrogen bonding ligands in particular are attractive in this respect due to their directional nature hence allowing discrimination among anions on the basis of their geometries and hydrogen-bonding abilities [3].

Among the anionic analytes, fluoride is smallest anion with a high charge density and is of particular interest due to its fundamental role in industry, food and toxicity etc. [4]. The fluoride anion also shows beneficial effects towards dental health and the treatment of osteoporosis [5]. Furthermore, it is also used in hypnotic and psychiatric drugs as well as for the refinement of uranium in nuclear technology [6]. However, excessive ingestion of  $F^-$  may also result in immune system disruption, kidney damage, cancer, [7] dental and skeletal fluorosis, lesions of the thyroid, liver and other organs etc. [8]. The fluorosis causes nephrotoxic changes in both humans and animals, and lead to urolithiasis [9]. There are at least 15 states in India which are affected by fluorosis and among them Gujarat is the most severely affected state due to high fluoride content in drinking water [10]. Hence, there is an urgent necessity

to develop a sensor for fluoride ions having low detection limit as well as high selectivity at affordable cost.

In recent years, many optical sensors have been developed for fluoride ion detection. Most of the synthetic chemosensors generally involve the covalent linkage between optical signaling chromophoric fragment and a neutral anion receptor containing amide [11] pyrrole [12], urea [13], thiourea [14], indole [15] subunits. These receptor units can provide one or more H bond donor sites for selective binding and sensing of some anions like  $AcO^-$ ,  $H_2PO_4^-$  and  $F^-$  etc. In these motifs,  $N-H \cdots X^-$ , plays very important roles for selective anion binding. Although deprotonation is an effective way to accomplish naked-eye recognition, but generally, the same cannot differentiate  $F^-$  from the matrix of other anions particularly from  $AcO^-$  and  $H_2PO_4^-$  due to their comparable basicity to that of  $F^-$  [16]. Hence, the selectivity is a paramount issue [17] to construct the colorimetric chemosensor with specific receptor for the fluoride ion. Hitherto the colorimetric sensors based on N–H proton donation by molecular scaffolds satisfying the above conditions are few only [18]. Our own few reports in this context are worth to be mentioned [19].

The present piece of work is the latest worth full addition in the same context from our lab. Here we coupled 4-nitrobenzohydrazide over the platform of thiophene-2,5-dicarboxaldehyde (**BSB**) (Fig. 1). Our design strategy of having nitro group at the 4th position of the benzene ring modulated the acidity of N–H proton in such a way that the same bound selectively with  $F^-$  only and not with other very similar anions like  $AcO^-/H_2PO_4^-$  having a comparable basicity with  $F^-$ . The position of nitro group on benzene ring allows it only for push-pull effect

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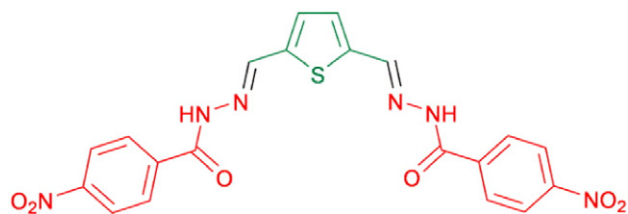


Fig. 1. Structure of BSB.

instead of direct electron withdrawing effect. The anchoring of the thiophene in the probe **BSB** is further justified through theoretical and HOMO-LUMO orbital calculations.

Furthermore, owing to the increasing demands of information technology the design and construction of molecular systems capable of performing complex logic functions such as logic gates [20–24], molecular keypad locks [25], information storage devices [26] is of great scientific interest nowadays. Such logic instruments are believed to transfer the molecular-level information in the form of observable optical signals [23a]. In the same context we are reporting hereby the ‘INHIBIT’ logic gate incorporating two chemical inputs viz.;  $F^-$  and  $H^+$  as two chemical inputs as a direct way of detecting congregations of chemical species.

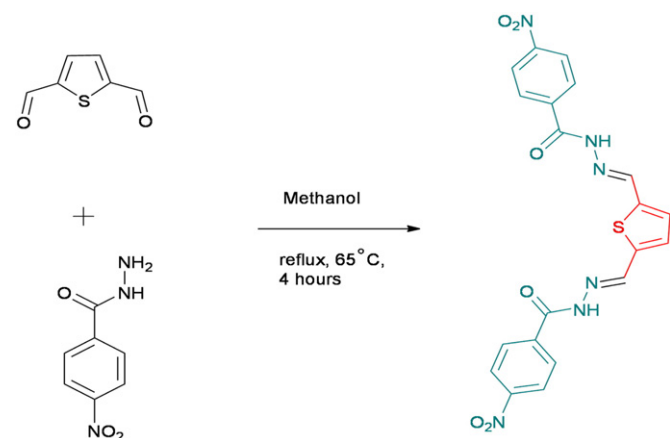
## 2. Experimental

### 2.1. Synthesis of BSB; (thiophene-2,5-diylbis(methanylylidene))bis(4-nitrobenzohydrazide)

The 2, 5-thiophene dicarboxaldehyde (140.16 mg, 1.0 mM) and 4-nitrobenzohydrazide (362.3 mg, 2.0 mM) were taken in dry MeOH (96%, 10 mL) in a 50 mL round bottom flask having catalytic amount of HCl (Scheme 1). The reaction mixture was stirred at room temperature for 10–30 min than refluxed for 4 h. A yellow crystalline precipitate isolated from reaction mixture by filtration, washed with hot MeOH for two times and dried in a vacuum oven. The desired compound was obtained as a light yellow crystalline solid (326 mg, 0.70 mM, yield ~70%). The **BSB** have been thoroughly characterized by various spectral techniques such as  $^1H$ ,  $^{13}C$  NMR, IR and ESI-MS (ESI; Figs. S1–S4).

### 2.2. Spectroscopic characterization of BSB

$^1H$  NMR (300 MHz, DMSO- $d_6$ ,  $\delta$  ppm): 12.20 (s, 2H, 2-N-H), 8.66 (s, 2H, -HC = N-), 8.38–8.35 (m, 4H, Ar-H), 8.14–8.11 (m, 4H, Ar-H), 7.53



Scheme 1. Synthesis of thiophene-based chemosensor BSB.

(2H, Ar-H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ ),  $\delta$  (ppm): 176.93, 149.32, 143.54, 138.96, 131.86, 129.20, 123.72, 121.12; IR (KBr)/ $cm^{-1}$ : 3432, 3291 (N-H Stretch), 3220 (N-H Stretch), 3065, 2852, 1673 ( $^1C = O$ ), 1600 ( $^1C = N$ ), 1519 ( $NO_2$ ; Stretch), 1457, 1346, 1272, 1137, 1109, 1013, 950, 905, 865, 851, 790, 714, 591, 509; ESI MS [M + H]: 467.6 Calc. for **BSB** [M] = 466.43.

## 3. Results and discussion

### 3.1. Description of the crystal structure of BSB

The structure of **BSB** was confirmed through its single crystal X-ray analysis. Crystals of receptor **BSB** were obtained by slow evaporation of its saturated DMSO- $CHCl_3$  (1:2, v/v) solution over a period of few weeks. Crystallographic data and details of structure determinations have been summarized in Table 1.

The receptor **BSB** crystallizes in the monoclinic system with  $P21/c$  space group. ORTEP representation of the **BSB** is shown in Fig. 2a which reveals its dipodal structure. The dihedral angle between C5-N1-N2-C6 and C13-N4-N5-C14 are  $-177.91^\circ$  and  $-179.42^\circ$  respectively, implying almost planar configuration about thiophene framework with two lateral 4-nitrobenzohydrazide. Two solvent molecules of DMSO were found to be trapped with **BSB** through hydrogen bonding interactions [ $N(2)H \cdots O(7)$ ,  $N(5)H \cdots O(8)$  with 2.026 Å, 2.050 Å respectively]. Furthermore, supramolecular interactions between sulphur atom of DMSO and oxygen atom of nitro of **BSB** were also seen;  $S(1) \cdots O(6) = 3.27$  Å, 3.30 Å. The bond angles of  $C6-N2-N1 = C14-N5-N4$  and  $C5-N1-N2 = C13-N4-N5$  were found to be  $\sim 119.5^\circ$  and  $\sim 114.5^\circ$  respectively (Fig. 2b).

### 3.2. Chromogenic responses and binding ability of BSB

The chromogenic responses of 50  $\mu M$  acetonitrile (ACN) solution of **BSB** were primarily investigated through naked-eye upon separate additions of several cationic and anionic analytes. The solution of **BSB** did not experience any significant colorimetric change with any chosen

Table 1  
Crystal data and structure refinement for **BSB**.

| Identification code               | BSB  |
|-----------------------------------|--|
| CCDC No.                          | 1407606  |
| Empirical formula                 | C <sub>24</sub> H <sub>26</sub> N <sub>6</sub> O <sub>8</sub> S <sub>3</sub>   |
| Formula weight                    | 622.69   |
| Temperature                       | 273(2)K  |
| Wavelength                        | 0.71073 Å  |
| Crystal system                    | Monoclinic   |
| Space group                       | $P21/c$  |
| Unit cell dimensions              | a = 12.4731(7)Å, alpha = $90^\circ$ ,<br>b = 19.2037(10)Å, beta = $94.942(2)^\circ$ ,<br>c = 11.6946(6)Å, gamma = $90^\circ$ |
| Volume                            | 2790.8(3)Å <sup>3</sup>  |
| Z                                 | 4  |
| Density (calculated)              | 1.482 Mg m <sup>-3</sup>   |
| Absorption coefficient            | 0.325 mm <sup>-1</sup>   |
| F(000)                            | 1164   |
| Crystal size                      | 0.32 × 0.21 × 0.16 mm  |
| Crystal colour and habit          | Colourless, rectangular  |
| Diffractometer                    | ‘Bruker APEX-II CCD’   |
| Theta range for data collection   | $1.95$ to $28.35^\circ$  |
| Limiting indices                  | $-16 \leq h \leq 16$ , $-25 \leq k \leq 25$ , $-14 \leq l \leq 15$   |
| Reflections collected / unique    | 27,700 / 6921 [R(int) = 0.0869]  |
| Completeness to theta = 25.00     | 99.1%  |
| Absorption correction             | None   |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>  |
| Data / restraints / parameters    | 6921 / 0 / 380   |
| Goodness-of-fit on F <sup>2</sup> | 1.041  |
| Final R indices [I > 2sigma(I)]   | R1 = 0.0770, wR2 = 0.1681  |
| R indices (all data)              | R1 = 0.1364, wR2 = 0.1949  |
| Largest diff. peak and hole       | 0.913, -0.688e·Å <sup>-3</sup>   |

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