Chinese Chemical Letters 26 (2015) 339–342

Contents lists available at ScienceDirect

Chinese Chemical Letters

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

Original article

# A highly efficient and selective probe for $F^-$ detection based on 1*H*-imidazo[4,5-*b*]phenazine derivative

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ARTICLE INFO

*Article history:*
Received 11 July 2014
Received in revised form 25 September 2014
Accepted 15 October 2014
Available online 5 November 2014

*Keywords:*
Imidazole
Phenazine
Fluoride anion probe
Naked-eye detection

ABSTRACT

A new colorimetric and fluorimetric chemosensor for $F^-$ detection based on 1*H*-imidazo[4,5-*b*]phenazine derivative has been designed and synthesized. It shows excellent fluorescent specific selectivity and sensitivity for $F^-$ in DMSO solution. Upon addition of $F^-$ to the solution of probe **1**, a remarkable color change from yellow to red could be observed easily by the naked-eye. The detection limit of this probe toward $F^-$ is $6.2 \times 10^{-6}$ mol/L. Analysis by $^1$H NMR proved that the imidazolyl N–H could be hydrogen-bonded with added fluoride anions, and results in the difference of colors.

## 1. Introduction

Fluoride anion has distinctive features than other anions due to its exceptional electronegativity and small radius [1]. Based on these unique characteristics, the fluoride anion plays an important role in biological, clinical and environmental fields, especially the function of preventing dental caries and the treatment of osteoporosis [2–5]. Meanwhile, fluoride overload is harmful to human health, which can cause fluorosis [6]. Excessive fluoride anion is also considered as potential danger to the environment [7]. Accordingly, the development of efficient probes for fluoride anion has attracted much more attention. A large number of synthetic fluorophores have been designed as chemosensors for $F^-$ in the past decade. However, some sensing systems suffer from several typical drawbacks, such as low limit of detection, poor selectivity for anions, difficulty of synthesis, and impossible recognition by the naked-eye [8–10].

It is well-known that the imidazole unit, due to the acidity of the N–H proton, acts as an excellent hydrogen bond donor in the molecular structure, which can be utilized in detecting fluoride. Tamiaki *et al.* [11] and Liu *et al.* [12] reported a series of imidazo[4,5-*f*]-1,10-phenanthroline metal-complexes as colorimetric and fluorescence chemosensors for fluoride anions, respectively. The results proved that the imidazolyl N–H could be hydrogen-bonded upon the addition of $F^-$ and results in the suppression of the photosensitization. These chemosensors were mainly designed on the coordination of the metal center (Eu, Re, Pt) with imidazolyl chromophores, which have the disadvantage of complicated preparation and relative high cost. In addition, phenazine derivatives have been widely used in the field of polymer conductive materials, exhibiting excellent luminescent properties and photophysical stabilities [13–16]. Zhang's group [17] reported a heteroacene based $F^-$ sensor, 2-(2,3,4,5-tetrafluorophenyl)-1*H*-imidazo[4,5-*b*]phenazine, which shows selectivity and multiple responses to $F^-$ through combined hydrogen bonding, deprotonation, and anion–$\pi$ interactions. However, the studies on the phenazine based $F^-$ sensors are still rare and the low detection limits prohibit their extensive application.

In this work, we designed and synthesized a new probe based on imidazole and phenazine structures (Scheme 1). The Br substituent was introduced with the aim of improving the selectivity and sensitivity for $F^-$ due to its moderate electronegativity. At the same time, the synthesis of this probe is simpler than other probes. The colorimetric and fluorescent characteristics of this chemosensor drastically change with the addition of fluoride anions in DMSO solution. Furthermore, paper test strips of this probe were prepared to detect $F^-$ in water-solvent system.

## 2. Experimental

All reagents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. The $^1$H

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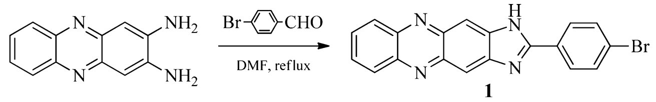
http://dx.doi.org/10.1016/j.cclet.2014.10.028



**Scheme 1.** Synthetic route for probe **1**.

(400 MHz) NMR and $^{13}$C NMR (100 MHz) spectra were recorded in DMSO-$d_6$ at room temperature using a Bruker Ultra Shield Plus 400 MHz instrument with tetramethylsilane (TMS) as internal reference. Melting points (m.p.) were measured on a Gal-lenkamp apparatus. Mass spectrometry analyses were acquired using MAT-212 instrument. Fluorescence spectra were collected using a Perkin-Elmer LS 50B spectrofluorometer. UV–vis absorption spectra were recorded using an Agilent 8453 spectrophotometer.

Synthesis of probe **1**: Both 2,3-diamino-phenazine (0.21 g, 1 mmol) and 4-bromobenzaldehyde (0.19 g, 1 mmol) were dissolved to DMF (8 mL). The solution was stirred under reflux for 16 h. After cooling to room temperature, the brown precipitate was filtered, washed with hot ethanol three times, then recrystallized with DMF–$H_2O$ to get a brown powdery product **1** (0.29 g, 78% yield). M.p. > 300 °C, $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 7.89 (q, 4 H, $J$ = 8.0 Hz), 8.23 (q, 2H. $J$ = 8.0 Hz), 8.32 (d, 2H, $J$ = 8.0 Hz), 8.39 (s, 2H), 13.51 (s, 1H), $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 158.87, 147.67, 141.34, 139.87, 131.90, 129.72, 128.93, 128.80, 124.62, 116.87, 109.88. ESI-MS $m/z$: $(M-1)^+$ calcd. for $C_{19}H_{11}N_4Br$ 374.02; found 372.9.

All UV–vis spectroscopy were recorded after the addition of tetrabutylammonium salts in DMSO [18,19], while keeping the ligand concentration constant ($1 \times 10^{-5}$ mol/L) on a Agilent 8453 spectrophotometer. The solutions of the anions were prepared from the tetrabutylammonium salts of $F^-$, $Cl^-$, $Br^-$, $I^-$ $OAc^-$, $H_2PO_4^-$, $HSO_4^-$ and $ClO_4^-$.

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For $^1$H NMR titrations, probe **1** was dissolved in DMSO-$d_6$, which was mixed different equiv. of $F^-$ in NMR tubes. The spectra were performed at 298 K [20].

## 3. Results and discussion

The selective properties of probe **1** ($1 \times 10^{-5}$ mol/L) in DMSO solution toward various anions were first evaluated. Fig. 1 illustrates the absorption spectra changes and color changes when probe **1** in DMSO solution was added to 5 equiv. of the $F^-$ and 20 equiv. of other anions. Absorption spectra show remarkable changes that the original absorption peak at 405 nm red-shift to 435 nm after adding $F^-$, while a broad absorption band at 550 nm appears. Furthermore, no obvious changes were observed after the addition of other halogen anions, such as $Cl^-$ and $Br^-$, $I^-$ and more complicated anions, such as $OAc^-$, $H_2PO_4^-$, $HSO_4^-$ and $ClO_4^-$. Simultaneously, when $F^-$ (5 equiv.) was added to the DMSO solution of probe **1** ($1 \times 10^{-4}$ mol/L), the color of the solution changed from yellow to red. This could be clearly observed by the naked-eye. The fluorescence of probe **1** in DMSO solution also exhibits significant differences upon adding various anions. When $F^-$ was added to the solution of probe **1** ($1 \times 10^{-5}$ mol/L), the intensity of the emission band at 530 nm decreased and a new emission band appeared at *ca.* 650 nm. The fluorescent color changed from green to red under a UV lamp (365 nm light irradiation), which could be distinguished by the naked-eye. Meanwhile, none of the other anions induced any significant changes in the fluorescence intensity at 530 nm compared with $F^-$ (Fig. S5 in Supporting information).

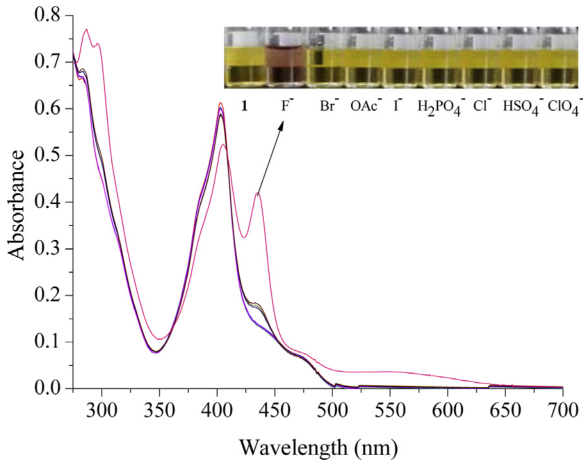

**Fig. 1.** UV–vis absorption spectra of probe **1** ($1 \times 10^{-5}$ mol/L) in DMSO, upon addition of $F^-$ (5.0 equiv.) and other anions (20.0 equiv of $Cl^-$, $Br^-$, $I^-$, $OAc^-$, $H_2PO_4^-$, $HSO_4^-$and $ClO_4^-$ as their TBA salts). Inset illustration: color change of sensor ($1 \times 10^{-4}$ mol/L) in DMSO after addition of 5 equiv. of different anions. From left to right: a solution of probe **1** and those after the addition of anions (as TBA salts): $F^-$, $Br^-$, $OAc^-$, $I^-$, $H_2PO_4^-$, $Cl^-$, $HSO_4^-$ and $ClO_4^-$.

A spectrophotometric titration method was used to investigate the interaction between probe **1** and $F^-$. When tetrabutyl

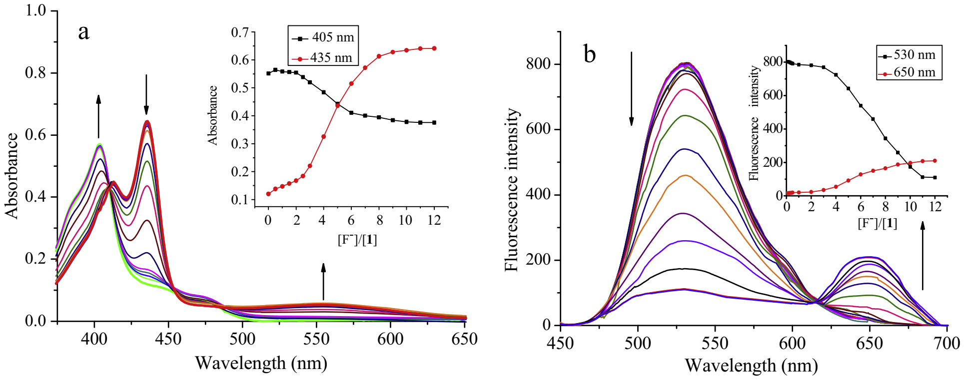

**Fig. 2.** (a) UV–vis absorption titration of probe **1** ($1 \times 10^{-5}$ mol/L) in DMSO solution (range of 0–12 equiv. of fluoride ions). Inset illustration: correlation curve of probe **1** at 435 nm (black) and 405 nm (red) adding different equivalents of $F^-$. (b) Fluorescence titration of probe **1** in DMSO solution ($1 \times 10^{-5}$ mol/L) (range of 0–12 equiv. of fluoride ions). Inset illustration: correlation curve of probe **1** at 530 nm (black) and 650 nm (red) adding different equivalents of $F^-$.