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ARTICLE

An efficient colorimetric and fluorescent probe for detection of fluoride ion based on a benzothiadiazole derivative

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In this paper, an efficient colorimetric and fluorescent probe based on benzothiadiazole derivative was developed for detection of fluoride ions (F⁻). Selectivity of this approach was capitalized on highly selective and straightforward chemical reaction between F⁻ and Si-O bond. Sensing behavior of this probe towards anions was monitored by UV-visible and fluorescence spectroscopies in a acetonitrile-aqueous buffer mixtures. Among tested anions: F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, NO₃⁻, CN⁻, HSO₄⁻, AcO⁻ and H₂PO₄⁻ only F⁻ induced a remarkable red-shift (149 nm) in the absorption spectrum concomitant with a color colorless to pink. This probe provides a new approach for naked-eyed detection of F⁻ and the detection limit was calculated to be 1.7 μM. Besides, a concomitant fluorescence decrease was also observed. These results demonstrated that the probe could detect F⁻ with an excellent sensitivity and selectivity in complicated samples.

Introduction

In recent years, anions sensing has drawn much attention from chemical and biological scientists and turned into a significant target in the field of analytical chemistry, because of their fundamental roles in daily life.¹⁻⁴ Fluoride ion, regarded as one of the most important anions, is widely used as an essential additive in toothpaste and even in drinking water due to its ability to prevent tooth decay.⁵ However, high level of fluoride ion in drinking water can lead to serious disease, for example, dental and skeletal fluorosis, gastric and kidney disorders, nephrotoxic changes and osteosarcoma.⁶⁻⁸ Hence, various approaches for detecting fluoride have been developed, such as electrochemical method,⁹⁻¹¹ ¹⁹F NMR analysis,¹² colorimetric¹³⁻²² and fluorescence sensing.²³⁻³² Among them, colorimetric and fluorescence sensors have attracted much more attention owing to their divers advantages over the other methods, such as high sensitivity, “naked-eye” detection convenience and on need of expensive equipment.

Although many colorimetric and fluorescent sensors for anion detection have been reported in the past decades, development of sensors for fluoride detection is still challenging, because of complicated procedure to synthesize,³³⁻³⁴ low sensitivity³⁵ and low feasibility in water-containing systems.³⁶⁻³⁷ Indeed, some sensors based on hydrogen-bonding interactions can only detect fluoride in organic solvents.³⁸⁻³⁹ To overcome these shortcomings, a strategy based on selective reaction between fluoride and silicon-oxygen

bond was developed. In this strategy, *tert*-butyl dimethylsilyl (TBDMS) and *tert*-butyldiphenylsilyl (TBDPS) were proved to be the best groups to be connected to the fluorescent molecules through a Si-O bond, which can only be selectively cleaved by fluoride catalysed hydrolysis. This cleavage could result in a remarkable spectral change depending on the concentration of F⁻, as first pioneered by Kim and Swager,⁴⁰ who reported a fluoride-sensing system in which fluoride induced the silicon-oxygen bond cleavage and formed a highly fluorescent coumarin derivative. Subsequently, several groups developed different chemodosimeters that can detect fluoride efficiently. However some of them were only work efficiently in organic solvent and need complicated organic synthesis.⁴¹

In this work, we tried to address the above-mentioned problems by developing a novel probe **3**, easily synthesized (Scheme 1) and applicable for fluoride detection in acetonitrile-aqueous water buffer mixtures with a low detection limit.

Benzothiadiazole derivatives are well-known due to their excellent optical-electronic properties, such as red light emission, high fluorescent yield, good photostability, large Stokes shift and large extinction coefficient. It was selected as the signal reporting site in probe **3**⁴² and Si-O bond was chosen as the reaction site for its high selectivity toward F⁻. To the best of our knowledge, it is the first probe in which a benzothiadiazole derivative is used to detect F⁻ with colorimetric response.

Results and discussion

Synthesis of probe 3

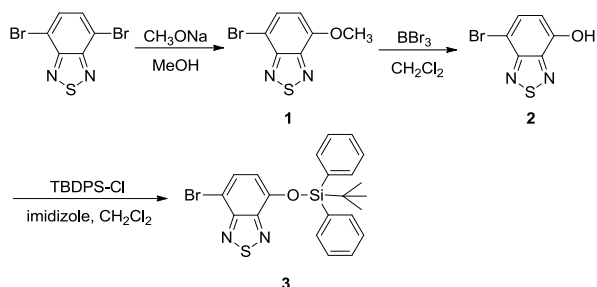
Synthesis of probe **3** was illustrated in Scheme 1. 4,7-dibromo-1,2,3-benzothiadiazole was treated with sodium methylate in methanol under reflux overnight to give the mono substituted compound **1** in 75% yield. Removal of the methyl group using a solution of BBr₃ in dichloromethane (1 M) at room temperature overnight led to 4-bromo-7-hydroxy-1,2,3-benzothiadiazole **2** in 80% yield. 4-bromo-7-((*tert*-butyldiphenylsilyl)-oxy)-1,2,3-benzothiadiazole

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ole **3** was prepared in 90% yield by treating the compound **2** with *tert*-butylchlorodiphenylsilane and imidazole in dichloromethane at room temperature for 3 h.



Scheme 1. synthesis of fluorescent probe **3**

Spectroscopic investigation of fluoride detection by probe **3**

In order to examine whether probe **3** can work in a water containing solution for fluoride detection, the absorption and fluorescence properties of probe **3** (10 μM) in the presence of F^- were investigated in a mixture of acetonitrile and Tris-HCl buffer ($v/v = 9:1$, $\text{pH} = 7.5$). As shown in Fig. 1, the maximum absorption band of **3** is at 370 nm. Incremental addition of F^- led to a progressive decrease of the absorption at 370 nm decreased ($A_{370\text{ nm}}$), while a new absorbance band appeared around 519 nm and the absorption at 519 nm increased. The $A_{519\text{ nm}}/A_{370\text{ nm}}$ ratio varied in function of the fluoride concentration and reached a plateau when 5 equiv. of F^- was used. The solution color changed from colorless to pink, owing to the cleavage of Si-O bond. As a consequence, compound **3** could be used as a "naked-eye" probe for detecting F^- . Moreover, there is a good linear relationship between the absorption value at 519 nm and the concentration of F^- in the range from 2.5 to 30 μM (Fig. 2). The linear equation is $y = 860.12x - 0.00136$, where x is the concentration of F^- and y is the absorption intensity at 519 nm. The coefficient of determination R^2 is 0.9960. The detecting limit for F^- was calculated to be 1.7 μM (Supporting Information).

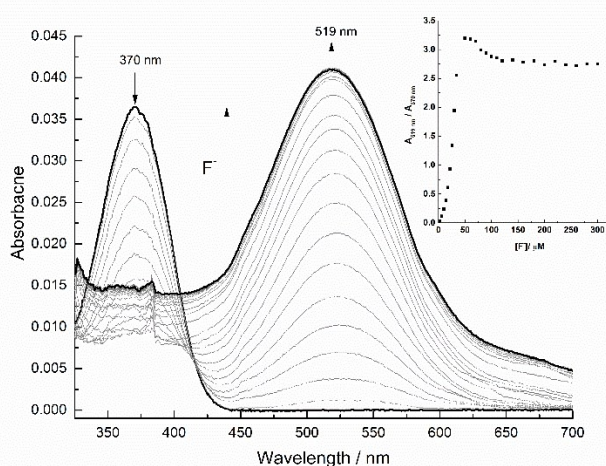


Fig. 1 Absorbance spectra of **3** (10 μM) in a mixture of acetonitrile and Tris-HCl buffer ($v/v = 9:1$, $\text{pH} = 7.5$) in function of fluoride concentrations; Inset: the absorption intensity ratio ($A_{519\text{ nm}} / A_{370\text{ nm}}$) versus concentration of fluoride.

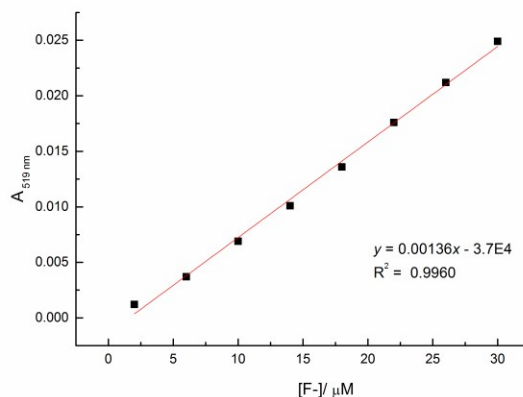


Fig. 2 Linear relationship between the absorption intensity at 519 nm and the fluoride concentrations (from 2.5 to 30 μM).

The fluorescence response of probe **3** (10 μM) towards F^- was also studied. As shown in Fig. 3, probe **3** has a maximum emission band at 493 nm upon excitation at 370 nm. Its fluorescence intensity decreased upon incremental addition of F^- and reached saturation upon addition of 50 μM F^- . The fluorescence intensity also exhibited a linear relationship with the concentrations of F^- in the range from 5 to 30 μM . The linear equation is $y = -2.5E4x + 1.112$, where x is the concentration of F^- and y is the fluorescent intensity at 493 nm. The coefficient of determination R^2 is 0.9915 (Supporting Information).

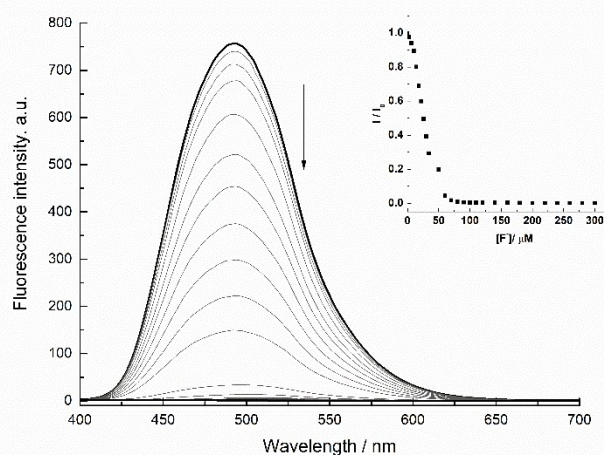


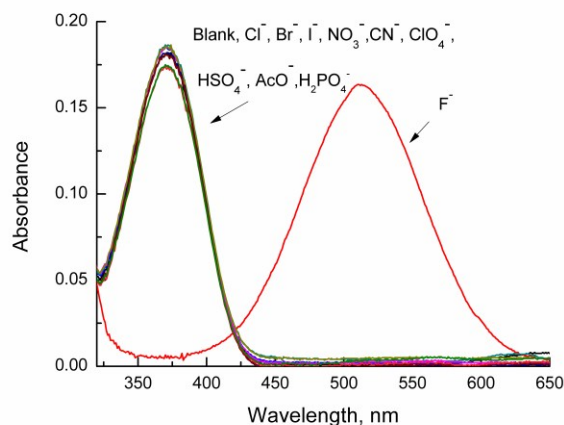
Fig. 3 The fluorescence spectra of probe **3** (10 μM) in function of fluoride concentrations (from 2.5 and 300 μM) in a mixture of acetonitrile and Tris-HCl buffer ($v/v = 9:1$, $\text{pH} = 7.5$); The excitation wavelength is 370 nm and the emission wavelength is 493 nm.

Selectivity

In addition to the sensitivity study, the selectivity of probe **3** (10 μM) towards F^- was also investigated. As shown in Fig. 4a, among the tested anions (F^- , Cl^- , Br^- , I^- , NO_3^- , CN^- , ClO_4^- , HSO_4^- , AcO^- and H_2PO_4^-), only addition of F^- induced the absorption band of probe **3** around 370 nm decreased, meanwhile a new absorption band around 519 nm appeared. Other anions lead to unchanged absorption responses.

More over, a addition of the same amount of each anions, respectively, just F⁻ resulted in an obvious color change from colorless to pink, which can be observed by the "naked-eye" (Fig. 4b). In addition, fluorescence responses of probe 3 (10 μM) to all anions mentioned above were also researched (Fig. 5a). Similar phenomenon to absorption spectra was observed, upon addition of each anions, respectively, only F⁻ lead to fluorescence quenching completely (Fig. 5b), some anions induced a slight fluorescence decreased. All the results show that probe 3 has a high selectivity to F⁻.

a

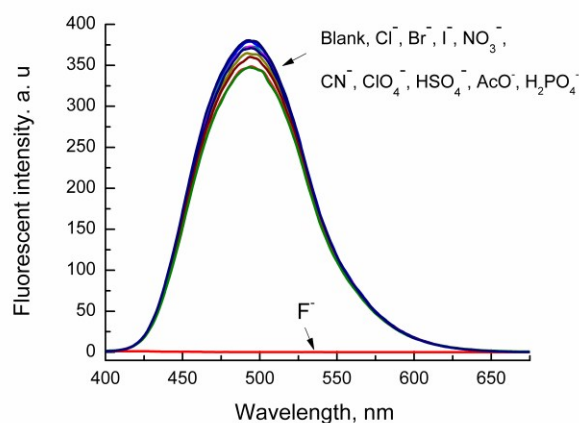


b



Fig. 4 (a) The absorption spectra and (b) color changes of probe 3 (10 μM) in the mixture of acetonitrile and Tris-HCl buffer (v/v = 9:1, pH = 7.5) after a addition of 200 μM different anions in the form of TBA⁺ salt at 25 °C. From left to right: probe 3, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, CN⁻, ClO₄⁻, HSO₄⁻, AcO⁻ and H₂PO₄⁻.

a



b

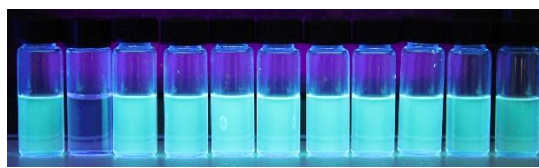


Fig. 5 (a) The fluorescence spectra and (b) color changes of probe 3 (10 μM) in the mixture of acetonitrile and Tris-HCl buffer (v/v = 9:1, pH = 7.5) after a addition of 200 μM different anions in the form of TBA⁺ salt at 25 °C.

Competition studies

To test the ability of probe 3 to detect F⁻ in a complicated environment, the competition experiment was carried out. As shown in Fig. 6, addition of various interfering anions, including Cl⁻, Br⁻, I⁻, NO₃⁻, CN⁻, ClO₄⁻, HSO₄⁻, AcO⁻ and H₂PO₄⁻ (100 μM) into the probe 3 (10 μM) solution, didn't induce any significant fluorescence decrease as compared to the blank sample. However, a total quenching of fluorescence was observed in all the interfering samples when F⁻ (50 μM) was added into them. This demonstrated the excellent selectivity of the actual approach for fluoride detection over the other anions.

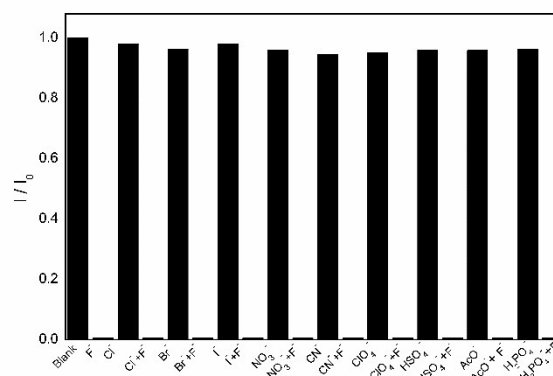


Fig.6 Fluorescence responses of probe 3 (10 μM) to various anions (100 μM) (Cl⁻, Br⁻, I⁻, NO₃⁻, CN⁻, ClO₄⁻, HSO₄⁻, AcO⁻ and H₂PO₄⁻) with and without F⁻ (50 μM) in the mixture of acetonitrile and Tris-HCl buffer (v/v = 9:1, pH = 7.5).

Mechanism studies

In order to confirm that the changes in the absorption and the fluorescence spectra of probe 3 induced by a addition of F⁻ are owing to the F⁻-assisted cleavage of Si-O bond and the probe 3 is transformed into 4-bromo-1,2,3-benzothiadiazole-7-olate, a ¹H NMR titration experiment was carried out in CD₃CN. As shown in Fig. 7, addition of 0.2 eq. F⁻ induced the protons 1 and 2 of probe 3 were shifted to downfield, while with the increasing amount of fluoride, the protons 1' and 2' were moved to the right. This indicates that,

addition of fluoride led to cleavage of Si-O to form 4-bromo-1,2,3-benzothiadiazole-7-olate concomitant with a decrease of the electron density of benzothiadiazole. Then, the increasing amount of TBAF·3H₂O resulted in the protonation of oxygen ion, the protons 1' and 2' were moved to the right, consequently.

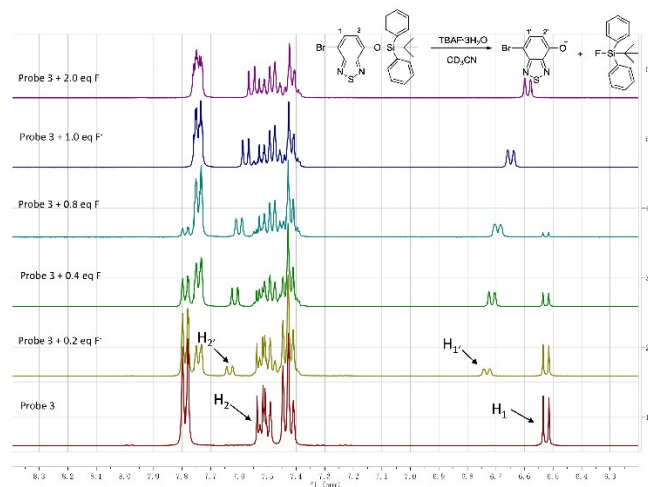


Fig. 7 The ¹H NMR spectra of probe **3** in CD₃CN in the presence of incremental amounts of fluoride from 0.2 and 2 equivalent.

Experimental section

Reagents and chemicals

4,7-Dibromobenzo[*c*]-1,2,5-thiadiazole, sodium methanolate, boron tribromide solution (1 M in CH₂Cl₂), *tert*-butylchlorodiphenylsilane, imidazole and all of tetrabutylammonium (TBA⁺) salts were supplied by Sigma-Aldrich without further purification. Organic solvents were purchased from Aladdin (Shanghai, China). Distilled water was used in all experiments. Reactions were monitored by TLC. Chromatography separations were executed using silica gel (200-300 mesh).

Apparatus

¹H NMR, ¹³C NMR spectra were collected on a Bruker Advance 400 MHz spectrometer. MS spectra were recorded on a Bruker amaZon SL instrument using standard conditions (ESI). UV-vis spectra were recorded on a Perkin Elmer Lambda 25 spectrometer. Fluorescence measurements were performed on a Perkin Elmer LS 55 spectrometer.

General method

Stock solutions of the anions of F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, NO₃⁻, CN⁻, HSO₄⁻, AcO⁻, H₂PO₄⁻ (10 mM) and probe **3** (1 mM) were prepared in acetonitrile. Test solution were used by diluting stock solution by acetonitrile and Tris-HCl buffer solution (9:1, V/V). All UV-vis and fluorescence spectra were recorded at room temperature in a 1.0 cm quartz cell.

Synthesis of probe

Synthesis of compound **1** (4-bromo-7-methoxy-1,2,3-

benzothiadiazole) 4,7-dibromo-1,2,3-benzothiadiazole (1 g, 3.4 mmol) and sodium methanolate (5.5 g, 10.2 mmol) were added to 30 mL methanol. After refluxing in a nitrogen atmosphere for 10 h, the solvent was removed under vacuum. Purification by column chromatography (CH₂Cl₂/petroleum ether: 1/5) gave compound **1** as yellow solid (0.8 g, 75% yield). m.p. 141.3 °C; ¹H NMR (400 MHz, CDCl₃) 7.75 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 4.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 154.11, 151.20, 147.77, 132.47, 106.37, 104.38, 56.43;

Synthesis of compound **2 (4-bromo-7-hydroxy-1,2,3-benzothiadiazole)** To a solution of compound **1** (0.5 g, 2.0 mmol) in dry CH₂Cl₂ (10 mL) was added BBr₃ (4 mL, 1M in CH₂Cl₂) slowly by syringe at 0 °C. The mixture was stirred at room temperature overnight. After the completion of reaction, 10 mL H₂O was added, then extracted with CH₂Cl₂ (2×10 mL). The combined organic layers were dried over MgSO₄, evaporated, then purified by column chromatography (CH₂Cl₂/petroleum ether: 1/1) to give compound **2** as a yellow solid in 80% yield. m.p. 168.7 °C ¹H NMR (400 MHz, CDCl₃) 7.75 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.50 (s, 1H, OH); ¹³C NMR (100 MHz, CDCl₃) 153.57, 147.34, 146.95, 133.25, 110.48, 103.68; HRMS: calculated for [M-H⁺]: 228.9071, measured: 228.9091.

Synthesis of compound **3 (4-bromo-7-((*tert*-butyldiphenylsilyl)-oxy)-1,2,3-benzothiadiazole)** To a solution of compound **2** (0.3 g, 1.3 mmol) in dry CH₂Cl₂ was added *tert*-butylchlorodiphenylsilane (0.5 mL, 1.95 mmol) and imidazole (132 mg, 1.95 mmol). The mixture was stirred overnight at room temperature. After the completion of reaction, removed the solvent under the vacuum condition. The crude product was purified by column chromatography (CH₂Cl₂/petroleum ether: 1/5) to give compound **3** as a light yellow solid in 90% yield. m.p. 121.5 °C ¹H NMR (400 MHz, CDCl₃) 7.75-7.74 (m, 4H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.43-7.36 (m, 6H), 6.38 (s, d, *J* = 7.8 Hz, 1H), 1.20 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 154.29, 149.82, 147.15, 132.45, 132.46, 131.68, 130.31, 127.97, 115.38, 104.77, 26.46, 19.74. HRMS: calculated for [M+Na⁺]: 491.0225, measured: 491.0240.

Conclusions

In conclusion, a high selective and colorimetric probe **3** for F⁻ detection was designed and synthesized in a quite simple route. This original probe works well in a mixture of acetonitrile and Tris-HCl buffer (v/v = 9:1, pH = 7.5) based on internal charge transfer mechanism, using Si-O bond as receptor of F⁻. Among the tested anions, only F⁻ could lead to a 149 nm red shift from 370 to 519 nm in absorption spectra and the solution color changes from colorless to pink with a low detection limit (1.7 μM). Furthermore, a concomitant fluorescence quenching of probe **3** was observed by addition of F⁻ without interference of other anions. All these results provide strong evidence that this probe represents attractive characters and may be useful for detecting F⁻ in environment applications.

Acknowledgements

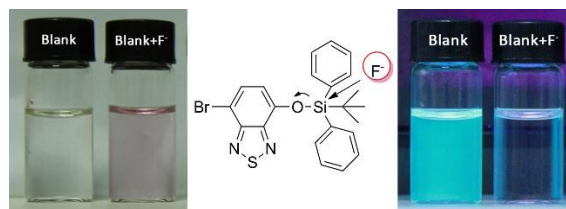
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Graphical Abstract

A novel colorimetric and fluorescent probe based on benzothiadiazole derivative was designed and synthesized, which showed excellent selectivity for fluoride.

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