A New Fluoride Chemodosimeter Based On 3-Ether-Substituted 1, 8-Naphthalimide Derivatives

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Research Article

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Abstract

We developed a new chromogenic and fluorescent "off–on" 1,8-naphthalimide-derived chemosensor **1** based on an F^- -triggered desilylation reaction. It showed significant variations in UV/Visible absorption (510 nm) and fluorescence emission wavelength (570 nm) for selective detection of fluorides in tetrahydrofuran. Moreover, chemodosimeter **1**-loaded test strips were successfully fabricated to detect fluorides efficiently.

Research Highlights

1. A new sensor based on an F^- -triggered desilylation reaction
2. The test strips loaded probe **1** exhibited efficiently detection of fluorides with significant changes in fluorescence.

Introduction

Fluoride ions widely exist in the nature and organisms, and play an extremely important role in the metabolic process of organisms. It is widely used in dental treatment, disease surveillance, and drinking water health control^[1–4]. Excessive fluoride ions leakage not only pollute the environment, but also cause irreversible harm to physiological condition, such as dental fluorosis, skeletal fluorosis, the acute reaction of gastrointestinal, and nephrotoxic lesions^[5–6]. Therefore, the development of new chemodosimeter to detect fluoride ions has attracted wide attention.

Among various fluorine ion detection technologies, the fluorescence method has been widely used in food detection, environmental monitoring, cell imaging, and other fields due to its high selectivity, rapid response, and strong anti-interference. Many sensor systems for fluoride detection have been developed to date for the detection of fluoride ions, including metal ion coordination^[7–8], Lewis acid base^[9–10], hydrogen bond^[11–15], and silicon-carbon bond cleavage^[16–17] sensing mechanisms.

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The fluorescent sensor based on fluoride-induced desilylation reaction has attracted much attention. Especially, those fluorophore have been investigated extensively such as the skeleton of BODIPY, coumarin, and 1,8-naphthalimide derivatives^[18–20]. However, in contrast to those probes for detection of fluoride, the chemodosimeter based on fluoride-induced desilylation reaction showing long wavelength response is limited (TableS1)^[21–24]. In view of fluorescent probes with long emission wavelength have low light damage, low self-fluorescence as well as the better deep tissue penetration^[25–28], it is very important to develop a new fluorescent chemodosimeter with the advantage of potential longer emission wavelength triggered by fluorine-induced desilylation reaction.

1,8-naphthalimide fluorophore has a rigid planar skeleton and a large π -conjugated system, which can be used as a good chromophore. One particularly intriguing approach is based on the construction of a donor-acceptor-type skeleton that introduces the binding site such as OH or NH group in the 4-position of 1, 8-naphthalimide derivatives. However, the 3-substituted 1, 8-naphthalimide derivatives as sensor are less investigated. Here, we reported a new colorimetric and fluorescent chemodosimeter **1** coupled with 4-(*tert*-butyldiphenylsilyloxy)benzylbromide (**3**) and 3-hydroxy-4-cyano-1,8-naphthalimide (**2**). The chemodosimeter showed significant color and fluorescent changes, highly selectivity and long wavelength response through the classical fluoride-induced desilylation reaction.

Experimental

General information

Unless otherwise noted, solvents and reagents were choosed and purchased from commercial channels. They were analytical reagents that can be directly used. The column chromatography using silica gel (200–300 sights) was performed. The intermediate **2** was synthesized according to the reported literature. We used SHIMADZU UV-1800 spectrophotometer to determine UV-visible absorption spectra. We used the Hitach F-4600 Fluorescence spectrophotometer to determine the fluorescence emission spectra. We used Bruker AVANCE III instrument to obtain the ^1H NMR and ^{13}C NMR spectra. Mass spectra analyses were performed on SolanX 70 FT-MS electrospray ionization high-resolution mass spectra.

Synthesis of probe 1

The synthesis of target chemodosimeter **1** is shown in Scheme 1. The intermediates 3-hydroxy-4-cyano-1,8-naphthaleneimide (**2**) and 4-(*tert*-Butyldiphenylsilyloxy)benzylbromide (**3**) were synthesized according to the literature^[29–30]. To a solution of 3-hydroxy- 4-cyano-1, 8-naphthaleneimide (**2**, 0.20 g, 0.68 mmol) in CH_3CN (20 mL) was added 3.0 equiv. of potassium carbonate (0.28 g, 2.04 mmol), and the mixture was stirred at 50 °C for 1 h. After adding 3.0 equiv. of 4-(*tert*-Butyldiphenylsilyloxy)benzylbromide (**3**, 0.87 g, 2.04 mmol), then the mixture was further refluxed for 24 h. After cooling of the reaction mixture, the residue was poured into dilute hydrochloric acid, and then extracted with ethyl acetate (20 mL×3), then the organic layer was further washed with brine, then dried with Na_2SO_4 and filtered. After the removal of solvent in vacuo, the residue was purified by chromatography (PE:EA = 10:1) to afford the probe **1** (0.21 g, 48%) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 8.51 (d, J = 7.0 Hz, 1 H), 8.40 (d, J = 8.5 Hz, 1 H), 8.34 (s, 1 H), 7.88 (t, J = 8.0 Hz, 1 H), 7.70 (d, J = 7.0 Hz, 4 H), 7.41 (t, J = 7.0 Hz, 2 H), 7.36 (t, J = 7.0 Hz, 4 H), 7.24 (s, 2 H), 6.80 (d, J = 8.0 Hz, 2 H), 5.34 (s, 2 H), 4.16 (t, J = 7.5 Hz, 2 H), 1.72–1.66 (m, 2 H), 1.09 (s, 9 H), 0.98 (t, J = 7.5 Hz, 3 H), 0.89 – 0.82 (m, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.3, 162.8, 160.8, 156.1, 135.6, 132.7, 132.7, 130.1, 123.0, 129.9, 129.9, 129.8, 128.9, 127.9, 127.8, 127.6, 127.2, 123.0, 122.9, 120.2, 119.8, 117.3, 114.2, 101.4, 71.8, 40.7, 30.2, 27.0, 26.6, 20.4, 19.5, 13.9; HRMS-ESI (m/z): $[\text{M} + \text{H}]^+$ Calcd. for ($\text{C}_{40}\text{H}_{38}\text{N}_2\text{O}_4\text{Si}$): 639.2674; Found:639.2680.

Results And Discussion

Sensing property of probe 1 for fluoride ions

Initially, the selectivity of chemodosimeter **1** was evaluated by measuring the changes of absorption spectra after the addition of different anions (Fig. 1). Only the addition of fluoride ions (1.8 equiv., TBAF), the new absorption peak at 510 nm was increased followed by the unique color change from colorless to yellow, indicating that fluoride-induced desilylation reaction takes place and the potential 3-hydroxy-4-cyano-1,8-naphthaleneimide was produced. However, the introduction of other anions, such as CN^- , AcO^- , H_2PO_4^- , I^- , Cl^- , NO_3^- , HSO_4^- , ClO_4^- , BF_4^- , Br^- , SCN^- , S^{2-} , GSH , OH^- ions (as their TBA salts) did not result in significant difference in color change, indicating the chemodosimeter **1** has the high selectivity for F^- . Next, with further increase of fluoride ion concentration, a significant color change from colorless to yellow was observed (Fig. 2, inset), and followed by the absorption peak at 345 and 390 nm decreases and a remarkable increase of new peaks at 273 and 510 nm. Three isotonic points appeared at 320 nm, 356 nm and 410 nm in THF (Fig. 2). In order to demonstrate the application of chemodosimeter **1** in water-containing conditions, similar UV-vis titrations were carried out in THF/ H_2O system (Fig. S5), and similar spectral responses were generated, but in the presence of excessive fluoride ions. It indicates that probe **1** is less effective in aqueous environments.

The most significant changes were observed in fluorescence titration studies. Upon excitation at 410 nm in THF, with the addition of F^- , probe **1** showed strong emission at 570 nm (Fig. 3). However, the introduction of other anions, such as F^- , CN^- , AcO^- , H_2PO_4^- , I^- , Cl^- , NO_3^- , HSO_4^- , ClO_4^- , BF_4^- , Br^- , OH^- ions (as their TBA salt), did result in no change in the emission intensity of probe **1** (Fig. 4). The unique orange fluorescence emission induced by fluorides was observed, which further showed the excellent selectivity of probe **1** for fluoride ions. In addition, this selectivity of probe **1** was further confirmed by competitive experiments (Fig. 5). The unique absorption and fluorescence bands produced by adding fluoride ions were not affected by other existing anions (including CN^- , AcO^- , H_2PO_4^- , I^- , Cl^- , NO_3^- , HSO_4^- , ClO_4^- , BF_4^- , Br^- , OH^-). The fluorescence detection limit of probe **1** was further determined to be $1.16 \mu\text{M}$ (Fig. S6).

In addition, to further demonstrate the practicability of this sensor, the test paper was prepared by immersing the test paper into THF solution of **1** (1.0 mM) and drying them in air. As shown in Fig. 6, the probe **1**-loaded test paper can be used as a 'life monitor' to detect F^- in the solution with significant color changes in fluorescence. This application provides a strong basis for further development of sensors similar to 'life monitor' method.

Possible reaction mechanism of probe 1 with fluoride ions

In order to confirm the sensing mechanism, the titration reaction of chemodosimeter **1** with F^- was analyzed by ^1H NMR spectra. ^1H NMR spectra confirmed that compound **2** was obtained by treating compound **1** with fluoride ions (Fig. S8). The results showed that compound **1** could react with fluoride

ions to generate the compound **2** by the classical desilylation reaction (Scheme 2). Therefore, a new colorimetric and fluorescent 3-hydroxy-4-cyano-1,8-naphthaleneimide-based probe **1** by the fluorine-triggered desilylation reaction was developed for the first time.

Conclusion

In general, a new and simply chemosensor **1** based on fluorine-triggered desilylation reaction was described, and the mechanism involving the cascade release reaction to obtain the fluorophore of 3-hydroxy-4-cyano-1,8-naphthaleneimide were studied. The probe **1** was shown excellent selectivity and sensibility to fluoride ions with significant dual changes in UV/vis and fluorescence spectra in aqueous THF solution. Significantly, the probe **1**-based test strips was successfully prepared and exhibited efficiently detection of fluorides with significant changes in fluorescence. Further work on this framework with 3-hydroxy-4-cyano-1,8-naphthaleneimide working in the aqueous solution is expected to yield novel fluoride-sensing probe with practical utility.

Declarations

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Author Contributions

All authors contributed to the study conception and design. Xi Chen carried out the experiments, Haibin Shao, Tingting Zhu, Zhihua Chen and Yan Hu conducted the data analyses, Hua Zhang and Chuanxiang Liu wrote and edited the paper.

Data Availability

Not applicable.

Code Availability

Not applicable.

Author information

Consent to Participate

Not Applicable.

Consent for Publication

Not Applicable.

Conflicts of interest

There are no conflicts of interest to declare.

Ethics Approval

Not Applicable.

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Figures

Figure 1

Absorption spectra responses of probe 1 (20 μ M) in THF with various anions (ca. 1.8 equiv.) (Inset: color changes of 1 from left to right: probe 1 only, F^- , CN^- , AcO^- , $H_2PO_4^-$, I^- , Cl^- , NO_3^- , HSO_4^- , ClO_4^- , BF_4^- , Br^- , SCN^- , S^{2-} , GSH , OH^-).

Figure 2

UV-visible titration of probe 1 (20 μM) with TBAF (5 mM, 0 to 1.8 equiv.) in THF. Inset: color change and plot of absorption changes at 390 and 510 nm versus TBAF.

Figure 3

Emission spectra of probe 1 (20 μM , $\lambda_{\text{ex}} = 410 \text{ nm}$) with TBAF (0 to 1.6 equiv.) in THF. The inset shows the fluorescence intensity at 570 nm as a function of TBAF concentrations.

Figure 4

Relative fluorescence changes of probe 1 (20 μ M) after treatment with 1.6 equiv. of TBA salt of various anions in THF at λ_{ex} =410 nm (from left to right: only probe 1, F⁻, CN⁻, AcO⁻, H₂PO₄⁻, I⁻, Cl⁻, NO₃⁻, HSO₄⁻, ClO₄⁻, BF₄⁻, Br⁻, OH⁻ ions)

Figure 5

Interference response of probe 1 (20 μ M) for F⁻ in the presence of other anions (1.6 equiv.). The black bars represent the emission at 570 nm of probe 1 in the presence of 1.6 equiv. of the other anion (from 1

to 11: CN^- , AcO^- , H_2PO_4^- , I^- , Cl^- , NO_3^- , HSO_4^- , ClO_4^- , BF_4^- , Br^- , OH^-). The red bars show the change that occurs upon subsequent addition of 1.6 equiv. of F^- to the solution containing probe 1

Figure 6

The changes of the probe 1-loaded test papers (1.0 mM) with F^- ; use hand-held UV lamp to irradiate the test strips at 365 nm.

Supplementary Files

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