A Simple Water-Soluble ESIPT Fluorescent Probe for Fluoride Ion with Large Stokes Shift in Living Cells

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ABSTRACT: Developing an effective method for monitoring fluoride ion in biological samples is meaningful because fluoride ion plays a vital role in biological processes. In this contribution, a simple water-soluble ESIPT fluorescent probe 2-(4-((tert-butyldiphenylsilyl)oxy)-1,3-dioxoisoinolin-2-yl)methyl)-1-ethyl-pyrindin-1-ium iodide (SPI) was constructed for monitoring fluoride ion. The probe SPI containing pyridinium salt group exhibited preeminent water solubility. The probe SPI introducing a trimethylphenylsilyl ether recognition group displayed excellent selectivity for fluoride ion over other biologically relevant species. Additionally, the probe SPI exhibited a fast response for a fluoride ion, suggesting that it could provide real-time fluoride ion detection. Importantly, the probe could detect fluoride ion with a linear range of 0–70.0 × 10⁻⁶ M and a low detection limit of 1.16 × 10⁻⁶ M. Furthermore, probe SPI could detect fluoride ion with a large Stokes shift (98 nm), which was attributed to ESIPT fluorescence sensing process. At last, probe SPI was successfully employed to monitor fluoride ion in living cells.

1. INTRODUCTION

As the smallest anion, fluoride ion (F⁻) is an indispensable and important anion in the treatment of osteoporosis and dental health. It is widely used as an additive in pharmaceutical agents, toothpaste, and drinking water. However, excessive ingestion can cause skeletal fluorosis, dental, nephrolithiasis, osteosarcoma, and metabolic dysfunctions. The detection of fluoride ion is particularly meaningful in environmental samples and biological systems. To date, several methods for detecting fluoride ion have been developed, such as spectrophotometry, electrochemical method, ¹³⁵⁵F NMR, high-performance liquid chromatography (HPLC), and ion chromatography. Even though the above detection techniques could monitor fluoride ion with excellent selectivity and sensitivity, they were not suitable for living biosystems owing to the need for destruction of cells or tissues. In contrast, fluorescent probes are recognized as ideal tools for the detection of fluoride ion by taking advantage of their high spatiotemporal resolution, real-time imaging capacity, non-destructive detection, and simplicity, which have attracted a lot of attention. Currently, a lot of fluorescent probes for fluoride ion have been fabricated, such as using the H-bond interactions, the interactions between F⁻ and Lewis acids, and Si–O bond cleavage. However, for probes based on the first two mechanisms, they suffered from unsatisfactory selectivity or irreversibility. Although desilylation-based probes for fluoride ion could overcome the above disadvantages, most of them could only need a high level of organic solvents or monitor tetrabutylammonium fluoride in organic solvents. Additionally, most of these reported had long reaction time or required cationic surfactant, cetyltrimethylammonium bromide (CTAB), to increase the reaction rate, which greatly restricted their practical application. Moreover, most of the fluoride ion fluorescent probes were developed with a small Stokes shift. The probes with a small Stokes shift was difficult to use for quantitative determination due to the interference of excitation light and self-absorption of fluorescence. Therefore, high specificity, fast response, and water-soluble fluorescent probes with large Stokes shifts are urgently required for fluoride ion.

As an ESIPT fluorophore, 3-hydroxypythalimide derivatives have attracted attention owing to their characteristics including simple structure, good photostability, extremely facile chemical modification, and large Stokes shift. Herein, we synthesized a new ESIPT-based fluorescent probe for fluoride ion in which 4-hydroxy-2-(pyridin-2-ylmethyl)isoindoline-1,3-dione was utilized as the fluorophore and a trimethylphenylsilyl ether was used as the recognition group (Scheme 1). The trimethylphenylsilyl ether was selected as a recognition unit of fluoride ion due to its high specificity for fluoride ion. The introduction of pyridinium salt could not only achieve fast reaction rate but also enhance the solubility in water. The probe 2-(4-((tert-
butyldiphenylsilyl)oxy)-1,3-dioxoisodolin-2-yl)methyl)-1-ethylpyridin-1-ium iodide (SPI) was a weak fluorescent, in which the protection of hydroxyl group with trimethyldiphenylsilyl ether blocked the ESIPT process. However, fluoride ion could cleave the trimethyldiphenylsilyl ether group, releasing the fluorophore; thus, the fluorescence appeared. The probe SPI displayed many advantages including high selectivity, fast response, excellent water solubility, and large Stokes shift. Moreover, the probe SPI could be used for fluoride ion imaging in living cells.

2. RESULTS AND DISCUSSION

2.1. Spectral Properties of SPI to F\(^-\). To demonstrate the capability of SPI for F\(^-\), the spectra of SPI (10 \(\mu\)M) to F\(^-\) were examined in phosphate-buffered saline (PBS) solution (20 mM, pH 7.4, containing 1% CH\(_3\)CN).

Figure 1. (a) Fluorescence emission spectra of SPI (10.0 \(\mu\)M) upon the addition of concentrations of F\(^-\) in PBS solution (20 mM, pH 7.4). (b) Fluorescence emission of SPI at 511 nm versus increasing F\(^-\) concentrations F\(^-\) (0–70 \(\mu\)M) in PBS solution (20 mM, pH 7.4, containing 1% CH\(_3\)CN).

Figure 2. Fluorescence spectral (A) and intensity (B) changes of SPI (10 \(\mu\)M) with various analytes (250 \(\mu\)M) in PBS solution (20 mM, pH 7.4, containing 1% CH\(_3\)CN): (1) none, (2) F\(^-\), (3) Cl\(^-\), (4) Br\(^-\), (5) I\(^-\), (6) S\(^2-\), (7) AcO\(^-\), (8) SO\(_3\)\(^2-\), (9) SO\(_4\)\(^2-\), (10) CO\(_3\)\(^2-\), (11) NO\(_2\)\(^-\), (12) NO\(_3\)\(^-\), (13) HPO\(_4\)\(^2-\), (14) H\(_2\)PO\(_4\)\(^-\), (15) SCN\(^-\), and (16) ClO\(_3\)\(^-\).
fluorescence intensity of SPI at 511 nm gradually increased with the continuous addition of F− concentration (Figure 1). When 250.0 μM F− was added, the fluorescence intensity became saturated. Additionally, the fluorescence intensities at 511 nm had a linear relationship with the F− concentrations at 0–70.0 μM. The detection limitation of F− was calculated to be 1.16 × 10−8 M (3σ/k). More importantly, the probe SPI showed a large Stokes shift (98 nm). The results indicated that the probe SPI can monitor F− with excellent sensitivity.

2.2. Selectivity Studies. The specificity selectivity is of importance for the chemosensor. Thus, to demonstrate the selectivity of SPI, the fluorescence response of SPI for biologically relevant species (F−, Cl−, Br−, I−, S2−, AcO−, SO32−, SO42−, CO32−, NO3−, NO2−, HPO42−, H2PO4−, SCN, and ClO3−) was examined in PBS solution (20 mM, pH 7.4, containing 1% CH3CN). As presented in Figure 2, the fluorescence emission of SPI at 511 nm displayed dramatic enhancement upon the addition of F−. While the fluorescence intensities had weak changes in other analyses of species. The results indicated that SPI had high selectivity toward F− over other competitive species.

2.3. Response Time. Next, time-dependent fluorescence variation of SPI was investigated by monitoring the fluorescence intensities changes at 511 nm in the absence and the presence of F− in PBS solution (20 mM, pH 7.4, containing 1% CH3CN). As depicted in Figure 3, the probe SPI itself had no fluorescence change with the prolonging time. Meanwhile, with the addition of F−, the fluorescent intensity of the probe SPI at 511 nm increased immediately and reached a maximal at about 8 min. The results indicated that SPI can serve as a fast response to F−.

2.4. pH Effect Studies. As pH is a critical parameter for evaluating the application of performance, the pH dependence of the probe SPI was examined before and after the addition of F− in PBS solution (20 mM, pH 7.4, containing 1% CH3CN). As shown in Figure 4, the probe SPI displayed a weak fluorescence and retained the negligible changes in the pH range of 2−12, which indicated that the probe SPI was stable over a wide pH range. However, upon treatment with F−, the fluorescence intensities of the probe SPI at 511 nm significantly increased in the pH range 4−7 and remained stable in the pH range 7−10. The results suggested that the probe SPI can be used for biological detection.

Figure 4. Fluorescence intensity of SPI (10 μM) alone (a) and in the presence of F− (b) under different pH values.

2.5. Proposed Sensing Mechanism. To validate the reaction mechanism of SPI toward F−, the proposed product PI from the reaction of SPI with F− was obtained and analyzed by 1H NMR spectra. As shown in Figure S5, there was difference from the 1H NMR spectroscopy of SPI. The methyl of trimethylphénylsilyl ether disappeared at around 1.16 ppm and the hydroxyl peak appeared at around 11.25 ppm in the spectra, which verified the release of hydroxyl and the separation of trimethylphénylsilyl ether. In addition, the mixture of PID with the addition of F− by high-resolution mass spectrometry (HRMS) spectra was investigated. As depicted in Figure S6, a mass peak at m/z 283.1084 [M] was observed, which agreed well with PI (calcd m/z 283.1083 [M]+). Those results suggested that the trimethylphénylsilyl ether in SPI could be cleaved into the −OH group by F− and gave compound PI. The possible sensing mechanism is described in Scheme 1.

2.6. Cell Imaging. Next, we assessed the ability of SPI for the detection of F− by confocal fluorescence imaging. As shown in Figure S7, when SPI was incubated with the cells, no fluorescence was observed. However, the green fluorescence was observed when NaF was added. The results suggested that SPI can be applied to detect F− in living cells.

3. CONCLUSIONS

In summary, through the ESIPT process, we developed a simple water-soluble fluorescent probe toward fluoride ion by combining 4-hydroxy-2-(pyridin-2-ylmethyl)isoindoline-1,3-dione fluorophore and F− capturing group trimethylphénylsilyl ether together. In the absence of fluoride ion, the ESIPT process of the probe was blocked and displayed a weak emission. When the fluoride ion was present, the ESIPT process was recovered, which resulted in green fluorescence emission. Meanwhile, the probe had rapid response, high specificity and selectivity, a wide working pH range, and a large Stokes shift for the fluoride ion, which is suitable for detecting fluoride ion in the living cells.

4. EXPERIMENTAL SECTION

4.1. Materials and Instruments. 4-Hydroxyisobenzofuran-1,3-dione, trimethylphenyl chlorosilicon, iodoethane, and pyridin-2-ylmethanamine were purchased from Energy Chemical. The other chemicals were analytical grade and bought commercially. Fluorescence data were recorded on a Shimadzu RF-5301PC luminescence spectrometer. UV−vis spectra were obtained on a Shimadzu UV-2501PC spectrophotometer.
HRMS was performed with an Agilent 6210 ESI/TOF/MS instrument. The NMR data were acquired on a Bruker Ascend-400 instrument.

4.2. Synthesis of Probe SPI. A mixture of SP (0.49 g, 1.0 mmol) and iodoethane (0.2 mL) in anhydrous CH$_3$CN (5 mL) was stirred at 90 °C for 12 h. The mixture was filtered to give SPI (0.28 g, 67%) (Scheme 2). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 9.53 (d, 2H, J = 6.4 Hz), 8.02 (d, 2H, J = 6.4 Hz), 7.75–7.73 (m, 4H), 7.48–7.45 (m, 2H), 7.42–7.37 (m, 5H), 7.30 (d, 1H, J = 8.4 Hz), 6.71 (d, 1H, J = 8.4 Hz), 5.10 (s, 2H), 5.08–5.03 (m, 2H), 1.72 (s, 3H), 1.16 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 167.2, 165.6, 156.1, 153.6, 144.9, 136.1, 135.4, 133.3, 131.4, 130.5, 128.1, 126.9, 118.8, 116.8, 57.2, 40.3, 26.3, 19.7, 17.4. HRMS calc for C$_{33}$H$_{33}$N$_2$IO$_3$Si [M – I]$^+$ 521.2260, found 521.2229.

4.3. Cell Imaging. The HepG2 cells were seeded in a 96-well plate and cultured with a fresh medium for 24 h. The cells were loaded with SPI (10 μM) for 30 min at 37 °C, washed with PBS for three times, and imaged. The probe SPI (10 μM) was pretreated with HepG2 cells and co-incubated for another 3 h, incubated with F$^-$ for another 30 min, then the cells were washed with PBS for three times, and imaged. Confocal fluorescence images were collected by a Leica TCS SP8 confocal microscope.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02589. Spectroscopic data, NMR, and MS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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