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Colorimetric fluoride sensor based on 1,8-naphthalimide derivatives

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ABSTRACT

A colorimetric chemosensor **TBS-NA**, 4-(*tert*-butyldimethylsilyloxy)-N-butyl-naphthalimide was designed and synthesized. Addition of fluoride ion to a CH_3CN solution of **TBS-NA** can result in an obvious color change (from colorless to yellow) and UV–Vis absorption spectral change in a short time. This indicated that **TBS-NA** had highly selectivity for fluoride detection over other anions, such as Cl^-, Br^-, I^-, HSO_4^-, ClO_4^- and AcO^- in CH_3CN solutions, and the selectively detection was due to the selective cleavage of Si–O bond in **TBS-NA** by fluoride. The detection limit was calculated to be 0.59 μM.

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1. Introduction

Anions play an important role in numerous kinds of chemical and biological processes, and in recent years the design and development of synthetic receptors and sensors for the detection of anions have received considerable attention [1–11]. Among the anions, fluoride ion is one of the most important anions because of its role in prevention of dental caries and the treatment of osteoporosis [12–15]. However excess intake fluoride can cause many serious disease such as gastric and kidney disorders, skeletal fluorosis [16,17]. Thus, the development chemosensor for fluoride anion is of great importance for environment and human health care. Recently, considerable efforts have been devoted to fluoride ion sensing via UV–Vis, fluorescence, or other methods [18–22]. Colorimetric sensor is more attractive for naked-eye detection through a vivid color change.

The construction of a chemosensor may couple at least two units, the binding site and the signaling subunit, which may be covalently or non-covalently linked. Commonly, most binding site for sensing fluoride is N–H fragment, such as urea, thiourea, amide and pyrrole, which can react with fluoride through the formation of a hydrogen bond. However, oxygen-containing anions may be possible interferents [23] during the fluoride sensing. In 2003, Kim and Swager develop a new method for fluoride determination which can avoid the interference [24]. In their report, *tert*-Butyldimethylsilyl (TBS) ethers were chosen as receptors, because Si–O bond of the silyl ether could be selectively cleaved by fluoride ion. Based on this mechanism, Hong and coworkers [25] successfully demonstrated a Si–O band-based fluoride receptor detecting fluoride quantificationally. Zhu et al. [26] synthesized a cyanine dye, 1-ethyl-4-(p-*tert*-bytyldimethylsilane ether styryl) quinolinnium iodide, and determined fluoride ion by colorimetric method. And more recently, Akkaya et al. [27] reported two Bodipy derivatives with silyl-protected phenol, which could selectively sense fluoride via UV and fluorescence methods.

Though optical probes for fluoride based on the fluoride-ion-triggered Si–O bond cleavage mechanism have been reported, some disadvantages can be cited about these probes, such as low sensitivity, longer reaction time. Here we reported a 1,8-naphthalimide derivative **TBS-NA** for fluoride determination in this paper. The sensor exhibits a high selectivity for fluoride ion over other anions with absorbance red-shift in CH_3CN. The absorbance of **TBS-NA** at 474 nm increased linearly with the concentration of fluoride from 10 to 100 μM, and the detection limit was calculated to be 0.59 μM. 1,8-naphthalimide dye was chosen as a fluorophore due to its outstanding chemical, thermal and photochemical stability as well as its fluorescence quantum yield [28,29]. The synthesis of **TBS-NA** started from 4-bromo-1,8-naphthalic anhydride **1**, via N-alkylation, substitution and hydrolysis steps, compound **4** was produced. Then *tert*-butyldimethyllchlorosilane was coupled with compound **4** to afford the target sensor **TBS-NA** in 79% yield, as shown in Scheme 1.

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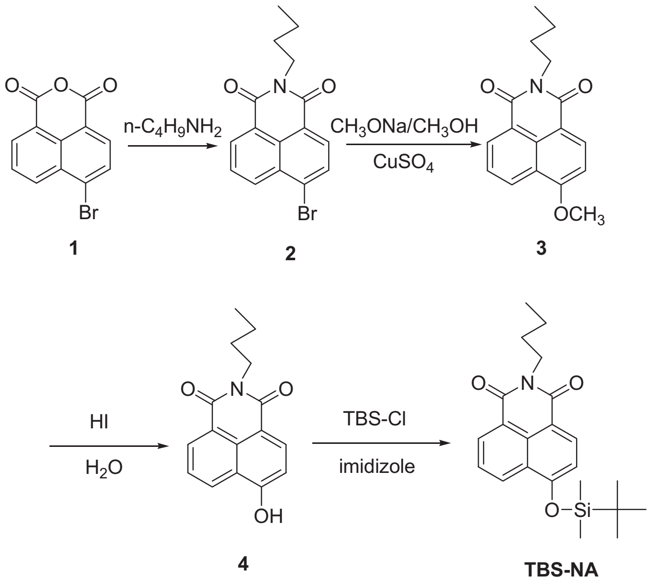


Scheme 1. The synthetic route of **TBS-NA**.

2. Materials and methods

2.1. Experimental

2.1.1. General

Unless otherwise noted, all chemicals were of analytical reagent grade obtained from commercial suppliers and used without further purification. Chloroform ($CHCl_3$) were refluxed with calcium hydride and distilled under atmospheric pressure. THF were refluxed with Na and distilled under atmospheric pressure. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from Qingdao Ocean Chemicals, China. The UV–Vis absorption spectra were measured by Shimadzu UV-2450 spectrophotometer at 25 °C. ^1H NMR spectra in $CDCl_3$ were recorded using Varian Unity Invoa-600 MHz spectrometer with chemical shifts reported as ppm (TMS as the internal standard).

2.2. Synthesis

2.2.1. Synthesis of 4-bromo-N-butyl-1,8-naphthalic anhydride **2**

A mixture of compound **1**(5 g, 18 mmol), 1-Aminobutane (1.7 g, 23.3 mmol) in 40 mL acetic acid was stirred under reflux in a nitrogen atmosphere for 6 h, After the completion of reaction, the reaction mixture was then poured into a mixture of cracked ice and water (200 mL) and filtered to get a pale yellow solid. The crude product was recrystallized from chlorobenzene to give 4.6 g light gray needles in a yield of 77%. Mp 109–110 °C. The product was used for next step directly.

2.2.2. Synthesis of 4-methoxy-N-butyl-1,8-naphthalimide **3**

A mixture of compound **2** (5.4 g, 16.3 mmol), CH_3ONa (7.0 g, 130 mmol) and $CuSO_4 \cdot 5H_2O$ (0.50 g, 2.0 mmol) in 50 mL CH_3OH were refluxed for 12 h. After the removal of the solvent and washing of the residue with water (30 mL × 3). Compound **3** was obtained as yellow needles in 89% yield. ^1H NMR ($CDC1_3$): $\delta = 0.95$(t, J = 7.2 Hz, 3H, $N-CH_2CH_2CH_2CH_3$), 1. 42 (m, 2H, $N-CH_2CH_2CH_2CH_3$), 1.70 (m, 2H, $N-CH_2CH_2CH_2CH_3$), 4.15(t, 2H, J = 7.8 Hz, $N-CH_2CH_2CH_2CH_3$), 4.11(s, 3H. $-OCH_3$), 7.02(d, J = 8.4 Hz, lH), 7.68(t, J = 7.8 Hz, 1H), 8.54(d, J = 7.8 Hz, 2H), 8.58(d, J = 7.2 Hz, 1H).

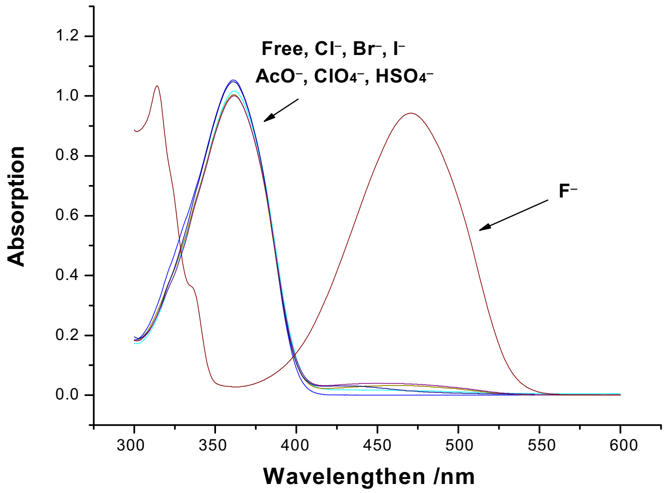


Fig. 1. UV–Vis absorption changes of compound 1(1×10^{-4} mol/L) upon addition of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, HSO_4^-, ClO_4^- and AcO^- (10 equiv) in CH_3CN.

2.2.3. Synthesis of 4-hydroxy-N-butyl-1,8-naphthalimide **4**

A mixture of compound **3** (4.0 g, 14.1 mmol) and 100 mL concentrated HI (57%) was refluxed for 3 h. After cooling and filtration, yellow needles of compound **4** were obtained in 82% yield. ^1H NMR ($CDC1_3$): $\delta = 0.97$ (t, J = 7.2 Hz, 3H, $N-CH_2CH_2CH_2CH_3$), 1.45 (m, 2H, $N-CH_2CH_2CH_2CH_3$), 1.72 (m, 2H, $N-CH_2CH_2CH_2CH_3$), 4.16(t, J = 7.8 Hz, 2H, $N-CH_2CH_2CH_2CH_3$), 5.61(s, 1H, -OH), 7.12 (d, J = 8.4 Hz, lH), 7.67 (t, J = 7.8 Hz, 1H), 8.43 (d, J = 8.4 Hz, lH), 8.47 (d, J = 8.4 Hz, lH), 8.57 (d, J = 7.2 Hz, 1H).

2.2.4. Synthesis of ***TBS-NA***

A mixture of compound **4** (0.540 g, 2.0 mmol), *tert*-butyldimethylsilyl chloride(0.331 g, 2.2 mmol), imidazole (0.163 g, 2.4 mmmol) in 10 mL dry $CHCl_3$ were stirred overnight at room temperature. At the end of the reaction, the solvent was removed in vacuum. After purification by column chromatography (200–300 mesh silica gel, 20:1 chloroform/acetone), the desired product was obtained as off-white solid in 79% yield. ^1H NMR ($CDC1_3$): $\delta = 0.35$(s, 6H, $-CH_3 \times 2$), 1.0(t, J = 9.6 Hz, 3H, $N-CH_2CH_2CH_2CH_3$), 1.08(s, 9H, $-(CH_3)_3$), 1.42 (m, 2H, $N-CH_2CH_2CH_2CH_3$), 1.68 (m,2H, $N-CH_2CH_2CH_2CH_3$), 4.14(t, J = 7.8 Hz, 2H, $N-CH_2CH_2CH_2CH_3$), 7.02(d, J = 8.4 Hz, lH), 7.68(t, J = 7.8 Hz, 1H), 8.46(d, J = 8.4 Hz, lH), 8.47(d, J = 8.4 Hz, lH), 8.57 (d, J = 7.2 Hz, 1H).

3. Result and discussion

The interaction of sensor **TBS-NA** with the anions was investigated through UV–Vis spectra. All the UV–Vis behavior of sensor

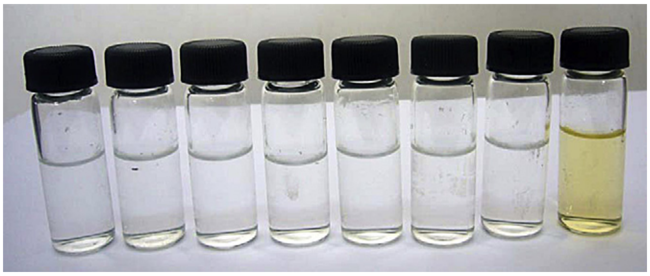
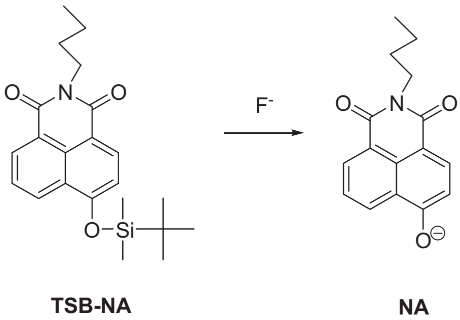


Fig. 2. Color changes of the compound 1 (1×10^{-4} mol/L) in CH_3CN with the addition of one equiv tetrabutylammonium salts (from left to right: free, Cl^-, Br^-, I^-, HSO_4^-, ClO_4^-, AcO^-, F^-).



Scheme 2. Cleavage of Si–O bond in **TBS-NA** by fluoride ion.

TBS-NA was studied in CH_3CN solution. In the absence of anions, the maximum absorption wavelength of **TBS-NA** is at about 362 nm. As shown in Fig. 1, when 10 equiv of TBAF was added to the solution of sensor **TBS-NA** (1×10^{-4} mol/L), the peak at 362 nm disappeared and the red-shift band at 474 nm was observed. In the same conditions, no significant changes happened when 10 equiv of tetrabutylammonium chloride, bromide, iodide, perchlorate, acetate, hydrogen sulfate were added. The results suggest that sensor **TBS-NA** has a high selectivity for the fluoride anion over other common anions.

Fig. 2 displays the visual aspects of fluoride ion recognition and sensing. Each vial contains a 10^{-4} mol/L of **TBS-NA** in CH_3CN. The addition of one equivalent of fluoride ions solution induced the appearance of a bright yellow color (the last vial), the addition of one equivalent of other anions did not induce any color change. This may be due to the high affinity of silicon toward fluoride ion which resulted in the cleavage of Si–O bond [16], as shown in Scheme 2. To conform the assumption, ^{1}H NMR was carried out (Fig. 3). The H_a, H_c and H_d proton shifted to upfield part obviously with the addition of fluoride, which due to the weak electron-withdrawing ability of phenolate anion.

The interaction of sensor **TBS-NA** with the fluoride was investigated through UV–Vis spectrophotometric titration by adding standard solution of TBAF (Fig. 4). As the concentration of fluoride ion increased, the absorbance intensity decreased at 362 nm, and a new band at 474 nm increased. The isobestic point at about 400 nm observed in both cases was attributed to the equilibrium between two species (**TBS-NA** and **NA**) throughout the titration process. Fig. 4 (inset) also shows that there was a good linearity between the absorbance at 474 nm and concentrations of F^- in the range from 10 μM to 100 μM, indicating that sensor **TBS-NA** can detect quantitatively relevant concentrations of F^-. The linear equation was found to be $y = 1.023 \times 10^4 x - 0.0631$ ($R = 0.9962$), where y is the absorbance at 474 nm measured at a given F^- concentration and x represents the concentration (10^{-4} mol/L) of F^- added. According to IUPAC, the detection limit was determined from three times the standard deviation of the blank signal (3σ) as 0.59 μM.

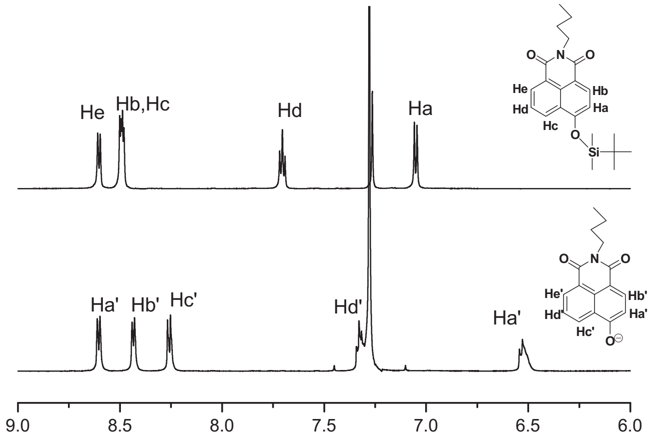


Fig. 3. Partial ^{1}H NMR spectra of sensor **TBS-NA** in $CDCl_3$ in the presence of 0 equiv (top), 1.5 equiv (b) (bottom) of TBAF.

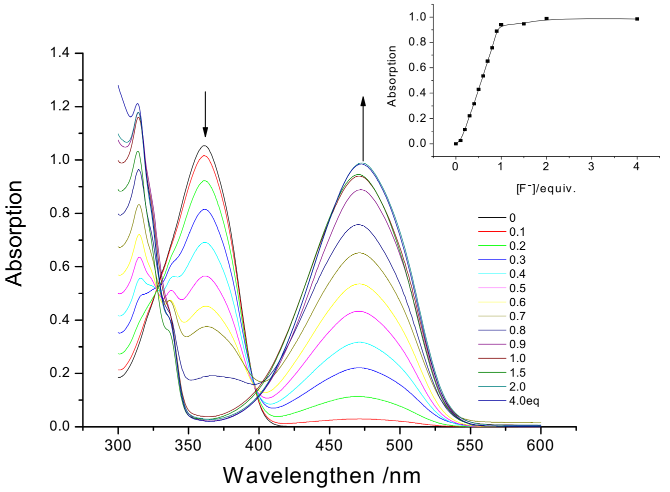


Fig. 4. UV–Vis titrations of sensor **TBS-NA** (1×10^{-4} mol/L) with TBAF in CH_3CN. Inset: UV absorption intensity at 474 nm *vs* concentration of F^-.

The effect of reaction time on the UV–Vis absorption spectra of the detecting system was studied. Adding 1 equiv of fluoride to CH_3CN solution of **TBS-NA**, 2 min later the absorbance at 474 nm of the system gets to maximum and does not change with more reaction time. It means the Si–O band of **TBS-NA** can be cleaved in a short time in CH_3CN system. 3 min was selected as the detection time in this paper.

4. Conclusions

In conclusion, a novel naphthalimide derivative **TBS-NA** has been synthesized by the couple reaction between *tert*-butyldimethyllchlorosilane and 4-hydroxy-N-butyl-1,8-naphthalimide. Addition of fluoride ion to a CH_3CN solution of **TBS-NA** can result in an obvious color change (from colorless to yellow) and UV–Vis absorption red-shift in a short time. The method was based on the selective cleavage of Si–O bond in **TBS-NA** by fluoride leading to a red-shift of the maximum wavelength. This makes the simple-to-use and naked-eye detection of fluoride ion possible.

Acknowledgments

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