



Novel 2,1,3-benzothiadiazole derivatives used as selective fluorescent and colorimetric sensors for fluoride ion



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ABSTRACT

Two novel 2,1,3-benzothiadiazole derivatives, used as colorimetric and fluorescent sensors for fluoride ion were designed, synthesized and characterized. These sensors contained single hydrogen-bond functional groups, which acted as interacting sites for fluoride ion. Both sensors displayed a red color in dimethyl sulfoxide solution. Binding studies revealed that they showed noticeable colorimetric and fluorescent responses only to F⁻ among the eight anions tested (F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻ and NO₃⁻). ¹H NMR titration proved that the interaction between compounds and fluoride ion: hydrogen bond at low fluoride ion concentration, deprotonation at high fluoride ion concentration. Moreover, those compounds showed high sensitivity and selectivity for fluoride ion by inhibiting the excited state intramolecular proton transfer processes, and the detective processes could be followed by direct visual observation.

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1. Introduction

Anions are known to play crucial roles in a wide range of chemical and biological processes [1–3], and construction of appropriate molecules for sensing of anions is a “hot” topic [4,5]. Fluoride ion is one of the most attractive targets owing to its smallest ionic radius, highest charge density and hard Lewis basic nature [6,7]. So far the sensors for fluoride ion can be classified several kinds as follows: (a) Lewis acids-based interactions [8,9]; (b) hydrogen-bond interactions [2,10,11]; (c) reaction-based interactions [12]; (d) polymer-based interactions [13]; (e) Quantum dots and gold nanoparticles-based interactions [14]; (f) mesoporous silica or silica particle-based interactions [15]. Their signaling mechanisms can be deduced as follows: photo induced

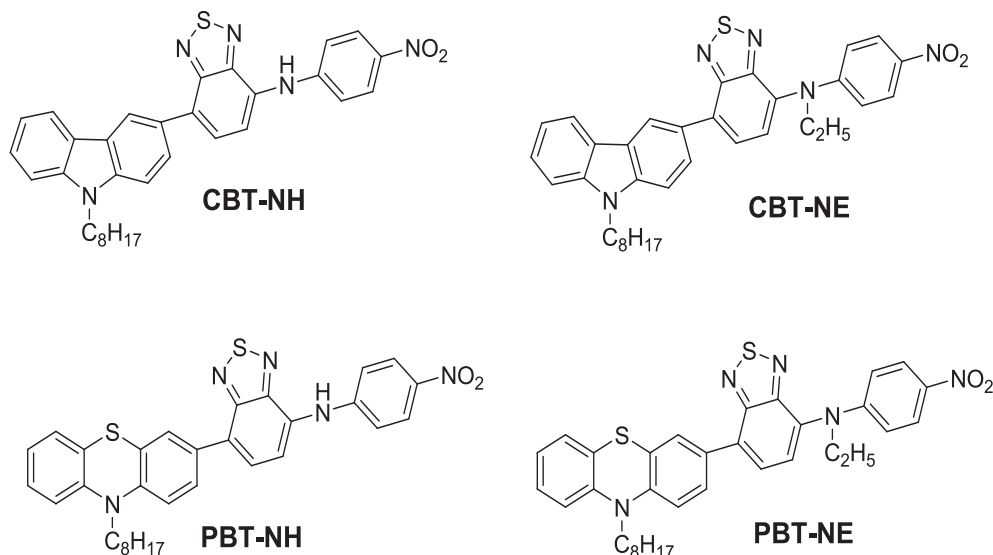
electron transfer (PET) [16], intramolecular charge transfer (ICT) [17,18], metal-to-ligand charge transfer (MLCT) and excited-state intramolecular proton transfer (ESIPT) [19,20].

Recently, some new methods which can quickly detect fluoride ion were reported [21]. In some cases, hydrogen bonds were utilized for fluorescent sensor sites and some acidic amidic NH groups could be deprotonated by fluoride ion for their relatively strong base [22]. At the same time, 2,1,3-benzothiadiazole (BTD) derivatives are a class of attractive fluorophores used in many photoelectrical materials [23]. Molecules containing 2,1,3-benzothiadiazoles usually show large molar extinction coefficients, good photostability and intense fluorescence [24]. Wang et al. [25] reported a benzothiadiazole derivative for fluoride ion detecting, the detective amount of fluoride was 0–300 equiv. Furthermore, Sreekanth et al. [26] reported bithiocarbohydrazones for a fluoride sensor, but these sensors also possessed response to acetate ion.

In this investigation, two compounds, 7-(9-octyl-9H-carbazol-3-yl)-N-(4-nitrophenyl)-benzo[c][1, 2, 5]thiadiazol-4-amine (CBT-

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Scheme 1. Molecule structures of compounds (CBT-NH, PBT-NH, CBT-NE and PBT-NE).

NH) and 7-(10-octyl-10H-phenothiazin-3-yl)-N-(4-nitrophenyl)-benzo[*c*][1, 2, 5]thiadiazol-4-amine (**PBT-NH**) (Scheme 1), were designed and synthesized, and used as fluorescent sensors for fluoride with the detection limits 0.86 μM and 4.25 μM , respectively. And their quantum yields were 0.034 and 0.015, respectively. **CBT-NH** and **PBT-NH** showed high selectivity for fluoride ion through the deprotonation action and the inhibiting ESIPT processes. More importantly, the molecules could detect fluoride ion by a fast method which was observable with the naked eye. And they showed a faster response (within 5 s) to fluoride ion than that of some related literatures [27,28].

2. Experimental

All the starting materials, reagents and solvents were AR grade purchased from J&K Chemical Co., which were received without further purification. ^1H and ^{13}C NMR spectra were measured on a Bruker AM-400 spectrometer at room temperature using *d*-chloroform or DMSO- d_6 as a solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as an internal standard. The UV/Vis spectra were recorded on a Nicolet CARY 100 and the Fluorescence spectra were measured on a CARY Eclipse. The stock solutions of **CBT-NH** and **PBT-NH** (5×10^{-5} mol/L) were prepared in DMSO solution. The TBA salts (F^- , Cl^- , Br^- , I^- , AcO^- , H_2PO_4^- , HSO_4^- , and NO_3^-) solutions were prepared at a concentration of 1×10^{-1} mol/L in DMSO solution. Different equivalents of TBA salts were added to the compounds and their corresponding UV-visible and fluorescence spectra were recorded at room temperature. Compounds (**CBT-NH** and **PBT-NH**) (6×10^{-3} mol/L in DMSO- d_6) were titrated with fluoride anion (as tetrabutylammonium salts) by addition of increasing equivalents of anion in DMSO- d_6 solution.

2.1. 3-Bromo-9H-carbazole (**1a**)

Carbazole (1.002 g, 5.997 mmol) was added into DMF solution (50 mL). Then the mixture of N-bromosuccinimide (NBS) (1.068 g, 6.000 mmol) and DMF (20 mL) was added dropwise into reaction flask in ice-water bath. After filtration and washed by water, white powder was obtained [29] (1.254 g, 85.0%). Mp: 199 °C. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ : 11.40 (s, 1H), 8.33 (d, $J = 8.4$ Hz, 1H), 8.12 (d, $J = 8.4$ Hz, 1H), 7.43 (m, 4H), 7.15 (t, $J = 7.6$ Hz, 1H).

2.2. 3-Bromo-9-octyl-9H-carbazole (**2a**)

Compound **1a** (0.615 g, 2.499 mmol) and K_2CO_3 (1.730 g, 12.50 mmol) were added into DMF (20 mL). Then $\text{C}_8\text{H}_{17}\text{-Br}$ (0.580 g, 3.003 mmol) was added dropwise into reaction flask, and the mixture was stirred overnight at 80 °C. After removal of the solvent, the residue was purified by column chromatography on silica (petroleum ether) to give a liquid [30] (0.740 g, 82.7%). ^1H NMR (CDCl_3 , 400 MHz, TMS) δ : 8.20 (s, 1H), 8.04 (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 7.22 (d, $J = 7.6$ Hz, 1H), 4.27 (t, $J = 7.2$ Hz, 2H), 1.40–1.20 (m, 12H), 0.85 (t, $J = 7.2$ Hz, 3H).

2.3. 9-Octyl-3-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)-9H-carbazole (**3a**)

A solution of Compound **2a** (0.716 g, 2.000 mmol) in anhydrous THF (20 mL) was cooled to -78 °C under a nitrogen atmosphere. N-BuLi (2.5 M, 2.400 mmol) was slowly added dropwise followed by stirred for another 1 h. Then isopropylpinacolylborate (2.04 mL, 10.01 mmol) was added and the mixture was stirred at -78 °C for 1 h. After that, the mixture was cooled to room temperature and stirred for 16 h. After removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ $\text{CH}_2\text{Cl}_2 = 3:1$) [31]. A white solid was obtained in a yield of 63.8% (0.5170 g). ^1H NMR (CDCl_3 , 400 MHz, TMS) δ : 8.53 (s, 1H), 8.06 (d, $J = 7.6$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 7.2$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 7.2$ Hz, 1H), 4.23 (t, $J = 7.2$ Hz, 2H), 1.33 (s, 12H), 1.30–1.10 (m, 12H), 0.80 (t, $J = 7.2$ Hz, 3H).

2.4. 10-Octyl-10H-phenothiazine (**1b**)

This compound was synthesized by the same procedure described for **2a** using 10H-phenothiazine and $\text{C}_8\text{H}_{17}\text{-Br}$ [32]. Yield: 75.6%. ^1H NMR (CDCl_3 , 400 MHz, TMS) δ : 7.14–7.10 (m, 4H), 6.91–6.84 (m, 4H), 3.40 (t, $J = 6.8$ Hz, 2H), 1.30–1.10 (m, 12H), 0.82 (t, $J = 6.8$ Hz, 3H).

2.5. 3-Bromo-10H-octyl-10H-phenothiazine (**2b**)

The compound was synthesized by the same procedure described for **1a** using compound **1b** and N-bromosuccinimide (NBS) [33].

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