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Boron–dipyrromethene based specific chemodosimeter for fluoride ion

M. Rajeswara Rao, Shaikh M. Mobin, M. Ravikanth *

Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India

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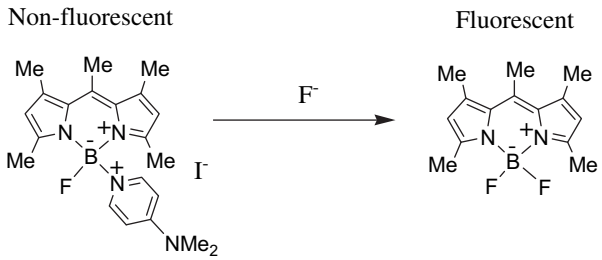
ABSTRACT

3,5-Bis(trimethylsilylethynyl)-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene [BODIPY(CCTMS)$_2$] has been synthesized by coupling of 3,5-dibromo-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene with trimethylsilylacetylene under pd(0) coupling conditions. The BODIPY(CCTMS)$_2$ was used as a selective colourimetric and fluorescent chemodosimeter for fluoride ion, following the F^- ion induced cleavage of trimethylsilyl group, the protecting group of ethyne functionality by monitoring the changes in UV–vis and fluorescence properties. The dosimeter BODIPY(CCTMS)$_2$ display clear changes in colour, absorption and emission bands selectively for F^- ion over other anions such as Cl^-, Br^-, I^-, ClO_4^- and HPO_4^{2-}.

1. Introduction

Anion recognition and sensing via artificial receptors are of current interest in supramolecular chemistry because of their importance in chemical and biological systems.[1] Among the anions, fluoride, the smallest anion, is of particular interest because of its role in preventing dental caries,[2] and treatment of osteoporosis.[3] However, an excess fluoride anion can lead to fluorosis, which is a type of fluoride toxicity.[4] The diversity of function, both beneficial and detrimental, necessitates the development of systems capable of detecting the fluoride anion. The available fluoride ion sensors in literature are mainly based on the approach of a binding site-signalling sub-unit (chemosensors).[5] Although considerable progress has been made in sensing of fluoride anion using various chemosensors, the chemodosimeter approach,[6] which involves the use of specific chemical reactions induced by the presence of target anions, has received much less attention comparatively. The chemodosimetric approach usually shows high selectivity and is based on the changes in the electronic properties of the fluorophore. It involves the use of specific chemical reactions, which are usually irreversible induced by the presence of target anions that are coupled to a colour, absorption or emission variation. In chemodosimetric approach, either the anion reacts with the chemodosimeter and remains covalently bonded to the product or it simply catalyzes a chemical reaction. In this approach, since the final compound is chemically different from the original one, the changes in the colour and the spectroscopic characteristics of the solution allows the determination of the anion. The underlying idea of these irreversible systems is to take the advantage of the selective reactivity that certain anions may display. Recently there are some reports on chromogenic and fluorescent chemodoimeters for fluoride anion.[7] Interestingly, boron–dipyrromethene dyes (BODIPY), which are used extensively as labelling reagents, fluorescent switches, chemosensors[8] etc., due to their excellent photophysical properties, to the best of our knowledge, there is only one report on BODIPY based chemodosimeter sensor for F^- ion. Hudnall and Gabbaï reported[9] a BODIPY boronium cation, which can act as chemodosimeter sensor for fluoride ion (Scheme 1).



Scheme 1. The reported chemodosimeter for fluoride ion.[9]

They used *p*-dimethylaminopyridine adduct of 1,3,5,7,8-pentamethylpyrromethene–boron fluoride, the non-fluorescent compound, which on reaction with F^- ion turn to brightly fluorescent difluoride complex. In this paper, we developed another example of boron–dipyrromethene based chemodosimeter for fluoride anion,

* Corresponding author.
E-mail address: ravikanth@chem.iitb.ac.in (M. Ravikanth).

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which exhibited drastic changes in colour, absorption and fluorescence properties selectively for F^- ion over other anions. We used the BODIPY dye BODIPY(CCTMS)$_2$ **1** containing trimethylsilylethynyl groups at 3,5-positons (Chart 1) to act as chromogenic and fluorescent sensor for fluoride anion (TBA^+, K^+ salts) by adopting simple chemodosimetric approach. We hypothesized that the electron-rich trimethylsilyl protective group[10] could be removed by F^- ion to reveal the electron-deficient ethyne group. This transformation of electron-rich trimethylsilylethyne group to electron-deficient ethyne group alter the electronic properties of the dye and should lead to changes in the colour and shifts in absorption and emission maxima and downfield shifts of certain protons in ^{1}H NMR spectrum. Furthermore, to show that the position of trimethylsilylethyne group(s) on BODIPY dye play any important role in designing chemodosimeter for fluoride ion, we synthesized an alternate BODIPY dye **2** in which the trimethylsilylethyne group is placed at the *para*-position of *meso*-phenyl group[11] (Chart 1).

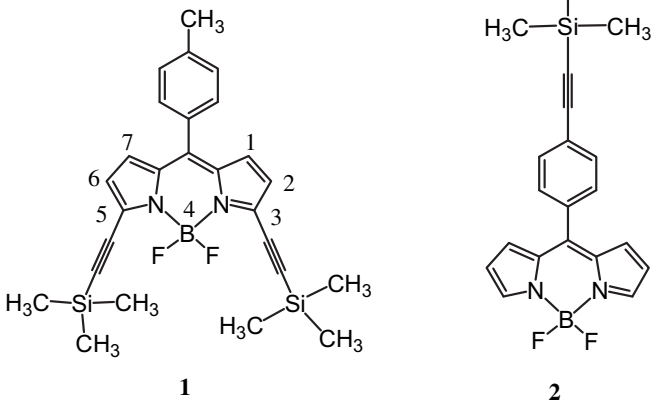
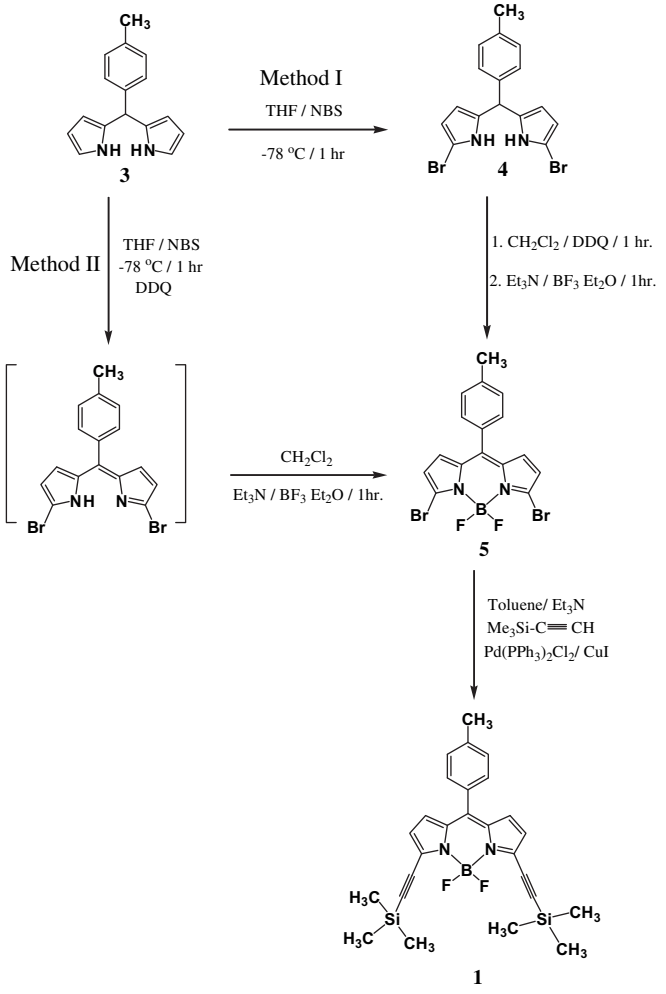


Chart 1.

2. Results and discussion

The BODIPY dye **2** was prepared by following the literature procedure.[11] The BODIPY dye **1** was prepared in three steps starting from *meso*-phenyl dipyrromethane **3** as shown in Scheme 2. The *meso*-(*p*-tolyl) dipyrromethane **3** was prepared as reported in literature[12] by treating one equivalent of benzaldehyde with 25 equiv of pyrrole in the presence of catalytic amount of $BF_3\cdot OEt_2$ at room temperature followed by work-up and column chromatographic purification. The *meso*-(*p*-tolyl)-3,5-dibromodipyrromethane **4** was prepared by treating **3** with two equivalents of *N*-bromosuccinimide at −78 °C for 1 h. The crude compound was subjected to flash column chromatography using CH_2Cl_2 and isolated compound **4** in 75% yield. The compound **4** was confirmed by ^{1}H NMR, mass and elemental analysis (Supplementary data). The BF_2 complex **5** was prepared in subsequent step by adopting two-steps in one pot reaction methodology (Method I).[13] In the first step, the compound **4** was oxidized with one equivalent of DDQ in CH_2Cl_2 for 1 h at room temperature to afford dipyrromethene. Without isolating the dipyrromethene, in the second step, the reaction mixture was first neutralized with triethylamine and then reacted with $BF_3\cdot Et_2O$ at room temperature for 1 h. The dark fluorescent crude reaction mixture was subjected to column chromatographic purification and afforded clean fluorescent BF_2 complex **5** in 25% yield. During the course of our synthesis, we realized that the compound **4** is not very stable hence we attempted to synthesize compound **5** in one step starting from compound **3** without isolating compound **4** (Method II). According to method II, we first brominated compound **3** by treating it with two equivalents of NBS at −78 °C in THF for 1 h, which was then followed by oxidation with DDQ at room temperature for 10 min. The solvent was removed on rotary evaporator in high vacuo and quickly flash chromatographed on silica. The resultant compound was dissolved in CH_2Cl_2 and treated with $BF_3\cdot Et_2O$ for 1 h.



Scheme 2. Synthesis of chemodosimeter **1**.

The TLC analysis of crude reaction mixture showed three spots corresponding to monobromo, dibromo and tribromo compounds. Column chromatography on silica gave pure **5** as second band in 64% yield. Although both methods work efficiently, we found that it is convenient to synthesize the compound **5** by following method II. The compound **5** was characterized by mass, NMR, absorption and fluorescence spectroscopic techniques. The M^+ ion peak at 421 confirmed the formation of BF_2 complex **5**. In ^{1}H NMR spectrum of **5**, the pyrrole protons appeared as two sets of doublets at 6.53 and 6.82 ppm, which shifted to downfield as compared to those in **4**. The absorption spectrum of **5** showed one sharp band at 520 nm, which was red shifted by 18 nm compared to **2** due to presence of two bromine atoms at 3, 5-position (Supplementary data). In the last step, the compound **5** was treated with trimethylsilylacetylene in toluene/triethylamine in the presence of $Pd(PPh_3)_2Cl_2$/CuI at 40 °C for 3 h (Scheme 2). The crude compound was subjected to column chromatographic purification and afforded the target compound **1** as blue crystals in 60% yield. The compound **1** was characterized by mass, NMR, absorption, fluorescence and single crystal X-ray analysis. In ^{1}H NMR spectrum, the methyl protons of trimethylsilyl group appeared as singlet at 0.31 ppm and four

pyrrole protons appeared as sets of two doublets at 6.68 and 6.92 ppm (Table 1). The absorption spectrum of **1** showed one strong sharp band at 571 nm, which was red shifted by ~50 nm compared to compound **5**. The single crystal of compound **1** was obtained from *n*-hexane/dichloromethane on slow evaporation over a period of one week. The single crystal X-ray diffraction (CCDC 728412) study of **1** revealed that the two pyrrole rings and the central six-membered ring containing the boron ring are planar (Fig. 1). The dihedral angle between the *meso*-aryl ring and the plane defining various dipyrrin atoms in compound **1** is almost same (53°) as that of reported unsubstituted *N*,*N*′-difluoroboryl-5-phenyldipyrrin complex[11] (~60°). However, there are slight variations in some bond lengths, such as pyrrole 'N'–B and B–F bonds in compound **1** as compared to *N*,*N*′-difluoroboryl-5-phenyldipyrrin[11] complex, which is attributed to alteration of electronic properties of boron–dipyrromethene due to the presence of electron releasing trimethylsilylethynyl substituents at 3,5-positions in **1** (Supplementary data).

Table 1
^{1}H NMR and Photophysical data of compounds **1**, **2**, **6** and **7**

Compound	^{1}H NMR (δ in ppm)		Absorption	Emission
	1,7-py	2,6-py	(λ_{nm})	(λ_{nm})
1	6.92	6.68	571	584
6	6.98	6.76	551	564
2	6.56	5.88	497	516
7	6.56	5.88	497	516

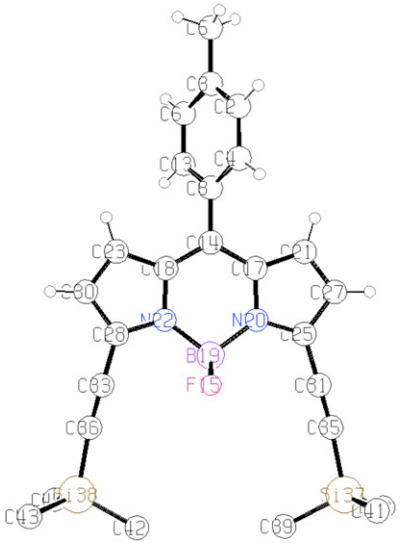
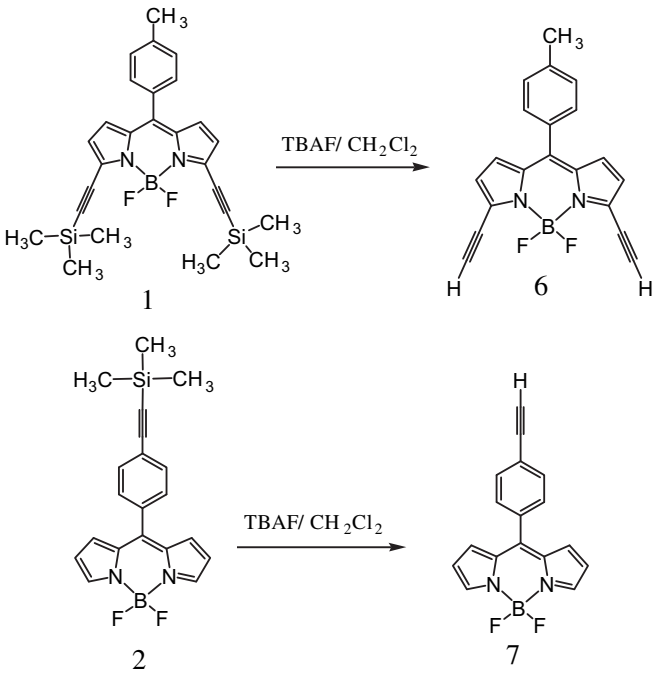


Figure 1. ORTEP diagram of compound **1**.

The compound **1** is freely soluble in all common organic solvents. The compound **1** exhibits one fluorescence band at 584 nm with a quantum yield of 0.29 and singlet state lifetime of 5.6 ns. The compound **1** can be used as fluorescent and as well as chromogenic chemodosimeter for fluoride ion detection based on selective fluoride ion catalyzed deprotection of ethyne functional groups present at the 3- and 5-positions of the dye. It is established that if functional group is in close proximity to a fluorophore, the change in electronic properties of the functional group due to protection/deprotection may influence the photophysical properties of the dye, which should lead to an observable change in the absorption/emission profile of the dye. Since the trimethylsilyl groups, the protective groups for ethyne functional groups, are electron donating groups and removal of trimethylsilyl groups from ethyne functional groups would alter the electronic properties of the dye, which in turn expected to result in changes in spectroscopic properties. Because of the high affinity of fluoride for silicon, the trimethylsilyl groups present at the 3,5-positions of **1** can be easily cleaved by fluoride ion but not by other anions to afford the BODIPY dye containing two ethynyl functional groups, thus **1** can act as specific chemodosimeter for fluoride ion (Scheme 3). This irreversible reaction can be monitored by following changes in NMR, absorption, and fluorescence spectroscopic features and also by following changes in the colour under naked eye and UV light conditions.



Scheme 3. Fluoride sensing chemodosimetric reaction.

The fluoride ion induced transformation of protected **1** to deprotected **6** can be systematically followed by ^{1}H NMR spectroscopy. The changes in the selected protons of dosimeter **1** on addition of increasing amounts of KF in CD_3OD are shown in Figure 2. We used maximum two equivalents of KF, which is required to cleave the two trimethylsilyl groups of **1**. As it is clear from

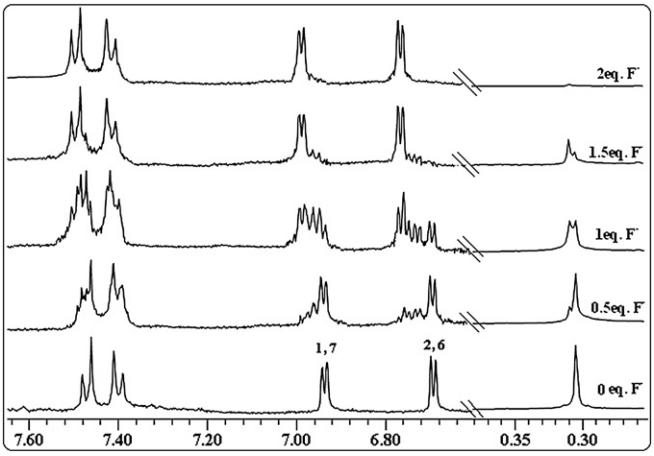


Figure 2. ^{1}H NMR spectra of **1** (in CD_3OD, 31 mM) in the presence of different concentrations of F^- ions. The final mole ratio of [F^-] to [**1**] is 0, 0.5, 1.0, 1.5 and 2.0, respectively.

Figure 2, on sequential addition of KF, the trimethylsilyl groups, which appear at 0.31 ppm slowly start disappearing and upon complete addition of two equivalents, the signal corresponding to trimethylsilyl groups completely disappeared supporting the formation of **6**. The systematic changes were also observed with pyrrole and aryl protons of **1** on sequential addition of increasing amounts of KF to **1**. For e.g., the 1,7 and 2,6-pyrrole protons, which appears at 6.92 and 6.68 ppm, respectively, in **1**, upon addition of two equivalents of KF, the protons experience slight downfield shifts and appears at 6.98 and 6.76 ppm, respectively, supporting the formation of **6** (Table 1).

However, on addition of one equivalent of F^- to **1**, the signals corresponding to the mixture of compounds, such as **1**, **6** and the intermediate compound containing one protected and one deprotected ethynyl functional groups are present. Thus, on complete addition of two equivalents of F^-, the pyrrole and aryl proton signals corresponding to **1** disappeared completely and the signals corresponding to **6** appeared. Although, the changes in chemical shifts are relatively small, it is enough to follow the progress of the reaction by ^1H NMR. Under same conditions, the other anions, such as Br^-, Cl^-, I^-, HPO_4^{2-} and ClO_4^- did not affect the changes in the pyrrole and aryl protons of **1** even after the addition of three equivalents of each anion. Similarly, the ^1H NMR studies were also carried out with compound **2** in which the trimethylsilylethyne group is present at the *para*–position of *meso*-phenyl group. The addition of F^- ion to compound **2** results in the deprotection of ethyne group and forms compound **7** (Scheme 3). The comparison of ^1H NMR spectra of compound **2** and compound **7** is shown in Figure 3. Although some negligible changes were noticed in the chemical shifts of aryl protons, no changes were observed in the chemical shifts of pyrrole protons on formation of compound **7** (Table 1). Thus, ^1H NMR study reveals that compound **1** can be used as chemodosimeter for fluoride ion, whereas compound **2** cannot be used.

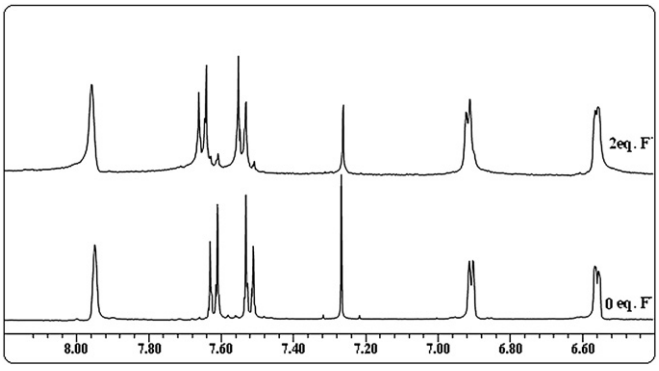


Figure 3. ^1H NMR spectra of **2** (in $CDCl_3$) in the presence of two different concentrations of F^- ions. The final mole ratio of [F^-] to [**2**] is 0 and 2.0, respectively.

The boron–dipyrromethene dyes, in general possess interesting absorption and fluorescence properties[8] and it is convenient to follow the changes in absorption and fluorescence peak maxima of **1** on addition of F^- ions. The systematic changes in absorption spectra of dosimeter **1** on increasing the concentration of TBAF in CH_2Cl_2 are shown in Figure 4. The addition of F^- ions to a dichloromethane solution of **1** showed nice ratiometric changes, which reflected in the decrease of the intensity of the absorption band at 571 nm corresponding to **1** and appearance of new band at 551 nm corresponding to **6**. This is also clearly evident in the plot, which shows the changes in the absorbance of band at 571 and 551 nm (A) versus the concentration of F^- (Fig. 4 inset).

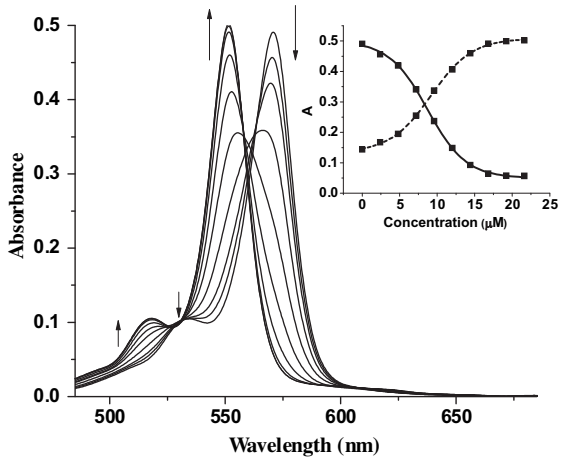


Figure 4. The absorption spectra of **1** in the presence of F^- in CH_2Cl_2 (8 μM). The F^- concentration is 0, 2.4, 4.8, 7.2, 9.6, 12.0, 14.4 and 16.8 μM, respectively. The inset shows the plot of changes in absorbance (A) at 571 nm (solid line) and 551 nm (dotted line).

Furthermore, the time dependence of the conversion of **1** to **6** at 551 nm in the presence of two equivalents F^- ion was monitored by means of absorption spectroscopy (Supplementary data). The results indicate that the reaction completes within 5 min duration (Supplementary data). Similar observations were made with fluorescence studies. The addition of fluoride ions to a solution of **1** in CH_2Cl_2 also results in clear ratiometric changes in fluorescence spectra, which reflected in the decrease of the intensity of emission band at 584 nm corresponding to dosimeter **1** and increase in intensity of new band at 564 nm corresponding to **6** (Fig. 5).

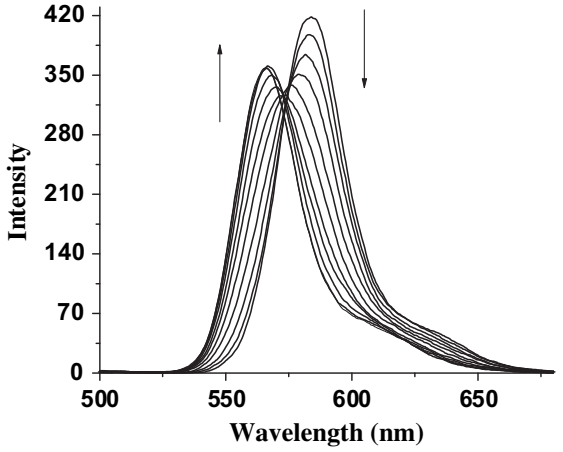


Figure 5. Fluorescence emission changes (ex 425 nm) of dosimeter **1** (2 μM) upon the addition of F^- in CH_2Cl_2. The F^- concentration is (equiv) 0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20 and 22.5 μM.

There are no changes in absorption and fluorescence bands of **1** on addition of any other anions, such as Br^-, Cl^-, I^-, HPO_4^{2-} and ClO_4^- as shown in Figure 6. Thus, these results support that the compound **1** can be used as chromogenic and fluorescent chemodosimter for fluoride anion. To show that only **1** can be used exclusively as chemodosimeter for fluoride ion, the absorption and fluorescence studies were carried out with compound **2** in which the trimethylsilylethynyl group is present on *meso*-phenyl group. The absorption and emission spectra of compound **2** on addition of excess amount of F^- ion are shown in Figure 7. The addition of F^- ion to **2** results in cleavage of trimethylsilyl group present at the *para*-position of *meso*-phenyl group, but there are no significant changes in absorption and fluorescence bands observed suggesting

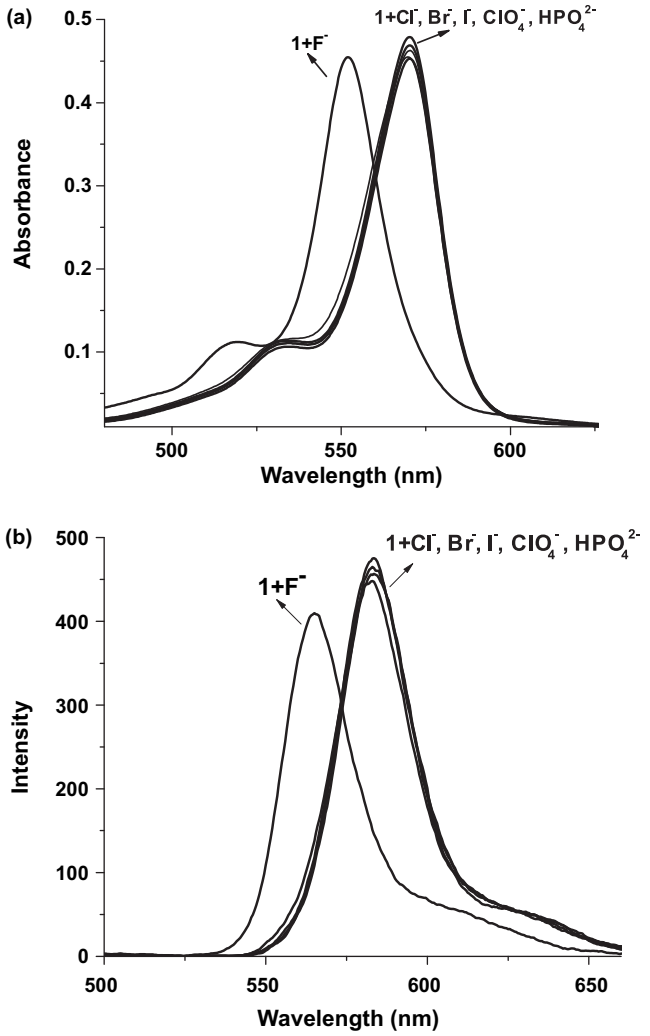


Figure 6. (a) Absorption spectra of **1** (8 μm) with F^- (excess equivalents), Cl^-, Br^-, I^-, ClO_4^- and HPO_4^{2-} (excess equivalents) (b) Emission spectra of **1** (2 μM) with F^- (excess equivalents), Cl^-, Br^-, I^-, ClO_4^- and HPO_4^{2-} (excess equivalents).

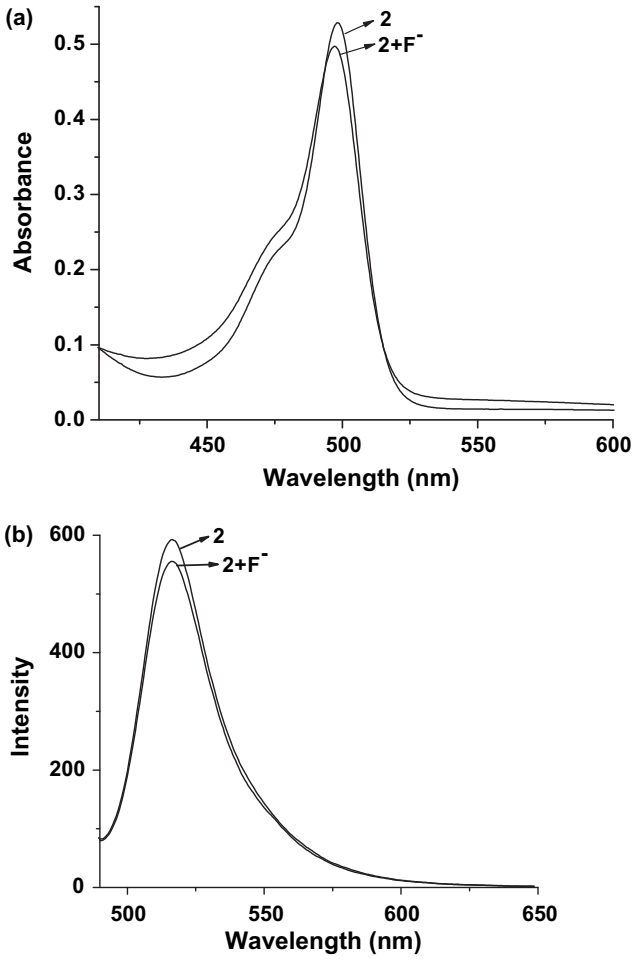


Figure 7. (a) Absorption spectra of **2** (8 μm) with excess of F^- (b) Emission spectra of **2** (2 μm) with excess of F^-.

that compound **2** cannot be used as chemodosimeter for F^- ion (Table 1).

This study also indicates that the location of functional group, such as trimethylsilylethynyl functional group on BODIPY plays a very important role in designing the chemodosimetric sensor. If the functional group is closer to the fluorophore as in **1**, the changes in the functional group alter the electronic properties of the dye resulting in significant changes in the spectroscopic properties. However, if the functional group is away from the fluorophore as in **2**, the changes in the functional groups do not reflect clearly in the spectroscopic properties. Apart from the shifts in absorption and fluorescent bands of compound **1** on addition of F^- ion, there is also visible colour change to naked eye as well as under UV light on addition of F^- ion to compound **1** as shown in Figure 8. This supports that **1** can also be used as colourimetric sensor (Fig. 8). The bright pink fluorescencent colour of compound **1** was turned to violet on addition of F^- ion, whereas compound **2** did not show any such changes in colour.

Similarly, under UV light, the bright orange fluorescence of **1** was changed to fluorescent green on addition of fluoride ion. The comparison of colour changes on addition of various anions, such as Br^-, Cl^-, I^-, HPO_4^{2-}, ClO_4^- and F^- to compound **1** is shown in Figure 9. As clear from Figure 9 that addition of only F^- ion to **1** results in clear colour change, where as the addition of other anions does not bring any noticeable colour change to the dye. Thus, compound **1** can be used exclusively as colourimetric and chemodosimeter sensor for fluoride ion.

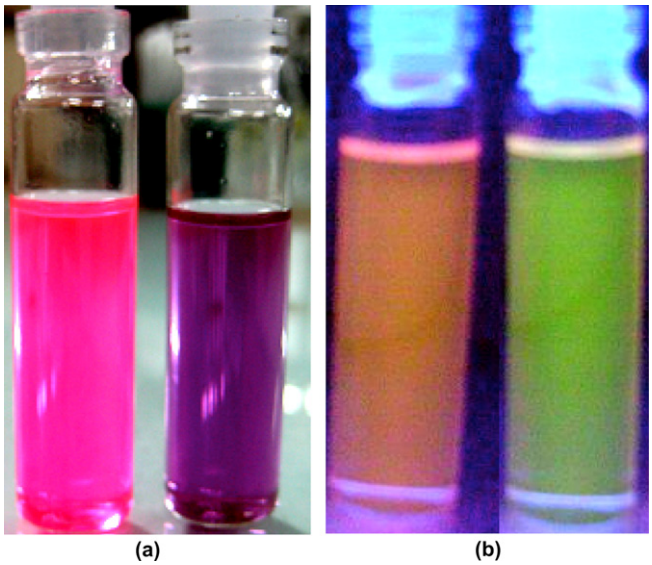


Figure 8. (a) Naked eye colour changes in compound **1** with (right) and without (left) F^- ion. (b) Under UV lamp colour changes in compound **1** with (right) and without (left) F^- ion.

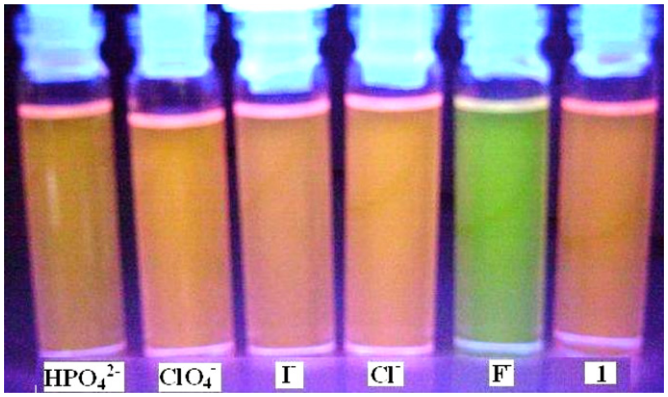


Figure 9. Under UV lamp colour changes in compound **1** on addition of two equivalents of various anions.

3. Conclusions

In summary, we have synthesized a simple boron–dipyrromethene (BODIPY) based chemodosimeter in three steps and demonstrated that it can be used as colourimetric and fluorescent chemodosimeter for fluoride anion. The chemodosimeter, which is based on well known desilylation reaction reveals that the fluorescent chemodosimeters for specific anion can be developed by making small alterations on the molecular structure of fluorescent dyes.

4. Experimental section

4.1. General

^1H, ^{13}C NMR (δ in ppm) spectra were recorded using Varian VXR 300 spectrometer. TMS was used as an internal reference for recording ^1H (of residual proton; δ 7.26) and ^{13}C (δ 77.0) signal of $CDCl_3$. Absorption and steady state fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and Lambda-55 instruments, respectively. The ES–MS mass spectra were recorded with a Q-Tof micro mass spectrometer. High-resolution mass spectrum was obtained from Q-TOF instrument by electron spray ionization (ESI) technique. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. THF and Chloroform were dried over sodium benzophenone ketyl and distilled prior to use. $BF_3\cdot Et_2O$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and trimethylsilylacetylene were used as obtained. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60–120 mesh).

4.2. X-ray diffraction studies

The intensity data collection for compound **1** have been carried out on a Nonius MACH3 four circle diffractometer at 293 K. Structure solution for the compound **1** was obtained using direct methods (SHELXS-97)[14] and refined using full-matrix least-squares methods on F^2 using SHELXL-97.[15] Other details pertaining to data collection, structure solution and refinement are given as Table S1 Supplementary data.

*4.2.1. meso-(p-Tolyl)-3,5-dibromodipyrromethane (**4**).* meso-(*p*-Tolyl)-dipyrromethane **3** (1.0 g, 4.23 mmol) was taken in dry THF (75 mL) and cooled to −78 °C under argon. *N*-Bromosuccinimide (1.6 g, 9.0 mmol) was added in two portions over 1 h period. After *N*-bromosuccinimide dissolved completely (~1 h), the reaction mixture was warmed to room temperature and the solvent evaporated by rotary evaporator. The residue was purified by silica gel column chromatography using of petroleum ether/dichloromethane (85:15) and afforded **4** as a red solid (1.27 g, 75%); mp 118–119 °C; ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.34 (s, 3H; $-CH_3$), 5.29 (s, 1H; –CH), 5.82 (m, 2H; Py), 6.06 (m, 2H; Py), 7.06 (d, ^3J (H, H)=7.8 Hz, 2H; Ar), 7.13 (d, ^3J (H, H)=7.8 Hz, 2H; Ar); ES–MS: ($C_{16}H_{14}Br_2N_2$). 394.2 [M^+], CHN calcd: C-48.76, H-3.58, N-7.11, Obsd, C-48.36, H-3.79, N-7.30.

*4.2.2. 3,5-Dibromo-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**5**).*

4.2.2.1. Method I. Compound **4** (500 mg, 1.31 mmol) was taken in CH_2Cl_2 (30 mL) and oxidized with DDQ (300 mg, 1.31 mmol) at room temperature. The reaction was allowed to stir for 1 h at room temperature. Triethylamine (6.38 mL, 46.0 mmol) followed by $BF_3\cdot Et_2O$ (8.20 mL, 65.8 mmol) was added, and continued stirring at room temperature for additional 1 h. The reaction mixture was washed with 0.1 M NaOH solution and water thoroughly. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The crude product was purified by silica gel column chromatography using of petroleum ether/dichloromethane (75:25) to afford compound **5** as a purple powder (208 mg, 25%); R_f (pet. ether/25% CH_2Cl_2) 0.70; mp 210–211 °C; IR (KBr, cm^{-1}) 737, 777, 827, 980, 1083, 1110, 1182, 1255, 1313, 1386, 1543, 1569, 2853, 2923; ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.46 (s, 3H; $-CH_3$), 6.53 (d, ^3J (H, H)=4.28 Hz, 2H; Py), 6.82 (d, ^3J (H, H)=4.28 Hz, 2H; Py), 7.32 (d, ^3J (H, H)=7.9 Hz, 2H; Ar), 7.38 (d, ^3J (H, H)=7.9 Hz, 2H; Ar); ES–MS: ($C_{16}H_{11}BBr_2F_2N_2$) 421.06 [M^+-F], CHN calcd: C-43.69, H-2.52, N-6.37, Obsd, C-43.60, H-3.99, N-7.41.

4.2.2.2. Method II. meso-(p-Tolyl)-Dipyrromethane **3** (500 mg, 2.15 mmol) was taken in dry THF (50 mL) and cooled to −78 °C under argon. *N*-Bromosuccinimide (762 mg, 4.31 mmol) was added in two portions over 1 h period. After *N*-bromosuccinimide dissolved completely (~1 h), DDQ (491 mg, 2.15 mmol) in THF was added dropwise over 10 min. The reaction mixture was warmed to room temperature and the solvent was evaporated on rotary evaporator under vacuum. The crude compound was subjected to flash column chromatography using CH_2Cl_2, concentrated on rotary evaporator, neutralized with triethylamine (10.49 mL, 75.4 mmol) and treated with $BF_3\cdot Et_2O$ (13.44 mL, 107.0 mmol) at room temperature for additional 1 h. The reaction mixture was washed with 0.1 M NaOH solution and water thoroughly. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The TLC analysis of crude compound showed three spots corresponding to monobromo, dibromo and tribromo derivatives and the desired dibromo derivative was the second spot. The crude product was subjected to silica gel column chromatography and second was collected using of petroleum ether/dichloromethane (75:25). The solvent was removed on rotary evaporator under vacuo and afforded **5** as purple powder (600 mg, 64% yield).

*4.2.3. 3,5-Bis(trimethylsilylethynyl)-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**1**).* Sample of **5** (50 mg, 113 μmol), was dissolved in toluene/triethylamine and trimethylsilylacetylene (38 μL, 284 μmol) was added under argon atmosphere the coupling was initiated by addition of catalytic amounts of CuI (4.2 mg, 22.6 μmol) and $Pd(PPh_3)_2Cl_2$ (9.5 mg, 13.6 μmol). After disappearance of the starting material as judged by TLC analysis, the solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel, using of petroleum ether/dichloromethane (40:60) and afforded **1** as blue crystals (32 mg, 60% yield); R_f (pet. ether/60% CH_2Cl_2) 0.58; mp 184–185 °C; IR (KBr, cm^{-1}) 710, 797, 874, 942, 1017, 1071, 1140, 1164, 1269, 1384, 1453, 1468, 1549, 1816, 2852, 2922; ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 0.31(s, 18H; $-Si(CH_3)_3$), 2.45 (s, 3H; $-CH_3$), 6.60 (d, ^3J (H, H)=4.39 Hz, 2H; Py), 6.81 (d, ^3J (H, H)=4.39 Hz, 2H; Py), 7.30 (d, ^3J (H, H)=7.8 Hz, 2H; Ar), 7.38 (d, ^3J (H, H)=7.8 Hz, 2H; Ar); HRMS

calcd for $C_{26}H_{29}BF_2N_2Si_2Na$ 497.1828, found 497.1814; CHN calcd: C-65.81, H-6.16, N-5.90, Obsd, C-66.20, H-5.85, N-5.80.

4.3. Procedure for anion sensing

Stock solutions of the anions (2.0 mM) were prepared in methanol and stock solution of **1** (1 mM) was prepared in CH_2Cl_2. For absorption measurements, the stock solution of **1** was diluted to 8 μM with CH_2Cl_2. Titration experiments were performed by placing 2.5 mL of solution **1** (8 μM) in a quartz cuvette of 1 cm optical path length, and various amounts of anions were added incrementally by means of a micro-pipette. For fluorescence measurements, 2 μM concentration of **1** was used. Excitation was provided at 425 nm, and emission was collected from 500–700 nm.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2009.12.039.

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