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ORIGINAL PAPER

A Reversible and Reusable Selective Chemosensor for Fluoride Detection Using a Phenolic OH-Containing BODIPY Dye by Both Colorimetric 'Naked-eye' and Fluorometric Modes

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Abstract A novel BODIPY-based probe **1** was designed and synthesized as a selective fluorescent and colorimetric chemosensor for fluoride. The spectral responses of **1** to fluoride in acetonitrile were studied: an approximately 118 nm red shift in absorption and 'turn-off' emission response was observed. The striking pink to indigo change in ambient light was thought to be due to the deprotonation of the phenol moiety by way of O–H···F hydrogen bonding interactions. Interestingly, when the nonfluorescent **1**-F^- solution treated with trifluoroacetic acid (TFA) resulted in color change from indigo to pink and a significant enhancement of fluorescence intensity (10-fold). Furthermore, the reversibility and reusability of probe **1** for the detection of F^- ion was tested for four cycles indicating the probe **1** could be used in reversible manner.

Keywords Colorimetric · Chemosensor · BODIPY · Fluoride · Fluorescence

Introduction

The recognition and detection of anions is extremely necessary because anions play so many positive and negative effects in the lives. Among the anions, fluoride ion (F^-) is of particular interest owing to its established role in dental care and clinical treatment for osteoporosis. An acute intake of a large dose or chronic ingestion of lower doses of F^-can result in gastric and kidney disorders, dental and skeletal fluorosis, and urolithiasis in humans, and even death. For these reasons, an improved method for the detection and sensing of F^- with high selectivity is of current interest.

A well developed strategy is to couple a chromogenic or fluorogenic signaling unit to a receptor unit that can interact with fluoride ions via hydrogen bonding. In this regard, hydrogen bonding interactions were applied to construct colorimetric or fluorescent sensors, using urea, thiourea, amide, pyrrole, amidourea, imidazolium, indole and phenol as receptor units of fluoride ions [1–11]. However, most of them show slow response times, low sensitivities and modest selectivity. The biggest bottleneck in developing probes for the fluoride is interference by acetate and other anions of comparative basicity. Furthermore, Most of these sensors are normally irreversible and one time use for sensing fluoride ion [12–15]. There are very few sensors available in the literature which can be used as reversible and reusable systems for sensing fluoride ion [16–18].

Recently, the attractive photophysical properties of boron-dipyrromethene (BODIPY) dyes were also utilized to construct fluoride ion colorimetric or fluorescent sensors using various recognition strategies such as chemical reactivity with silicon, Lewis acidic boron, hydrogen bonding, etc. [19–28]. Despite the OH group can interact with fluoride ions via hydrogen bonding [29], there are only a few colorimetric or fluorescent sensors based on BODIPY for detection fluoride ions by way of O–H···F hydrogen bonding interactions [30].

Understanding the nature of intermolecular hydrogen bonding of phenol and fluoride ion is necessary to develop a fluoride ion selective sensor. Herein, we reported a reversible and reusable BODIPY probe **1** (Scheme 1) for the rapid detection and colorimetric sensing of fluoride ion in CH_3CN. The prepared probe **1** contained two phenol moieties serving as receptor units to form hydrogen bonds via the disposal of OH groups in the presence of fluoride ion. In particular, the presence of two electrondonating vinylidene substituents on the *para* position of the phenol in probe **1** decreased the

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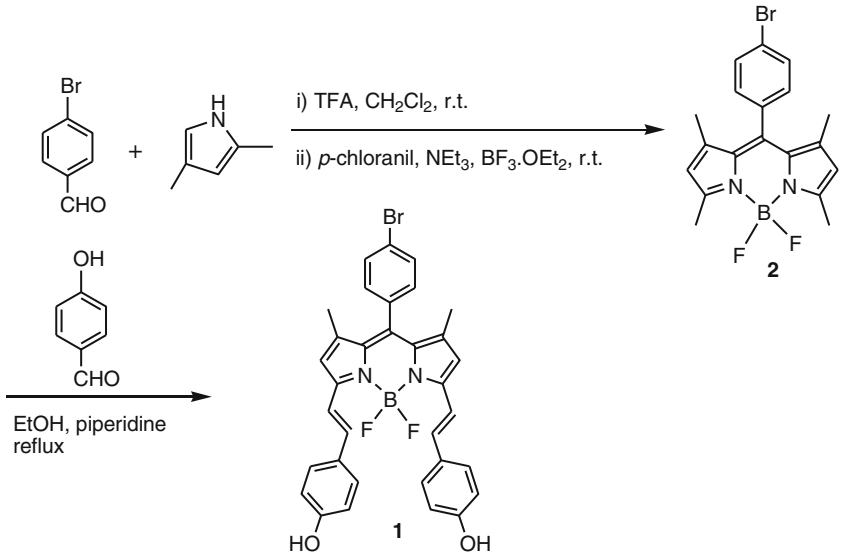
Scheme 1 Synthesis of probe **1**



acidity of its active sites and hence enhanced binding selectivity to F^- over other anions. Thus, probe **1** allowed highly selective and sensitive F^- detection by both colorimetric 'naked-eye' and fluorometric analyses. The F^--induced clear color change from pink to indigo and quenching of orange fluorescence were simply driven by hydrogen bonding interaction between the phenolic OH proton of **1** and F^-.

Experimental

Chemicals and Instruments

Nuclear magnetic resonance spectra were recorded on Bruker Avance III 400 MHz and chemical shifts are expressed in ppm using TMS as an internal standard. The UV–vis absorption spectra were recorded using a Helios Alpha UV–vis scanning spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 FL spectrophotometer with quartz cuvette (path length=1 cm).

The solutions of anions (F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, ClO_4^-) were prepared from their tetrabutylammonium salts. **1** was dissolved in CH_3CN at room temperature to afford the stock solution (10^{-3} M). Test solutions were prepared by placing 1 mL of **1** stock solution into a 100 mL volumetric flask, adding an appropriate aliquot of each metal stock, and diluting the solution to 100 mL with CH_3CN. The resulting solution was shaken well before recording the absorption and emission spectra.

Synthesis of Compound **2**

4-Bromobenzaldehyde (1.000 g, 5.4 mmol) and one drop of trifluoroacetic acid were added to a solution of 2,4-dimethylpyrrole (1.23 mL, 12.0 mmol) in dried CH_2Cl_2. The mixture was stirred at room temperature for 24 h. Then *p*-chloranil was added and stirred at room temperature for another 1 h. Followed by a subsequent addition of triethylamine (15.8 mL) and $BF_3.Et_2O$ (15.8 mL), the mixture was stirred for another 2 h at room temperature. The reaction was stopped by the addition of the distilled water (200 mL), and then was washed 3 times with the distilled water. The organic layer was then dried over Na_2SO_4, filtered and the solvent removed. Crude product was treated with chromatography on silica gel (PE/EA, 30:1 as eluent) to yield 419.3 mg red and metallic luster solid **2** in 19 % yield. m.p. 189 °C-191 °C.

^{1}HNMR ($CDCl_3$, 400 MHz, δ, ppm): 7.64 (d, 2H), 7.17 (d, 2H), 5.99 (s, 2H, pyrrole-H), 2.55 (s, 6H), 1.41 (s, 6H).

Synthesis of Probe **1**

Compound **2** (0.34 g, 0.87 mmol), 4-hydroxybenzaldehyde (0.466 g, 0.382 mmol) and one drop of piperidine in EtOH (20 mL) were stirred for 24 h at 72 °C. After completion of the reaction, the organic layer was then dried over Na_2SO_4, filtered and the solvent removed. Chromatography on silica gel (PE/EA, 5:1 as eluent) yield 77.8 mg purple sold **1** in 11 % yield. m.p. 205 °C-207 °C.

^{1}HNMR (DMSO-d_6, 400 MHz, δ, ppm): 9.98 (s, 2H, −OH), 7.78 (d, 4H), 7.47 (d, 4H), 7.40 (d, 4H), 6.87 (d, 4H, olefin-H), 6.20 (s, 2H, pyrrolic-H), 2.49 (s, 6H).

Results and Discussions

Design and Synthesis of **1**

A convenient synthetic route to chemosensor **1** was developed as shown in Scheme 1. Compound **2** was synthesized through

a condensation of 4-bromobenzaldehyde and 2,4-dimethylpyrrole in the presence of trifluoroacetic acid (TFA) as catalyst, followed by oxidation with *p*-chloranil. The boron difluoride bridge was introduced by treatment with boron trifluoride diethyl etherate ($BF_3.Et_2O$) in the presence of triethylamine. **1** can be obtained in 11 % yield by condensation of **2** with 4-hydroxybenzaldehyde using the Knoevenagel condensation method.

Effect of Solvent Polarity on Optical Properties of 1

The absorption and emission properties of **1** were studied in different solvents of varying polarity. As shown in Fig. 1a, **1** showed a characteristic strong band corresponding to a $S_0 \rightarrow S_1$ transition at 573 nm with one vibronic component on the higher energy side at 531 nm which was separated from the main transition. The absorption band at 339 nm for **1** can be assigned to the intramolecular charge transfer (ICT) band due to an electron-donating 4-hydroxystyryl group. However, the remarkable bathochromical shifts at 579, 544 and 347 nm of the maximum absorption wavelengths of **1** were present in DMSO, respectively.

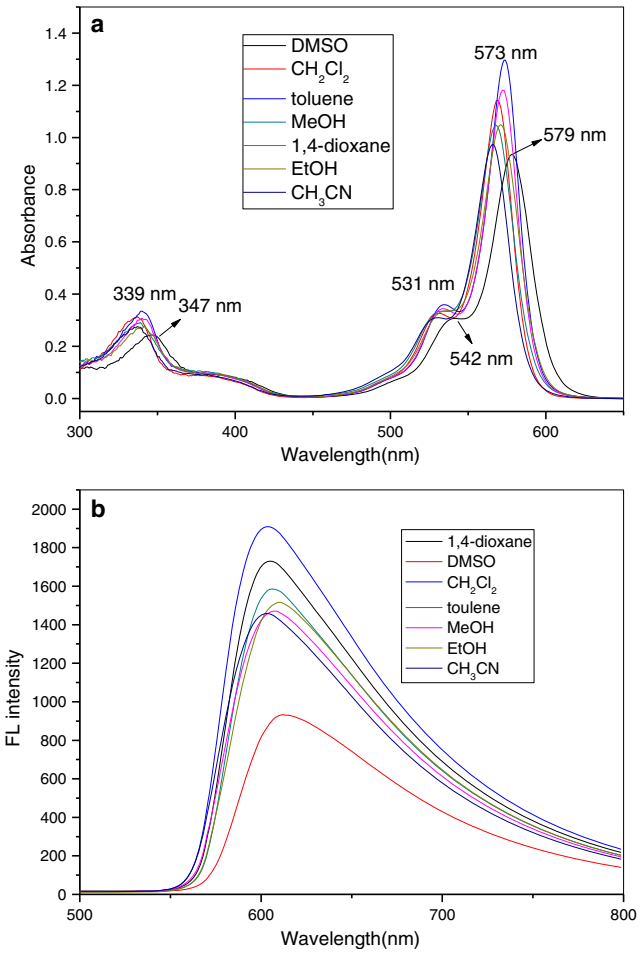


Fig. 1 **a** UV–vis (10 μM) and **b** fluorescence spectra of **1** (1 μM) in different solvents (λ_{ex}=565 nm)

With the increase in the polarity of the solvent, the fluorescence band of **1** was bathochromically shifted and emission intensity was decreased (Fig. 1b). For example, in the case of 1,4-dioxaneand DMSO, **1** showed maximum emission bands at 602 and 613 nm, respectively.

Spectroscopic Responses of 1 to Anions

The anion binding abilities of the probe **1** with F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, ClO_4^- in CH_3CN were studied through UV–vis, fluorescence spectra and naked eye color changes. The anions tested were used as their tetrabutylammonium salts while probe **1** was taken as its 1.0×10^{-5} M CH_3CN solution.

Upon addition of 20 equiv. of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, ClO_4^-) to **1**, there were no significant UV–vis spectral change in the nature of the spectra except for F^-, as shown in Fig. 2a. It was interesting to observe that upon interaction of **1** with F^-, two new absorbance peaks emerged at 402 and 683 nm. Meanwhile, the absorbance peaks at 337, 528 and 565 nm were greatly decreased. However, addition of AcO^- and $H_2PO_4^-$ only gave minor response to **1**, where absorbance peak at 565 nm slightly decreased and weak absorbance peak at 683 nm appeared.

The difference in **1** response to anions could thus be used to develop a colorimetric assay. The color change from pink to indigo occurred very rapidly (within 10 s), which was sufficiently distinct to be discriminated from other anions through naked eye itself. The corresponding naked eye changes were present in Fig. 2b.

A titration of **1** with F^- indicated that there was a gradual increase in the absorbance at 402 and 683 nm upon increment of the F^- concentration up to 50 equivalents, as shown in Fig. 3a. At the same time, the absorbance peaks at 337, 528 and 565 nm greatly decreased. This observation was ascribed to the modulation of ICT by extension of π-conjugation as the consequence of fluoride binding through –OH of the receptor **1**. Two clear isosbestic points at 484 and 587 nm were observed during the titration process, indicating formation of intermediates species with the receptor **1**. Figure 3b showed the color photographs of **1** in the presence of different F^- concentrations. With increased F^- concentrations, color of **1** solution gradually changed from pink to indigo, an agreement with the appearance of a new absorption band at about 698 nm in the corresponding UV/Vis spectra, which offered the feasibility of naked-eye detection. So **1** was a selective and sensitive colorimetric probe for F^-.

1 was decently fluorescent with maximum emission band at 602 nm upon excitation at 565 nm. The quantum yield of **1** in CH_3CN was 0.34, which was determined at 25 °C using fluorescein in 0.1 M NaOH aqueous solution as standard

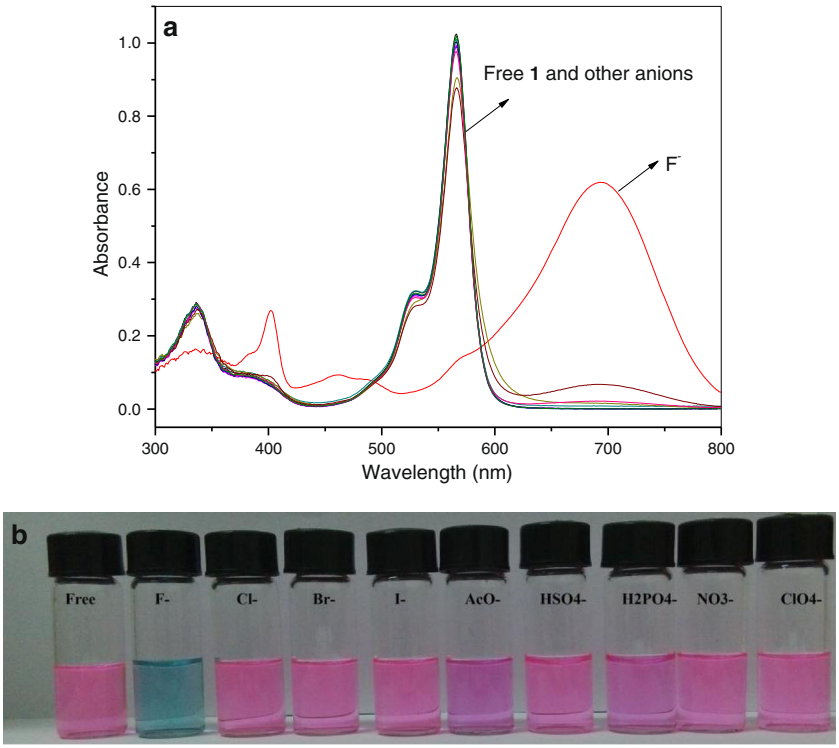


Fig. 2 **a** UV–visible spectra of **1** (10 μM) in ethanol in the presence of 20 equivalents of different anions. **b** Visual changes observed for **1** in the presence of different anions under daylight

(λ_{ex}=490 nm, Φ=0.85) [31]. On addition of F^- to the solution, the fluorescence quenching of 98 % was observed and the emission peak underwent a minor blue shift from 602 nm to 593 nm, suggesting that the new species is much less luminescent than the original one. This may be ascribed to the O–H···F hydrogen bonding, which enhanced the electron-

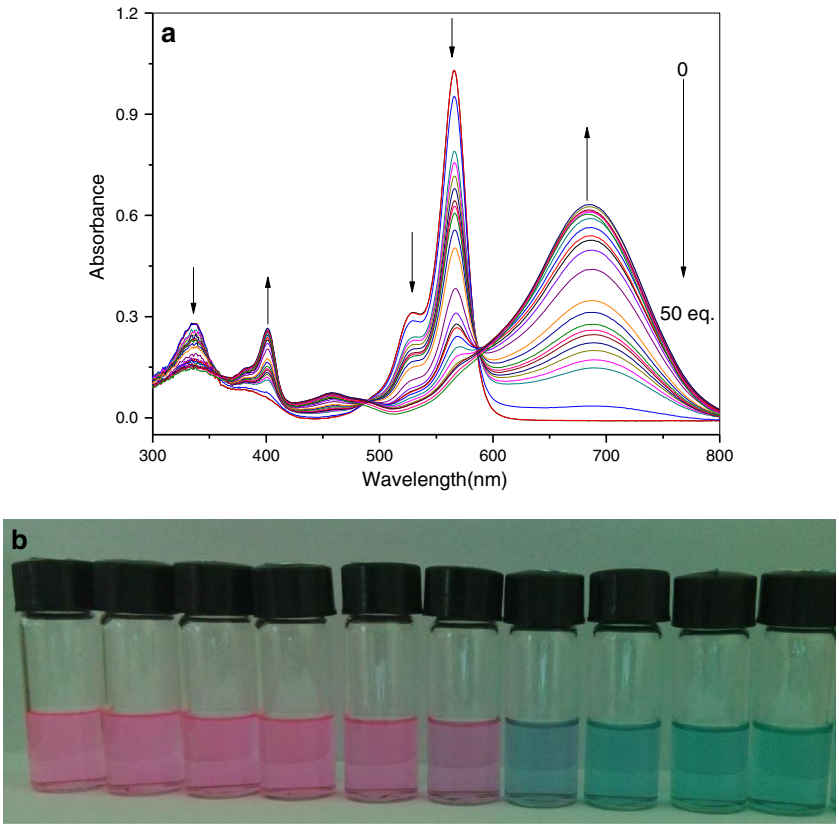


Fig. 3 **a** UV–vis spectra of **1** (10 μM) in the presence of varying concentration of F^- in CH_3CN. **b** Photographs of **1** (10 μM) in CH_3CN with F^- ranging from 0, 10, 20, 30, 40, 50, 100, 150, 200 and 300 μM from left to right

donating ability of phenolic OH and facilitated the intramolecular photoinduced electron transfer from the phenolate moiety to the excited BODIPY core, resulting in fluorescence turn-off. But addition of Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, ClO_4^- resulted in insignificant changes in the fluorescent spectra (Fig. 4a). In the case of AcO^- and $H_2PO_4^-$ anions, fluorescence quenching rates of 29 and 21 % were obtained, respectively. However, these changes were smaller in magnitude when compared to F^-. Thus, the significant change in the fluorescent intensity of **1** with a clear color change from fluorescent orange solution to nonfluorescent solution in presence of F^- was present, an agreement with the appearance of fluorescence quenching of 98 % in the corresponding fluorescence spectra. In the presence of the other anions no changes in fluorescence were observed. The corresponding naked eye fluorescence changes were present in Fig. 4b. All these findings suggested that **1** allowed selective and sensitive F^- detection over other anions by both colorimetric and fluorometric analyses. The possible reason maybe that the introduction of electrondonating vinylidene substituents on the *para* position of the phenol decreased the acidity of the proton, and thus the hydrogen bonding ability was reduced. **1** can only interact with fluoride ions due to its higher electronegativity and its smaller size compared to the other halides.

To test whether **1** can detect F^- selectively even in the presence of other anions, competitive anion titrations were carried out. **1** was treated with 20.0 equiv. of F^- in the presence of 20.0 equiv. of all other anions. The results indicated miscellaneous competitive anion did not lead to any significant spectral change and F^- ions still resulted in the similar fluorescence quenching in the presence of competitive anions, as shown in Fig. 5. Thus, the selectivity of **1** toward F^- was not affected by the presence of other anions. All the above results clearly indicated that **1** could be used as a new chemosensor for F^- by the colorimetric and fluorescence dual mode.

The quenching constant of **1** by F^- was estimated by Stern−Volmer equation, and the quenching constant was found to be 1.15×10^5 M^{-1}, as shown in Fig. 6. In addition, limits of detection (LOD) were determined from the equation $LOD = K\times Sb_1/S$, where K =3, Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve [32]. The obtained result was 1.2 μM for F^- with **1** using emission measurements.

For determination of stoichiometry between **1** and F^-, Job's plot analyses were used. The method is that keeping total concentration of **1** and F^- at 20.0 μM, and changing the molar ratio of F^- (X_M; $X_M=[F^-]/\{[\mathbf{1}]+[F^-]\}$) from 0.1 to 0.9. From Fig. 7, when molar fraction of F^- was 0.3, the absorbance at 698 nm got to maximum, indicating that forming a 1:2 complex between **1** and F^-.

Moreover, the binding stoichiometry and the binding constant to F^- were determined by Benesi–Hildebrand double reciprocal method following Eq. (1) [33, 34]. Here I_0 and I_m are the fluorescence intensities at zero and the maximum concentrations of F^-, $[F^-]$ is the total F^- concentration, K_b is the binding constants for 1:2 binding mode. For probe **1**, a good linear fit could be obtained by Eq. (1), indicative of the

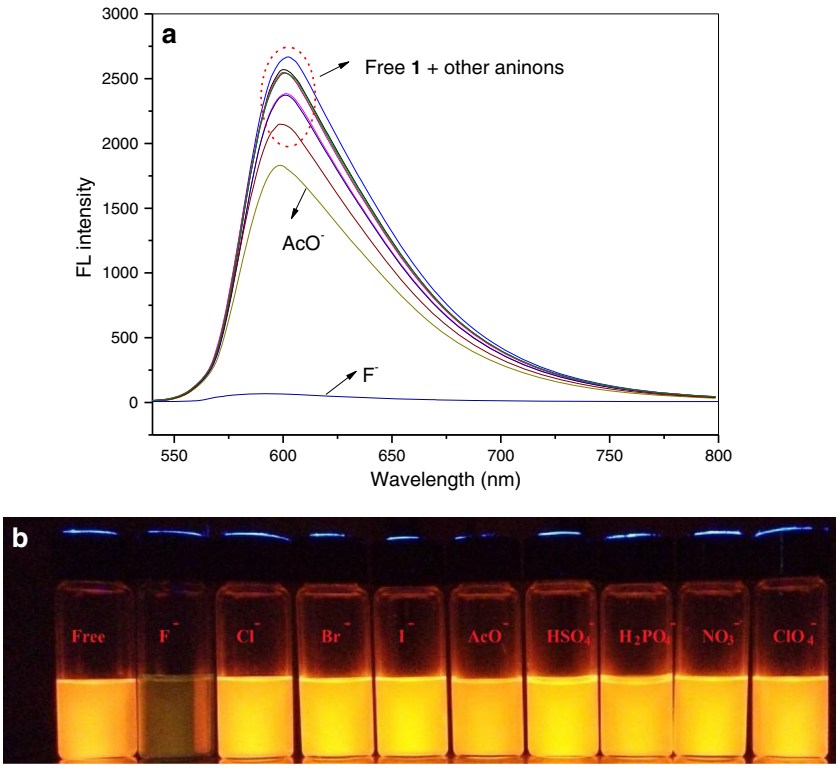


Fig. 4 **a** Fluorescence emission spectra of **1** (10 μM) in ethanol in the presence of 20 equivalents of different anions. **b** Visual emission changes observed for **1** in the presence of different anions under 365 nm

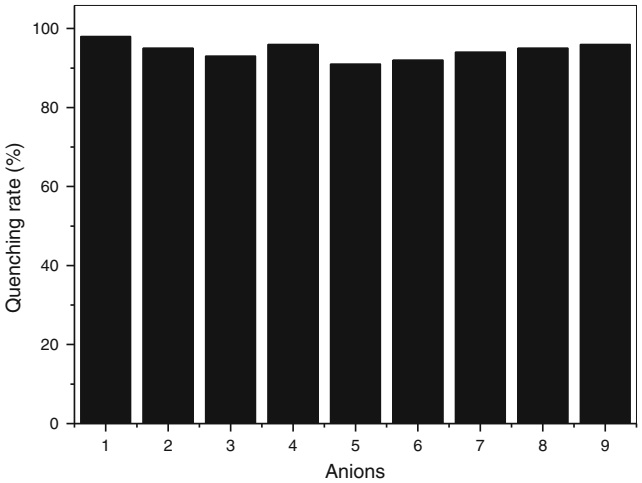


Fig. 5 Fluorescence quenching rate of **1** (10 μM) in the presence of 200 μM F^- and with the addition of 200 μM different anions. 1: **1**+ F^-; 2: **1**+ F^-+Cl^-; 3: **1**+ F^-+Br^-; 4: **1**+ F^-+I^-; 5: **1**+ F^-+AcO^-; 6: **1**+ F^-+ HSO_4^-; 7: **1**+ F^-+$H_2PO_4^-$; 8: **1**+ F^-+NO_3^-; 9: **1**+ F^-+ClO_4^-

binding stoichiometry of 1:2, which conformed to the presence of two phenolic OH groups in probe **1**. The binding constant was found to be 8.95×10^9 M^{-2}. Similar results have been reported for fluoride ion sensing by use of other BODIPY dyes [30].

$$\frac{1}{/_{0^-}/} = \frac{1}{[/_{0^-}/][1]}\left(1+\frac{1}{K_b[F^-]^2}\right) \quad (1)$$

^{1}H NMR Studies

^{1}H NMR chemical shift of the phenolic OH is a good measure of its acidity. The OH proton chemical shift of **L** located at 9.98 ppm in DMSO- d_6, suggesting that the OH acidity was

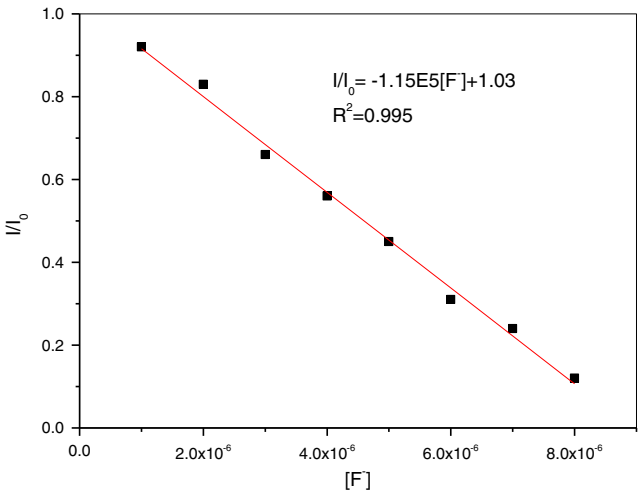


Fig. 6 The linear relation for concentration of F^- in the range of 0–8 μM. I_0 and I are the emission intensities at 602 nm of **1** in the absence and presence of F^-, respectively

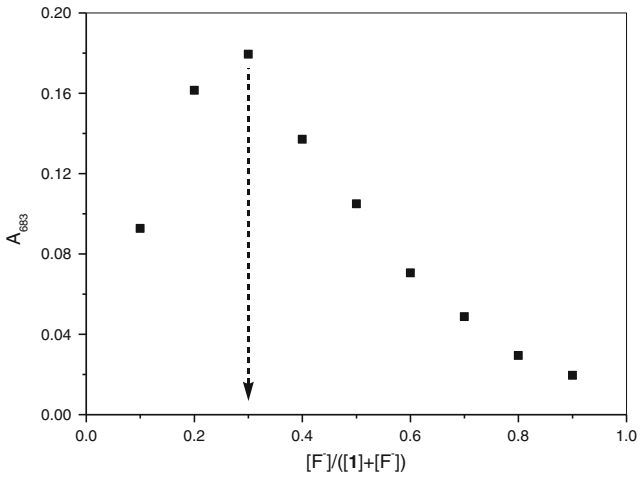


Fig. 7 Job's plot of probe **1** with F^- in CH_3CN using their absorbance changes measured at 683 nm

low due to presence of the electron-donating ability of the substituent. Similar results have been reported by Wang's group in the case of phenolic OH-containing BODIPY dyes [30]. They found the variation of the substitution position of OH group and the presence of ancillary substituent, e.g., methoxy group and *t*-butyl group, may lead to significant differences in F^- binding selectivity.

As the visible changes were observed with only fluoride hence, ^{1}H NMR titrations of **1** were performed with fluoride by its concomitant additions as its tetrabutylammonium salts to the 5×10^{-3} M solution of **1** in DMSO-d_6. The partial ^{1}H NMR spectra were given in Fig. 8. Upon addition of F^-, the signal of –OH underwent a remarkable decrease in intensity. The completely vanishing of –OH took place at 2.0 equiv. for fluoride, which was in agreement with formation of 1:2 complex between **1** and F^- from Job's plot. At the same time, the chemical shifts of 4-bromophenyl protons were almost unchanged, whereas all the other protons of phenyl ring, pyrrole and vinylidene were upfield-shifted. Similar phenomena were often observed for F^- sensors based on hydrogen-bonding interaction mechanism [35, 36]. At large excess of F^-, we did not observe any signal for $[HF_2]^-$ in its ^{1}H NMR spectral titrations even up to δ 20 ppm probably due to its instability in highly polar solvents like DMSO [37].

Practical Application

To examine the practical application of probe **1** for the detection of F^-, we investigated the recognition of F^- by probe **1** while supported on silica. The color and emission changes of **1** on silica before and after addition of F^- were shown in Fig. 9. Firstly, a solution of **1** in CH_3CN (20 mL, 10^{-4} M) was added to silica (200–300 mesh, 2.00 g, colorless), stirred for 1 min, after which time the solvent was removed to provide a pink silica. The silica was treated with a solution

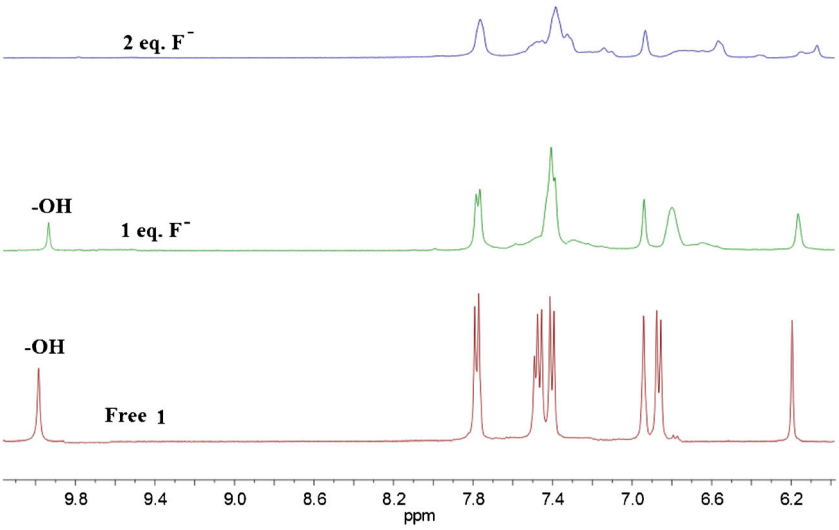


Fig. 8 Partial ^{1}H NMR spectra of **1** in DMSO-d_6 in the presence of 0, 1.0 and 2.0 equiv. of fluoride ions

of F^- (2 mL, 10^{-3} M) in CH_3CN. An instant color change from pink to indigo was noticed. The solvent was removed under reduced pressure, and the silica samples were dried in an oven to obtain indigo materials, as shown in Fig. 9a. Moreover, the bright fluorescence of **1** silica being completely quenched was clearly visualized by bare eyes when it was immersed into CH_3CN solution of F^- (2 mL, 2×10^{-3} M) in CH_3CN. Since the color change was rapidly and clearly detected, probe **1** has the potential for use in practical applications such as optical solid sensors [38, 39].

Reversibility and Reusability of the Probe **1**

Most of the F^- ion sensors available in the literature are irreversible and can be used only one time. It is very beneficial if a probe can be reversible in nature and be reusable for sensing selective anion. To test the reversibility and reusability of **1**, we carried out systematic titration studies of **1**-F^- complex upon addition of increasing amounts of trifluoroacetic acid (TFA) by absorption and fluorescence techniques. The absorption spectral titration of **1**-F^- complex with increasing addition of TFA (0–10 equiv.) in CH_3CN solution is shown in Fig. 10a. Addition of increasing equivalents of TFA to a solution of **1**-F^- complex resulted in the significant increase in the absorption bands at 337, 528 and 565 nm, whereas two absorbance peaks at 402 and 683 nm were greatly decreased. It was clearly shown that addition of 10 equiv. of TFA to **1**-F^- complex was needed to go back to the initial spectrum of original **1**. These findings supported protonation of the phenolic oxygen negative ion. Similarly, we also monitored the systematic titration studies of **1**-F^- complex upon addition of increasing equivalents of TFA by fluorescence studies in CH_3CN solution. Upon addition of increasing amounts of TFA to **1**-F^- complex, the fluorescence emission gradually increased, and emission peak underwent a minor red shift from 593 nm to 602 nm. Finally, 10-fold enhancement was observed on addition of 10 equiv. of TFA (Fig. 10b). Thus, upon F^- ion addition, the phenol moiety was electron-rich via deprotonation and engaged in photoinduced electron transfer quenching of the BODIPY excited state. But, upon titration

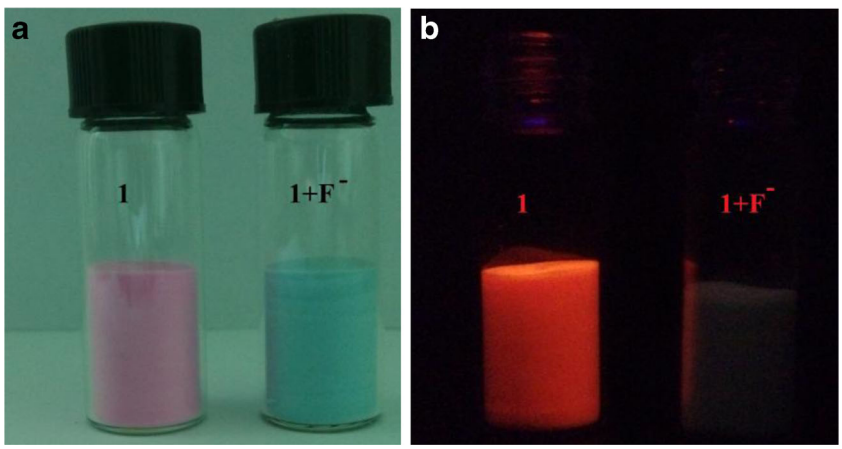


Fig. 9 Color change of **1** on silica before and after addition of F^- under daylight (**a**) and UV lamp (**b**)

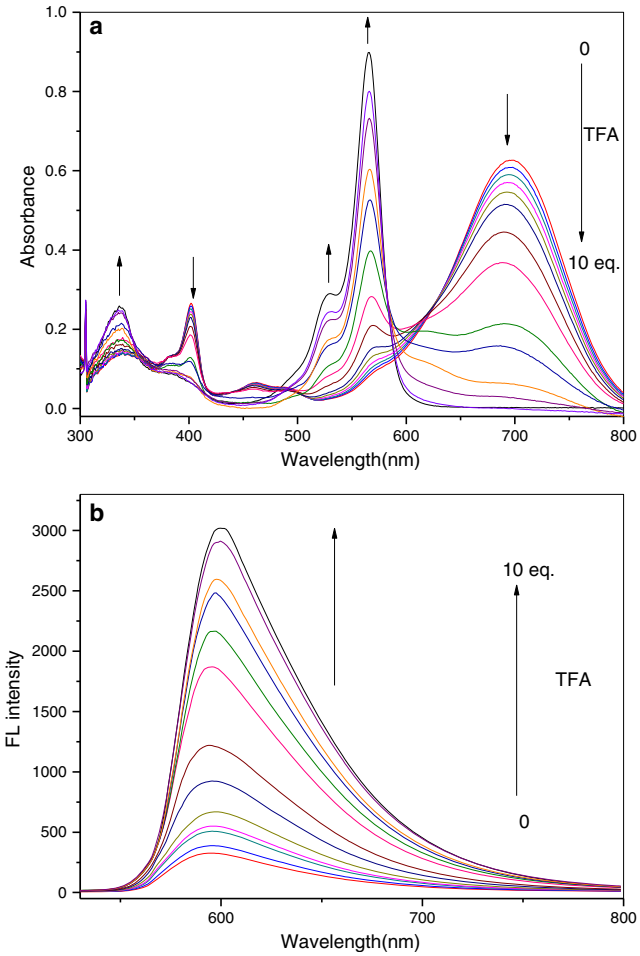


Fig. 10 **a** Absorption and **b** emission spectral changes of **1**-F^- solution (10 μM) upon addition of increasing equivalents of TFA (0–10 equiv.) in CH_3CN solution. Excitation wavelength used was 565 nm

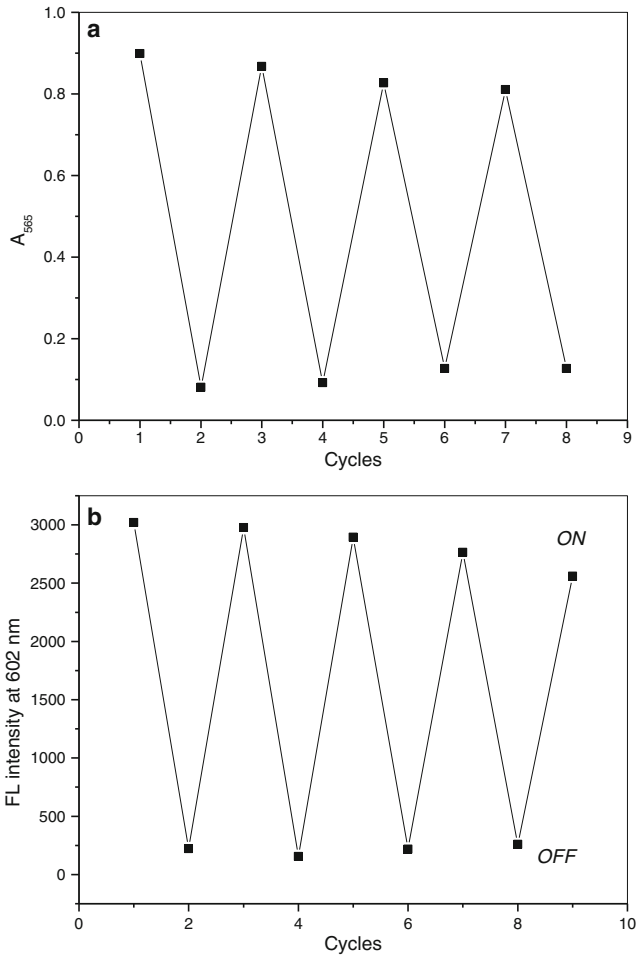
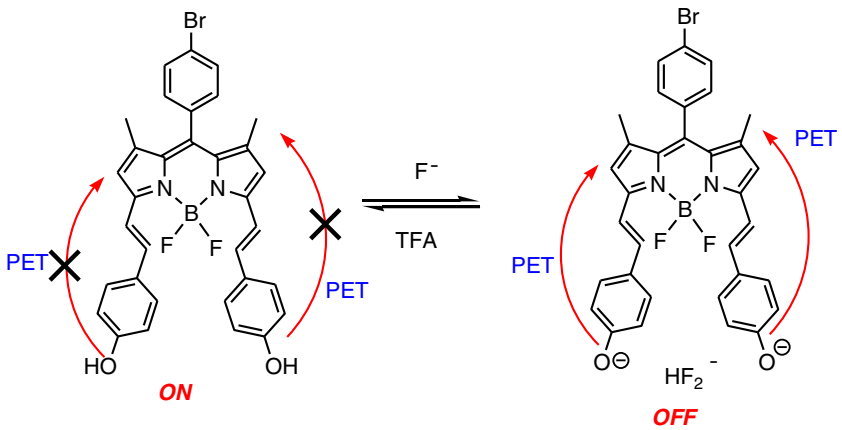


Fig. 11 Reversibility and reusability of **1** for sensing F^- sequentially: **a** relative absorbance data at 565 nm and **b** relative fluorescence intensity at 602 nm obtained during the titration of **1** with F^- and H^+ (TFA) in CH_3CN solution

with TFA, the photoinduced electron transfer quenching was prevented because of protonation of phenolic oxygen negative ion. So, the absorption and fluorescence properties were reverted (Scheme 2). The reversible and reusable response of **1** was demonstrated by carrying out four alternate cycles of titration of **1** with F^- ion followed by addition of TFA by absorption and fluorescence measurements (Fig. 11). Titration of **1** with F^- ion resulted in quenching of fluorescence due to the formation of **1**-F^- complex, thus acting as an OFF switch. However, titration of the **1**-F^- complex with TFA resulted in

Scheme 2 Proposed mechanism of fluorescence On/Off for **L** upon addition of fluoride and TFA causes operation of photoinduced electron transfer process



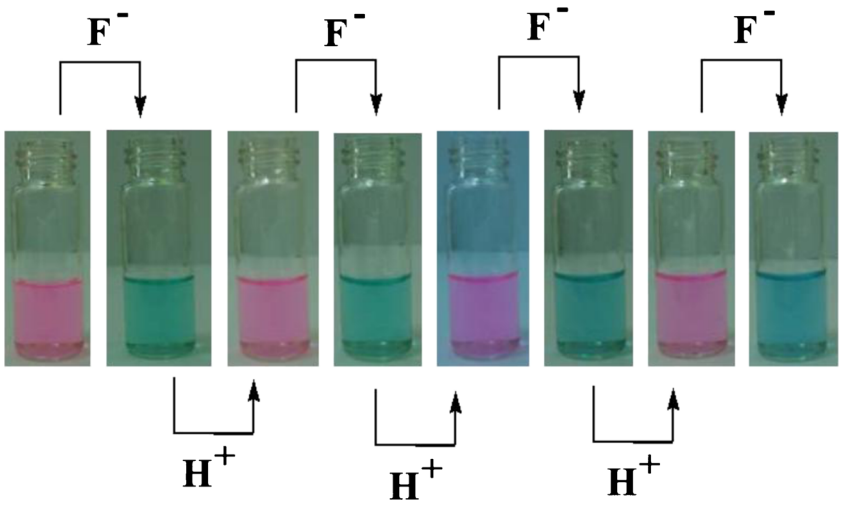


Fig. 12 Visual color changes of **1** after each sequential addition of F^- and H^+ ions

protonation of the phenolic oxygen negative ion and formed **1**, which was accompanied by significant increase in the fluorescence intensity, thus acting as an ON switch (Fig. 11b). The repeated demonstration of the OFF/ON behavior of fluorescence as well as visual color changes from pink to indigo and then back to pink was shown in Fig. 12, demonstrating the reversibility and reusability of probe **1**. Herein, in the presence of 10 equiv. TFA, the color change from indigo to pink and fluorescence recovery occurred very rapidly (within 10 s), indicating high efficiency was the unique feature of **1**. This was impressive as some reported reversible F^- probes require long reaction time to reach a maximal spectral signal. For example, Madhu et al. reported the maximal spectral signals were recovered after the addition of TFA to BODIPY-F^- system for 10 min [5j].

Conclusions

Our studies clearly showed that **1** can act as a sensitive probe for the detection of F^- over various other anions. Addition of F^- ions to a solution of **1** led to a complete quenching of fluorescence of the BODIPY moiety accompanied by a visually detectable color change from pink to indigo. Competitive binding experiments in the presence of various anions demonstrated that **1** could specifically detect F^- ions. The reversible binding properties of **1**, a crucial key point for the development of regenerable probes, was clearly highlighted. Interestingly, systematic addition of TFA to nonfluorescent [**1**-F^-] solution resulted in the significant enhancement of fluorescence intensity. The reversibility and reusability of **1** for sensing the F^- ion had been demonstrated by sequential addition of F^- ions followed by TFA over four cycles, indicating **1** could be used as a reversible and reusable probe for F^- ion.

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