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Extending the Chemistry of Reaction between BODIPY and Cyanide Ions: An Application in Selective Sensing of Fluoride and Cyanide Ions

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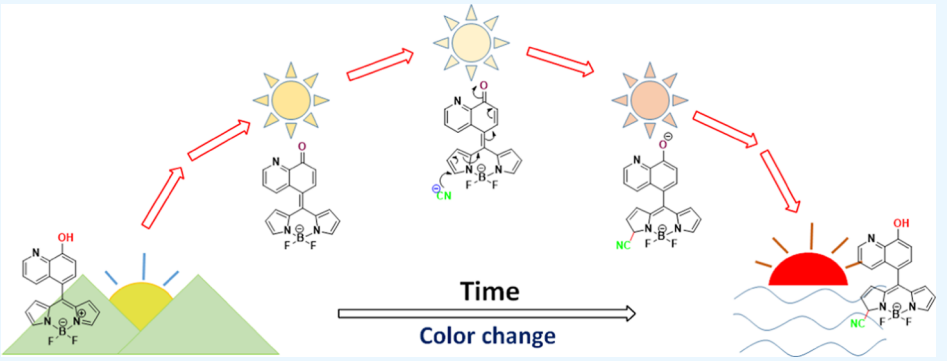

ABSTRACT: A novel colorimetric BODIPY-based probe for selective detection of fluoride and cyanide has been developed. The color of the solution significantly changes upon addition of fluoride and cyanide ions with detection limits of 2.2×10^{-7} and 1.8×10^{-7} M calculated by UV−vis absorption method for F^- and CN^- respectively. An unprecedented phenomenon about the interaction of cyanide ions with the probe was discovered which has not been reported yet. The green color of the paper strip in the presence of cyanide ions changes with time. This observation indicates that unlike fluoride, the cyanide ion interaction with the probe is beyond mere deprotonation of the phenolic group rather envisaged as nucleophilic addition reaction. The phenomenon was also observed in the solution phase and subsequently the reaction order and rate constant of the reaction were determined from absorption versus time graph which were found to be first order and 0.3465 s^{-1} respectively. The emission spectra also showed different behavior of interaction with time for the two ions. The rate of the reaction was found to be independent of the solvent polarity. The plausible mechanism of the reaction between cyanide and fluoride ions with the probe was proposed based on ^1H NMR titration experiments and mass spectrometry.

INTRODUCTION

Anions play important roles in biological, physiological and industrial cases.[1] Among them fluoride and cyanide ions are being considered most alarming owing to their terrific effect on health and environment.[2−7] Therefore, developing sensors for selective detection of F^- and CN^- below their permissible limit is of great importance.

Among the different mechanisms of sensing, the most common one is based on hydrogen bond interactions with the anion. Other methods involve anion-induced reaction to form new compounds.[8] The latter method of detection of anions is advantageous over the former since anions with similar basicity can interfere the detection process. Based on this mechanism, sensors containing BODIPY moiety are reported owing to their high molar absorption coefficient, photo and chemical stability, high quantum yield and so on.[9−11] Fluoride and cyanide ions show nucleophillic displacement reactions to break the BODIPY moiety which in turn change the color of the solution.[12] Unlike fluoride ions, CN^- can also bind to the BODIPY moiety through nucleophilic addition reaction to the pyrrole ring of BODIPY. Moreover, reactions between BODIPY and cyanide ions for instance nucleophilic addition reactions to unsaturated double bonds through Michael addition, nucleophilic addition to formyl group, etc., are also used for selective detection of cyanide ions.[13−18] Various research groups around the world have designed and synthesized BODIPY-based sensors for selective detection of fluoride and cyanide with detection limits calculated by the fluorometric method; these are much below the range of their

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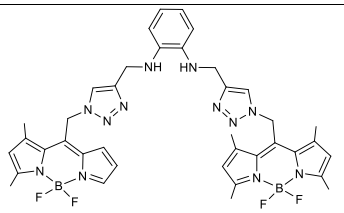
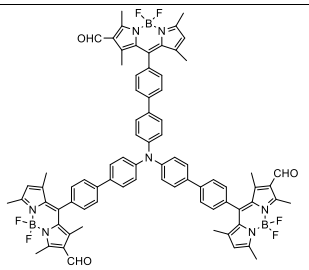
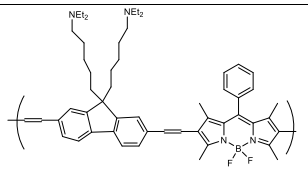
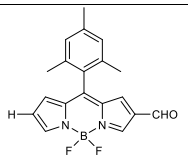
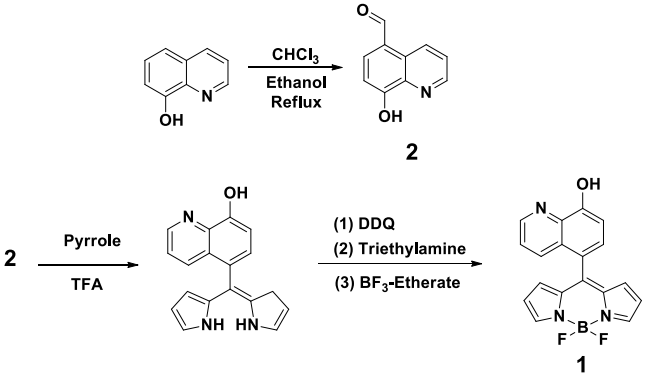
Table 1. List of BODIPY-Based Sensors for F^- and CN^- Ions

Sl no.	Probe	Detection limit (in molar)		Method	Ref.
		F^-	CN^-		
1		8.3×10^{-8}	7.2×10^{-8}	Fluorometric	20
2		3.45×10^{-7}	1.35×10^{-7}	Fluorometric	21
3		5.23×10^{-7}	2.96×10^{-7}	Fluorometric	12
4		N/A	2.5×10^{-7}	Fluorometric	22

permissible limit. Some of them are listed in the table below (Table 1).[12,15,19−22]

Based on these observations, we have designed a novel BODIPY-based sensor derived from 8-hydroxyQuinoline-5-carbaldehyde (Scheme 1). The sensor selectively detects fluoride and cyanide ions in the presence of other commonly associated anions. Also, it shows anomalous behavior in the case of CN^- ions, which is not reported so far. The color of the solution containing CN^- changes with time and finally disappears, whereas in the case of fluoride ions, it remains the same. The color change of the solution with time may be envisaged as the progress of the reaction between BODIPY and cyanide ions, which allows real-time monitoring of the progress of the reaction with naked eye. This study of the reaction kinetics may create a new avenue of monitoring reaction progression with naked eye. Moreover, this unprecedented phenomenon indicates different mechanisms of sensing for F^- and CN^- ion dissimilarity to the usual sensors reported so far.

Scheme 1. Synthesis of 8-Hydroxyquinoline-5-carbaldehyde (2) and Its BODIPY Derivative (1)



EXPERIMENTAL SECTION

General Methods. All the chemicals purchased were of analytical grade and used without further purification. 8-Hydroxyquinoline was purchased from Merck, India. $BF_3.OEt_2$, Et_3N and pyrrole were purchased from Spectrochem Pvt. Ltd. Solvents used were of spectroscopic grade. UV−vis spectra were recorded on a Shimadzu UV-1700 PharmaSpec spectrophotometer with a quartz cuvette featuring a path length of 10 mm with 2 mL solution against a solvent reference. LC−MS spectra were recorded on a Thermo Fischer Ultimate 3000/TSQ Endura spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer applying tetramethylsilane as an internal standard. Chemical shifts are given in ppm.

Synthesis of 8-Hydroxyquinoline-5-carbaldehyde. 10 g of NaOH in 8 mL of water was added into a solution of 8-hydroxyquinoline (5 g) in ethanol at 40 °C. The mixture was then heated to 65 °C; 0.013 g of CTAB (cetyltrimethylammonium bromide) was added into it, and then 5 mL of

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chloroform was dropped into it through a separating funnel within 30 min. The mixture turned black, and this resulting mixture was refluxed for another 10 h at 80 °C. Then solvents were evaporated, the residue was poured into cold water (150−200 mL), and the pH of the solution was adjusted to ca. 5 using acetic acid (checked by pH paper). The precipitate obtained was then filtered and dried. The precipitate was then further dissolved in a large quantity of chloroform and filtered again. The filtrate was evaporated and further purified by silica gel column chromatography (hexane/ethylacetate). The desired product 8-hydroxyquinoline-5-carbaldehyde was obtained as a pale-yellow powder, 0.580 gm (13% yield). LC-MS-$[M + H^+]$ peak at m/z 174.17. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.15 (s, 1H), 9.70 (d, J = 8.5 Hz, 1H), 8.88 (d, J = 3.0 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.68 (dd, J = 8.4, 4.0 Hz, 1H), 7.30 (overlapped with residual $CHCl_3$ signal at δ 7.28, d, J = 7.9 Hz, 1H), 5.32 (s, 1H).

Synthesis of HQ-BODIPY (1). The probe was synthesized using some literature methods with modification.[23] 8-hydroxyquinoline-5-carbaldehyde (0.173 g, 1 mmol) and pyrrole (0.134 g, 2 mmol) were dissolved in 60 mL of dry dichloromethane and stirred in a nitrogen atmosphere at room temperature for a few minutes. A few drops of TFA (trifluoroacetic acid) were added into the mixture, and the mixture was again stirred until complete consumption of the aldehyde (checked by TLC). The solution was then treated with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (0.227 g) (1 mmol), and stirring continued for another 2 h. After that, Et_3N (2 mL) was added, followed by addition of $BF_3{\cdot}OEt_2$ (2 mL). Then the resulting mixture was stirred for another 6 h. The reaction was quenched by washing with water. The organic phase was dried over $MgSO_4$ and evaporated. Further purification was done by silica gel column chromatography (ethyl acetate/hexane). The desired compound was obtained as brown-green crystals, 70 mg, (21%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.87 (d, J = 5.3 Hz, 1H), 8.28 (d, J = 8.6 Hz, 1H), 7.99 (s, 2H), 7.64 (d, J = 7.9 Hz, 1H), 7.46 (dd, J = 8.6, 4.1 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 6.71 (d, J = 4.1 Hz, 2H), 6.51 (d, J = 3.8 Hz, 2H) 5.33 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 114.05, 119.99, 122.46, 126.42, 128.81, 129.50, 130.85, 130.90, 132.44, 134.67, 139.31, 146.80, 162.27, 167.86. LC-MS-$[M + H^+]$ peak at m/z 336.17.

RESULTS AND DISCUSSION

The probe was synthesized following the modified reported procedure and characterized by LCMS, ^{1}H NMR, and ^{13}C NMR spectroscopy. The spectral properties of the probe with different anions were examined by UV−vis spectroscopy. Anions, namely, F^-, Cl^-, Br^-, I^-, CN^-, ClO_4^-, AcO^-, HSO_4^- and HCO_3^- were taken as tetrabutyl ammonium salts, and solutions of both anions and the host were prepared in acetonitrile. The UV−vis spectra of the probe (10^{-4} M) show absorptions at approx. 330 and 494 nm. On addition of TBACN solution, the absorbance at 330 and 494 nm decreases with the emergence of peak at a longer wavelength (680−685 nm) (Figure 1a). Consequently, the color of the solution turns yellow to green, enabling naked eye detection of cyanide ions (Figure 2). The isosbestic point at a wavelength of 570 nm indicates one-to-one interaction between the probe and anion. The titration experiment with the cyanide ion was completed within 30 min.

Based on the changes in absorption, the binding constant of the interaction between the cyanide ion and the probe was calculated using the Benesi−Hildebran equation and found to be 1.37 × 10^4 M^{-1}. A similar change in absorption was observed upon addition of fluoride ions with a binding constant of 6.11 × 10^3 M^{-1} (Figure S6). The binding constant of the former was found to be higher, which may be attributed to higher basicity and nucleophilicity of the cyanide ion compared to fluoride. The detection limits were found to be 2.2 × 10^{-7} and 1.8 × 10^{-7} M for F^- and CN^- respectively, which fall within the recommended concentration range of the WHO (Figure S7). Similar titrations were also carried out for anions such as chloride, bromide, iodide and perchlorate, bicarbonate, bisulfate and acetate. The changes in absorption in these titrations are insignificant, and their presence does not interfere the detection of fluoride and cyanide ions (Figures S8 and S9).

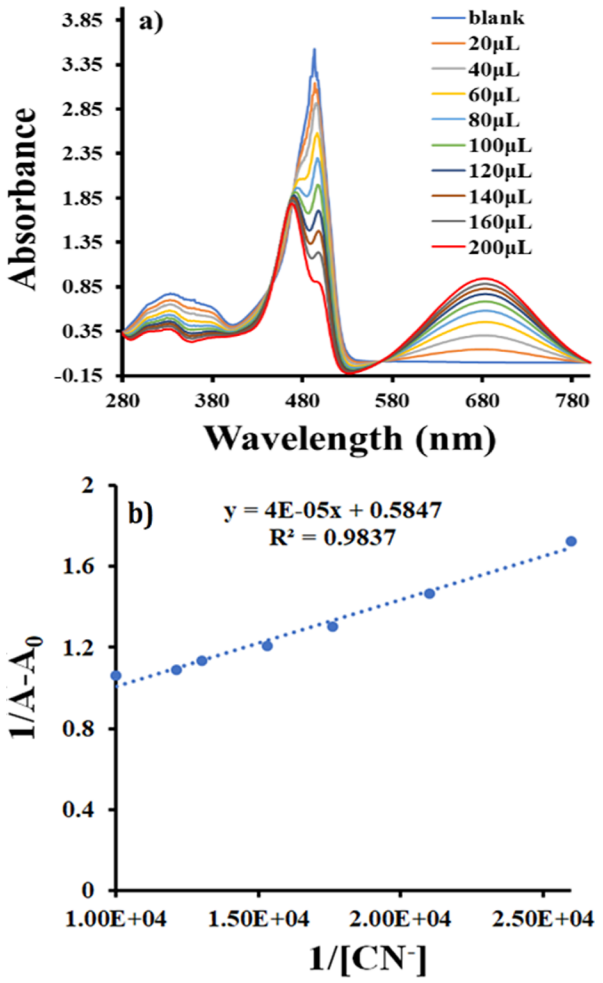

Figure 1. (a) Overlaid absorption spectra of compound **1** (10^{-4} M) with TBACN (10^{-3} M) in acetonitrile; (b) binding constant plot at 680 nm.

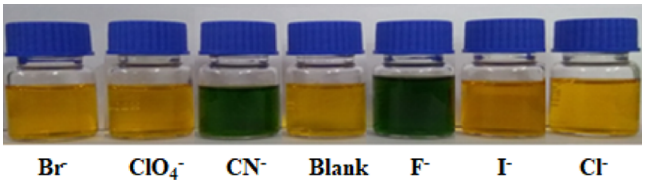

Figure 2. Colorimetric responses of compound **1** in the presence of different anions in acetonitrile.

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To make the probe, more practical paper strip experiments were performed. Paper strips were prepared by immersing the strips of filter paper in chloroform solution of the probe and subsequently dried. Then these strips were dipped into the different anionic solutions prepared in acetonitrile and dried. As expected only for F^- and CN^- the strips showed color change (Figure 3). The difference in colors of the strips on treatment with the respective anionic solution is clearly visible with naked eye.

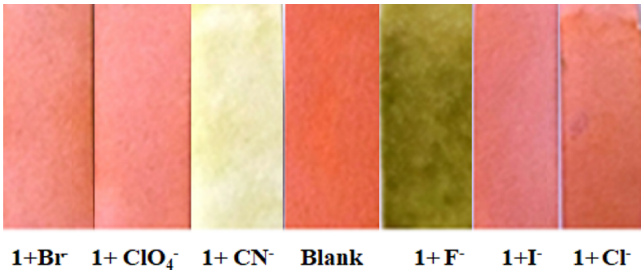

Figure 3. Change in color of the probe on paper strips after treating with different anions.

Interestingly, an unprecedented phenomenon was observed in the above experiment. The green color of the strip on treatment with cyanide solution changes with the progress of time, which was not observed with fluoride ions. This change of color with time enabled recognition of these ions from each other as well as from other associated ions. To get further insight into the phenomenon, we have carried out the study in the solution phase. In the study, the color change of the 1:1 (host:CN^-) solution in acetonitrile with time was monitored. As mentioned above, the instantaneous color of the solution is green, which turned light brown and then red after each 2 h interval, and finally, the solution was almost colorless after 6 h (Figure 4a). The corresponding change in the absorption of the solution was also monitored. The absorption at 680 nm gradually decreases with time. As anticipated, the peak which appeared on addition of cyanide ions disappears completely after 6 h (Figure 4b). This phenomenon is not observed in the case of fluoride (Figure S10), which clearly indicates that different mechanisms of sensing are involved in the case of cyanide ions.

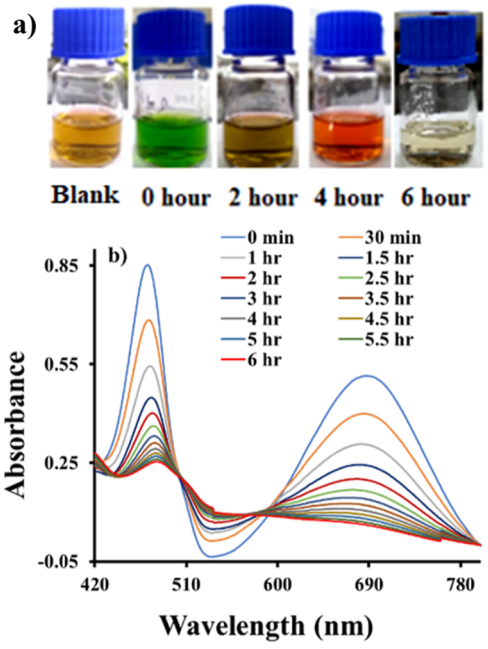

Figure 4. (a) Color change of the solution containing cyanide ions with time; (b) corresponding decrease in absorption of the solution with time.

The time required to change the color of the solution from green to colorless may be envisaged as the duration of the reaction between the host and cyanide ions. Based on this assumption, the absorption (λ_{max} = 680 nm) versus time graph was plotted to determine the rate constant of the reaction between CN^- and the host. The graph fits well for lnA versus time, which indicates that the reaction between the host and CN^- is first order (Figure 5) and the rate constant of the reaction was found to be 0.3465 s^{-1}.

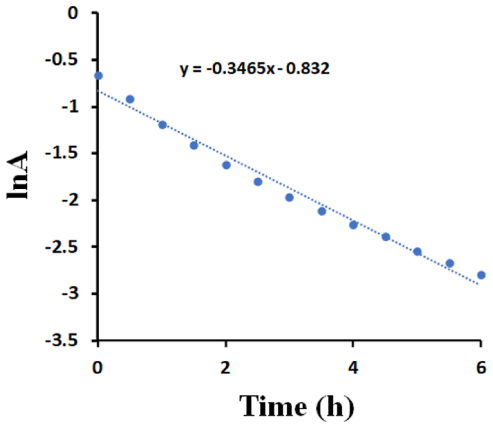

Figure 5. Absorbance vs time plot of the probe after addition of TBACN in acetonitrile.

To understand the mechanism of the sensing between the two ions and the probe, ^{1}H NMR titration and mass spectra analysis were carried out at different time intervals. Upon addition of cyanide ions, the peak at δ = 4.35 ppm corresponding to the proton of phenolic OH immediately disappeared owing to its deprotonation in the presence of CN^- ions (Figure 6). A significant change in the spectra was observed when recorded at different time intervals. After 2 h from addition of cyanide, only two peaks appeared at around 7.6 and 8.7 ppm, which may be attributed to the disruption of aromaticity of the system in the process of reaction between CN^- and the pyrrole ring of BODIPY moiety. However, at 4 h in addition to the aromatic protons, new peaks appeared in the range of δ 5.3 to 6.2 ppm, which correspond to olefinic protons with regeneration of the phenolic OH peak. The regeneration of the phenolic proton indicates reaction of cyanide ions with the probe.

Based on these pieces of evidence, we have proposed a mechanism for the reaction between cyanide ions and the probe. According to the proposed mechanism, at first deprotonation takes place resulting in the formation of phenoxide ions which imparts an intense green color to the solution due to the extension of conjugation. After a while, the color of the solution further changes as shown in Figure 4a and the solution becomes almost colorless at the end after ca. 6 h. From the literature of reaction between cyanide and BODIPY moiety, it is found that cyanide adds to the α-position of BODIPY moiety through nucleophilic addition reaction.[15,16,22]

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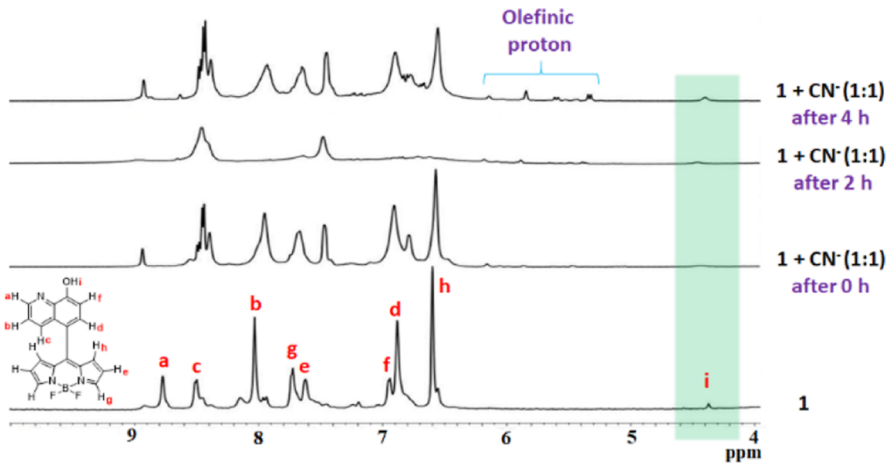

Figure 6. ^{1}H NMR spectral change of the probe in the absence and presence of TBACN in DMSO-d_6 at different time intervals.

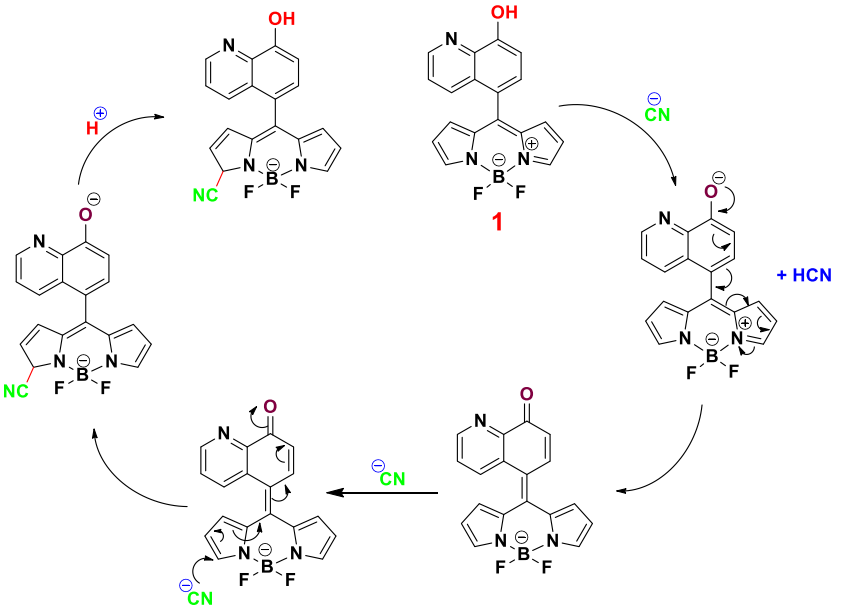

Figure 7. Probable mechanism of reaction between BODIPY and cyanide ions.

Thus, there is a possibility of nucleophilic addition of cyanide to the pyrrole ring of BODIPY moiety which results in disruption of the aromaticity of the system as shown in the mechanism. After completion of the reaction between cyanide and the probe, an addition product is generated, as shown in Figure 7. Consequently, the phenolic group retracks to its original state which decreases the conjugation existing in the system. In the process, the color of the solution changes and consequently there is change in absorption of the solution with time. The nature of interaction between cyanide and the probe contributes more insight to the type of reaction between cyanide and the BODIPY moiety.

To further confirm this plausible mechanism, mass spectral analysis was performed with the progress of time. When mass was recorded in the presence of cyanide instantaneously, a peak at m/z 334.67 was obtained which corresponds to the deprotonated form of the probe. Then for the same solution, mass spectra were recorded after ca. 4 h. A peak at m/z 361.42 was obtained which corresponds to the final addition product of the probe with cyanide (Figures S11 and S12).

To check the solvent dependency of this phenomenon, similar experiments were carried out with different solvents, namely, chloroform, THF, acetonitrile, DMF and DMSO with varying polarity. However, no obvious solvent dependency was observed, and only a slight red shift of approx. 10 nm in the absorption maxima was observed with increasing polarity from chloroform to DMSO. As mentioned, no such phenomenon was observed in the case of fluoride and no related literature studies were found after sincere efforts. Unlike cyanide, nucleophilic addition of fluoride is unusual since it behaves more like a base than a nucleophile. Thus, the difference in nucleophilicity of these two anions leads to different modes of interaction with the probe (Figure 8).

The sensing of fluoride was further investigated by ^{1}H NMR titration in the presence of F^- ions (Figure S13). When NMR spectra were recorded in DMSO-d_6, a peak at 12.0 ppm appears, which corresponds to the phenolic OH proton. Although in the titration experiment for CN^- it was found at 4.35 ppm, this time, in a totally different experiment, the peak appeared at 12.0 ppm, which may be attributed to different experimental conditions, for instance, temperature or possi-

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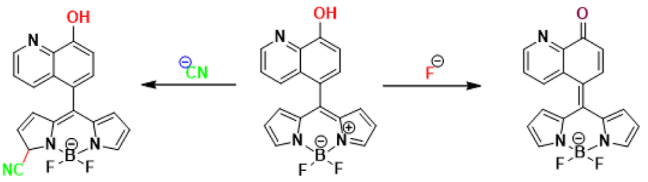

Figure 8. Possible interactions of the probe with fluoride and cyanide ions.

bility of intramolecular H-bonding between the OH proton and quinoline nitrogen atom, which can make it more downfield. Moreover, ^{1}H NMR spectra of OH/NH protons are not fixed in a particular position and may vary with experimental conditions. Upon addition of fluoride ion solution in DMSO-d_6, this peak disappeared immediately and simultaneously, the peaks in the aromatic region upfielded slightly. This upfield shift can be ascribed to the increase in electron density in the system owing to deprotonation. This increase in electron density accounts for the enhanced shielding effect of the aromatic system. When NMR spectra of the same solution were recorded again after 4 h, no further changes were observed. Mass spectra of this solution give a peak at m/z 334.33 (Figure S14), which corresponds to the deprotonated form of the probe. Thus, it may be confirmed that the sensing of the fluoride ion is merely based on deprotonation of the sensor unlike that observed in the case of cyanide ions.

Also, the fluorescence emission spectra of the compound were recorded in the presence of both the ions (i.e. F^- and CN^-). The compound shows λ_{max} at 600 nm in acetonitrile on excitation at a wavelength of 366 nm. In both the cases, on addition of the ion, the fluorescence intensity decreases gradually (Figure S15). This quenching of fluorescence intensity might be a consequence of active photoinduced electron transfer (PET) from deprotonated quinoline moiety to the BODIPY moiety. The fluorescence spectra of the compound after addition of F^- and CN^- were recorded again after 24 h. On comparison, a significant difference in fluorescence intensity was observed between the two systems, which might be attributed to the difference in interaction of the compound with fluoride and cyanide ions.

Moreover, competitive experiments were also performed with both fluoride and cyanide ions (Figure 9). It was found that the probe can detect cyanide in the presence of fluoride but not vice versa. This may be attributed to higher basicity of cyanide compared to fluoride.

CONCLUSIONS

In summary, we have developed a colorimetric BODIPY-based probe for selective detection of fluoride and cyanide over other anions. Addition of both the anions resulted in remarkable changes in color and electronic properties of the probe, which enabled their naked eye detection. The detection limit of these two anions falls below the WHO's recommended lower concentration level. The probe also differentiates fluoride and cyanide ions through different mechanisms of sensing. Plausible mechanisms of the reaction between the probe and these two ions were studied through UV−vis, fluorescence emission and ^{1}H NMR spectroscopy, which gave great insight into the nucleophilic addition reaction between the pyrrole ring of BODIPY and CN^- and merely deprotonation of the probe in the presence of F^- ions. Subsequently, the rate

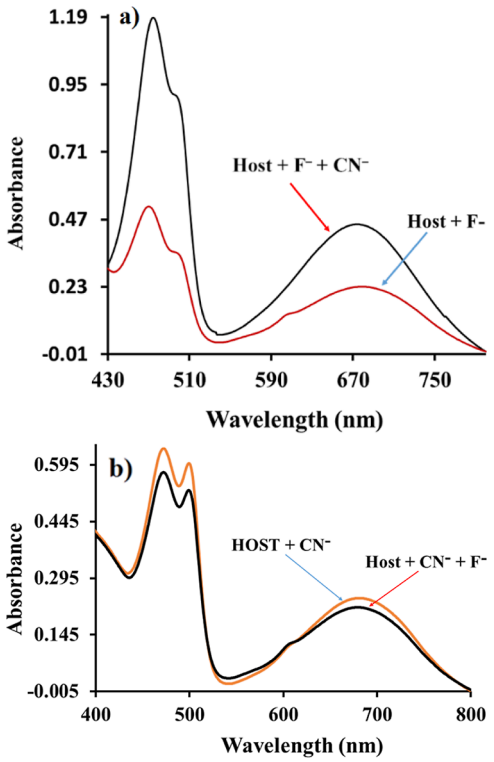

Figure 9. Competitive experiment of the probe; (a) CN^- in the presence of F^- and (b) F^- in the presence of CN^- ions.

constant and order of the reaction between cyanide and the probe was determined.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04422.

^{1}H and ^{13}C NMR spectra, LC−MS spectra, detection limit plot, binding constant plot, and UV−vis and fluorescence spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) El-Ballouli, A. O.; Zhang, Y.; Barlow, S.; Marder, S. R.; Al-Sayah, M. H.; Kaafarani, B. R. Fluorescent detection of anions by dibenzophenazine-based sensors. *Tetrahedron Lett.* **2012**, *53*, 661−665.

(2) Hudnall, T. W.; Gabbaï, F. P. A BODIPY boronium cation for the sensing of fluoride ions. *Chem. Commun.* **2008**, 4596−4597.

(3) Rao, M. R.; Mobin, S. M.; Ravikanth, M. Boron−dipyrromethene based specific chemodosimeter for fluoride ion. *Tetrahedron* **2010**, *66*, 1728−1734.

(4) Wang, L.; Li, L.; Cao, D. Dual binding site assisted chromogenic and fluorogenic discrimination of fluoride and cyanide by boryl functionalized BODIPY. *Sens. Actuators, B* **2016**, *228*, 347−359.

(5) Kumari, N.; Jha, S.; Bhattacharya, S. Colorimetric probes based on anthraimidazolediones for selective sensing of fluoride and cyanide ion via intramolecular charge transfer. *J. Org. Chem.* **2011**, *76*, 8215−8222.

(6) Ghosh, K.; Panja, S. Naphthalene-cholesterol conjugate as simple gelator for selective sensing of CN− ion. *Supramol. Chem.* **2017**, *29*, 350−359.

(7) Saikia, E.; Dutta, P.; Chetia, B. A Novel Benzimidazolyl-based Receptor for the recognition of Fluoride and Cyanide Anion. *J. Chem. Sci.* **2017**, *129*, 1−7.

(8) Wang, L.; Fang, G.; Cao, D. A novel phenol-based BODIPY chemosensor for selective detection Fe3+ with colorimetric and fluorometric dual-mode. *Sens. Actuators, B* **2015**, *207*, 849−857.

(9) Kubota, Y.; Hara, H.; Tanaka, S.; Funabiki, K.; Matsui, M. Synthesis and fluorescence properties of novel pyrazine−boron complexes bearing a *β*-iminoketone ligand. *Org. Lett.* **2011**, *13*, 6544−6547.

(10) Chen, Y.; Wang, H.; Wan, L.; Bian, Y.; Jiang, J. 8-Hydroxyquinoline-substituted boron−dipyrromethene compounds: synthesis, structure, and OFF−ON−OFF type of pH-sensing properties. *J. Org. Chem.* **2011**, *76*, 3774−3781.

(11) Zhao, X.; Gao, C.; Li, N.; Liu, F.; Huo, S.; Li, J.; Guan, X.; Yan, N. BODIPY based fluorescent turn-on sensor for highly selective detection of HNO and the application in living cells. *Tetrahedron Lett.* **2019**, *60*, 1452−1456.

(12) Wang, L.; Fang, G.; Cao, D. Highly selective and sensitive detection of F− and CN− ions simultaneously by a reaction-based BODIPY-containing conjugated polymer. *Sens. Actuators, B* **2015**, *221*, 63−74.

(13) Wang, L.; Ding, H.; Ran, X.; Tang, H.; Cao, D. Recent progress on reaction-based BODIPY probes for anion detection. *Dyes Pigm.* **2020**, *172*, 107857.

(14) Wang, L.; Li, L.; Cao, D. A BODIPY-based dye with red fluorescence in solid state and used as a fluorescent and colorimetric probe for highly selective detection of cyanide. *Sens. Actuators, B* **2017**, *239*, 1307−1317.

(15) Dvivedi, A.; Kumar, S.; Ravikanth, M. Nucleophilic addition of CN− ion to CN bond of aza-BODIPY leading to turn-on fluorescence sensor. *Sens. Actuators, B* **2016**, *224*, 364−371.

(16) Wu, F.; Liu, H.; Zhong, C.; Zhu, L. Revealing a nucleophilic addition reaction between aza-BODIPY and cyanide anion. *Tetrahedron Lett.* **2016**, *57*, 5120−5123.

(17) Guliyev, R.; Ozturk, S.; Sahin, E.; Akkaya, E. U. Expanded bodipy dyes: anion sensing using a bodipy analog with an additional difluoroboron bridge. *Org. Lett.* **2012**, *14*, 1528−1531.

(18) Aydıner, B. A chemodosimeter approach for selective colorimetric and fluorimetric cyanide detection using coumarin based fluorescent dyes. *J. Photochem. Photobiol., A* **2019**, *382*, 111916.

(19) Yu, Y.; Shu, T.; Fu, C.; Yu, B.; Zhang, D.; Luo, H.; Chen, J.; Dong, C. A novel colorimetric sensor based on BODIPY-coumarin dye for simultaneous detection of cyanide and fluoride. *J. Lumin.* **2017**, *186*, 212−218.

(20) Saiyasombat, W.; Eiamprasert, U.; Chantarojsiri, T.; Chainok, K.; Kiatisevi, S. Bis-BODIPY-based fluoride and cyanide sensor mediated by unconventional deprotonation of C−H proton. *Dyes Pigm.* **2022**, *206*, 110643.

(21) Wang, L.; Li, L.; Cao, D. Synthesis, photoluminescence, chromogenic and fluorogenic discrimination of fluoride and cyanide based on a triphenylamine-tri(2-formyl BODIPY) conjugate. *Sens. Actuators, B* **2017**, *241*, 1224−1234.

(22) Wu, Q.; Wang, S.; Hao, E.; Jiao, L. Highly selective, colorimetric probes for cyanide ion based on *β*-formyl BODIPY dyes by an unprecedented nucleophilic addition reaction. *Spectrochim. Acta Mol. Biomol. Spectrosc.* **2021**, *247*, 119102.

(23) Christianson, A. M.; Gabbaï, F. P. Anion sensing with a Lewis acidic BODIPY-antimony (V) derivative. *Chem. Commun.* **2017**, *53*, 2471−2474.

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