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FULL PAPER

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Isophorone-boronate ester: A simple chemosensor for optical detection of fluoride anion

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A highly selective isophorone-boronate ester based chemosensor, (**1**), having a dicyanovinyl moiety as a convenient colorimetric probe, has been designed. Different types of anionic analyte such as CH_3COO^-, ClO_4^-, Cl^-, F^-, PF_6^-, Br^- and HSO_4^- were tested and among them only highly nucleophilic F^- anion displayed significant response towards the sensor. Addition of the fluoride anion across the boron atom disrupts the π-conjugation thereby shifts the absorption wavelength towards the redshift region due to the decrease in the HOMO-LUMO energy gap and a colour change from yellow to blue is observed under visible light condition. The detection limit of this probe was calculated to be 3.25×10^{-8} M for fluoride anion. The binding constants and the detection limits of the sensor were calculated using absorption titration studies. The silica gel TLC strips dip-coated by the chemosensor (**1**) revealed a colour change from yellow to brick red to naked eye.

KEYWORDS

boron derivatives, chemosensor, fluoride anion sensing, optical Spectroscopy

1 | INTRODUCTION

One of the most potential and active research field in supramolecular chemistry has been the advancement of optical chemosensor for neutral and charged species detection.[1] Owing to its tremendous importance in environmental and biological purposes, the selective detection of inorganic anions has catapulted as an important area of research during the past few decades.[2] The variations in the physical properties of anions such as size, shape, charge distribution and the solvation in polar and protic solvents make the detection of anion as an intriguing subject.[3] The chemosensors relying on the colorimetric and/or optical response can be transformed into a cheap, operationally simple, low detection limit technologies.[4] A range of host/guest strategies to bind fluoride anion have been developed.[5–8] Apart from the role of fluoride anion in the dental health as well as treatment of osteoporosis, the fluoride overexposure can adversely affect bones, brain, thyroid gland and pineal gland etc. Moreover, the use of excess fluoride can also cause acute gastric and kidney problems.[9]

Typical methods employed to analyse fluoride anion, involving the use of sophisticated instrumental methods, such as titrimetric, voltammetric, potentiometric, electrochemical as well as ion exchange chromatography often exhibit high detection limits.[10] While these techniques are time-consuming, optical sensors which rely on either colour change or fluorescence intensity variations have been studied over the past few decades.[4,10] Design of anion-selective chemosensors is often based on the high nucleophilicity of fluoride anions.

By virtue of its high Lewis acid character, the boron centre has played key a role in frustrated Lewis pairs,[11] anion sensing[12,13] and carbohydrate detection.[14] However, there exists several means and ways to increase the Lewis acidic character of boron atom in an ensemble.[15] These include for instance, linking of electron withdrawing groups such as perfluorinated aryl moieties,[13,16] coulombic interactions with cations,[12a, 17] boron incorporated anti-aromatic systems[18] and boron containing extended π-conjugated arrays.[19] As illustrated in (Figure 1), different types of boron containing fluorescent probes have been studied in diverse fashion.[20] Moreover, the Lewis-acid based approaches are most effective due to their ability for quick detection, easy visualization and sensitivity.

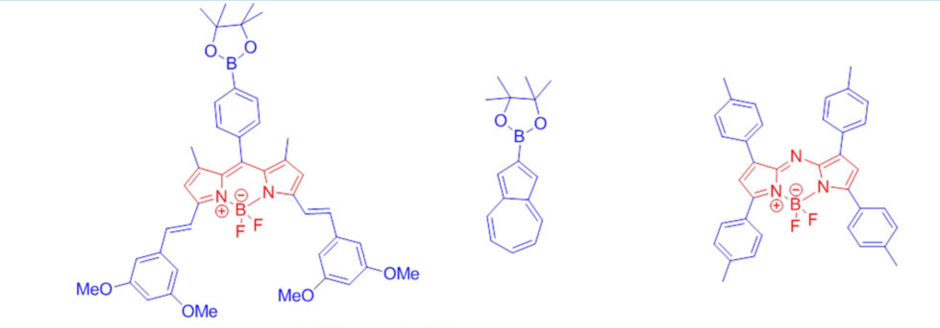
A typical Lewis acid probe consists of a binding site and a covalently linked signalling unit. The binding site captures the anion and subsequently the signalling unit exhibits an optical or fluorescent change indicating anion detection. The binding affinity, sensitivity and detection limit of the F$^-$ anion can be tuned by modulating the binding site as well as the signalling unit.[21] In order to design a turn-on receptor, it is necessary to tune the electronic interaction around boronic esters. One of the promising approaches can be the introduction of an electron-withdrawing unit π-conjugated with a tri-coordinated boron ester. The polarised π-system thus produced can significantly enhance the intramolecular charge-transfer interactions.[22] Keeping this in mind, a boron containing compound having a conjugated organic signalling unit and a sensitive pinacol boronate binding site has been designed. The coordination of a strong Lewis base, like F$^-$ anion onto the vacant Boron p-orbital can disrupt the π-conjugation thereby decreasing the HOMO-LUMO gap along with a redshift in the absorption spectra.

The isophorone unit present in the organoboron derivative has been extensively studied for its sensing abilities. This unit acts as a colour reporting group having unique optical and biocompatibility. Isophorone is a well-known push-pull charge transfer dye chemosensor which can undergo intramolecular charge transfer (ICT). Lee et al. reported a group of isophorone-based fluorescent materials as red emitters for use in OLEDs.[23] A series of isophorone based near-infrared solid state emitters have been reported, and all of the crystalline compounds were fluorescent in the solid state.[24] Linking dicyanovinyl isophorone unit onto a Boron moiety might augment enhanced sensing capabilities.

Recently our group has designed multichannel sensors for the detection of Hg^{+2}, Co^{+2}, Cu^{+2} and Zn^{+2} cations using absorption and emission spectroscopy.[25,26] Hence, herein, we describe the synthesis, characterization, anion sensing abilities and DFT calculations of a pinacol boronate linked dicyano isophorone sensor (**1**).

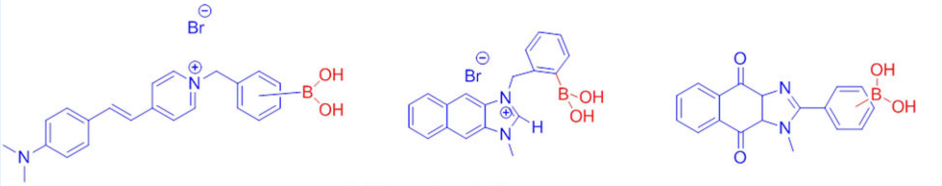
2 | RESULTS AND DISCUSSION

The pinacol boronate linked dicyano isophorone sensor, (**1**) was synthesized in three steps as shown in Scheme 1. The dicyanovinylene substituted isophorone (L-1) was prepared in the first step followed by the pinacol protection of 4-formyl phenyl boronic acid (L-2) according to the previous reports. The Knoevenagel Condensation of L-1 and L-2 under standard conditions formed the desired



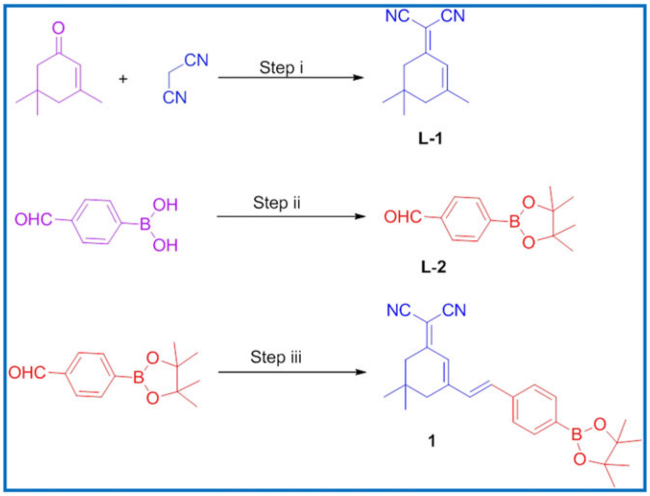
(a) Boronate Ester sesors

(b) BODIPY derivative Sensor



(c) Boronic acid Sensors

FIGURE 1 Different types of boron containing chemosensors suitable for anion detection



SCHEME 1 Synthesis of Boron based chemosensor (**1**). Reagents and reaction conditions used:Step (i): Piperidine, Dry Ethanol, 60 °C, 8 hours. Step (ii): L-1, Pinacol, Diethyl ether, 25 °C, 24 hrs. Step (iii): Knoevenagel Condensation of L-1 and L-2, Dry Ethanol, 40 °C, 8 hrs

sensor (**1**). The L-1, L-2 and sensor (**1**) were characterized by various spectroscopic tools such as, ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, HRMS, and IR analyses (Figure S1-S12 in the Supporting Information). In the ^{1}H NMR spectra, the proton chemical shifts of the phenyl ring appeared as two doublets at δ 7.75 ppm and δ 7.45 ppm, while those for the conjugated ethylene protons appeared as a singlet at δ 6.99 ppm and the conjugated olefinic proton of the isophorone moiety appeared at δ 6.79 ppm. The two methylene units of isophorone appeared as two doublets around δ 2.53–2.40 ppm and a singlet at δ 1.01 ppm appeared for the two methyl groups of isophorone. In the ^{13}C NMR spectra, the aromatic phenyl carbon appeared as singlets around δ 123.25 ppm and δ 115.31 ppm. The ethylene carbons appeared at δ 102.15 ppm and the pinacol carbons were observed in the regions δ 4.25 ppm and δ 10.71 ppm. The ^{11}B NMR spectra of the boronate ester (**1**) exhibit a broad singlet at δ 22.29 ppm which suggests the presence of boronate esters in the chemosensor (FIGURE S8 in the Supporting Information). In addition, the probe (1) was also confirmed by HRMS (Figure S10 in the Supporting Information). Similar way (**1.F**)$^{-}$ was also confirmed by ^{11}B NMR and HRMS mass spectrometry (Figure 4) (FIGURE S9, S11 in the supporting information).

The coordination of Lewis bases at the Boron centre results in the modification of the electronic properties of the Boron centre and thus changes the UV–Vis. absorption behaviour of (**1**). The complexation studies were carried out with the fluoride anion as a strong Lewis base.

2.1 | UV–Vis. Spectroscopic Studies of sensor (1) in the absence and presence of F^{-} anion

Sensor (**1**) was highly stable at 25 °C and was soluble in tetrahydrofuran (THF), dichloromethane (DCM) and acetonitrile (ACN). The solution of (**1**) appeared yellow in colour (FIGURE S13 in the Supporting Information) in THF and exhibited a band at 425 nm ($\varepsilon = 73333\ M^{-1}\ cm^{-1}$) in the absorption spectra. {(Figure 2) and (FIGURE S14 in the Supporting Information)} The sensing ability of the chemosensor (**1**) was examined by using colorimetric and fluorescence titration experiments. It was observed that among most of the anions such as OAc^{-}, ClO_4^{-}, Cl^{-}, PF_6^{-}, F^{-}, HSO_4^{-} and Br^{-} ions, the chemosensor (**1**) responded spontaneously to F^{-} anion (TBAF is the source of fluoride ion).

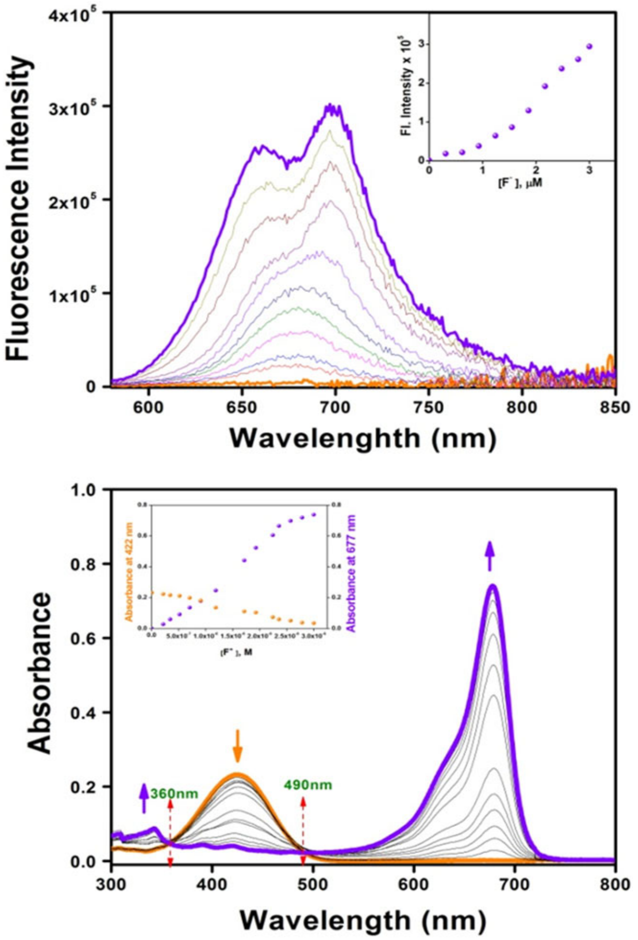
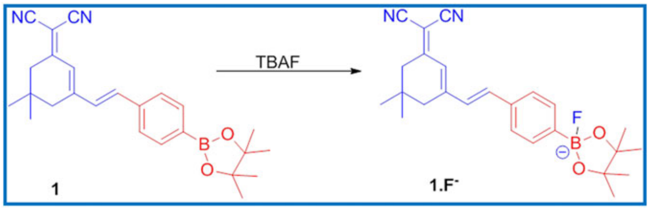


FIGURE 2 Fluorescence emission spectral changes observed when variable concentrations (1×10^{-7}-9×10^{-6} M) of F^{-} solution were added to the solution of (**1**) (3×10^{-6} M) (TOP). UV–vis. Spectral changes observed when variable concentrations (1×10^{-7}-9×10^{-6} M) of F^{-} solution were added to the solution of (**1**) (3×10^{-6} M) (BOTTOM)

The colour of sensor (**1**) changes from yellow to blue (FIGURE S13 in the Supporting Information) and generates a new F^{-} adduct on addition of tetrabutylammonium fluoride (TBAF) (Scheme 2). The F^{-} anion-adduct (**1.F**)$^{-}$ exhibited absorption at 670 nm, which can be assigned to the strong nucleophilic strength of F^{-} anion. {Figure 2 (TOP) (FIGURE S15 in the Supporting Information)} Further, various concentrations of F^{-} anions were titrated and the corresponding absorptions were recorded. Significant spectral changes were observed in the UV–Vis. spectra. On addition of the F^{-} anion, a gradual decrease of the band at 425 nm was observed and simultaneous rise of a new intense band at 676 nm with two clear isosbestic points at 360 nm, and 490 nm was observed. {Figure 2 (TOP)} HOMO-LUMO energy gap of the (**1**) and (**1.F**)$^{-}$ was found to be 2.50 eV and 1.73 eV respectively. These energy gaps were calculated from the onset absorption wavelengths 495.4 nm, 715.5 nm of (**1**) and **(1.F),**$^{-}$ respectively.



SCHEME 2 Sensing of fluoride anion

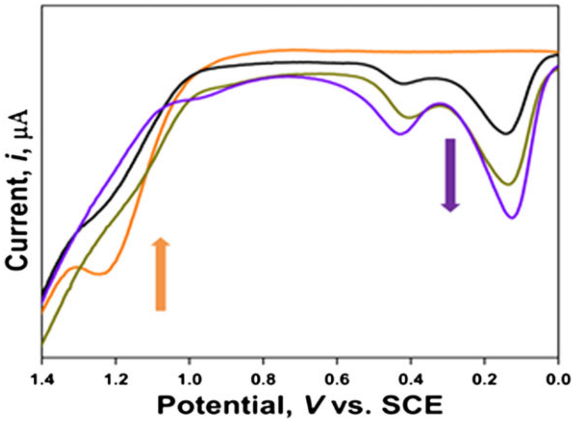


FIGURE 3 Electrochemical [differential pulse voltammogram (dpv)] titration experiment of (**1**) with F^{-} ion

From the absorption titrations and Benesi–Hildebrand (B-H) plot[27] (equation 1 in the experimental section), the binding constant (K) was found to be $K = 1.73 \times 10^{5}\ \mathrm{M}^{-1}$ for the complex (**1.F**)$^{-}$ formed in the reaction. The detection limit was obtained from the UV–Vis. data. The standard deviation $\sigma = 0.002$ was determined from the deviation in absorption spectra recorded over the concentration range (1×10^{-7} M - 9×10^{-6} M) on titration with the fluoride salt. The slope from the absorbance versus concentration plot was calculated to be $k = 2.76 \times 10^{5}$ for the fluoride anion (FIGURE S16 in the Supporting Information). The chemosensor (**1**) was found to possess certain virtues such as sensitivity, stability, and ambient working conditions. A ratio of 1:1 for **(1)** and F^{-} anion was obtained from the Job's plot using absorption titration experiment. (FIGURE S18 in the Supporting Information). The detection limit was calculated as 3.25×10^{-8} M for F^{-} anion (FIGURE S19 in the Supporting Information).

2.2 | Fluorescence Emission Studies of sensor (1) in the absence and presence of F^{-} anion

Further, in the fluorescence spectra, a weak band at 580 nm was obtained upon excitation of (**1**) at 435 nm, while a similar excitation at 570 nm failed to produce any spectra. However, the fluorescence titrations by varying F^{-} anion concentrations led to an incremental increase of emission band at 693 nm on exciting at 570 nm. {Figure 2

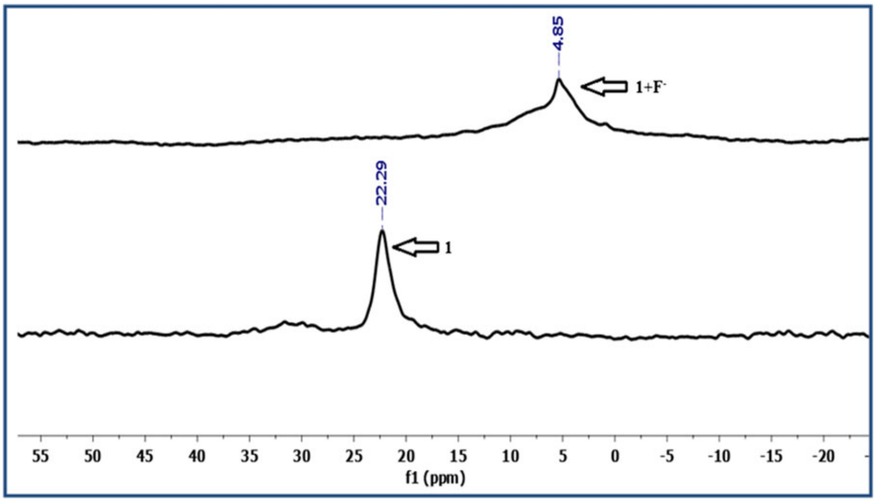


FIGURE 4 ^{11}**B** NMR spectra of (**1**) ($CDCl_3$) and in the presence of one equivalent of fluoride anion (**1.F**)$^{-}$

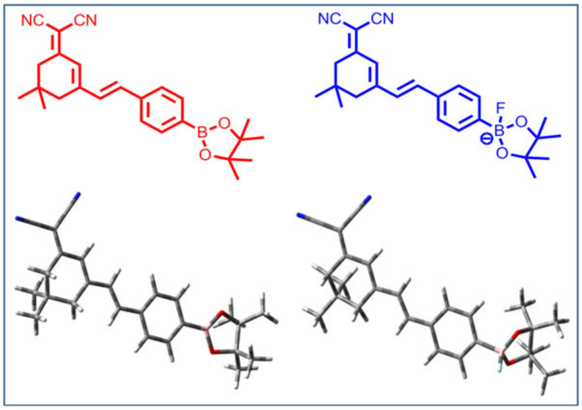


FIGURE 5 Chemical structure and DFT Optimized Geometry of Chemosensor (**1**) and complex (**1.F**)$^-$

(BOTTOM)} The binding affinity of the fluoride anions were evaluated from the (B-H) plot and equation (2) in the experimental section, while the binding constant (K) were determined to be K = 2.59× 10^5 M^{-1} for the complex (**1.F**)$^-$ (FIGURE S17 in the Supporting Information). The standard deviation $\sigma = 0.003$ was determined from the deviation observed when fluorescence intensity and concentration spectra were recorded over the concentration range (1×10^{-7} M $^{-9} \times 10^{-6}$ M) on titration with the fluoride salts. The slope from the fluorescence intensity versus concentration plot was calculated to be k = 1.025 × 10^{11} and for the fluoride anion detection limit was calculated to be 8.77× 10^{-14} M for F^- anion. (FIGURE S20 in the Supporting Information).

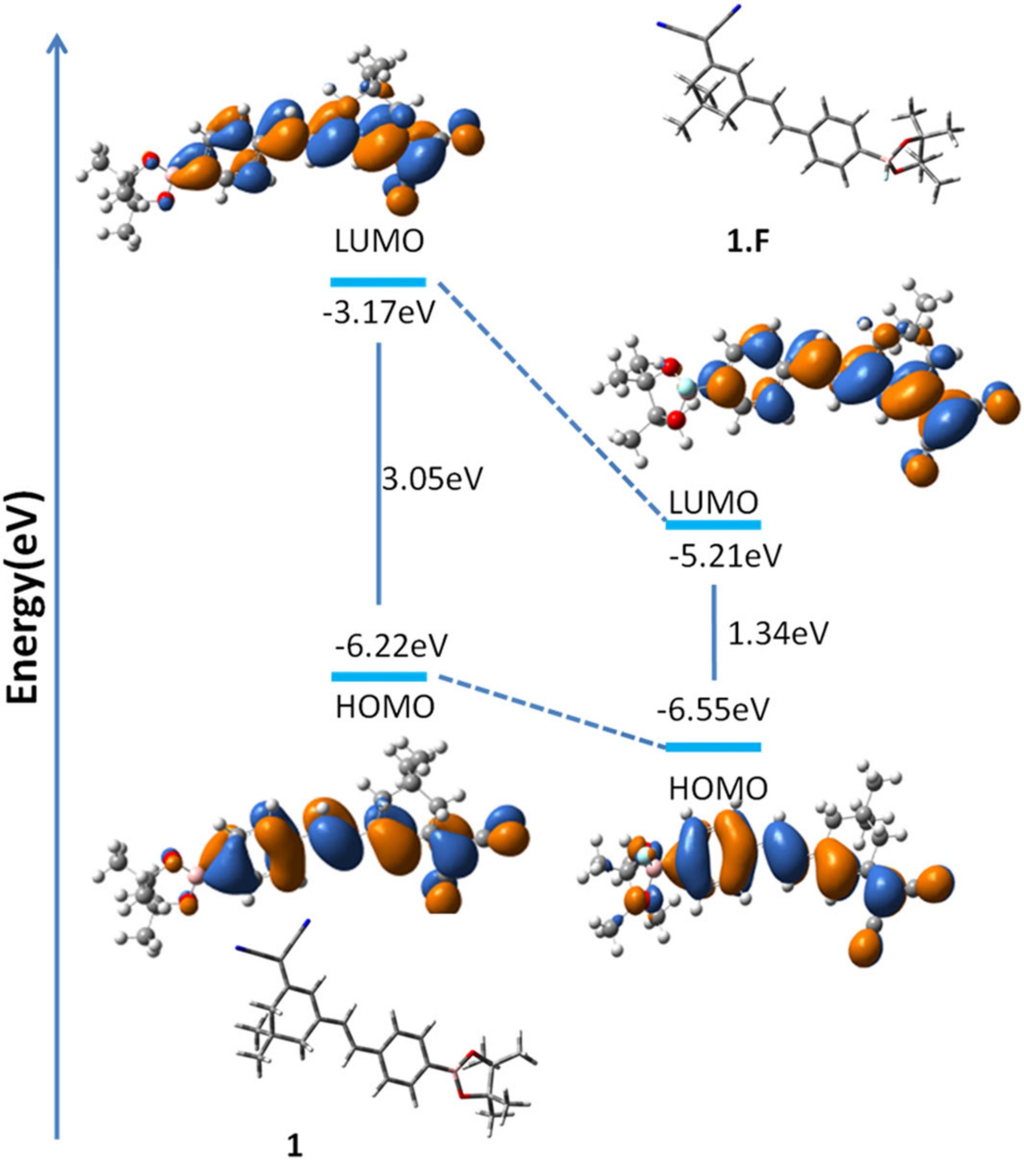


FIGURE 6 DFT energy levels diagram of (**1**) and (**1F**)$^-$

2.3 | Electrochemical Titration Studies of Probe 1 with F⁻ anion

The electrochemical (dpv) titration experiments were performed between (**1**) and F⁻ anions. Chemosensor (**1**) has an oxidation potential at 1.27 V vs SCE and upon subsequent titration with multiples of 0.33 eq. up to a total of 1 eq. of fluoride anion, new peaks appeared at 0.112 V and 0.446 V for F⁻ anion vs. SCE. The corresponding peak of the sensor (**1**) diminished in dpv on addition of up to one equivalent of F⁻ anion. This indicated the formation of 1:1 ratio of the corresponding complex (**1.F**)⁻. (Figure 3)

2.4 | ^{11}B NMR Studies

In order to confirm the coordination of the Lewis acidic Boron on sensor (**1**) with the incoming F⁻ anion, ^{11}B NMR was run in $CDCl_3$. An upfield shift in the NMR signal was observed.

Addition of TBAF generates the corresponding adduct (**1.F**)⁻. The formation of this complex is confirmed by an upfield shift in the ^{11}BNMR resonance at δ 4.85 ppm (Figure 4) as typically found in four-coordinate aryl boronate esters.[28,29]

2.5 | Theoretical Studies

The mechanism was explained for the interaction between (**1**) and F⁻ anion using density functional theory (DFT) calculations. These calculations are performed with B3LYP functional using 6–31 + G(d) basis set with Gaussian 09 program package.[28] The optimized geometries of (**1**) and (**1.F**)⁻ are shown in Figure 5. Through the DFT calculations, the energy gap, dipole moment and Bond length alteration (BLA) of probe (**1**) and (**1.F**)⁻ were observed. However, the HOMO-LUMO energy gap (eV) and dipole moment of (**1.F)**⁻ was found to be smaller than the free probe (**1**) (Table S1 in the Supporting Information).

The ground state optimized geometry of (**1**) undergoes drastic twisting, upon interaction with F⁻ anion, from trigonal planar to tetrahedron boron. This twist increases the Lewis base character of boron which enhances the ICT of overall system, resulting in a considerable redshift in the UV–Vis spectrum.

The different BLA is observed in the conjugated carbon chain in (**1**). The binding of F⁻ to the chemosensor (**1**) decreases the BLA upon formation of the complex (**1.F**)⁻. This perhaps originates from the collective electron donating effects of the tetrahedral boron moiety (BpinF)⁻ and the electron-rich π-bridge. (FIGURE S23 in the Supporting Information)

The HOMO-LUMO energy levels of **(1)** as shown in Figure 6 were calculated using this method. The HOMO-LUMO energy gap of probe (**1**) was 3.05 eV and drastically decreasing after fluoride anion binding (**1.F**)⁻ is 1.34 eV these energy gaps are agreed with Experimental UV–Vis. Spectra (Table S1 in the Supporting Information). Compound (**1**) has only one probable binding sitei.e., the boron end, hence the optimized geometries for (**1**) suggested that the electron density on both HOMO and LUMO levels was located on electron withdrawing vinyl cyanide end thereby generating an electron deficiency at the boronic ester end which initiates the binding of F⁻ ions. According to the electrostatic potential (ESP) data, it was found that the boron atom was more prone to the binding of F⁻ anion than dicyanovinyl quaternary carbon. ESP surfaces of molecules (**1**) and (**1.F**)⁻ with Mulliken atomic charges at

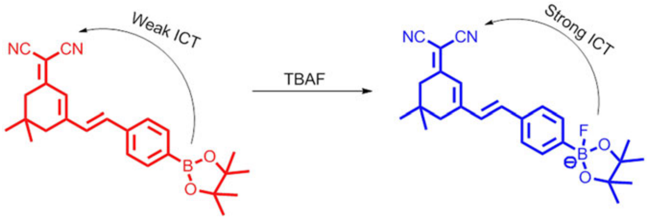


FIGURE 8 Plausible mechanism for the formation of coordination complex (**1.F**)⁻

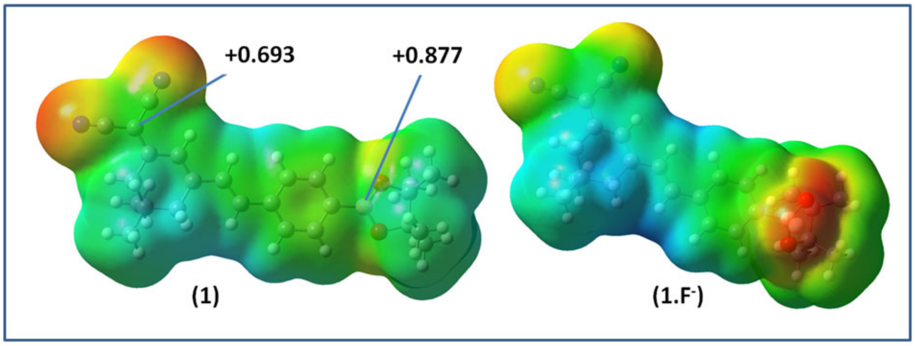


FIGURE 7 ESP surfaces of (**1**) and (**1.F**)⁻ (isovalue = 0.0004)

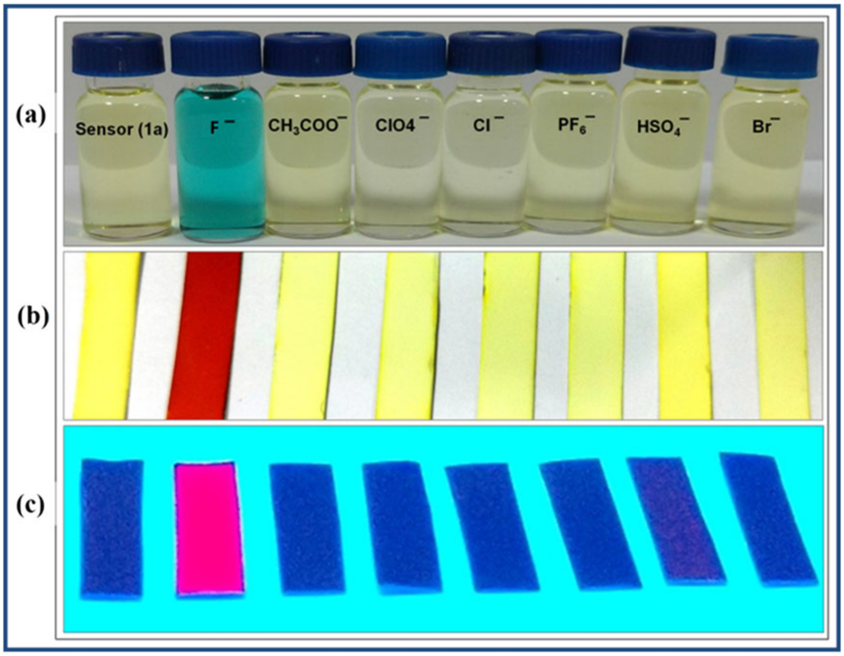


FIGURE 9 Demonstration for F^- ions sensing (a) Solutions colours of (**1**) in the presence of various anions (b) Strips colour under the white light (c) Strips colour under the UV light (long wavelength)

dicyano quaternary carbon and boron in the conjugate (**1**) are shown in Figure 7. The Boron atom on the ester with the Mulliken charge of +0.877 has more positive potential than that of dicyano quaternary carbon (Mulliken charge = +0.6930).

Similarly, TD-DFT for (**1**) and (**1.F**)$^-$ was calculated to know the electronic contribution from HOMO-LUMO in different level. This was performed with B3LYP/6–31 + G(d) basis set and TD-DFT calculations included the solvent effect (CPCM).[29] The results of transitions of (**1**) and (**1.F**)$^-$ are summarized TABLE S2 in the Supporting Information. The calculated wavelengths in the absorption spectra of (**1**) and (**1.F**)$^-$ were 437 nm and 1424 nm (FIGURE S24, S25 in the Supporting Information) respectively with oscillator strengths of 1.67 and 0.32. The predicted absorption spectra were commensurate with the experimentally observed ones.

Finally, following the experimental (stoichiometric UV–vis. and electrochemical titrations) and DFT studies, a plausible mechanism can be proposed in the Figure 8, wherein, in the first step, on addition up to one equivalent of F^- anion to the chemosensor (1), the F^- anion gets coordinated with the Lewis acidic B atom, without the cleavage of five member cyclic ester ring, to form a stable four coordinate boron adduct as reported in the literature.[30] Upon addition of another equivalents of F^- anion to previous adduct, no changes were observed in ^{11}B-NMR and absorption spectrum. Thus, it can be concluded that the combination of sensor (**1**) and F^- anion in 1:1 ratio forms the four coordinated B. F adduct.

2.6 | Silica Gel Dip-Strips of Probe (1) to detect F^- anions

Superior sensing capability of (**1**) towards F^- ion detection in solution phase was observed with the bare eye {Figure 9 (a)} and further used for the in-field device level applications, wherein, solution of (**1**) was introduced on the silica gel sheets and the response was inspected towards F^- anion sensing. The colour was clearly identified with the naked eye when the silica gel sheet colour changed from yellow to brick red {Figure 9 (b)} (FIGURE S26 in the Supporting Information) in the presence of white light and also the distinguished fluorescent behaviour was observed under the portable UV lamp {Figure 9 (c)}. These results can be helpful to the development of a selective fluoride chemosensors of practical convenience.

3 | CONCLUSIONS

In conclusion, we have successfully synthesized newly designed highly sensitive Lewis acidic (Boron) based chemo sensor by introducing cyclicborane unit into precursor compound's signalling unit. The chemo sensor (**1**) was well characterized by various spectroscopic techniques such as IR, ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, and HRMS. Further (**1**) was used for F^- anion sensing studies in solvent media. By using UV–Vis. fluorescence, and electrochemical titrations the binding constants, detection limits, and stoichiometry between (**1**) and F^- were evaluated. Application of probe (**1**) was showed in the practical use such as in-field device level utilization. Based on the experimental and theoretical results probable mechanism for F^- anion binding with probe (**1**) was proposed.

4 | EXPERIMENTAL SECTION

All chemicals such as isophorone, malononitrile, 4-formyl boronic acid, pinacol, piperidine, fluoride and other TBA salts were purchased from Sigma Aldrich and used as supplied. All the reactions were carried out in the absence of air using standard Schlenk techniques unless stated otherwise. Solvents were deoxygenated, purified and dried prior to use. Sensing experiments were carried out and monitored in freshly distilled tetrahydrofuran (THF). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on Bruker Avance 400 (or) Varian Inova 500 spectrometer in $CDCl_3$ as solvent; Chemical shifts (δ) for protons were reported in ppm down field from TMS as internal standard and the carbon shifts were referenced to the ^{13}C signal of $CDCl_3$ at 77.0 ppm. Coupling constants (J) were expressed in Hz. MALDI were recorded on a Shimadzu Biotech Axima. FT-IR spectra were recorded on a Thermo Nicolet Nexus 670 using spectrophotometer using KBr discs. Melting points were determined using a Toshniwal apparatus and are uncorrected. The UV–vis. Spectra were recorded on a UV 3600 (Shimadzu) spectrophotometer over the range of 200–550 nm in CH_3CN and THF solution. The cyclic voltammetry (CV) was performed with a conventional three-electrode configuration consisting of glassy carbon working electrode, platinum wire auxiliary electrode and saturated calomel (SCE) reference electrode. The cyclic voltammograms were recorded on CHI620 model electrochemical analyser in the presence of 0.1 M tetrabutylammonium perchlorate (TBAP) supporting electrolyte at a scan rate of 0.1 Vs^{-1}. Elemental analyses were performed with an Elementar Vario MICRO analyzer. For HRMS, m/z values were expressed in atomic mass units.

4.1 | Synthesis of compound 2-(3,5,5-trimethylcyclohex-2-en-1-ylidene) malononitrile (L-1)

A catalytic amount of piperidine (23 mg, 0.276 mmol) was added to the solution of isophorone (3.8 g, 27.6 mmol) and malononitrile (1.82 g, 27.6 mmol) in dry ethanol (150 ml) and resulting clear solution was stirred at 60 °C under nitrogen atmosphere till starting material disappeared (detected by TLC plate). The reaction mixture was cooled to room temperature, the solution was slowly poured into cold water (200 ml) and extracted with CH_2Cl_2, organic layer was evaporated and recrystallization from hexane affords a brown solid. Yield: 4.5 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.62 (dd, *J* = 2.8, 1.4 Hz, 1H, -CH=), δ 2.51 (s, 2H, $-CH_2-$), δ 2.17 (s, 2H, $-CH_2-$), δ 2.03 (d, *J* = 1.0 Hz, 3H, $-CH_3$), δ 1.01 (s, 6H, $-CH_3$ of $-CMe_2$). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 170.40, 159.78, 120.60, 113.20, 112.42, 45.70, 42.66, 32.39, 27.84, 25.33.

4.2 | Synthesis of compound 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzaldehyde (L-2)

The mixture of 4-formyl boronic acid (1.5 g, 10 mmol), anhydrous pinacol (1.2 g, 11.0 mmol) in anhydrous diethyl ether (15 ml) was stirred under nitrogen atmosphere till the starting materials disappeared (detected by TLC plate). After completion of the reaction, reaction mixture was washed with water; the ether phase was collected and dried with $MgSO_4$. The organic fraction was dried to give the pale yellow solid compound. Yield: 92%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 10.05 (s, 1H, -CHO), δ 7.96 (d, *J* = 8.1 Hz, 2H, Ar-CH), δ 7.88–7.83 (m, 2H, Ar-CH), δ 1.36 (s, 12H, -CH_3 of pinacol (4Me)). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 192.69, 138.13, 135.24, 128.72, 84.36, 24.91. ^{11}B NMR: (128 MHz, $CDCl_3$, ppm) δ 30.69 ppm.

4.3 | Synthesis of compound (E)-2-(5,5-dimethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)cyclohex-2-en-1-ylidene) malononitrile (1)

Under argon, 2-(3,5,5-trimethylcyclohex-2-enylidene) malononitrile (0.186 g, 1 mmol) and the corresponding 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzaldehyde (0.234 g, 1 mmol) was dissolved in dry ethanol (50 ml). Piperidine (0.01 mmol) is added and the solution is stirred at 45 °C till starting material disappeared (detected by TLC plate). The solution is concentrated and the product is purified by flash column chromatography (hexane: ethyl acetate 10:1, *v*/v). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.75 (d, *J* = 8.1 Hz, 2H, Ar-CH-), δ 7.45 (t, *J* = 10.0 Hz, 2H, Ar-CH-), δ 6.99 (s, 2H, -CH=CH-), δ 6.79 (d, *J* = 6.8 Hz, 1H, =CH-), δ 2.53 (d, *J* = 6.2 Hz, 2H, $-CH_2-$), δ 2.40 (d, *J* = 9.9 Hz, 2H, $-CH_2-$), δ 1.28 (s, 12H, $-CH_3$ of pinacol (4Me)), δ 1.01 (s, 6H, $-CH_3$ of CMe_2). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 155.34, 140.53, 123.15, 115.31, 112.38, 108.34, 102.15, 44.35, 31.10, 28.91, 25.12, 17.91, 17.46, 13.91, 11.63, 10.71, 4.25. ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ 22.29. IR (KBr) 3195.74 (=C-H), 2940.21 (=C-H), 2816.76 (30-C-), 2218.82 (-O-C-), 1600.32 (-CH=CH-) 1553.76 (=CN), 1016, 765 (-CH3), 740 (-CH3) cm^{-1}. HRMS [M + H] + = 401.00 (calculated = 400.32).

4.4 | UV–Vis. and Fluorescence Spectroscopic Studies

Stock solutions of (1) (1×10^{-3} M) and F^- anion (1×10^{-3} M) were prepared in anhydrous THF. For every new experiment the stock solution of (1) was diluted to 3×10^{-6} M and 3 mL was transferred into a quartz cuvette, subsequently, various concentrations of anionic solution was added with micropipette and the absorption and emission spectra was recorded after the thorough mixing of the solution. Emission spectral data was collected between 435/850 nm upon exciting at 422 nm and 570 nm wavelengths respectively.

4.5 | Detection of Binding Constant for the Complex $(1.F)^-$ Formation

Probe **(1)** solution was prepared in the THF solvent to get final concentration 3×10^{-6} M and used for the UV–Vis. and fluorescence spectral titration studies. 1×10^{-3} M concentrations of anionic stock solutions were prepared and titrated with (**1**) by varying final concentrations between 5.5×10^{-7} to 1.45×10^{-5} M.

4.6 | Calculations to evaluate Binding Constants by Using Spectroscopic Data

Binding constants were calculated for the formation of (**1. F**)$^-$ complexes by substituting UV–Vis. and Fluorescence spectral titration data in the Benesi-Hildebrand (B-H) plot equations 1 and (2).

$$1/(A - A_0) = 1/\{K\,(A_{max} - A_0)\,C\} + 1/(A_{max} - A_0) \quad (1)$$

$$1/(I - I_0) = 1/\{K\,(I_{max} - I_0)\,C\} + 1/(I_{max} - I_0) \quad (2)$$

Where A_0, A are absorption intensities of (**1**) of the absorption maximum at $\lambda = 678$ nm observed in the absence and presence of F^- anion at a certain concentration (C). A_{max} was the maximum absorption intensity value that was obtained at $\lambda = 678$ nm, during titration with varying F^- concentrations, K was the binding constant which was determined from the slope of the linear plots in constructed graphs. Also, I_0 and I are emission intensities of sensor (**1**) at emission maximum at 693 nm in the absence and presence of F^- anion at a certain concentration (C). I_{max} is the maximum emission intensity value that was obtained at $\lambda = 693$ nm during titration with varying F^- anion concentrations, K is the binding constant determined from the slope of the linear plots from the constructed graphs.

4.7 | Evaluation of Detection Limits for Probe (1)

Detection limits were determined by using UV–Vis. titration data between probe (**1**) and F^- anion. The standard deviations (σ) were calculated from the absorption spectrum, upon averaging ten titrations between the sensor and F^- anion, and the slope k was obtained from the graph which was plotted between absorbance and concentration of the [F^-]. Further obtained values were substituted in equation (3) to determine exact F^- anion detection limit of sensor (**1**).

$$\text{Detection limit} = 3\,\sigma/k \quad (3)$$

4.8 | Electrochemical Studies of the Chemosensor (1)

Electrochemical titration experiments of (**1**) in the absence and presence of F^- were carried out using differential pulse voltammogram (dpv) method (FIGURE S22 in the Supporting Information). The concentration of the chemosensor **(1)** was used 1×10^{-3} M and anionic solutions were maintained in the range of 1×10^{-3} M to 3×10^{-3} M.

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