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Selective detection of Fluoride *via* amplified Donor-Acceptor interaction of 6H-indolo[2,3-b]quinoline

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ABSTRACT

In this report, 6H-indolo[2,3-b]quinoline (hereafter **2a**) was synthesized and employed as an optical chemosensor for fluoride. The sensitivity of **2a** towards fluoride was established from the change in both the absorption and emission signals. The various *in-situ* ^{1}H NMR, UV-Vis, and density functional studies indicate that the 1:2 binding interaction between **2a** and fluoride followed by deprotonation to its corresponding di-anion ($\mathbf{2a^{2-}}$), which in turn boosted the donor-acceptor interaction between indole and quinoline moiety in $\mathbf{2a^{2-}}$ *via* expansion of torrision angle by 10.2° as compared to **2a**. Consequently the significant changes in both the absorption and emission signal of **2a** allow us to detect and estimate the concentration of fluoride up to 0.2 μM fluoride from the mixture of different anions.

1. Introduction

The sensing and recognition of fluoride has grown into an area of great interest in supramolecular and biological chemistry because of its applications in many areas.[1] Fluoride is well known for its important application in dental care and in the treatment of osteoporosis.[2] However excess fluoride can cause bone fluorosis, immune system disruption, thyroid disorder, kidney damage, and even cancer.[3] Furthermore, high intake of fluoride in plants may inhibit photosynthetic capacities and hence affect biomass productivity.[4] Thus, there is a growing interest on the development of optical chemo sensor, where the interaction with an anion leads to a change in the absorbance (color) or fluorescence properties of the receptor, for selective detection and estimation of fluoride from a mixture of other anions and are the most widely studied class of anion sensor.[5] To date, there are a number of ways in which optical anion sensing can be achieved. One frequently used strategy is to functionalize an anion binding group with a chromophoric or fluorophoric group capable of signaling the binding event into corresponding change in absorbance or emission signal.[6] The signaling unit is either directly attached to the receptor or separated from the receptor through a short covalent linker. In both the cases, formations of a supramolecular anion−receptor complex through noncovalent interactions lead to a change in the absorbance or emission properties of the signaling unit. [7,8] “Chemodosimeters” are another type of discrete optical sensors, in which anion reacts with the sensor (or catalyzes a reaction) to create a new molecule with different optical properties. [9] In most of the cases, the principle of the sensing methods rely either on strong interactions between Lewis-acidic boron or silicon with fluoride (Fig. 1), or hydrogen bonding and other types of interactions involving fluoride as a participant or a disrupter (Fig. 1).[10] Towards this, Gabbai and co-workers developed colorometric fluoride sensor based on; (i) B-F interaction in highly delocalized aryl substituents containing boron compounds, (ii) charge transfer (CT) or intramolecular charge transfer (ICT) process in fluoride binding to triarylboranes with extended π-conjugation, and (iii) metal-to-ligand charge transfer (MLCT) absorption bands from the interaction between fluoride and boron center of borylated ligands in transition metal complexes (Fig. 1). [11] On the other hand, in most of the silicon based sensor, electrofugal tert-butyldiphenylsilane (TBDPS) group has been attached with chromogenic fragment. The interaction of fluoride with Lewis acidic silicon promotes the cleavage of Si-O bond, which undergo dramatic changes in the UV−vis absorption properties of the chromogenic unit, corresponding to a change in color (Fig. 1). [12]

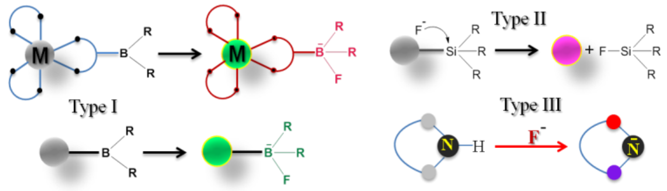


Fig. 1. Sensor based on "chemodosimeters". Sensing through strong interactions between Lewis-acidic boron and fluoride (Type I). Sensor based on fluoride promoted cleavage of Si-O bond (Type II). Sensor based on fluoride induced deprotonation (Type 3).

There is another type of sensors, in which strongest hydrogen bonding interaction between N-H fragment(s) of amides, sulfonamides, pyrroles, indoles, ureas and fluoride has been utilized for the deprotonation of N-H to generate the corresponding anionic molecule.[13] The extra charge brought through deprotonation caused a change in the dipole associated to the charge-transfer transition, which ultimately modifies absorption and emission signal of the molecule (Fig. 1). Owing this strategy, various class of molecule containing indole moieties *viz.* tris(indolyl) methanes,[14] bis(indolyl) methanes,[15] hydrazone based indoles,[16] indole-linked quinolone derivative,[17] oxidized bis(indolyl) methanes,[18] bisindole diazine,[19] BODIPY-indole conjugate[20] DNP derivative of bis(indolyl) methane[21] etc. with varying degrees of affinity and selectivity towards fluoride have been developed. In the present work, we wanted to utilize the 6H-indolo[2,3-b]quinoline (**2a**) as chemosensor for the detection of anions. The donor acceptor interaction between indole and quinoline moiety of **2a** is expected to be modified after the interaction with anions as both the moieties are not in the same plane. In fact, strongest hydrogen bonding interaction between N-H of indoles and fluoride followed by deprotonation resulted the formation of di-anion (**2a**$^{2-}$). The extra charge in **2a**$^{2-}$ caused more delocalization between indole and quinoline *via* expansion of torrision angle by 10.2° in **2a**$^{2-}$ as compared to **2a.** Thus, the fluoride induced boosted interaction modifies the absorption and emission signal of **2a** and has been utilized for the selective detection of fluoride in presence of other anions.

2. Experimental Section

2.1. Synthesis of 6H-indolo[2,3-b]quinoline (2a)

In a 10 mL round bottom flask equipped with a magnetic bar and refluxed condensor, was charged with Fe(ox)–Fe_3O_4 (0.05 mmol) in water (3 mL) stirred vigorously for 5 min in open air. [25] After that, 2-nitro benzaldehyde (1 mmol) and Indole (2.2 mmol) was added to it and placed into a constant temperature bath and refluxed at 110 °C for 6 h under vigorous stirring. After completion of the reaction, the product was extracted with ethylacetate (20 mL×3) and washed with water (10 mL×3), brine (10 mL) and dried over anhydrous Na_2SO_4. After removing the solvent the crude residue was used as it is for next step. A solution of **1a** (1 mmol) and $SnCl_2$. $2H_2O$ (5 mmol) in methanol (4 mL) was refluxed for 3 h. The solution was allowed to cool at room temperature and was then poured into ice. After that, 5% aqueous $NaHCO_3$ solution was added to it to make the solution slightly basic (pH ≈ 8). After that, ethylacetate (50 mL) was added to the reaction mixture and filtered through a bed of Celite. The organic layer was washed with water (50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4

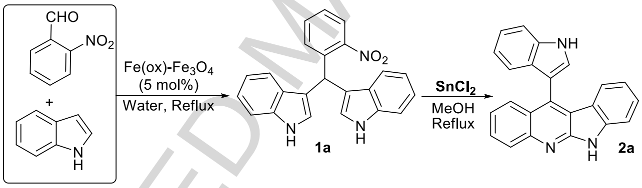
and evaporated to dryness under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate to afford pure **2a.** Yield = 58% IR (KBr): 3333, 3427, 3030, 2280, 1708 cm^{-1}. ^{1}H NMR 400 MHz (DMSO): δ (ppm) 7.05 (t, 1H, *J*=8 Hz), 7.10 (d, 1H, *J*=12 Hz), 7.17-7.25 (m, 2H), 7.42 (t, 1H, *J*=7.6 Hz), 7.49-7.53 (m, 2H), 7.59-7.63 (m, 2H), 7.83 (s, 1H), 7.92 (d, 1H, *J*=8 Hz), 8.22 (d,1H, *J*=8 Hz), 8.34 (d, 1H, *J*=8 Hz), 10.82 (s, 1H, N-H), 11.75 (s, 1H, N-H) ^{13}C NMR 109.2 MHz (DMSO): 107.8, 112.4, 112.6, 119.7, 119.9, 120.1, 120.6, 121.6, 121.8, 122.2, 124.7, 126.0, 126.3, 127.1, 127.3, 129.7, 129.8, 132.0, 137.8, 144.5, 144.6, 145.7.

2.2. Computational Details

The molecules were fully optimized without any geometry constraints at Becke, three-parameter, Lee-Yang-Parr (B3LYP) level of theory using 6-311+G** basic set. [22] Frequency calculations have also been performed at the same level of theory to characterize the nature of the stationary states. All geometries were found to be local minimum with real frequencies. The fluorescence spectra of **2a** and **2a-F**$^-$ were computed within the TD-DFT framework using B3LYP/6-311+G** level of theory in solution phase (using DMSO as the solvent with dielectric constant 46.7). For solvent phase calculations, polarizable continuum model (PCM) has been used.[23] All calculations were performed using Gaussian09 suite of program.[24]

3. Results and Discussion

The Fe(ox)-Fe_3O_4 promoted condensation reaction between 2-nitro benzaldehyde and 2 equivalent of corresponding indole leads to the bis(indollyl)methane (**1a**) in 82% yield.[25] The corresponding 6H-indolo[2,3-b]quinoline moiety was synthesized *via* following a reported $SnCl_2$ mediated intramolecular cyclization of **1a** *via* C–N bond formation by Kundu and co workers (Scheme 1).[26]



Scheme 1. Synthetic route of 6H-indolo[2,3-b]quinoline.

3.1. UV-vis and DFT study

The compound **2a** showed three peaks at 222, 312, and 422 nm with extinction coefficients (ε, mol^{-1}Lcm^{-1}) of 5×10^4, 4×10^3, and 3.22×10^3 in dimethyl sulfoxide (DMSO). Upon gradual addition of tetrabutyl ammonium fluoride (TBAF) to DMSO solution of compound **2a** (50 µM), the absorbance at 422 nm increases, while a new band centered at 485 nm is gradually appears due to the interaction between **2a** and fluoride (Fig. 2). However the absorbance at 422 nm reaches maximum after the addition of 5 equivalent fluorides. Further addition of fluoride leads to an increases in the absorbance at 484 nm band with decrease in the absorbance for band at 422 nm.[27] The new band at 484 nm may be attributed due to the association or association-dissociation equilibrium between two different type of N–H of **2a** and fluoride. This phenomenon can occur either stepwise or single step. Initially, to get an idea about the binding stoichiometry between fluoride and compound **2a**, Job's plot experiment with a fixed fluoride and **2a** concentration of 100 µM was done by using UV-vis study. The binding stoichiometry between compound **2a** and fluoride was found to be 1:2. So, two chemically different N–H present in compound **2a** interacting with two different fluoride. The calculated binding constant from the corresponding absorbance change upon gradual addition of fluoride to **2a** was found to be 5.0 ×10^3 M^{-2} using Bensi-Hildenberg equation.[28] So, fluoride promoted H-bonded interaction or interaction followed by deprotonation between **2a** and fluoride is responsible for the corresponding colour change. To check this, [Bu$_4$N]OH was added in the DMSO solution of compound **2a**, which brought the same colour and spectral changes of **2a** as those observed with fluoride anions. The strong base [Bu$_4$N]OH will definitely leads to deprotonation in compound **2a** by abstracting two N–H proton. Further, to check the reversibility of the process, protic solvent such as; methanol or water was added in brown colour solution of **2a** after treated with fluoride or [Bu$_4$N]OH. In both the cases, brown colour solutions turned into light yellow and revert back to its original absorption spectra, which indicate that the proton dissociation–association process is reversible in nature. To clarify the change in absorption spectrum after the interaction of fluoride, geometry of **2a**, **2a-2F**$^-$ and its di-anion (**2a^{2-}**) were optimized at B3LYP/6-311+G** level of theory and their HOMO-LUMO energy gap were determined.

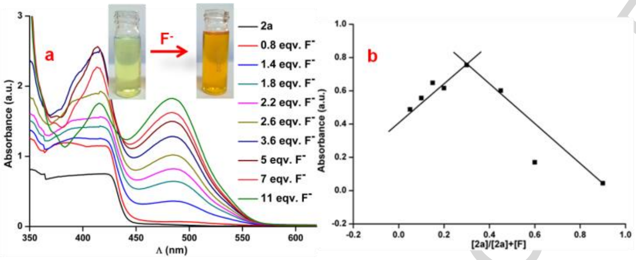


Fig. 2. The changes in UV-vis spectra of **2a** recorded in DMSO (50 μM) after gradual addition of fluoride (a) and Job's plot for compound **2a** with a fixed concentration of **2a** and fluoride of 100 μM (b).

In compound **2a**, HOMO primarily resides on both indole and quinoline moiety and LUMO localized majorly on the quinoline moiety (Fig. 3). The 1:2 hydrogen bonding interaction between two different N–H protons and fluoride promotes a negative charge transfer around indole and quinoline moieties, resulting decrease in HOMO-LUMO energy gap in **2a-2F**$^-$, which further decrease in dianion (**2a**$^{2-}$) and shows corresponding transition at 485 nm (Fig. 2-3).

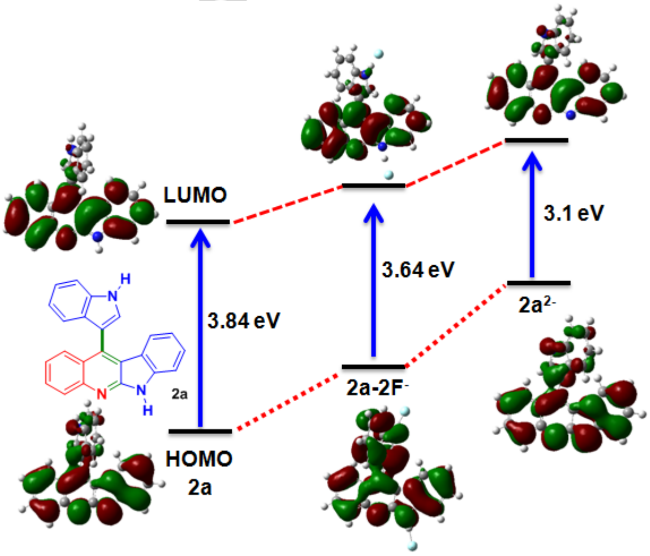


Fig. 3. Calculated HOMO LUMO energy gap of **2a, 2a-2F**$^-$, and **2a**$^{2-}$

3.1. NMR study

Further, to get an idea about the binding phenomenon of compound **2a** with fluoride, ^{1}H NMR titration of compound **2a** was done with gradual addition of fluoride in DMSO-*d*$_6$. After addition of 0.5 equivalent of TBAF salt to compound **2a** leads to complete disappearance of both the N–H proton of quinoline and indole moiety, which indicate very fast H-bonded association-dissociation equilibrium because of highly acidic quinoline and indole N–H proton (Fig. 4). Although complete disappearance of both the N–H proton was observed at lower equivalent of TBAF, but no generation of corresponding peak for $[HF_2]^-$ was observed at lower equivalent of TBAF.[29] However, addition of 20 equivalent of fluoride resulted a new triplet peak at 16.1, indicates the formation of $[HF_2]^-$ *via* the abstraction of both the indole and quinoline N–H proton of **2a** (Fig. 4).[30] Further ^{19}F NMR of **2a** in DMSO-d_6 after the addition of 20 equivalent of fluoride shows a signal at -146.1 ppm corresponding to $[HF_2]^-$ due to the deprotonantion of **2a**. On the other hand gradual addition of TABF to DMSO-d_6 solution of **2a** results down field shift of H_c proton of indole moiety as well as up-field shift of both H_d and H_e proton. Both the up-field and down-field shift of corresponding ring proton increases with increasing amount of TBAF, which suggest the delocalization of electron around the molecule increases with subsequent generation of di-anion of **2a**. The down-field shift of indole C–H (H_c) proton and up-field shift of quinoline C–H proton indicates that the negative charge brought after the abstraction of indole N–H results the flow of electron from indole to quinoline moiety, which is responsible for change in both absorption and emission signal of **2a** after the interaction with fluoride.[31] Further to check the donor-acceptor interaction between indole and quinoline moiety, both the structure **2a** and its di-anion **2a**$^{2-}$ were optimized in DMSO solvent at B3LYP/6-311+G** level of theory. In compound **2a**, the torrision angle between indole and quinoline moiety was found to be 108.6˚, which suggest the possible donor-acceptor interaction between indole and quinoline moiety of **2a**. However expansion of torrision angle by 10.2˚ in di-anion (**2a**$^{2-}$) is likely to be indicative of more planarity between indole and quinoline moiety, which is also indicative of more electron flow from indole to quinoline moiety after deprotonation (Fig. 5). The more electron donation from indole to quinoline moiety in **2a**$^{2-}$ is also likely to be responsible for corresponding lower HOMO-LUMO energy gap and subsequent red shift of the existing band in **2a** to low energy band at 485 nm in **2a**$^{2-}$.

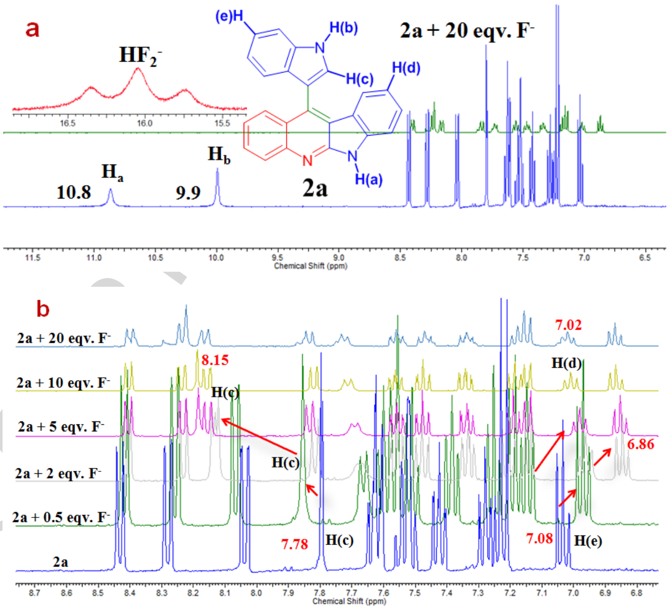


Fig. 4. ^1H NMR spectra of compound **2a** in DMSO-d_6 upon gradual addition of TBAF; change of the N–H proton (a) and change of other protons (b).

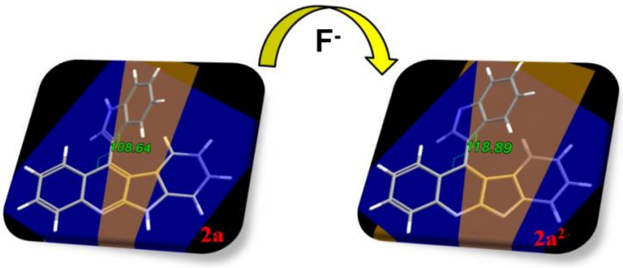


Fig. 5. Calculated torrision angle between indole and quinoline moiety in **2a** and **2a**$^{2-}$

3.1. Emission study

The fluorescence emission spectra of **2a** consist of one band with maxima at 490 nm corresponding to the neutral species upon photo irradiation at 420 nm. Upon gradual addition of TBAF in DMSO solution of **2a**, a significant enhancement of the existing 490 nm band was observed due to the interaction between fluoride and two N–H of **2a**. On the other hand, after addition of TBAF to DMSO solution of **2a**, a new band appears at 535 nm upon photo irradiation at 485 nm, which is found to be absent in **2a** (Fig. 6). To get a theoretical insight of the corresponding transition, the fluorescence spectra of **2a** and **2a-F**$^{-}$ were computed within the TD-DFT framework using B3LYP/6-311+G** level of theory[32] in polarizable continuum model (PCM) using DMSO solvent[33] using Gaussian09 suite of program.[34] The calculated fluorescence bands are in very good agreement with the experimental one (Fig. 6-7). For compound **2a**, the calculations showed two bands; one intense band at 486 nm (oscillator strength, $f = 0.029$) and the other at 472 nm (oscillator strength, $f = 0.010$). The band at 486 nm was assigned to the transition from HOMO to LUMO, while the transition at 472 nm is assigned to the transition from HOMO-1 to LUMO. The fluorescence band for fluoride bonded structure (**2a-F**$^{-}$**)** was also calculated at same level of theory in DMSO. The calculation revealed one band at 536 nm ($f = 0.012$) for HOMO to LUMO and another at 482 nm ($f = 0.054$) for HOMO-1 to LUMO transition (Fig. 7). The assigned calculated band positions as well as its oscillator strength are found to be in good correlation with experimentally observed result.

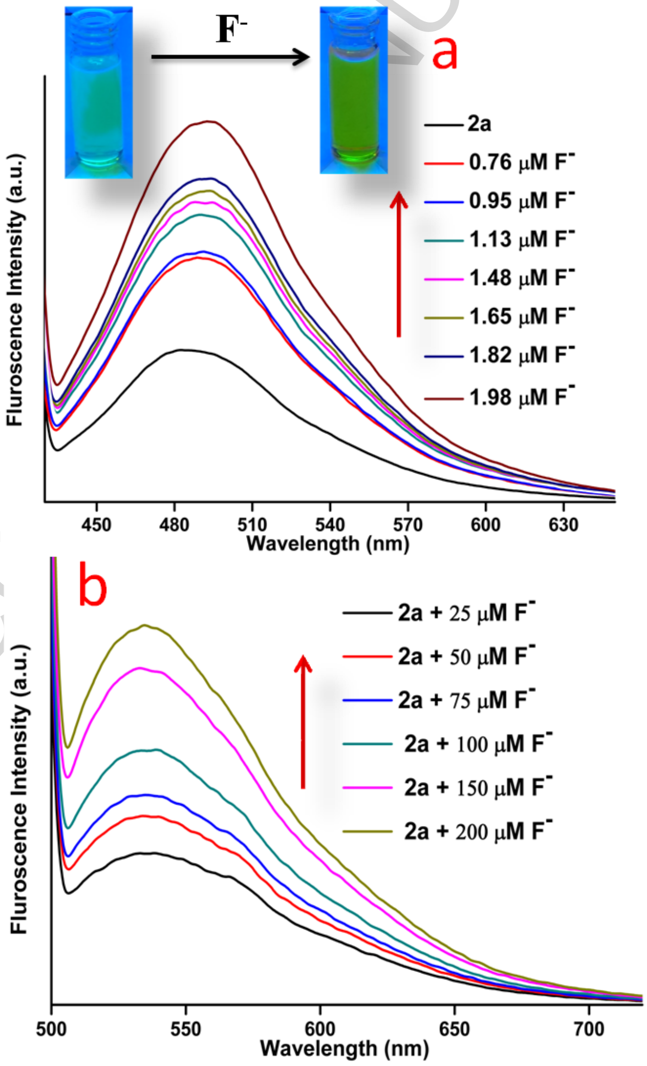


Fig. 6. The changes in emission spectra of **2a** recorded in DMSO (5 μM) after gradual addition of fluoride upon photoirradiation at 420 nm (a) and at 485 nm (b).

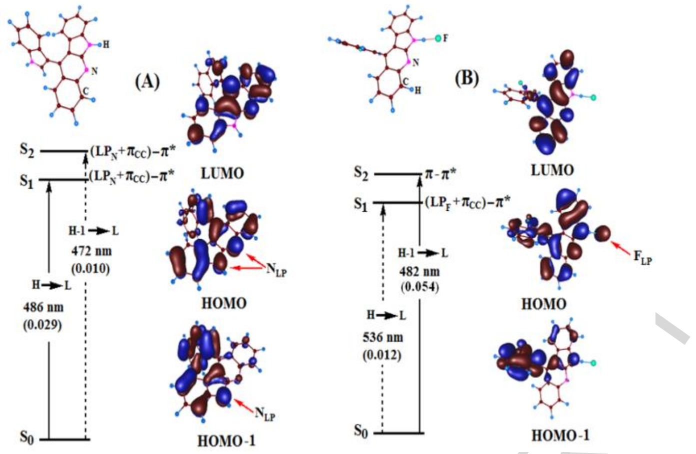


Fig. 7. TD-DFT calculated fluorescence spectra of compounds **2a** and **2a-F**$^{–}$.

3.1. Selectivity in presence of other anions

To verify the anion specificity, UV-vis monitoring of **2a** was performed with other tetrabutylammonium salts (TBA-X: X= Cl, Br, I, CH$_3$COO, BF$_4$, PF$_6$, SbF$_6$, H$_2$PO$_4$, PO$_4$, HF$_2$, and HSO$_4$) in DMSO. Under identical experimental condition, no appearance of peak at 485 nm was observed with other anions in spite of their presence in large excess compared to fluoride. However, in most of the anions, a decrease in intensity of 422 nm peak was observed in most of the cases.[35] The generation of new peak at 490 nm is also observed in a mixture of different anions containing fluoride, which shows the selectivity of **2a** towards fluoride in presence of other anions (Fig. 8).

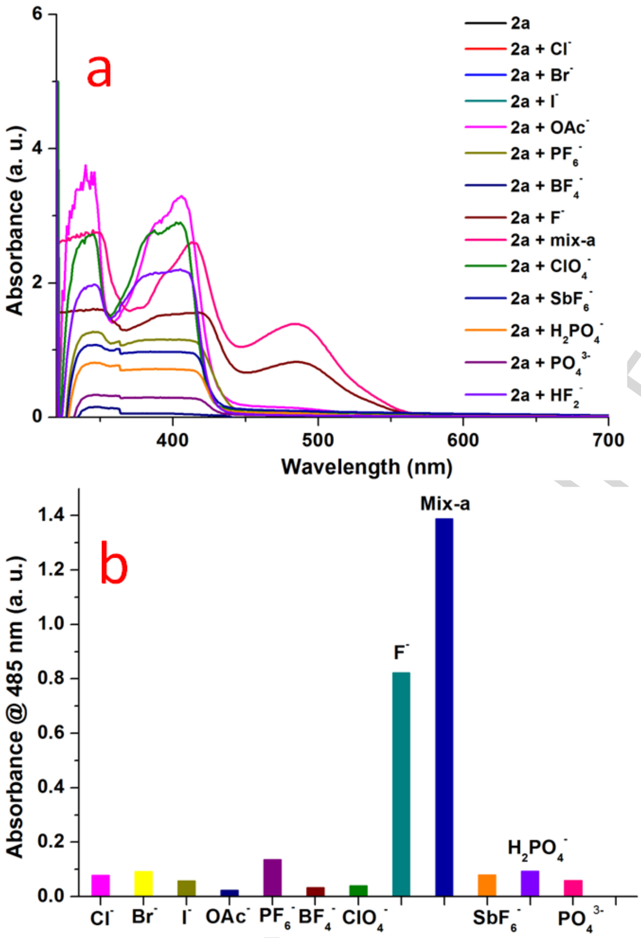


Fig. 8. The change in UV-vis spectra of **2a** (in 50 μM DMSO solution) after the addition of different anions (50 μM) (a); change of absorbance at 485 nm after the addition of different anions (b).

Further selectivity of compound **2a** was tested from emission study. Room temperature emission spectrum of **2a** solution in DMSO shows a single and structured band peaking around 490 nm upon photoirradiation at 420 nm, which is ascribed to the neutral species. The enhancement in intensity of 490 nm peak was found to be observed upon gradual addition of fluoride. On the contrary, nearly no detectable fluorescence enhancement was observed upon addition of large excess of other tetrabutylammonium salts (TBA-X: X= Cl, Br, I, CH_3COO, BF_4, PF_6, SbF_6, and HSO_4). Gratifyingly, a distinct difference in fluorescence enhancement of the existing 490 nm peak of compound **2a** could also able to detect variable concentration of fluoride in presence of different anions (Fig. 9).

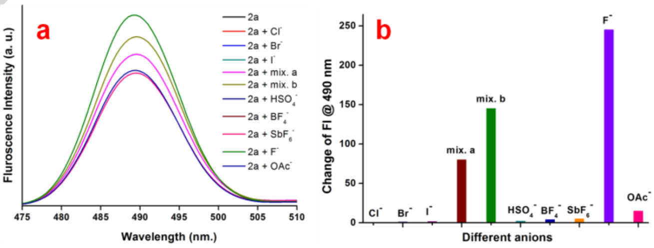


Fig. 9. The change in emission spectra of **2a** (in 5 μM DMSO solution) after the addition of different anions (100 μM), mix. a and mix. b represent two different mixture of eight different anion (10 μM) with 5 and 10 μM of fluoride respectively (a); and change of fluorescence intensity at 490 nm after the addition of different anions (b).

4. Conclusions

In summary, 6H-indolo[2,3-b]quinoline (**2a**) was synthesized and applied as a selective chemosensor for fluoride *via* color changes as well as change in both the absorption and emission signals. The observed evidences from in-situ ^{1}H NMR, UV-Vis, emission and density functional studies suggest that torrision angle between indole and quinoline moiety in **2a** is likely to be enhanced during the fluoride induced deprotonation of **2a**, which is amplifying the donor-acceptor interaction between indole and quinoline moiety and is responsible for the spectroscopic change in **2a**. The selective detection of fluoride in presence of other anions using both the absorbance and emission signal is also found to be suitable with **2a** and allow us to detect and estimate the concentration of fluoride up to 0.2 µM.

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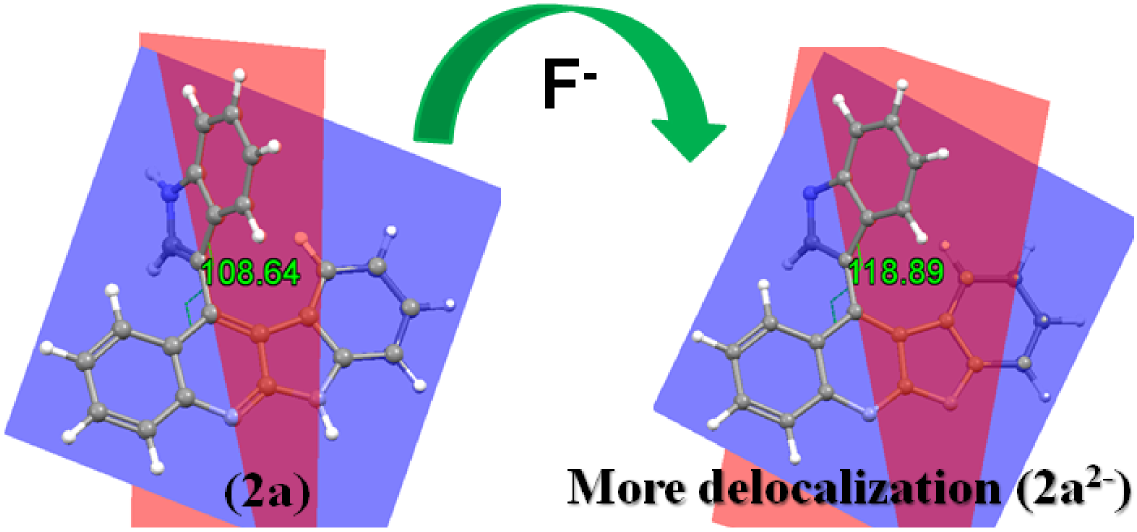
[35] The selectivity of **2a** towards fluoride in presence of other anions in aqueous medium was checked after the addition of aqueous solution of mixture of 10 different anions to DMSO solution of **2a** (DMSO : H_2O = 9:1, 2.7 : 0.3 mL). However we did not observe any change in the absorbance spectra of **2a**. The presence of water inhibits the formation of di-anion *via* inhibiting the fluoride induced deprotonation process.

Graphical abstract



Highlights

6H-indolo[2,3-b]quinoline (**2a**) was synthesized and applied as a selective chemosensor for fluoride, in which torrision angle between indole and quinoline moiety in **2a** is likely to be enhanced during the fluoride induced deprotonation of **2a**, which is amplifying the donor-acceptor interaction between indole and quinoline moiety and is responsible for the spectroscopic change in **2a**.