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ARTICLE

A selective ratiometric fluoride ion sensor with (2,4-dinitro phenyl)hydrazine derivative of bis(indolyl) methane and its mode of interaction

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In this report, a new easy-to-synthesis chemosensor, 2,4-dinitrophenylhydrazine (DNP) derivative of 4-(di(1H-indol-3-yl)methyl)benzaldehyde (hereafter **2a**) was designed, synthesized and employed as a selective optical chemosensor for fluoride through naked eye detection *via* pattern of color changes as well as change of absorption signals. The binding interaction between **2a** and fluoride from ¹H NMR, UV-Vis, and density functional studies suggests fluoride-induced interaction followed by deprotonation to its corresponding tri-anion is responsible for the significant color and spectral changes in the absorption properties of **2a**. The ratiometric responses of **2a** specifically to fluoride ion allow us to detect and estimate the concentration of fluoride ion accurately up to 2 μM.

Introduction:

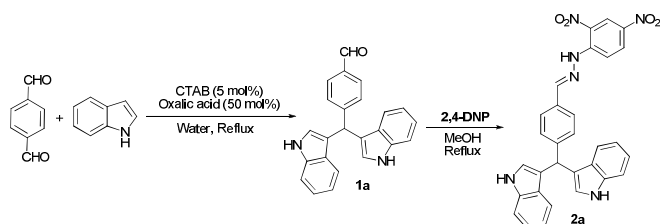
There exists a growing interest on the synthesis of colorimetric neutral chemo sensors for fluoride ion because of its long association with a diverse array of biological, medical, and technological processes.¹ Over the last 2-3 decades, one frequently used strategy to produce a colorimetric anion sensor is to functionalise an anion binding group with a chromogenic moiety capable of signaling the binding event through intramolecular charge transfer processes *via* the hydrogen bonding interaction or advanced stage of the proton transfer reactions between binding group and anion, which leads to a change of colour visible to eye.² Towards the development of colorimetric neutral chemosensor, various research groups have proposed a wide range of anion sensors utilizing hydrogen-bond donors *viz.* calixpyrroles, polyamines, urea, thiourea, dipyrrolylquinoxalines, dipyrrolyl derivatives, sulfonamide, amide, imidazoliums/imidazole, etc. that present varying degrees of affinity and selectivity towards different anions such as F⁻, H₂PO₄⁻, I⁻, OAc⁻, Cl⁻.³ In this regard various indoles, oxidized bis(indolyl) methanes,⁴ tris(indolyl) methanes,⁵ bis(indolyl) methanes,⁶ hydrazone based indoles,⁷ indole-linked quinolone derivative,⁸ bisindole diazine,⁹ BODIPY-indole conjugate¹⁰ etc. are noteworthy as a colorimetric fluoride sensor.¹¹ However, in most of the cases the sensing rely on the change in spectroscopic behavior at a particular wavelength in the presence of the analyte, and only a few systems are known that exhibit a ratiometric approach in absorption.¹² But the ratiometric approach depends upon several factor like; phototransformation, sensor concentration, and electronic

environment around the chromogenic unit, contribution to single band intensity. In this regard, ratiometric spectroscopic change of a system, which involves measurement of the changes in the ratio of the optical response at two different wavelengths, is preferred over the conventional method of monitoring the absorbance variation at a single wavelength.¹³ Herein, we introduce (2,4-dinitrophenyl)hydrazine (DNP) derivative of bis(indolyl)methane from the simple condensation reaction between 4-(di(1H-indol-3-yl)methyl)benzaldehyde and (2,4-dinitrophenyl)hydrazine for the selective sensing of fluoride *via* naked eye detection. The compounds showed selective ratiometric sensing of fluoride in presence of other anions. The binding mechanism between fluoride and compound was determined by the monitoring ¹H NMR of compound **2a** with gradual addition of fluoride, which also suggests stepwise binding of fluoride to compound **2a**. Since both hydrogen bonding and proton transfer mechanisms often give rise to a very similar kind of optical response of the receptor, so experimental findings were validated with theoretical calculation to get an idea about the mechanism of the signaling process, which showed stepwise binding of fluoride followed by deprotonation of N-H proton leads to a colour change.

Results and Discussion:

The Fe(ox)-Fe₃O₄ promoted condensation reaction between terephthaldehyde and 2 equivalent of corresponding indole leads to the bis(indolyl)methane (**1a**) in good yield.¹⁴ In **1a**, free aldehyde was further condensed with 2,4-dinitro phenyl

hydrazine in methanol to get the desired compound **2a** (Scheme 1). The compound **1a** showed three peaks in DMSO at 266, 322, and 445 nm with extinction coefficients (ϵ , $\text{mol}^{-1}\text{Lcm}^{-1}$) of 5×10^3 , 2.64×10^3 , and 2.2×10^2 . Upon gradual addition of tetra butyl ammonium fluoride (TBAF) salt to compound **1a** (500 μM) in DMSO, two new band at 524 and 462 nm appeared due to interaction between **1a** and Fluoride, while the color of the solution turned to pink (Figure 2). The absorbance of both the peak began to decrease after adding 3.05 equivalent of TBAF.¹⁵



Scheme 1. Synthetic route of all the compounds

Upon decreasing the concentration of **1a** from 500 μM to 100 μM , a characteristic colour change was observed after the addition of 50 equivalents of fluoride. Further decrease in concentration of **1a** from 100 μM to 50 μM leads to colour change upon addition of 70 equivalents of fluoride. Upon addition of strong base like $[\text{Bu}_4\text{N}]\text{OH}$, which definitely leads to deprotonation, also brought the same color and spectral changes of **1a** as those observed with fluoride anions. Upon progressive additions of protic solvent (such as methanol or water), the pink colour solution turned into light yellow and revert back to its original absorption spectra, which indicates the proton dissociation–association process is reversible in nature. The binding stoichiometry between fluoride and compound **1a** was determined from the Job's plot experiment with a fixed fluoride and **1a** concentration of 1000 μM , which suggests 1:2 binding between **1a** and fluoride (Figure 2). On the other hand, compound **2a** showed peaks in DMSO at 262, 312, and 405 nm with extinction coefficients (ϵ , $\text{mol}^{-1}\text{Lcm}^{-1}$) of 8.4×10^4 , 1.9×10^4 , and 0.62×10^4 . Condensation of 2,4-dinitrophenylhydrazine (DNP) to compound **1a** leads to more electron accepting ability of the molecule as DNP has more electron accepting capacity compared to aldehyde. So, we would expect higher sensitivity of compound **2a** compared to **1a** towards colorimetric detection of fluoride. To know the sensitivity of the compound **2a**, titration was done with variable concentration of **2a** in UV-vis spectroscopy. Gratifyingly, colorimetric sensing of fluoride with compound **2a** could be possible even at 5 μM . The Fig. 3 shows the change in absorption spectra upon gradual addition of F^- with compound **2a** at two different concentrations (60 μM and 20 μM). Upon gradual addition of fluoride to **2a** in DMSO, a unique new broad absorption band at 560 nm appears with a parallel decrease in the band at 401 nm corresponding to the neutral species with a clear isosbestic point around 457 nm indicating strong interaction between **2a** and fluoride ion (Fig. 3).

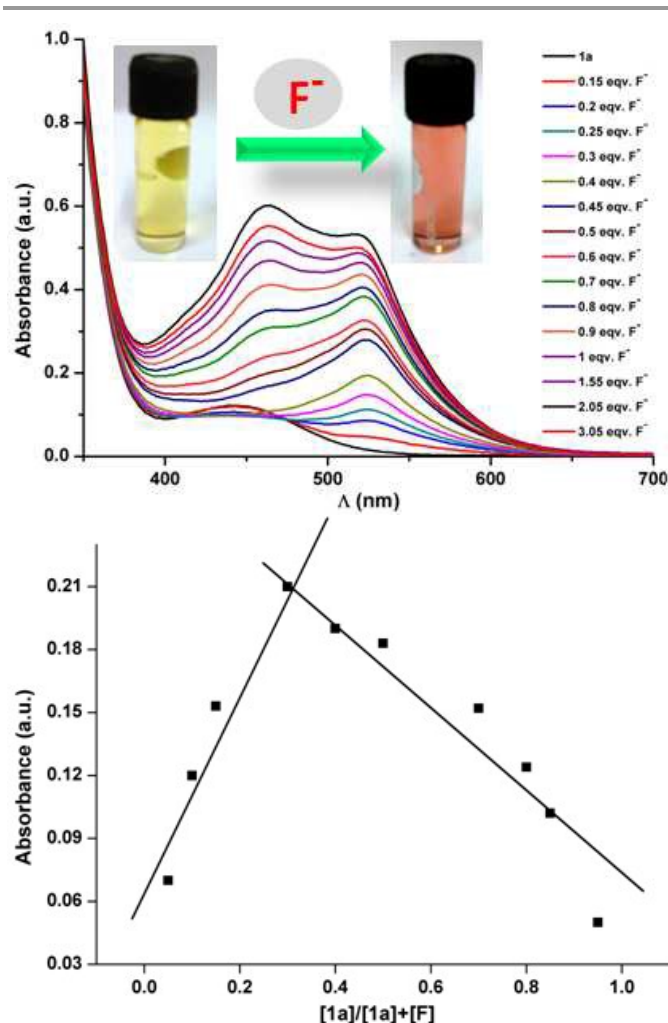


Figure 2. The changes in UV-vis spectra of **1a** recorded in DMSO (500 μM) after gradual addition of fluoride and Job's plot for compound **1a** with fixed concentration of **1a** and fluoride of 1000 μM .

Interestingly, after the addition of nearly 2.2 equivalent fluorides, the isosbestic point slightly shifted from 457 nm to 445 nm, with one additional blue-shift band centered at 520 nm, while the color of the solution turned from purple to orange. The shifting of the isosbestic point and the corresponding absorption band may be assigned to the formation of tri-anion of **2a** after deprotonation of two indole N-H and one hydrazine N-H.²¹ To get an idea about the binding phenomenon of compound **2a** with fluoride, ^1H NMR titration of compound **2a** was done with gradual addition of fluoride in acetone- d_6 . With addition of 0.2 equivalent of TBAF salt to compound **2a** leads to complete disappearance of N-H proton of hydrazine moiety, which indicates very fast H-bonded association-dissociation equilibrium with N-H proton of hydrazine because of its higher acidity (Fig. 4). On the other hand, the potential hydrogen bonding pocket, defined by the indole $-\text{NH}-$ protons, tends to bring the fluorides to the vicinity of indole groups. So, gradual addition of fluoride to compound **2a** leads to the broadening of the indole N-H signals with downfield shifting, which indicates the H-bonded interaction of fluoride with indole N-H proton.

The indole N-H signals in compound **2a** appeared at 10.01 ppm, which was shifted to 12.72 ppm upon addition of 7.0 equivalent of TBAF. Further, addition of 50 equivalent of fluoride resulted a new triplet peak at 16.04 with a coupling constant of 120 Hz, indicates the formation of $[\text{HF}_2]^-$ via the

abstraction of indole N-H and N-H proton of hydrazine in **2a**.¹⁶ So, in the first step, abstraction of most acidic N-H proton of hydrazine occurs in presence of lower equivalent of fluoride, followed by deprotonation of two indole N-H at higher equivalent of fluoride.

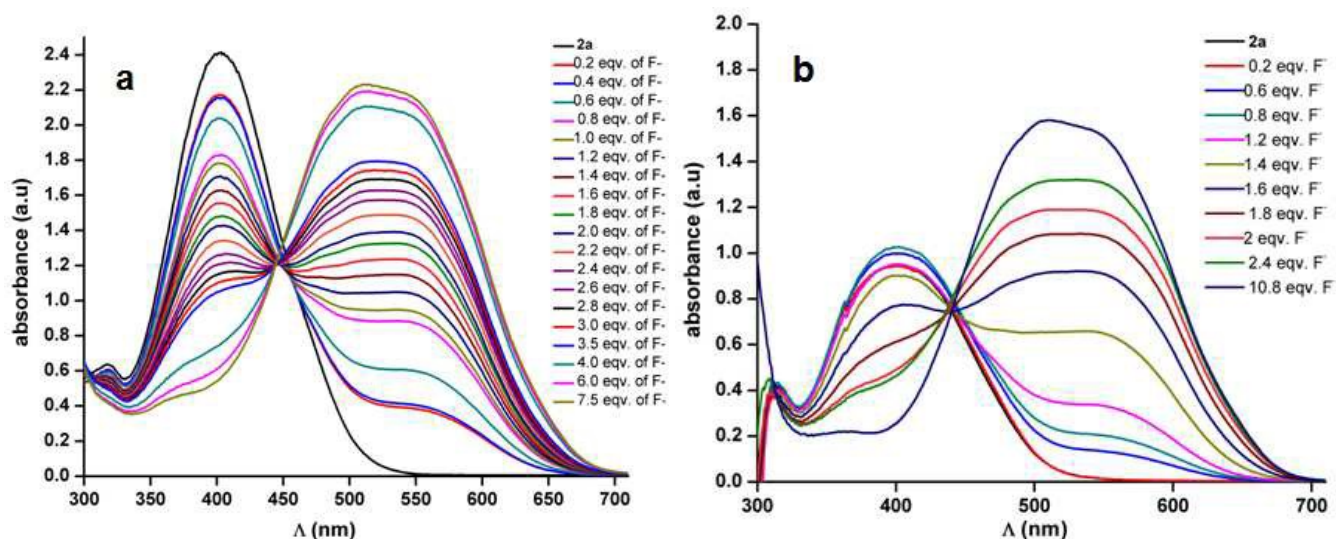
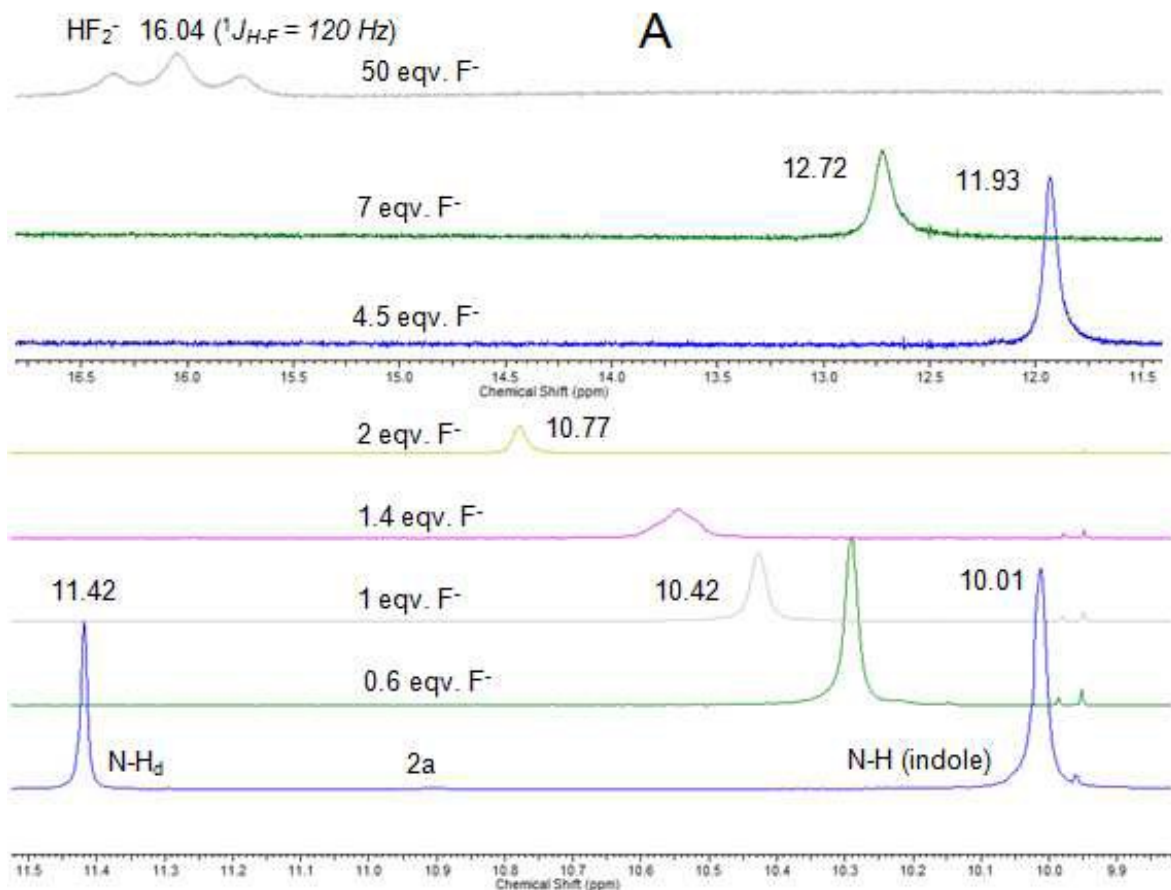


Figure 3. The changes in UV-vis spectra of **2a** (60 μM ; a and 20 μM ; b) recorded in DMSO after gradual addition of fluoride.



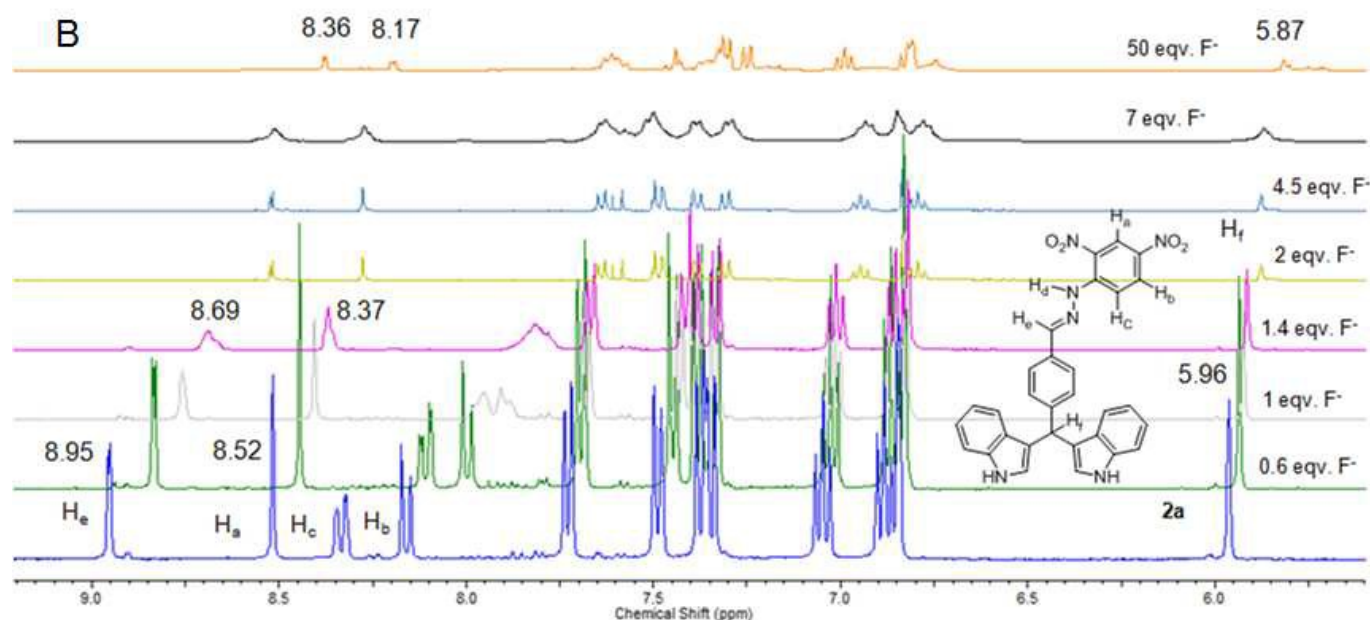
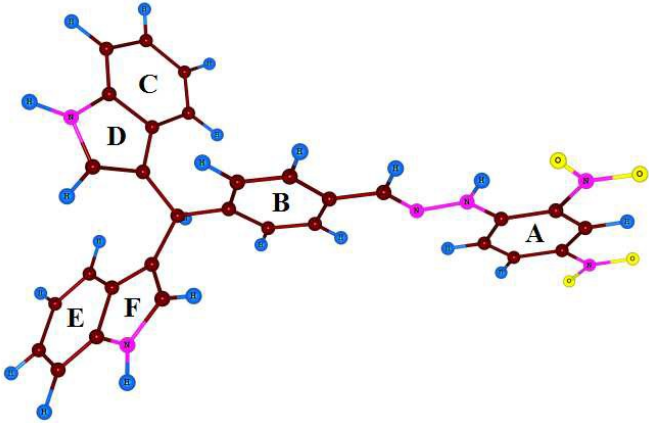


Fig 4. ^1H NMR of compound **2a** in acetone- d_6 upon gradual addition of TBAF change of the N-H proton (A), change of other proton (B).

Further ^{19}F NMR was carried out after the addition of 50 equivalent fluoride to **2a** in DMSO- d_6 , which indicates the signal of $[\text{HF}_2]^-$ at -146.1 ppm, due to the complete deprotonation of **2a** and the formation of $[\text{HF}_2]^-$. The deprotonation of hydrazine N-H resulted in the generation of negative ion at the nitrogen, which brought the 2,4 dinitrophenyl moiety in conjugation with aryl moiety of bis(indolyl)methane *via* imine. So, we would expect up field shift of DNP ring proton. While, after addition of 0.2 equivalent of fluoride, complete disappearance of N-H proton of hydrazine occurs, but negligible shift of DNP ring proton was observed. However, after the addition of 1.0 equivalent of fluoride, more up field shifting of imine proton (H_e) as well as DNP ring proton (H_a , H_b , and H_c) was observed. Further addition of fluoride leads to more up field shift of imine proton and ring proton of DNP (Fig. 4). The up field shift indicates that negative charge brought after the abstraction of hydrazine N-H results the delocalization of negative charge around 2,4-DNP ring. On the other hand, after deprotonation of two indole N-H in **2a** by excess fluoride do not able to brought the aryl and indole moiety in conjugation because of the non planar Sp^3 carbon in between them will inhibit the delocalization process. However aryl and 2,4-DNP ring will withdraw some electron from deprotonated indole moiety due to their negative inductive effect. So, we are expecting electron flow from indole to 2,4 DNP moiety after deprotonation of all the three N-H proton. To explain the shift in NMR signals of **2a** upon gradual removal of protons or electron flow after deprotonation, we carried out nucleus independent chemical shift (NICS)¹⁷ calculations at B3LYP/6-31G(d) level of theory using Gaussian-09.^{18,19} The NICS values at geometric mean of the centre is designated as NICS(0) while the values at 1Å above the ring is designated as

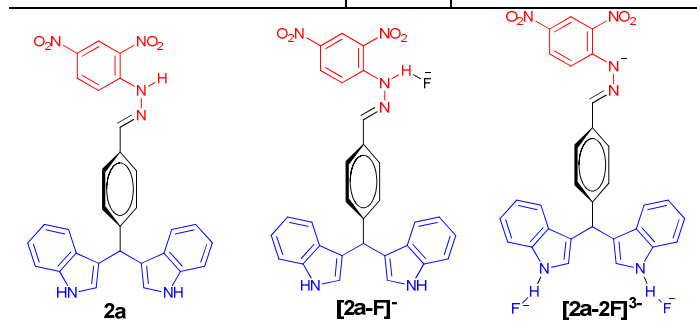
NICS(1). The values along with the designations of different rings in **2a** are shown in Table 1. It is evident from Table 1 that NICS values calculated at 1Å above the rings are slightly higher than that of NICS(0) values. Moreover, upon gradual removal of protons, the NICS values of the ring A (the benzene ring of 2,4-dinitrophenyl moiety) decreases while that of others increases. The lower NICS value of ring A after deprotonation also suggest less aromaticity of ring A, which is also consistent with the upfield shifts of 2,4-DNP ring in ^1H NMR. Although the step-wise deprotonation of **2a** could not be monitored, theoretical calculations suggest that after deprotonation more delocalization occurs at the indole moiety and flow of electron from indole to 2,4-DNP increases the electron density of 2,4-DNP moiety, hence up-field shift of corresponding proton in 2,4-DNP moiety. Although the stepwise deprotonation of **2a** ultimately leads to its corresponding trianion but, in this case N-H-F interaction between highly acidic N-H proton of DNP and fluoride followed by formation of stable $[\text{HF}_2]^-$ species will generate corresponding monoanion (**2a**⁻). After that, two fluorides will simultaneously interact with two chemically equivalent indole N-H to form the adduct (**2a-2F**⁻). Finally, the adduct (**2a-2F**⁻) will form the corresponding tri-anion (**2a**³⁻) after the interaction with another two equivalent of fluoride. Further, theoretical calculation was performed to know the energetic of the stepwise binding phenomenon. All the possible intermediates in stepwise binding pathway was optimized at B3LYP/6-31G* level of theory in gas phase. To know the solvent effect on the binding process, single point calculation is done on the optimized geometry in DMSO solvent utilizing PCM model at B3LYP/6-31G* level of theory.

Table 1. NICS values of compound **2a** and its corresponding anion after deprotonation at B3LYP/6-31G(d) level of theory


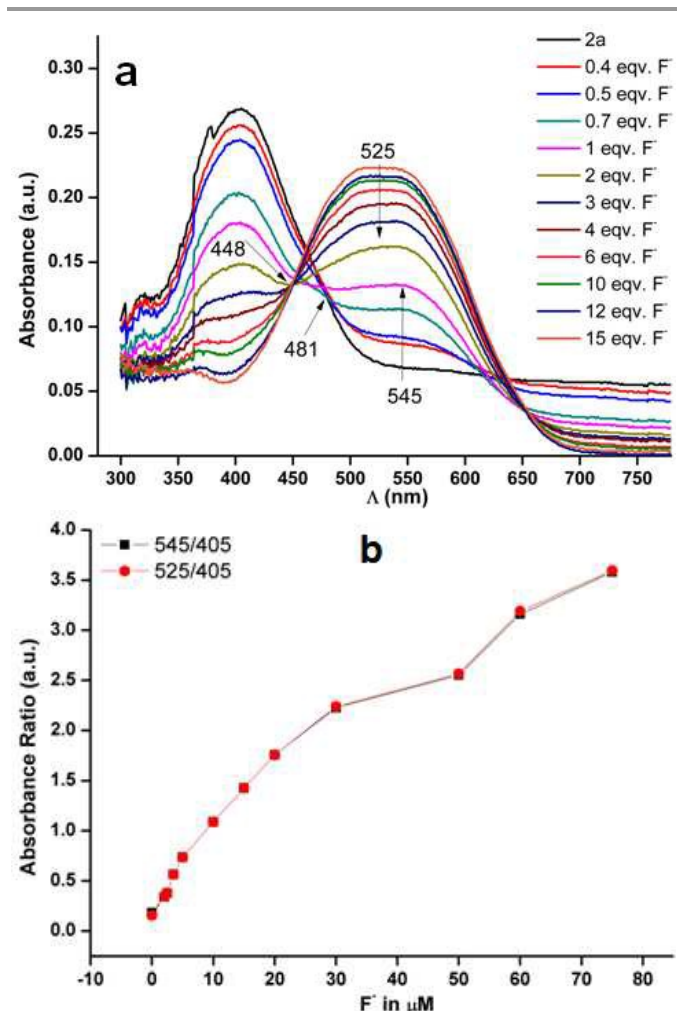
Compound	Ring	NICS(0)	NICS(1)
2a	A	-5.63	-5.88
	B	-6.87	-7.05
	C	-10.14	-10.83
	D	-11.66	-12.13
	E	-9.78	-10.76
	F	-10.97	-12.32
2a⁻	A	-5.09	-5.12
	B	-7.09	-7.21
	C	-11.33	-11.45
	D	-12.70	-13.27
	E	-11.31	-12.33
	F	-12.89	-14.12
2a³⁻	A	-3.02	-3.45
	B	-7.19	-8.15
	C	-10.96	-11.87
	D	-13.45	-14.12
	E	-11.20	-11.98
	F	-12.90	-14.11

Table 2. Plausible intermediates from the interaction between **2a** and fluoride and their calculated free energy of formation.

Plausible interaction and their intermediates	ΔG_f in Kcal/mol (gas phase)	ΔG_f in Kcal/mol (DMSO)
$2a + F^- \rightleftharpoons [2a-F]^-$	-93.6	-40.7
$[2a-F]^- + F^- \rightleftharpoons 2a^- + HF_2^-$	-50.4	-32.8
$2a^- + 2F^- \rightleftharpoons [2a-2F]^{3-}$	-56.7	-63.6
$[2a-2F]^{3-} + 2F^- \rightleftharpoons 2a^{3-} + 2HF_2^-$	-77.9	-53.8



The free energy of formation (ΔG_f) was determined from the free energy difference between product and reactant with zero-point energies (ZPE) and thermal corrections at 298 K. The negative free energy of formation of each of the step in both the gas phase and DMSO (ZPE and thermal corrections at 298 K are taken from gas phase data) suggests the feasibility of the interaction process between **2a** and fluoride. On the other hand, highest negative formation in step 3 (from **2a⁻** to **2a-2F³⁻**) in DMSO indicates the more affinity of fluoride to indole N-H (Table 2). For this reason, interaction of both the highly acidic N-H of DNP and indole N-H was observed even after addition of little amount of fluoride (vide NMR and UV-vis titration). The compound **2a** shows ratiometric response in presence of fluoride. The compound **2a** shows three peaks at 262, 312, and 405 in DMSO. Upon gradual addition of fluoride, a decrease in absorbance at 405 nm was observed, while a new peak at 545 nm was appeared (Fig. 5).²⁰

**Figure 5.** The changes in UV-vis spectra of **2a** (5 μM solution in DMSO) after the gradual addition of fluoride; a and Ratio of absorbance versus fluoride concentration plot of **2a**; b.

However, upon increasing the fluoride ion concentration, the band centered at 545 nm display a blue shift of 20 nm to a new band centered at 525 nm with a decrease in absorbance of the

existing band at 405 nm, while the isosbestic point also shifted from 481 nm to 448 nm (Fig. 5).²¹ We subsequently measured the absorbance ratio between 545 nm/405 nm and 525 nm/405 nm wavelengths to detect the fluoride concentration. In both the cases similar response was observed. The plot between ratios of the absorbance at the two selected bands *versus* fluoride concentration allows one to detect the fluoride accurately up to 2 μ M (Fig. 5). To verify the anion specificity, some assays with **2a** was performed with other tetrabutylammonium salts (TBA-X: X= Cl, Br, I, CH₃COO, BF₄ and HSO₄). Under identical experimental condition, negligible ratiometric change of **2a** was observed in spite of their presence in large excess compared to fluoride. So, in presence of other anions, fluoride can be detected quantitatively by measuring relative absorbance at 545 to 405 or at 525 to 405 nm (Fig. 6). This ratiometric chemosensory response could be conveniently used as a fingerprint to discriminate this particular anion.

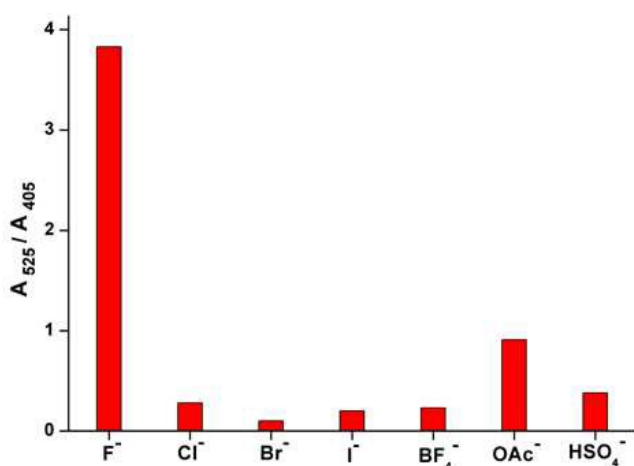


Fig. 6 Ratiometric response of **2a** in UV-vis spectroscopy.

Conclusions

In conclusion, we have designed and synthesized (2,4-dinitrophenyl)hydrazine derivative of bis(indolyl) methane (**2a**) from the condensation reaction between 4-(di(1H-indol-3-yl)methyl)benzaldehyde (**1a**) and (2,4-dinitrophenyl)hydrazine. Both the compound shows selective sensing of fluoride *via* naked eye detection of a pattern of colour changes as well as of absorption signals. The binding stoichiometry between fluoride and **1a** was determined from Job's plot experiment, which showed 1:2 binding. The binding interaction between **2a** and fluoride from ¹H NMR, UV-Vis, and density functional studies suggests stepwise fluoride-induced interaction followed by deprotonation of 2,4-dinitrophenyl)hydrazine N-H and two indole N-H proton to its corresponding tri-anion is responsible for the significant color and spectral changes in the absorption properties of **2a**. The compound **2a** shows ratiometric responses to fluoride ion in presence of other anions, which allows fluoride ion detection even at the submicromolar level, accurate up to 2 μ M.

Experimental Section:

Synthesis of 1a:

In a 10-mL round bottom flask equipped with a magnetic bar, was charged with Fe(ox)-Fe₃O₄ (0.05 mmol) in water (3 ml) in open air and stirred vigorously for 5 min. After that the appropriate aldehyde (1 mmol) and Indole (2.2 mmol) was added to it and placed into a constant temperature bath at 110 °C and allowed to continue. After completion, the reaction mixture was cooled and the addition of 2-3ml distilled water gives solid product. The solid product extracted with ethylacetate (20 mL×3) and washed with water (10 mL×3), brine (10 mL) and dried over anhydrous Na₂SO₄. After removing the solvent the residue was subjected to silica gel column chromatography (60-120 mesh, ethyl acetate-petroleum ether, and gradient elution) to afford pure product. Yield = 84%; Anal. Calc. for C₂₄H₁₈N₂O C, 82.26; H, 5.18; N, 7.99; Found C, 81.88; H, 5.08; N, 8.26, FT-IR ν_{\max} (Cm⁻¹), N-H (3404), 3093(C-H), 2923(C-H), 1690(C=N), 1614(C=C), 1505(NO₂), 1329(C-N) cm⁻¹; ¹H NMR (400 MHz, acetone-d₆) δ (ppm): 6.02 (1H, s,), 6.83-6.9 (4H, m), 7.05 (2H, t, J= 8 Hz), 7.35(4H, m), 7.59 (2H, d, J = 8 Hz), 7.81 (2H, d, J=8 Hz), 9.6 (1H, s), 10.1(2H, s). ¹³C δ C(100 MHz, acetone-d₆) 111.5, 118, 118.6, 119.3, 121.5, 123.9, 127.1, 129.4, 129.5, 135.1, 137.3, 152.1, 191.7.

Synthesis of 2a:

The compound **1a** (0.5 mmol) was taken in 10 ml round bottom flask equipped with a magnetic bar and reflux condenser and stirred vigorously for 5 min. After that, 2 ml methanol solution of (2,4-dinitrophenyl)hydrazine (0.5 mmol) was added to it and placed into a constant temperature bath at 110 °C and allowed to continue. After completion of the reaction, an orange colour precipitate was filtered and washed with methanol 3-4 times and dried under vacuum. Yield = 170 mg (64% **2a**); Anal. Calc. for C₃₂H₂₂N₆O₄ C, 67.92; H, 4.18; N, 15.84; Found: C, 67.64; H, 4.16; N, 16.09; FT-IR, ν_{\max} (Cm⁻¹), 3404(N-H), 3046(C-H), 2922(C-H), 284 3(C-H), 2738(C-H), 1685(C=O), 1597(C=C) ¹H NMR (400 MHz, acetone-d₆) δ (ppm): 5.99 (1H, s,), 6.88-6.93 (4H, m), 7.03-7.06 (2H, m,), 7.37-7.42 (6H, m,), 7.49 (2H, d, J = 8.0 Hz), 7.76 (2H, d, J=7.0 Hz), 8.19 (2H, d, J = 8.0 Hz), 8.36 (2H, d, J = 8.4 Hz), 8.51 (1H, s,), 8.95 (1H, s), 10.1(2H, s), 11.42 (1H, s); ¹³C δ C(100 MHz, acetone-d₆) 111.4, 116.8, 118.4, 118.6, 119.4, 121.4, 123, 123.8, 127.2, 127.5, 129.3, 129.7, 131.9, 137.3, 137.7, 145, 148.4, 149.2. m/z (MALDI-TOF-MS): 529.598.

Instruments

Absorption spectra were recorded in a Dynamica Halo DB-30 double beam digital spectrophotometer (Switzerland) attached with a Lab Companion RW-0525G chiller, and also in SHIMADZU UV 2550 spectrophotometer with quartz cuvette. All the samples for FTIR study were properly washed with distilled water at least five times, and then dried under vacuum. Finally, samples for the FTIR spectra were recorded using IMPACT 410 Thermo-Nicolet instrument from a thin

transparent KBr pellet. ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra (chemical shifts referenced to signals for residual solvent) were recorded on JEOL 400 MHz spectrometer at 298 K.

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Notes and references

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- (a) C. H. Park and H. E. Simmons, *J. Am. Chem. Soc.*, 1968, **90**, 2431 (b) F. Jäkle, *Coord. Chem. Rev.* 2006, **250**, 1107. (c) H. Miyaji and J. L. Sessler, *Angew. Chem. Int. Ed.*, 2001, **40**, 154. (d) M. Wenzel, J. R. Hiscock and P. A. Gale, *Chem. Soc. Rev.*, 2012, **41**, 480. (e) B. P. Hay, *Chem. Soc. Rev.*, 2010, **39**, 3700. (f) J. S. Kim and D. T. Quang, *Chem. Rev.* 2007, **107**, 3780.
- ² (a) P. A. Gale, S. E. Garrido, J. Garric, *Chem. Soc. Rev.* 2008, **37**, 151. (b) R. Martinez-Manez, F. Sancenon, *Chem. Rev.*, 2003, **103**, 4419. (c) T. Gunnlaugsson, P. E. Kruger, P. Jensen, J. Tierney, H. D. Paduka Ali, G. M. Hussey, *J. Org. Chem.*, 2005, **70**, 10875-10878. (d) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 191; (b) J. L. Sessler, S. Camiolo, P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 17; (e) J. L. Sessler, J. M. Davis, *Acc. Chem. Res.*, 2001, **34**, 989; (f) P. D. Beer, P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (g) P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79. (h) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge and F. P. Gabbaï, *Chem. Rev.*, 2010, **110**, 3958. (i) H. Zhao, L. A. Leamer, F. P. Gabbaï, *Dalton Trans.*, 2013, **42**, 8164 and references therein.
- ³ (a) P. A. Gale, P. Jr. Anzenbacher, J. L. Sessler, *Coord. Chem. Rev.*, 2001, **222**, 57; (b) P. A. Gale, *Coord. Chem. Rev.*, 2000, **199**, 181; (c) P. D. Beer, J. Cadman, *Coord. Chem. Rev.*, 2000, **205**, 131; (d) H. Miyaji, W. Sato, J. L. Sessler, *Angew. Chem., Int. Ed.*, 2000, **39**, 1777; (e) T. S. Snowden, E. V. Anslyn, *Curr. Opin. Chem. Biol.*, 1999, **3**, 740. (f) K. Choi, A. D. Hamilton, *Coord. Chem. Rev.*, 2003, **402**, 101; (g) C. R. Bondy, S. J. Loeb, *Coord. Chem. Rev.*, 2003, **240**, 77. (h) P. Bose and P. Ghosh, *Chem. Commun.*, 2010, **46**, 2962. (i) X. J. Peng, Y. K. Wu, J. L. Fan, M. Z. Tian and K. L. Han, *J. Org. Chem.*, 2005, **70**, 10524. (j) Y.-M. Zhang, Q. Lin, T.-B. Wei, X.-P. Qin and Y. Li, *Chem. Commun.*, 2009, 6074. (k) T. Gunnlaugsson, P. E. Kruger, T. C. Lee, R. Parkesh, F. M. Pfeffer and G. M. Hussey, *Tetrahedron Lett.*, 2003, **44**, 6575. (l) M. Suresh, A. Ghosh and A. Das, *Chem. Commun.*, 2008, 3906. (m) S. P. Mahanta, B. S. Kumar, S. Baskaran, C. Sivasankar and P. K. Panda, *Org. Lett.*, 2012, **14**, 548. (n) D. A. Jose, D. K. Kumar, B. Ganguly and A. Das, *Org. Lett.*, 2004, **6**, 3445. (o) I. Ravikumar and P. Ghosh, *Chem. Soc. Rev.*, 2012, **41**, 3077. (p) P. Bose and P. Ghosh, *Chem. Commun.*, 2010, **46**, 2962. (q) S. K. Kim and J. L. Sessler, *Acc. Chem. Res.* 2014, **47**, 2525.
- ⁴ X. He, S. Hu, K. Liu, Y. Guo, J. Xu and S. Shao, *Org. Lett.*, 2006, **8**, 333.
- ⁵ (c) L. Wang, X. He, Y. Guo, J. Xua and S. Shao, *Org. Biomol. Chem.*, 2011, **9**, 752.
- ⁶ A. Mallick, U. K. Roy, B. Haldar and S. Pratihar, *Analyst*, 2012, **137**, 1247.
- ⁷ O. Li, Y. Guo, J. Xu and S. Shao, *J. Photochem. Photobiol. B: Biology* 2011, **103**, 140.
- ⁸ L. Panzella, A. Pezzella, M. Arzillo, P. Manini, A. Napolitano and M. d'Ischia, *Tetrahedron* 2009, **65**, 2032.
- ⁹ Y. Shiraishi, H. Maehara and T. Hirai, *Org. Biomol. Chem.*, 2009, **7**, 2072.
- ¹⁰ Y. Shiraishi, H. Maehara, T. Sugii, D. Wang, D. and T. Hirai, *Tetrahedron Lett.* 2009, **50**, 4293.
- ¹¹ (a) M. Shiri, M. A. Zolfigol, H. G. Kruger and Z. Tanbakouchian, *Chem. Rev.* 2010, **110**, 2250. (b) P. A. Gale, *Chem. Commun.*, 2008, 4525. (c) G. Pereira, E. M. S. Castanheira, P. M. T. Ferreira and M. -J. R. P. Queiroz, *Eur. J. Org. Chem.* 2010, **3**, 464. (c) Q. Yi, Q. Sanyin, Y. Lin, H. Jianli and Q. Dahui, *Sensors and Actuators B* 2012, **173**, 225. (d) Z. Hui, H. Juan and Q. Da-Hui, *Org. Lett.*, 2012, **14**, 2334. (e) Y. Zhou, J. F. Zhang and J. Yoon, *Chem. Rev.* 2014, **114**, 5511 and references therein
- ¹² (a) J. R. Lakowicz *Principles of Fluorescence Spectroscopy*, Plenum Press, New York 1999. (b) D. Esteban-Gómez, L. Fabbrizzi and M. Licchelli, *J. Org. Chem.* 2005, **70**, 5717.
- ¹³ (a) X. Zhang, S. Lee, Y. Liu, M. Lee, J. Yin, J. L. Sessler and J. Yoon, *Sci. Rep.* 2014, **4**, 4593. (b) Z. Guo, N. R. Song, J. H. Moon, M. Kim, E. J. Jun, J. Choi, J. Y. Lee, C. W. Bielawski, J. L. Sessler and J. Yoon, *J. Am. Chem. Soc.* 2012, **134**, 17846. (c) Y. Du, B. J. Lim, B. Li, Y. S. Jiang, J. L. Sessler and A. D. Ellington, *Anal. Chem.* 2014, **86**, 8010
- ¹⁴ R. Pegu, K. J. Majumdar, D. J. Talukdar and S. Pratihar, *RSC Adv.*, 2014, **4**, 33446.
- ¹⁵ The decrease in absorbance may be due to the lowering in concentration of corresponding anion of **1a**, which is due to the aggregated assembly between the anion of **1a** and the corresponding tetrabutyl ammonium (TBA) cation of added TBAF.
- ¹⁶ (a) M. Pecul, J. Sadle, and J. Leszczynski, *J. Chem. Phys.*, 2001, **115**, 5498. (b) I. G. Shenderovich, S. H. Smirnov, G. S. Denisov, V. A. Gindin, N. S. Golubev, A. D. Dungen, R. Reibke, S. Kirpekar, O. L. Malkina, and H.-H. Limbach, *Ber. Bunsenges. Phys. Chem.*, 1998, **102**, 422.

- ¹⁷ (a) P. V. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. V. E. Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317. (b) *Aromaticity and Metal Clusters*; P. K. Chattaraj, Ed.; CRC Press: Boca Raton, FL, 2010. (c) P. K. Chattaraj, S. Giri and S. Duley, *Chem. Rev.*, 2011, **11**, PR43.
- ¹⁸ (a) B3LYP is Becke's three-parameter hybrid method using the LYP correlation functional. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785–789.
- ¹⁹ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P. J.; Dannenberg, J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision D.02, Gaussian, Inc.: Pittsburgh, PA, **2009**.
- ²⁰ The absorbance in **Fig. 5** at different amount of fluoride ion within the wavelength longer than 700nm is not zero, while that of other UV spectra within the same range is zero these may be explained from the solvation effect of **2a** with polar DMSO solvent. The higher absorbance in **Fig. 5** may be attributed to the more no of interaction between DMSO and **2a** at low concentration (5 μ M of **2a**) compared to its high concentration.
- ²¹ The blue shift of 545 nm band at higher concentration of TBAF may be attributed to the aggregated assembly between the anions (mono, di, or tri) of **2a** and the corresponding tetrabutyl ammonium (TBA) cation of added TBAF. Author thanks one of the reviewers for pointing out this. For reference please see; (a) J. Steffen and T. J. Nicolas, *Macromolecules*, 1995, **28**, 22. (b) R. M. Josep, C. Jouquim, F. Joan-Anton and V. L. Maria, *J. Chem. Soc., Chem. Commun*, 1994, 681.

