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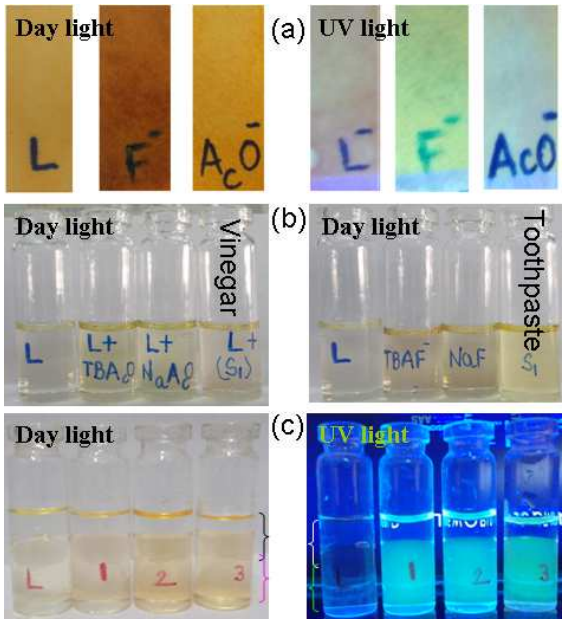
Graphical Abstract

A novel receptor (**L**) bearing catechol and phenol groups was synthesized and investigated for the dual sensing of F^- and AcO^- by naked-eye and spectral (UV-Vis and fluorescence) responses. The receptor **L** was tested for live breast cancer cell imaging and can be applied to the breast tumour diagnosis.



Anion selective chromogenic and fluorogenic chemosensor and its application in breast cancer live cell imaging

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Abstract

A novel Schiff base receptor (**L**) bearing catechol and phenol groups was synthesized and characterized by various spectral (FTIR, ^{1}H NMR and mass) data. The anion recognition ability of **L** was investigated by experimental (UV-Vis, fluorescence and ^{1}H NMR) and theoretical (B3LYP/6-31G**) methods. Among the tested anions, the receptor **L** showed both naked-eye detectable color change from light-yellow to intense brownish-yellow and spectral (hyperchromic shift at 450 nm and 'turn-on' fluorescence at 480 nm) changes selectively towards F^- and AcO^- in DMSO and mixed DMSO-H_2O medium because of the formation of hydrogen bonded anion-receptor complex followed by the deprotonation of **L**. The receptor **L** was tested for live breast cancer cell imaging and can be applied to the breast tumour diagnosis.

Keywords: Anion recognition, Chemosensor, Colorimetric, Fluorescence, F^-, AcO^-.

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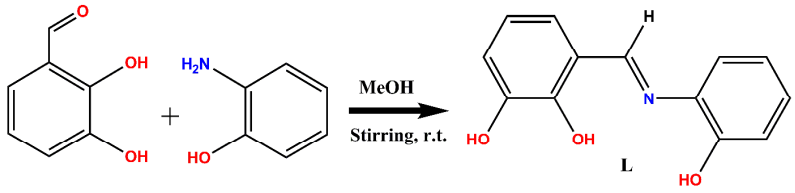
Introduction

The recognition and sensing of bioactive anions using colorimetric and fluorescence based chemosensor has gained an immense interest in the field of supramolecular chemistry.[1-2] Many reported sensing systems are known to exhibit self-assembling structures that are linked with a range of weak interactions viz. hydrogen bonding, π-π stacking, and van der Walls interaction etc. Owing to their property of exhibiting self-assembling structures, such chemosensors have the potential ability in controlling the functionalities of bio-macromolecules and thus provide the understanding regarding the structural and functional details of bio-macromolecules. This will, in turn, help these chemosensors to find possible applications in the field of analyte sensing and data storage.[3-5] Moreover, the presence of two or more hydrogen bonding moieties, mostly in combined form, leads to the increase in the anion binding affinity through synergistic action in these structures and allowed to sense the biologically significant anions or more precisely known as the Hofmeister series of anions. Usually the anion sensing ability of these sensors gives rise to internal charge transfer (ICT) with a naked-eye detectable color change and UV-Vis/fluorescence response, which can be easily detectable. Among the wide range of anions present in the Hofmeister series of anions, acetate (AcO^-) and fluoride (F^-) anions constitute an important class of analyte owing to their diversified applications in the biochemical processes, catalysis, environmental chemistry and pharmaceutical industry.[6-9] Fluoride is effective for the prevention of dental caries and useful in the treatment of osteoporosis.[10] However, high levels of fluoride in drinking water have been associated with both dental or skeletal fluorosis, kidney problems and nephrolithiasis.[11] Similarly, acetate is also equally important due to its possible tracer for malignancies and extensive use in prostate cancer and its metastases.[12] Hence, there is bourgeoning need of low-cost and easy-to-synthesize chemosensors for naked-eye (colorimetric) detection of anions because of the simplicity, sensitivity and selectivity.[13-19]

Herein, as a part of our ongoing research on anion recognition[20], we have developed a simple Schiff base receptor **L** (Scheme 1) bearing catechol and phenol units for the selective sensing of AcO^- and F^-. The anion recognition ability of **L** was investigated by both spectroscopic (absorbance, fluorescence and ^1H NMR) and density functional theory (DFT) methods. Finally, the receptor was applied for the sensing of intracellular F^- in live cells.



Scheme 1. Synthesis of the receptor **L.**

Results and discussion

The receptor **L** was synthesized by a Schiff base condensation reaction of 2,3-dihydroxybenzaldehyde with 2-aminophenol (Scheme 1). Then, the anion sensing ability of receptor **L** was investigated in detail through naked-eye, UV-Vis absorption and fluorescence spectroscopy in DMSO and mixed solvent DMSO/H_2O. In DMSO, the UV-Vis spectra of **L** (5×10^{-5} M) in the absence and presence of different anions (F^-, Cl^-, Br^-, I^-, HSO_4^-, AcO^-, $H_2PO_4^-$) were shown in Fig. 1a. The absorbance spectrum of free **L** exhibited a main absorption band at 350 nm and a weak band at 450 nm can be assigned due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions, respectively. The presence of a weak peak above 400 nm indicates that the enolimine form of **L** is predominantly existed in solution. On addition of F^- and AcO^- anions, the band at 350 nm of **L** was disappeared whereas the intensity of band at 450 nm was enhanced remarkably. Also, the color of the receptor solution was changed instantaneously from light yellow to intense brownish-yellow (Fig. 1a inset). However, such spectroscopic and color changes were not noticed with other tested anions even at abundance.

Next, the anion recognition ability of the receptor **L** toward different anions was investigated by fluorescence spectroscopy under similar conditions. The receptor **L** (5×10^{-5}

M) exhibited an emission centred at 440 nm upon excitation (λ_{exc} = 350 nm). Upon addition of AcO^- and F^- (Fig. 1b), the receptor **L** showed a remarkable fluorescence increment at 480 nm. Also, a weak fluorescence enhancement at 480 nm was observed in the presence of $H_2PO_4^-$. However, no meaningful fluorescence changes were observed with other anions. Then, the vials were visualized under UV light which showed a bluish-green fluorescence selectively only in the presence of AcO^- and F^- (Fig. 1b inset). Further, the results of competitive experiments inferred that the AcO^- and F^- detection ability of **L** was not significantly influenced in the presence of equimolar amounts of other interfering anions such as Cl^-, Br^-, I^-, $H_2PO_4^-$ and HSO_4^- (Fig. S1-2). All the above results clearly delineated the high selectivity, sensitivity and specificity of the receptor **L** for the detection of AcO^- and F^-.

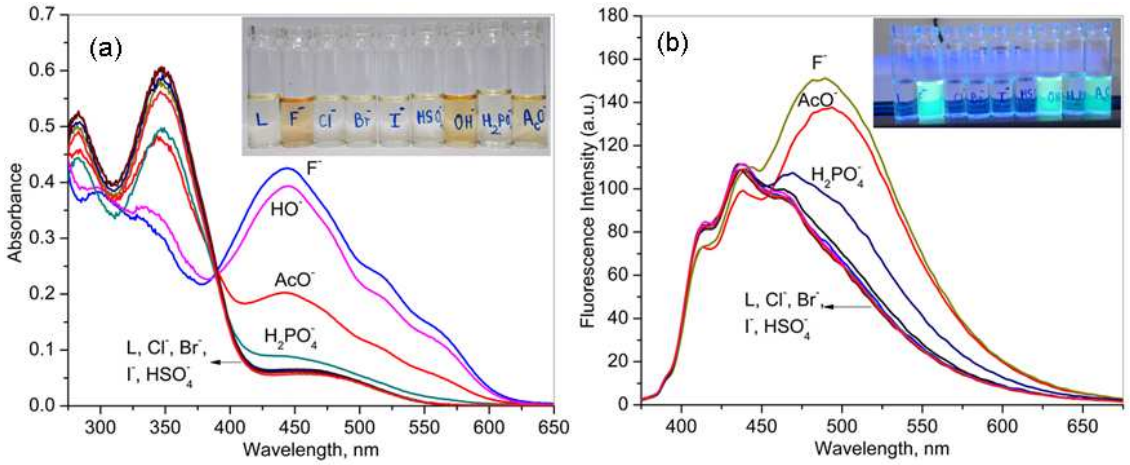


Fig. 1. (a) UV–Vis and (b) fluorescence spectra of **L** (5 x 10^{-5} M) in the absence and presence of 10 equivalents of different anions in DMSO. Inset showing the color change of **L** under day and UV light.

The spectral (absorption and fluorescence) titrations of **L** were performed with incremental addition of TBAF and TBAAcO in DMSO. Upon stepwise addition of F^- and AcO^- ions to the DMSO solution of **L** (5 × 10^{-5} M), the intensity of absorbance at 350 nm was reduced and enhanced gradually at 450 nm with the formation of an isosbestic point at 392 nm (Fig. 2a and Fig. S3). The formation of an isosbestic point indicates the interaction

occurred between the receptor **L** and the anion added. Then, the association/binding constants (K) of **L** with F^- and AcO^- were determined by Benesi–Hildebrand (B–H) analysis by using the spectroscopic titrations data (Fig. S4-5). The anion binding affinities for **L** were found to be higher in presence of F^- ($K = 3.02 \times 10^5\ M^{-1}$) compared to AcO^- ($K = 1.83 \times 10^5\ M^{-1}$) because of the higher basicity. Further, the absorption titrations data inferred that the receptor showed a good linearity range (5 μM to 47 μM) for the detection of F^- and AcO^- with the estimated detection limit (3σ/slope) of 5.7 μM and 6.2 μM respectively. In fluorescence titrations of **L** with anions (Fig. 2b and Fig. S6), the fluorescence at 480 nm was gradually enhanced upon successive addition of F^- and AcO^- to receptor **L** (5×10^{-5} M) solution in DMSO. The turn-on fluorescence can be attributed to the inhibition of excited state intramolecular proton transfer (ESIPT) process at the excited state. The receptor **L** showed a linear fluorescence response towards F^- and AcO^- between 5-70 μM and 5-25 μM, respectively.

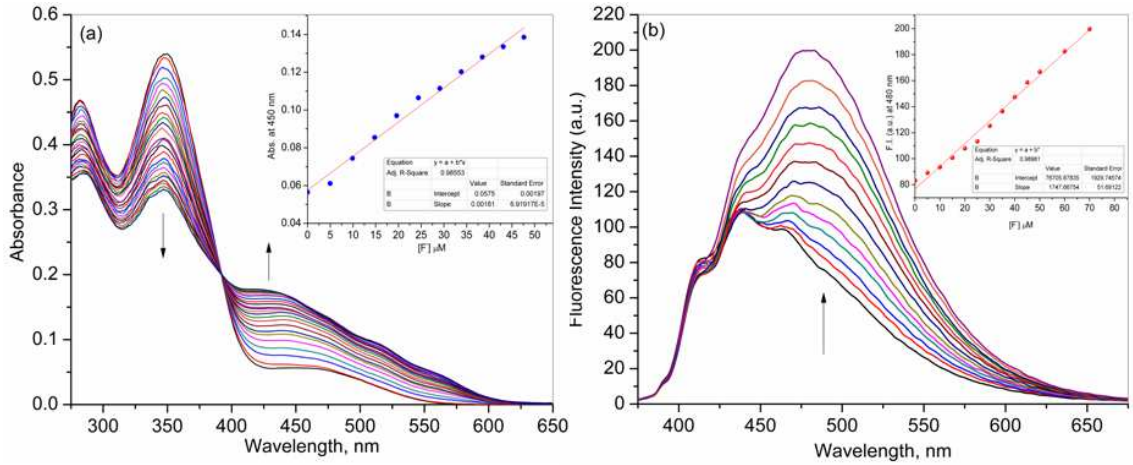


Fig. 2. (a) UV-Vis and (b) fluorescence (λ_{exc} = 350 nm) spectral changes of **L** (5 x 10^{-5}M) upon incremental addition of TBAF in DMSO. Inset showing the calibration plots.

The spectral changes of **L** on recognition with the hydrogen bond forming anions may reduced the O-H bond strength and facilitate deprotonation which increases the charge delocalization, which intensified the yellow coloration. The spectral and naked-eye detectable color changes of **L** upon addition of TBAOH (Fig. 1a and Fig. S7) were found to be identical to those obtained with TBAF and TBAAcO. Further, the effect of pH on the anion recognition of **L** (5 x 10^{-5} M, in DMSO) was examined by naked-eye detection method. As shown in Fig. 3a, the receptor alone showed visually detectable color changes under day and UV light on increasing the pH above ~9.67. When the receptor **L** was interacted with TBAF and TBAAcO, the pH of the solution was found to be 12.03 and 11.40, respectively (Fig. 3b). On decreasing the pH by addition of 0.1 M HCl, the detectable color changes were observed up to pH ~9.82 and ~10.53 respectively in the presence of F^- and AcO^- ions. The above results clearly delineated that the sensing of anions involves deprotonation of the catechol/phenol moieties in the presence of more basic anions (F^- and AcO^-) in DMSO. Moreover, the naked-eye detectable color changes of **L** in the presence and absence of the chemical inputs (F^-/AcO^- and H^+) can be used for the fabrication of Boolean type logic gate at molecular level.

Fig. 3a. Naked-eye detectable color changes of **L** (5 x 10^{-5} M, in DMSO) under UV (left) and day light.

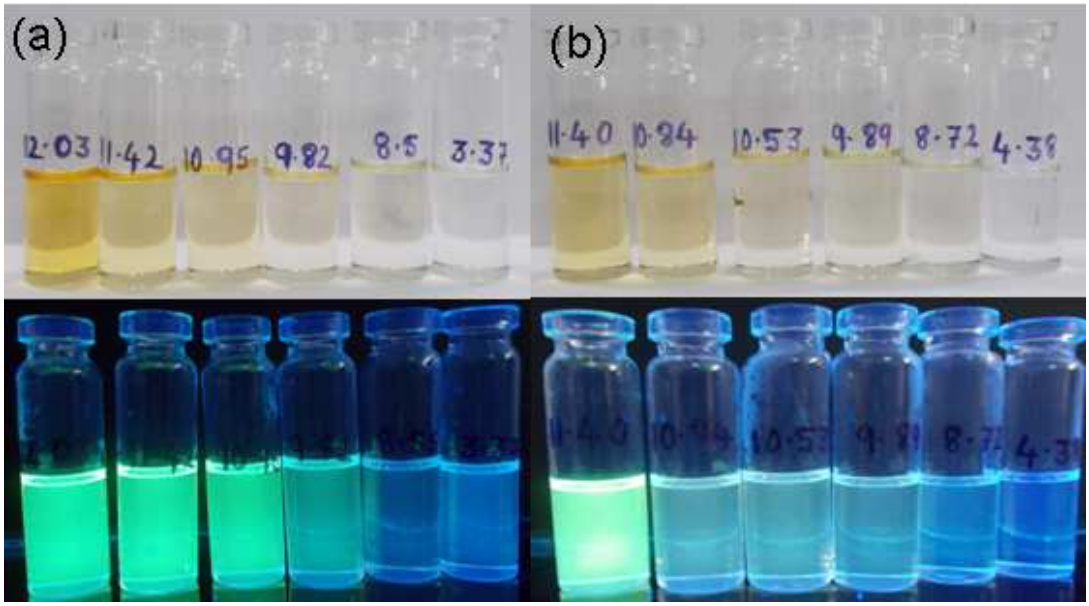


Fig. 3b. Naked-eye detectable color changes of **L** (5 x 10^{-5} M, in DMSO) containing 10 equivalents of (a) TBAF and (b) TBAAcO under day (above) and UV light (below).

In order to get fuller insight into the nature of the intermolecular interaction between the receptor **L** and anions, ^{1}H NMR titration experiment of **L** was carried out in the absence and presence of different equivalents of TBAF in DMSO-d_6 (Fig. S8). The free receptor showed three broad peaks at 14.21, 9.85 and 9.05 ppm respectively due to the two –OH groups of catechol and phenolic-OH. The appearance of peak at downfield (14.21 ppm) indicates the presence of an intramolecular hydrogen bond between the catechol-OH and imine-N. Upon addition of 0.5 equivalent of TBAF, dramatic changes occurred in the ^{1}H NMR spectrum of **L** with the disappearance of catecholic-OH peaks. Simultaneously, the peaks due to aromatic protons were shifted upfield. The upfield shift of the signals can be attributed to the increase in the electronic density of the aromatic system that enhanced the shielding effect owing to the through-bond effects. The shifting of aromatic peaks was continued up to the addition of 1.0 equivalent of TBAF. The shifting of peaks was stopped on further addition of TBAF, which indicates that the interaction of F^- with the receptor is mainly due to proton-transfer to the F^- i.e. deprotonation process rather than hydrogen-

bonding. Also, the deprotonation mechanism was confirmed from the appearance of a new broad peak at ~16.1 ppm due to the formation of FHF^- dimmer.[21]

The density functional theory (DFT) calculations were performed with the Gaussian 09W[22] computer program to complement the deprotonation mechanism proposed for the selective recognition of F^- and AcO^- by **L**. The receptor **L** and its **L**.(F^-/AcO^-) complexes were optimized by applying B3LYP/6-31G(d,p) method in the gas phase (Fig. 4). The enolimine form of **L** was energetically found to be more stable than its ketoamine form by 0.72 kcal/mol. The receptor also showed the presence of intramolecular hydrogen bonds (Fig. 4a-b). Upon interaction with F^- and AcO^- (Fig. 4c-d), the bond length of –OH groups of **L** were slightly elongated on forming intermolecular hydrogen bonds with the anions. However, the hydrogen bonded host-guest complexes failed to alter the band gap between HOMO and LUMO as compared to free receptor (Fig. S9). Also, the calculated absorption bands by TDB3LYP/6-31G(d,p) method for **L**, **L**.(F^-) and **L**.(AcO^-) were obtained respectively at 336 nm (oscillator strength, f = 0.4354), 363 nm (f = 0.2123) and 344 nm (f = 0.2236). These bands were closed to each other and below 400 nm to induce any perceptible color change. However, noticeable intramolecular charge transfer (ICT) and the lowering of band gap was observed for the deprotonated forms of **L** (Fig. S9). Also, the calculated absorption band for the mono-deprotonated and di-deprotonated forms of **L** were obtained at 425 nm (f = 0.2466) and 681 nm (f = 0.1523) respectively, which supports the deprotonation mechanism proposed with the help of experimental observations.

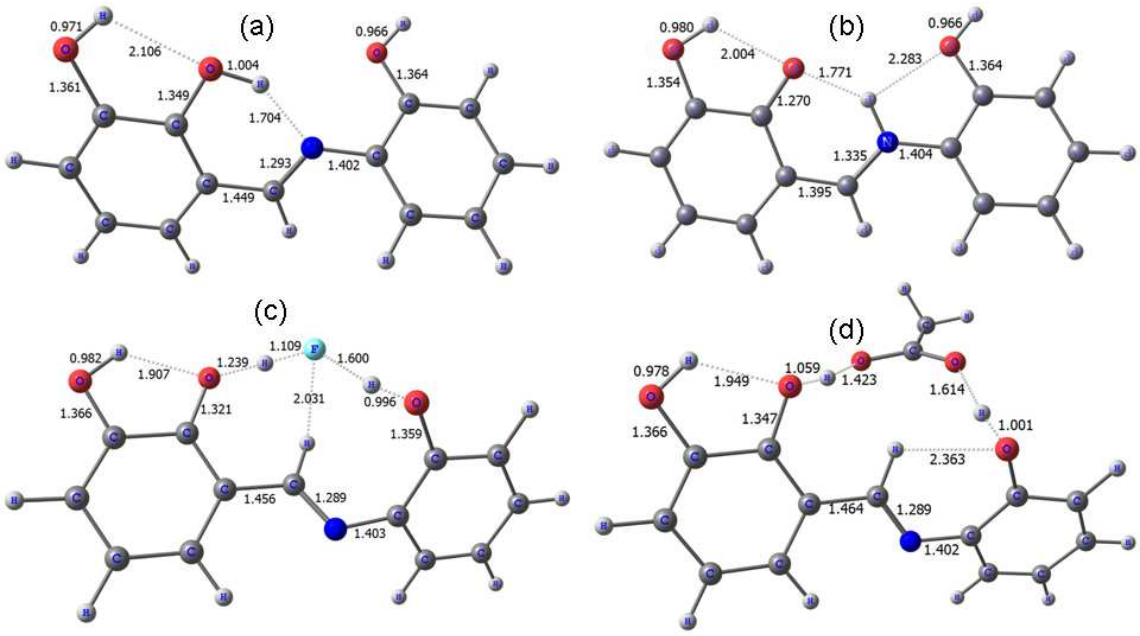


Fig. 4. DFT computed optimized structure of the (a) enolimine form of **L**, (b) ketoamine form of **L**, (c) **L**.(F^-) and (d) **L**.(AcO^-).

The possible analytical application of the receptor **L** for the detection of F^- and AcO^- was first explored in mixed solvent DMSO/H_2O. Anions are strongly solvated in aqueous medium due to their high hydration free energy which makes the detection of anions in water medium much more difficult. The protic solvents such as water can compete with anions for binding sites and disturb the hydrogen-bonded sites between the host and the anionic guest which lead to a reversal of the visual color and spectral responses. In case of receptor **L**, the anions (F^- and AcO^-) showed detectable color and spectral responses in mixed solvent DMSO/H_2O containing 6% H_2O (Fig. 5 and Fig. S10).

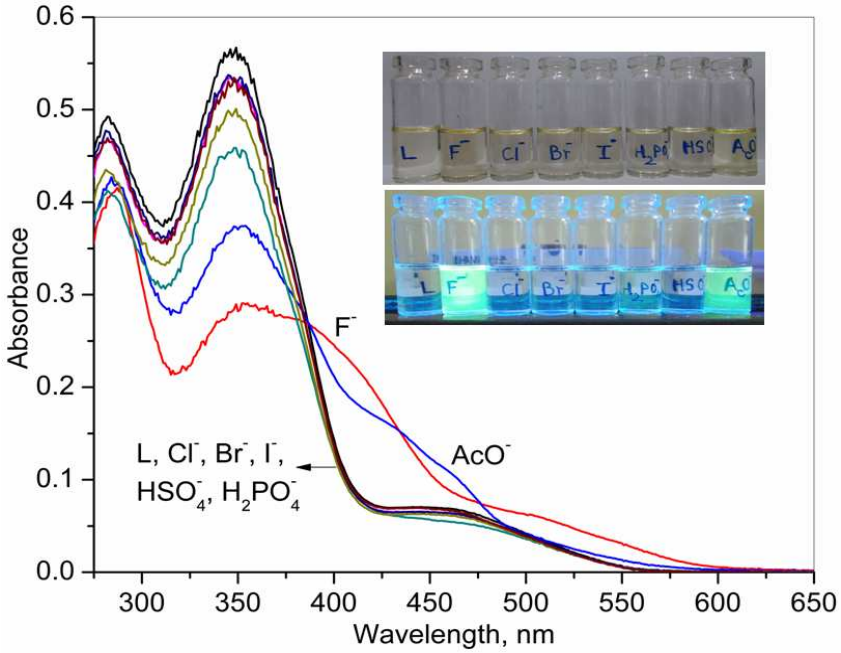


Fig. 5. UV-Vis absorption spectra of **L** ($5x10^{-5}$ M) in the absence and presence of different anions in DMSO/H_2O (94:6, v/v). Inset showing the color change under day and UV light.

The practical application of receptor **L** was next investigated by paper-made test strips for easy and rapid qualitative detection of F^- and AcO^-. The filter papers were prepared by immersing into a CH_3CN solution of **L** ($1X10^{-3}$ M) and then dried (Fig. 6a). The test strips were utilized to sense different anions. The obvious color change under day and UV light was observed only with the F^- and AcO^- anions. Then, the sensing system **L** was evaluated for the determination of F^- and AcO^- ions present in commercially available toothpaste and vinegar (Fig. 6b). The test solutions for this experiment were prepared by adopting our recently reported method.[23] Upon addition of 50 μL of toothpaste, NaF ($5X\ 10^{-3}$ M) and TBAF ($5X\ 10^{-3}$ M), a distinct color change of **L** was observed for the qualitative detection of F^-. Similar changes were noticed with vinegar solution. In another approach (Fig. 6c), the extraction of fluoride from aqueous solutions (NaF of $3X10^{-4}$ M, $1X10^{-3}$ M and $1.5X10^{-3}$ M) to the receptor solution in CH_2Cl_2 ($1\ X\ 10^{-4}$ M) was performed by using a liquid–liquid extraction strategy in

the presence of TBACl (2X 10^{-3}M) as a phase transfer agent. The perceptible color change of **L** under day and UV light clearly delineated the fluoride extraction ability of the receptor **L** from aqueous solution.

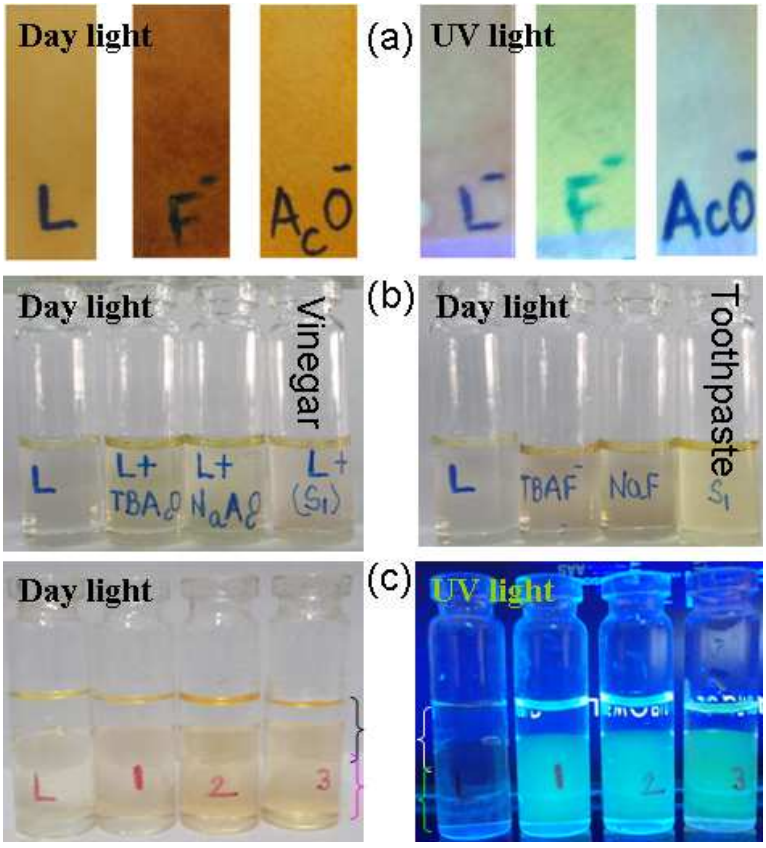


Fig. 6. Qualitative anions detection: (a) color change of paper-made test strips of **L** with F^- and AcO^-, (b) real sample analysis for the qualitative detection of F^- and AcO^-, and (c) F^- extraction and detection from aqueous solution by **L** using TBACl as phase transfer agent.

Finally, the biological application of **L** was tested for the detection of intracellular F^- in the human breast cancer cell MCF-7. The cytoplasmic uptake of F^- was monitored by fluorescence microscopy in the presence of receptor L. It was observed there was increase of fluorescence intensity in the increasing of concentration of NaF and receptor L (Fig. 7). It was also observed that cellular uptake of F^- can be visualized by the receptor L in the cytoplasmic area only. There is a clear central gap existing in the fluorescence image, which

shows that no fluorescence is coming from nucleus. Fluoride ions is extensively used for the fluoride PET/CT for breast tumour detection.[24] Thus, the receptor **L** can be used for the PET/CT for the breast tumour diagnosis**.**

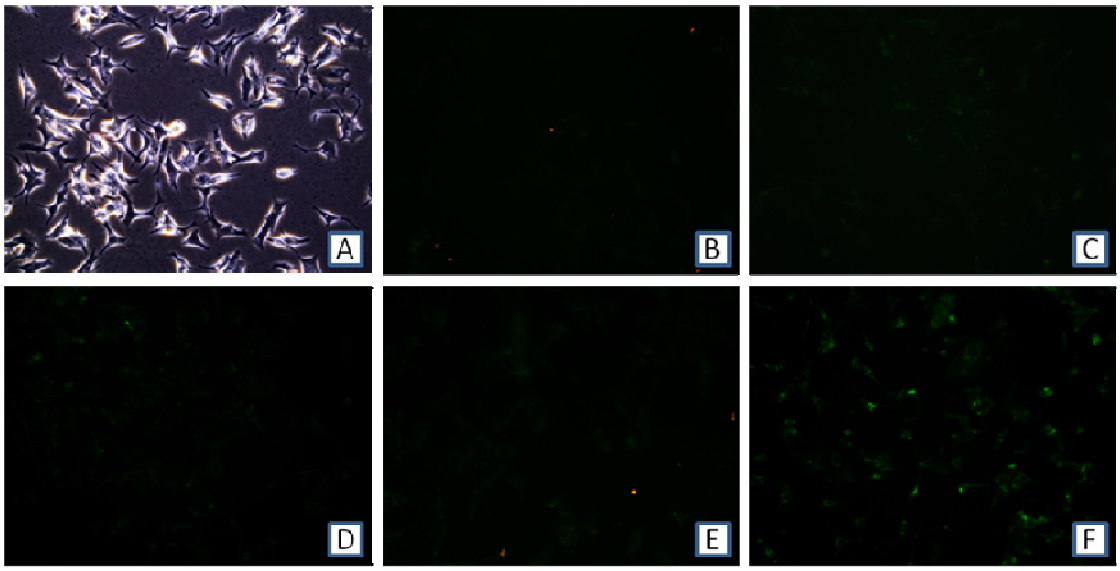


Fig. 7. (A) Phase contrast image of the cells, (B) fluorescence image of the cells after incubating the cells only with **L** (2.2 mM), (C) fluorescence image of the cells after incubating the cells with both **L** (2.2 mM) and NaF (8.7 mM), (D) fluorescence image of the cells after incubating the cells with both the **L** (2.2 mM) and NaF (17.4 mM), (E) fluorescence image of the cells after incubating the cells with both the **L** (4.4 mM) and NaF (8.7 mM) and (F) fluorescence image of the cells after incubating the cells with both the **L** (4.4 mM) and NaF (17.4 mM). All the images were observed using excitation filter 480 nm and photographs taken at 20X magnification.

Conclusion

A novel catechol based fluorescent and colorimetric sensor was developed for the highly selective and sensitive detection of AcO^- and F^- in DMSO and mixed solvent DMSO/H_2O with the detection limit down to micromolar level. The deprotonation of catecholic-OH groups was proposed for the anion selective colorimetric and spectral

responses. The sensor was applied for the qualitative detection of inorganic F^- and AcO^- from aqueous medium. Finally, the effectiveness of the sensor **L** was successfully assessed for the intracellular detection of F^- in breast cancer cell imaging for diagnosis of breast tumor.

Experimental

Materials and methods

All chemicals and solvents used for the synthesis were obtained commercially and used without further purification. In all the spectroscopic experiments, the anions were added in the form of tetra-n-butyl ammonium (TBA) salts and were purchased from Spectrochem Pvt. Ltd., India. UV-Vis spectra were recorded on a VARIAN CARY 50 spectrophotometer in the wavelength range of 300-700 nm with a quartz cuvette of 1 cm path length. The fluorescence spectra were recorded in a HORIBA FluroMax-4 spectrometer. ^{1}H NMR spectra were recorded in DMSO-d_6 on a BRUKER AVANCE II 400 MHz NMR using tetramethylsilane (TMS) as an internal standard.

All spectroscopic experiments were carried out at room temperature. Stock solutions of receptor **L** (1.0×10^{-4} M) and different anions (1.0×10^{-3} M) in DMSO were prepared and stored in the dark chamber. These solutions were used for all spectroscopic studies after appropriate dilution. Appropriate amounts of anions and receptor were taken into cuvette with the help of micropipette and diluted further for different spectroscopic experiments.

Synthesis of receptor L

Receptor **L** was synthesized by stirring 2,3-dihydroxybenzaldehyde (0.3 gm, 0.0021 mmol) with 2-aminophenol (0.23 gm, 0.0021 mmol) in methanol (15 mL). The yellow color precipitates were separated out in quantitative yield. These precipitate were filtered and dried. Yield: 98%. Mp. 181°C, IR (KBr, υ, cm^{-1}, Fig. S11): 3345, 3306, 3183, 3125, 3071, 2947, 2824, 2673, 2361, 1890, 1744, 1640, 1539, 1412, 1361, 1215, 1076, 1015, 868, 709; ^{1}H NMR (300 MHz, δ, ppm, DMSO-d_6, Fig. S12): 14.21 (1H, br, catechol-OH), 9.85 (1H, br,

catechol-OH), 9.05 (1H, br, phenol-OH), 8.95 (1H, s, CH=N), 6.72 (1H, t, Ar-H), 6.90 (2H, t, Ar-H), 6.98 (1H, d, Ar-H), 7.04 (1H, d, Ar-H), 7.14 (1H, t, Ar-H), 7.42 (1H, d, Ar-H).

Breast cancer cell live imaging

Human breast cancer cell MCF-7 was procured from NCCS, Pune, India. The cells were grown at 35 mm culture dish in Dulbecco's Modified Eagle Medium (DMEM) supplemented with 10% FBS and L-glutamine-penicillin-streptomycin and maintained at 37°C in a humidified atmosphere with 5% CO_2. When the cells have reached nearly 60% confluence, complete media was replaced with serum free media. The receptor **L** was added (2.2 mM and 4.4 mM) and incubated for 1 hour. After incubation, media was changed with fresh serum free media and NaF was added (8.7 mM and 17.4 mM). For live cell imaging culture dishes were placed on the stage of the inverted fluorescence microscope (Leica DMI6000B) and studied using excitation filter 480nm. Fluorescence images of the cells were captured through an attached CCD camera using image acquisition software (LAS 4.2).

Acknowledgments

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