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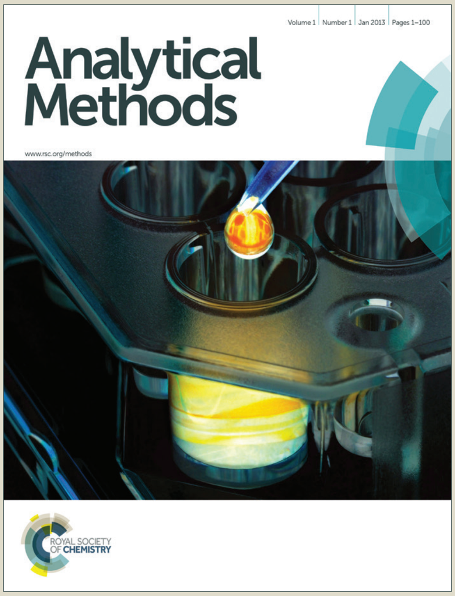

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New calix[4]arene based highly selective fluorescent probe for Al^{3+} and I^-

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Abstract

This approach highlights the synthesis of 2-hydroxy naphthalene functionalized a new calix[4]arene based fluorophoric Schiff base, *i.e.* **C4SB.** The ion-binding property of **C4SB** fluoroionophore was probed with a selected number of cations as well as anions and their recognition event was monitored by UV-visible and fluorescence spectral changes. Probe **C4SB** based on PET mechanism that exhibited selective "turn-on" response toward Al^{3+} and "turn-off" for I^- in the presence of other competing ions with certain observable spectral changes. The selective behavior of probe was visualized in the presence of different co existing competent ions. Interference study reveals that Hg^{2+} causes some disturbance in **C4SB** and Al^{3+} interaction. Probe **C4SB** forms (1:1) stoichiometric complex with both Al^{3+} and I^- and their binding constants calculated as 2.49×10^5 and 9.24×10^3 respectively. Moreover, complex was characterized through FT-IR spectroscopy.

Keywords: Calix[4]arene; fluorescent; PET; complex; FT-IR spectroscopy.

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Introduction

After oxygen and silicon, aluminum is the third most prevalent element in lithosphere and ample metal in the earth's crust. It has variety of applications in daily life [1, 2]. It is not only therapeutically beneficial but superfluous ingestion produces negative impacts on human beings as well as aquatic ecosystem [3, 4]. Its accumulation in human body tissues and organs causes their dysfunctions and toxicity [5- 6]. It inhibits the functioning of iron and sulphur containing proteins and causing bone and joints diseases by defective mineralization and osteomalacia [7]. Beside this neuronal disorder leading to dialysis encephalopathy, dementia, myopathy, idiopathic Parkinson's disease, impairment of memory, Alzheimer's disease [8-9] and its accretion even causes lung, breast and bladder cancer [10]. Moreover it is associated with anemia by increasing hemolysis, decreasing heme and globulin synthesis. It directly effects on iron metabolism, retards its absorption and transportation [11]. People are generally exposed to aluminum toxicity because of its widespread use in various food and pharmaceutical utensils. According to a World Health Organization report the average daily human intake of aluminum is approximately 3-10 mg day^{-1}. Tolerable weekly aluminum intake in the human body is estimated to be 7 mg kg^{-1} of body weight [12-13].

On the other hand, a prodigious research has devoted for the selective sensing of anions because of their significant importance in biological, medicinal, catalytic, environmental and chemical sciences [14]. Among the anionic species to be recognized and detected, I^{-} has received progressively more attention due to its elemental form widely utilized in chemistry for the synthesis of drugs and dyes [15]. It is one of the biologically important anions and is significant micronutrient which plays a key role in many biological pathways such as brain development, metabolism, neurological functions and thyroid gland activity [16]. It is essential element for life and biosynthesize thyroid hormones which is necessary for metabolism and mental growth [17]. The recommended daily intake of iodide is 150 μg/day. Its deficiency results severe delays in neurological development, cretinism and endemic goiter. Conversely, an excessive ingestion can also cause hyperthyroidism [18].

Thus, detection of cations and anions are currently a stint of major considerations in modern research owing to their widespread applications in chemical, biological and environmental assays. Determination of anions is more challengeable task as compared to metal ions as they are usually discriminated on the basis of charge and size whereas anions having complexity in structure and larger size [19] In this regard, number of traditional advanced analytical techniques like ion chromatography [20], capillary electrophoresis [21], atomic absorption spectroscopy [22], gas chromatography–mass spectrometry (GC–MS) [23], inductively coupled plasma (ICP)-MS [24], electrochemical methods [25], inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) most commonly employed analytical techniques[26] are used for the determination of for both iodide and aluminum. Among them the fluorescence spectroscopic method is widely used because of their rapidity, sensitivity, selectivity, simplicity and cost-effectiveness [27]. Consequently, efficient and selective fluorescent probes can be proving valuable implements for the sensation of biologically and environmentally important ions. Thus, the development of probes possessing high selectivity for Al^{3+} and I^- over other commonly coexistent ions in various media is of substantial meaning for environmental protection and human health. Due to considerable significance in various assays ground the extensive exploration of fluorescent probes for these important ions. Part of this effort varieties of fluorescent probes have recently been exploited for the determination of Al^{3+} and I^-. In literature there are few examples relating to “turn-on” and “turn-off” type of fluorescent probes are available for both ions [28-39].

With the advancement of supramolecular chemistry, one of the most fascinated approaches is mainly motivated on the development of highly specific, facile, and cost-effective chromogenic/fluorescent sensors for ions is an important objective of biological milieu such as enzymes, antibodies or genes and is fundamental to supramolecular chemistry [40, 41]. In this regard, macrocyclic calixarenes remain an area of interest due to their unique properties such as biomimic functions [42] ionic and molecular recognition [43] along with potential applications in fundamental and applied sciences as well as importance in coordination chemistry [44]. For ionic or molecular recognition calix[4]arenes are the most extensively employed molecular scaffolds as fluorescent sensors [45]. The synthesis of selective fluorescent sensors is fundamental target for scientists. So far, there are some successful achievements in the development of calix[4]arene framework based fluorescent probes for Al^{3+} [46] and I^- [47-49] .

Herein we designed and synthesized a new calix[4]arene based Schiff based fluorescent probe (**C4SB**), which displays highly selective and sensitive fluorescence “turn-on” recognition to Al^{3+} and turn-off fluorescence emission behavior for I^-.

Experimental

Chemicals

All reagents and solvents used were of standard analytical grade purchased from Alfa Aesar (Germany), Merck (Darmstadt, Germany) and were used without further purification. All metal nitrate salts and sodium salts of anions were purchased from Sigma and Aldrich. All aqueous solutions were prepared with deionized water that had been passed through a millipore milli Q Plus water purification system.

Instrumentation

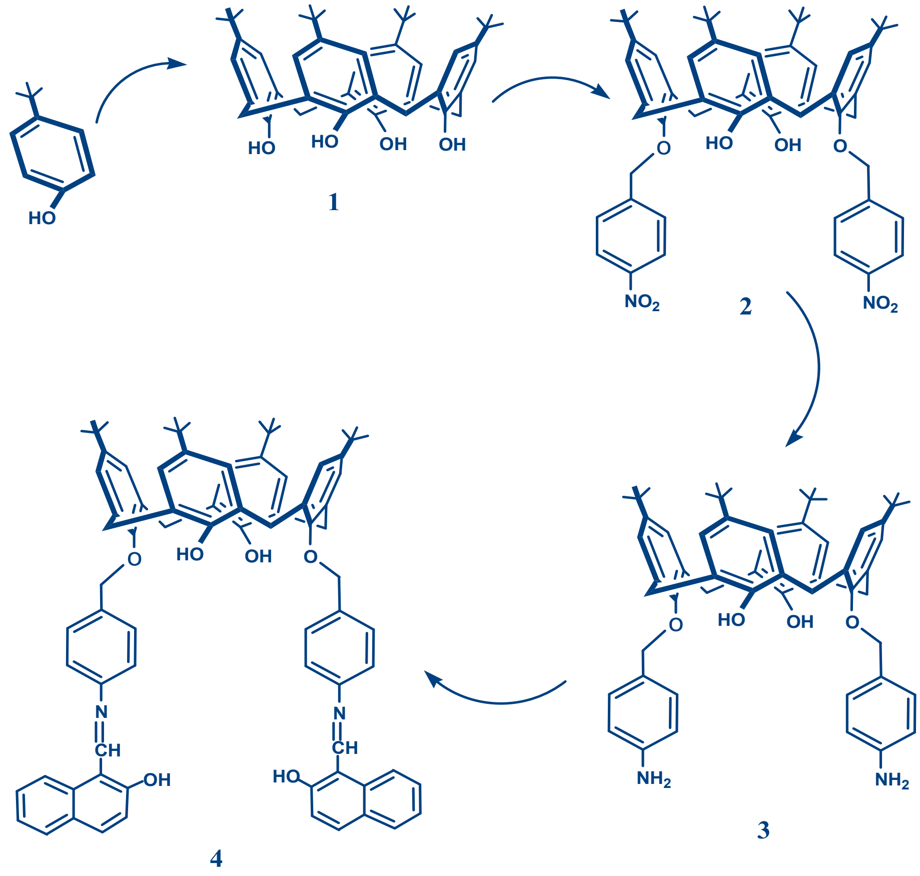
Melting points were determined on a Gallenkamp (UK) apparatus in a sealed capillary tube. Elemental analyses (CHNS) were performed using Flash EA 1112 elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded with an Agilent 400 MHz spectrometer in DMSO using tetramethylsilane (TMS) as an internal standard at room temperature. Thermo Nicollet AVATAR 5700 FT-IR spectrometer was used for recording IR spectra within a spectral range from 4000 to 400 cm^{-1}. Analytical TLC was performed on pre-coated silica gel plates (SiO_2, Merck PF_{254}).Absorption spectral investigation of **C4SB** and its complexes were performed on a Perkin Elmer Lambda-35 double beam spectrophotometer using standard 1.00 cm quartz cells whereas emission spectra were recorded on a Photon Technologies International Quanta Master Spectrofluorimeter (model QM-4/2006).

Synthesis

Synthesis of target compound (**4**), i.e. **C4SB** was carried out by stepwise synthesis as shown in (Scheme 1). The starting material *p-tert*-butylcalix[4]arene (**1**), dinitro derivative of *p-tert*-butylcalix[4]arene (**2**) and its aminated derivative (**3**) were prepared by earlier published procedures [50-51].

Synthesis of **C4SB**

To a stirred solution of calix[4]arene **(3)** (0.5 g, 0. 58 mmol) in absolute ethanol (10 ml) was added a solution of 2-hydroxynaphthaldehyde (0.3 g, 1.16 mmol) and the mixture was stirred for 30 minutes at room temperature followed by refluxing for 36 h to obtain a light greenish yellow precipitates. The precipitate was filtered and washed with ethanol. The residue obtained was further recrystallized from dichloromethane/methanol to furnish compound **4**. Yield (0.6 g, 0.51 mmol, 68%); m.p. 285 ^{o}C decompose, FT-IR (KBr):3353 cm^{-1} (OH), 1651 cm^{-1} (C=O), 1601 cm^{-1}, 1480, 1361 and 1232 cm^{-1} (N-H), 1190 cm^{-1} (C-N); ^{1}HNMR (400 MHz, DMSO, TMS, ppm): δ_H: 1.11 (18 H, s, *t*-Bu), 1.17 (18 H, s, *t*-Bu), 2.48 (4H, s, ArCH$_2$-O) 3.47 (4H, d, *J* =13.2 Hz, ArCH_2Ar), 4.1 (4H, d, *J* =13.2 Hz, ArCH_2Ar), 5.1 (2H, s, Ar *Napth -OH*), 6.73 (4H, s, Ar*H*), 6.84 (4H, s, Ar*H*), 7.1 (8 H, s, Ar *Benz*), 7.18 (2H, s, Ar -*OH*),7.30 (4 H, trip, Ar *Napth*), 7.5 (2 H, s, Ar *Napth*), 7.6 (2 H, d, Ar *Napth*), 8.0 (2 H, d, Ar *Napth*), 8.2 (2H, s, N=C-H) (Fig. S1 supl. Mat), $\delta_{C:}$ 31.4, 31.5. 32.9, 34.1, 75.8, 118.4, 123.3, 123.7, 124.1, 125.2, 126.6, 126.8, 128.0, 128.4, 132.1, 158.5, 160.3, Anal. Calc. for $C_{80}H_{80}N_2O_6$; C, 82.47; H, 8.47; N, 2.40 Found: C, 82.96; H, 8.25; N, 2.36.



Scheme 1 Synthesis of resin **C4SB**: (1) HCHO/OH^{-} (2) $BrCH_2C_6H_4NO_2/K_2CO_3$ (3) $NH_2NH_2.H_2O$/Raney Ni (4) 2-hydroxynapthaldehyde.

Synthesis of metal complex with **C4SB**

For FT-IR characterization, complexes of **C4SB** with Al^{3+} and I^{-} was synthesized according to stoichiometric ratio. For this saturated solution of **C4SB** in THF was prepared in round bottomed flasks separately. Stoichiometric amount of Al^{3+} and I^{-} were added into each respective reaction contents flasks. The mixture was stirred at room temperature for 24 hours. Solution was filtered and remaining residue was washed with small amount of water. Filtrate was evaporated at reduced pressure. The resultant crystals were dried in vacuum oven.

Spectroscopic measurements

UV-visible and fluorescence studies of **C4SB** toward different metals and anions were performed at a specific concentration of both host and guests. Stock solution of ligand ($2.6x10^{-3}$ M) was prepared in 25 mL of THF and followed by dilution to ($2.58x10^{-5}$ M) into 100 ml. Fluorogenic behavior of receptor **C4SB** was investigated using titration experiments in a binary solvent composition of THF: H_2O (1:1v/v). 10 molar equivalents of the appropriate each metal and anion were measured using a 1 cm absorption cell. In 10 ml test tubes, 2 ml of ligand solution of ($2.6x10^{-5}$ M) and 2 ml of metal/anion salts solution ($2.6x10^{-4}$ M) in were mixed together. UV-visible response of ligand before and after addition of ions solution was recorded. Emission intensities of **C4SB** were measured at 330 nm for metals and 280 nm for anions at room temperature. For the interfacial study of co-existing ions 10 equivalent solution of other metals ($2.6x10^{-4}$ M) were taken into same solvent system containing **C4SB** complexes with Al^{3+}/ I^{-}.

Determination of complex stoichiometry

Continuous variation method, i.e. Job's plot [52] was applied for the determination of stoichiometric ratio **C4SB** with Al^{3+} and I^- in THF+H_2O as a binary solvent system. For this method equimolar solution ($2.6x10^{-5}$ M) of both host and guest, i.e. **C4SB** and Al^{3+}/I^- were mixed under the condition that sum of the ligand-metal concentration remains constant. The absorbance was measured at 230 and 220 nm for Al^{3+} and I^- complexes respectively.

Results and discussion

UV-Visible study

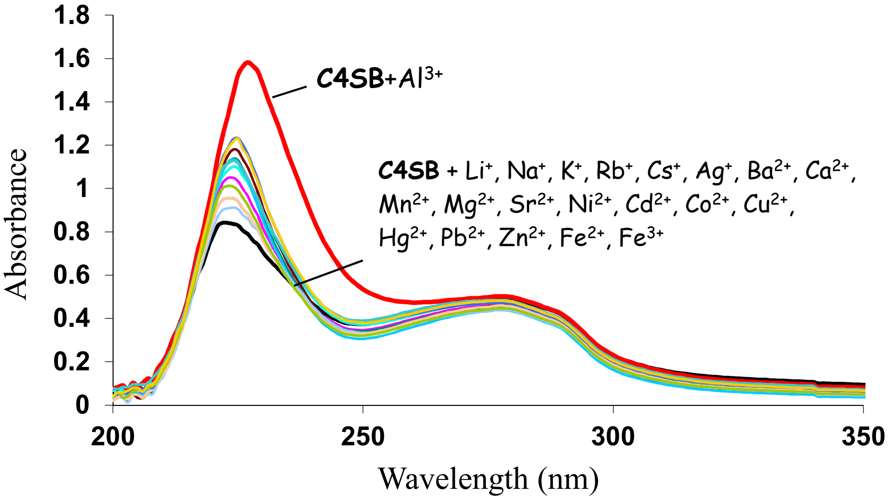


Figure 1 Absorption spectra of **C4SB** (2.6×10^{-5} M) and with different metals (10 eq.) in THF+ H_2O.

To examine the chromogenic behavior and selectivity of **C4SB** titration experiments were carried out in THF:H_2O binary solvent system for selected series of mono, di and tri valent cations Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Ba^{2+}, Ca^{2+}, Mn^{2+}, Mg^{2+}, Sr^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+},

Pb^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+}. Preliminary investigations reveal that free ligand **C4SB** before complexation exhibit two characteristics bands. One band at 280 nm is comparatively smaller in absorption than the other band at 220 nm. These absorption bands ascribe to the π-π* and n- π* transitions respectively (Fig.1). There was nominal changes occurring and only a minimal enhancement in the absorption intensities was observed by the contact of different metal ions. But on addition of Al^{3+} a prominent changes noticed in the absorption behavior of **C4SB**. A hyper chromic shift along with bathochromic shift was observed at 220 nm to 230 nm, i.e. the band intensities was surprisingly enhanced from 0.8 to 1.6 (Fig. 1). This spectral change of **C4SB**-Al^{3+} complex at 221 and 280 nm could be assigned due to the presence of π-electrons of (C=N) imine aromatic rings and lone pair of electrons present on oxygen/nitrogen that reflects to O/N-metal charge transfer absorption upon Al^{3+} contact with 2-hydroxynapthalimide moiety of **C4SB** [53].

Furthermore, selectivity and binding ability of **C4SB** for different anions like of F^{-}, Cl^{-}, Br^{-}, I^{-}, CO_3^{2-}, HCO_3^{-}, $CH_3CO_2^{-}$, SO_4^{2-}, HSO_4^{-}, CN^{-}, SCN^{-}, NO_3^{-}, ClO_4^{-}, $Cr_2O_7^{2-}$ and S_2O_7 also investigated under same conditions (Fig. 2). The distinctive UV-visible absorption changes were recorded upon the addition of sodium salts solution of anions into **C4SB** (2.6×10^{-5}M). Different anions produce slight variations in spectral properties of probe. However, a dramatic effect was observed in spectral response of **C4SB** on addition of I^{-} which caused emergence of two new band at 366 nm in the visible region. While hyper chromic effect along with red shift was observed in the bands at 280 and 220 nm. These bands at 280 and 220 nm shifted ≈14 and 12 nm to longer wavelength region respectively. Since strong absorption in the region 220 nm along with appearance of a new band in the visible region at 335–430 nm is the indication of complex formation. **C4SB**-I^{-} selective complexation can be explained by the hydrogen bonded interaction between I^- and hydroxyl protons (-OH) of **C4SB**. This response suggests very strong and selective affinity of **C4SB** toward Al^{3+} and I^-.The presence of hard donor site for hard acid and involvement of hydrogen bonding reflects the dual selectivity. Besides this thermodynamic stability, ionic radii, cavity size as well as geometry of ligand and ions are also important aspects for specificity which confers the affinity of ligand toward a both cation and anion.

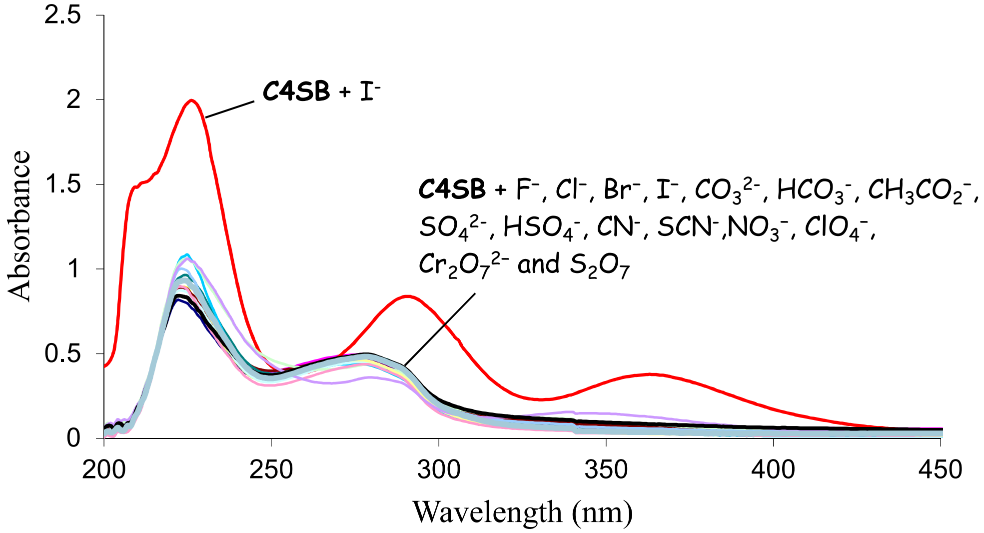


Figure 2 Absorption spectra of **C4SB** (2.6×10^{-5} M) and **C4SB** with different anions (10 eq.) in THF+ H_2O.

Fluorescence study

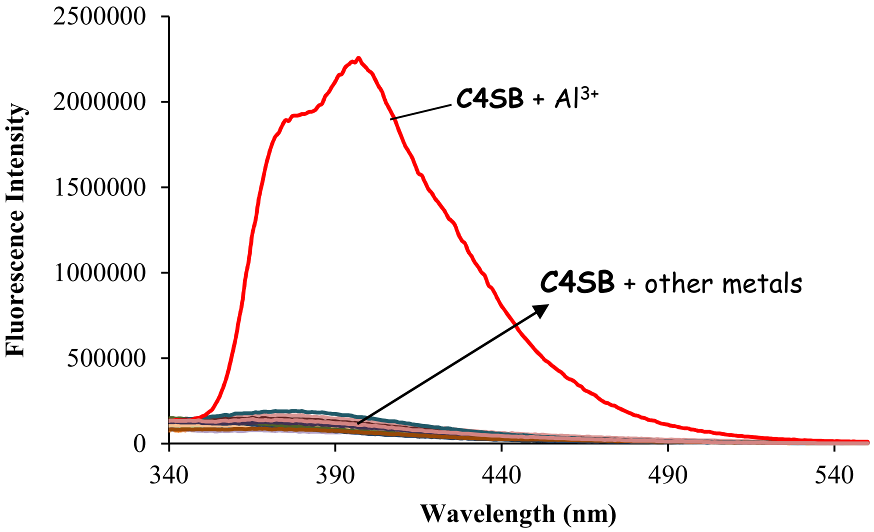


Figure 3 Fluorescence emission spectra of **C4SB** (2.6×10^{-5} M) and **C4SB** with different metals (10 eq.) in THF+ H_2O at 330 nm.

Further exploration for the fluorescent behavior of **C4SB** was performed toward different metals and anions under same aforementioned condition for UV-visible studies. The titration measurements were carried out with (10 eq.) of ions with probe (2.6×10^{-5} M). Fluorescence response of probe **C4SB** did not produce any substantial variations upon interaction with metals. However, **C4SB** exhibited prominent fluorescence response toward Al^{3+}. Upon addition of small amount (10 eq.) of Al^{3+} into the solution of **C4SB** (2.6×10^{-5} M) causes the formation of a new stronger band with high emission intensity at 398 nm. The emission intensity at band 398 nm was remarkably increased up to 95 fold along (Fig. 3). These pronounced result obtained after Al^{3+} addition among series of various cations confirms the **C4SB** as Al^{3+} selective potential probe. The increase in fluorescence during complexation is attributed to deactivation of the PET (photoinduced electron transfer) process occurring between the 2-hydroxy naphthalene moiety and the imine functional group site. Upon contact of Al^{3+}

within **C4SB** cavity O and N drift their electrons to Al^{3+} and thus diminish the PET process by reducing the delocalization into naphthalene ring [54].

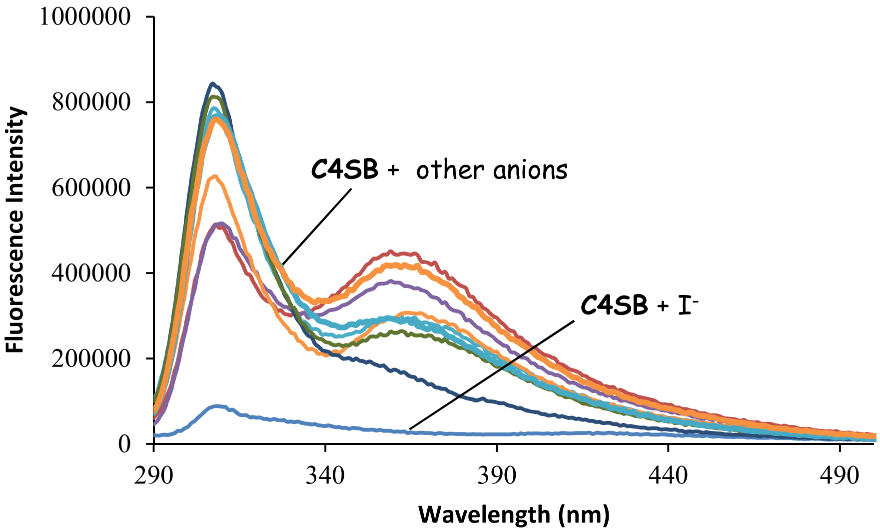
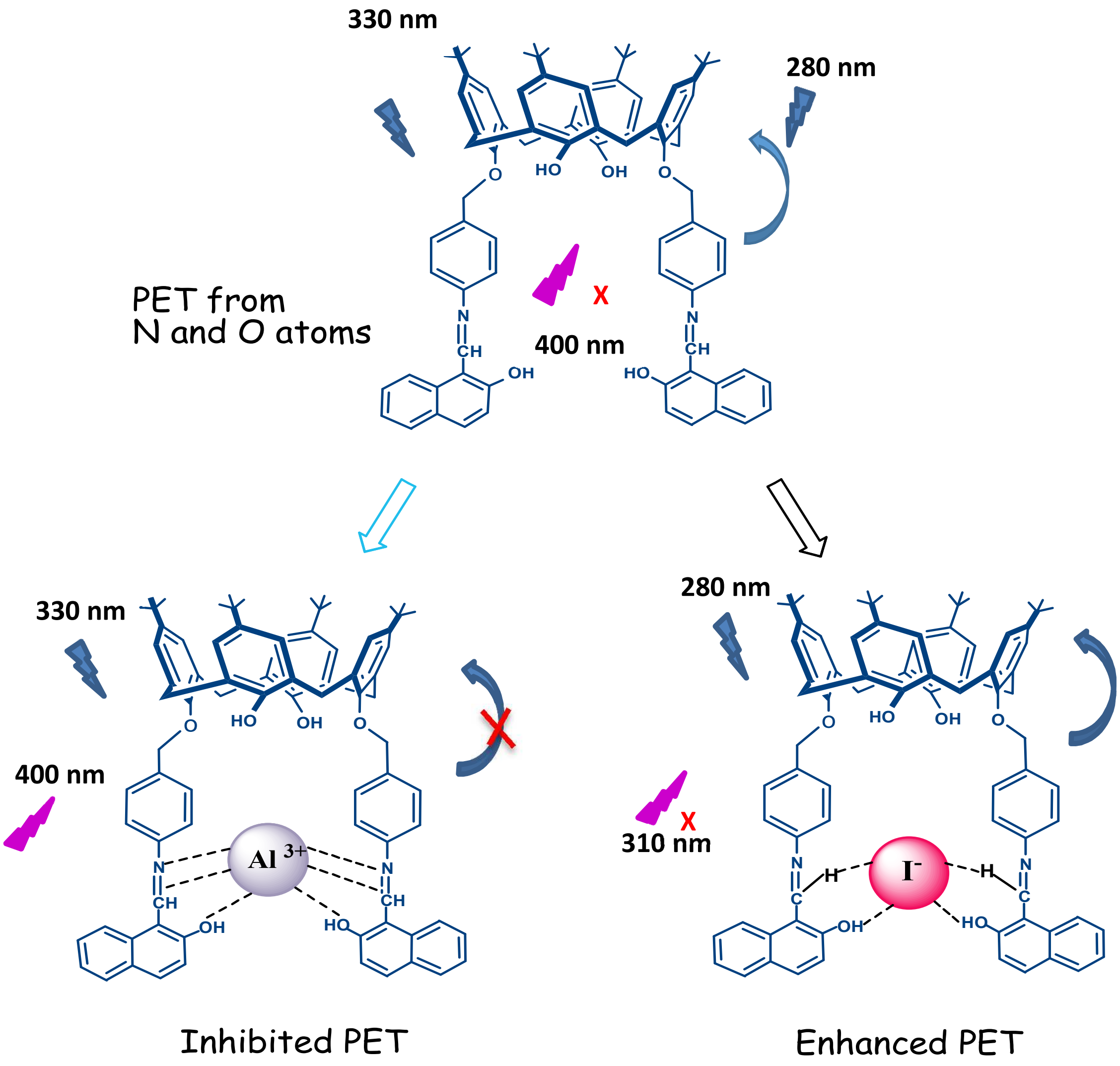


Figure 4 Fluorescence emission spectra of **C4SB** (2.6×10^{-5} M) and **C4SB** with different anions (10 eq.) in THF+ H_2O at 280 nm.

Similarly more investigations were also made for **C4SB** as I^- selective fluorogenic sensor. Discriminating response of **C4SB** for I^- was reflected by prominent fluorescent changes in the behavior of probe after interaction with different anions. The strong emission band at 309 nm in the parent spectrum was dramatically quenched upon the addition of (10 eq.) of I^-, i.e. considerable reduction in the emission intensity up to 85 % followed which was ascribed to **C4SB**–I^- complex (Fig. 4). While under similar conditions fluorescence ability of **C4SB** for other selected aforementioned anions also scrutinized. However, no substantial fluorescence variations observed in the presence of (10 eq.) of other anions, which confers the high specificity of **C4SB** toward I^-. Furthermore, the change in fluorescence intensity of both ions was measured by repeating the process for four times. Fluorescent response of both complexes with error bars are shown in (Fig. S2 (a) and (b), Supl. Mat) was remained unchanged.

Probe **C4SB** exhibit very low fluorescence intensity at 398 nm due to switched on PET (Photo-induced Electron Transfer) mechanism. Since, probe **C4SB** contains 2-hydroxy naphthalene and phenyl fluorophore rings along with imine functional group having N and O electron donating atoms. Two hydroxyls blocked by interamolecular hydrogen bonding while N atom in imine group conjugates its electrons with fluorophore rings that switched on the PET process causing complete quenching of the fluorescence response of the probe. After bonding with Al^{3+}, remarkable fluorescence enhancement was mainly induced by residing of Al^{3+} within the macrocyclic cavity of **C4SB** and coordination with N and O donors. The interamolecular PET fluorescence quenching effect derived from the electron pairs of N and O donor atoms to the fluorophores were fully blocked and relieved by reducing the electronic density of lone pairs through metal–donor binding interaction and consequently increases the probe emission. On the other hand large quenching of fluorescence emission on contact with I^- is the distinguishing feature of **C4SB** for the fluorometric identification of I^- among rest of the anions. This quenching behavior is attributed due to the formation of hydrogen bonding between I^- and hydroxyl protons of the fluorophore rings. This hydrogen bonding increases the electron density on hydroxyl oxygen atom which conjugates its electron pair in fluorophore ring. Thus the PET process triggered by donating lone pair of electrons of N and O to the fluorophore and resulted in the fluorescence being quenched on interaction with I^-.

Thus, the large quenching of emission in the presence of I^- is the characteristic feature of **C4SB** for the fluorometric identification of I^- among rest of the anions in present study. Other factors may also responsible for this quenching of emission are complementarity in size of iodide with **C4SB** cavity, its binding site and heavy atom effect of I⁻.



Scheme 2 Fluorescence mechanism of **C4SB** toward Al^{3+} and I⁻.

Concentration effect

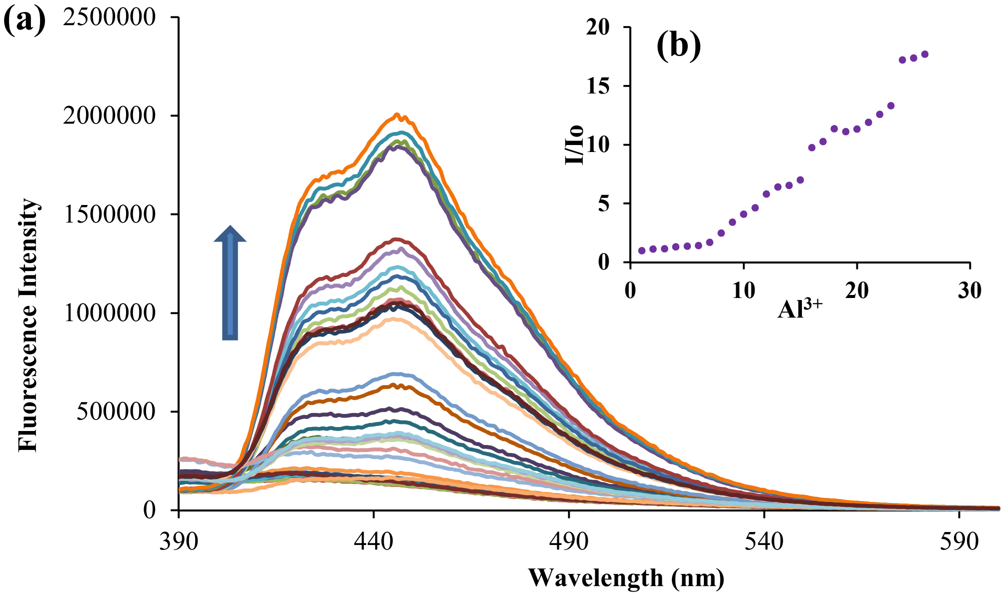


Figure 5 Influence of the addition of increasing amounts (0→10 eq.) of Al^{3+} on the emission spectra of **C4SB** (2.6×10^{-5} M) in THF+ H_2O.

Quantitative binding of **C4SB** for Al^{3+} and I^- was evaluation by examining the fluorogenic behavior with gradual increment of their concentration. There were spectral variations noticed by continuous enhancement in concentration of ion up to 10 equivalents to probe. Linear enhancement in the fluorescence intensity at 445 nm was observed with the increase of Al^{3+} ion concentration (Fig. 5 inset). The binding of Al^{3+} to **C4SB** reduced the electron-donating ability of N and O to aromatic rings, thus suppressing PET process and causing a remarkable increment in the emission intensity as shown in (Scheme 2). Therefore **C4SB** displays clear 'turn-on' fluorescence response and considerably high selectivity toward Al^{3+}. While on addition of I^- amount to **C4SB** solution its emission intensity quenched slowly by increasing the concentration (Fig. 6). Gradual increase in concentration strengthen the hydrogen bonding of I^- which in turn reinforce the electron density to fluorophore that enhance the PET process and causing significantly quenching of emission as shown in (scheme 2). By plotting the ratiometric variations in the fluorescence intensities as a function of Al^{3+} and I^- ion concentrations, Hoerl curve was obtained and is shown in inset of (Fig. 5 b and 6 b).

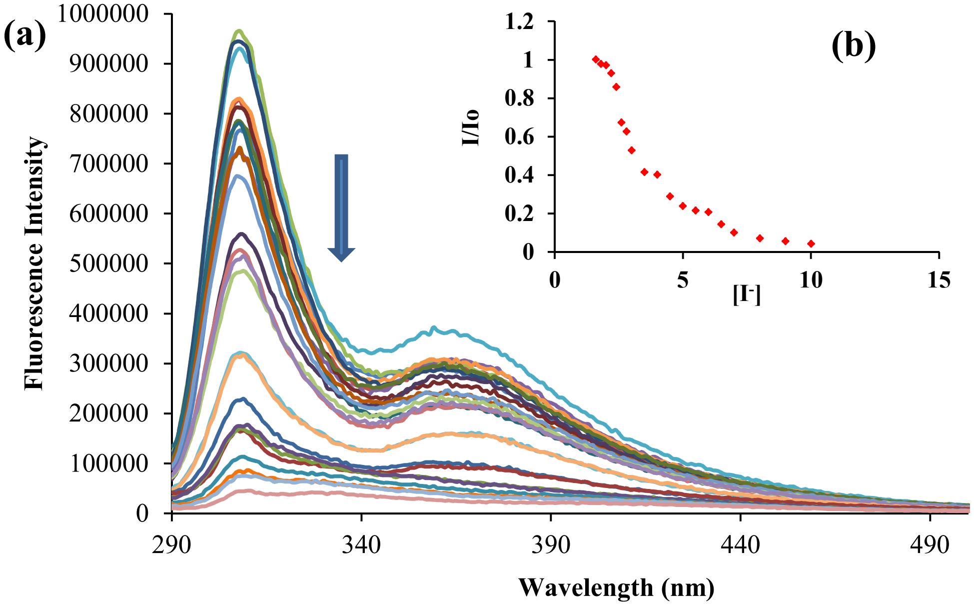


Figure 6 Influence of the addition of increasing amounts (0→10 eq.) of I^- on emission spectra of **C4SB** (2.6×10^{-5} M) in THF+ H_2O.

For this complexation binding constants of **C4SB**-Al^{3+}/I^- complexes were also determined by using Benesi–Hildebrand equation [55]. A plot of the ratio $I_o/(I-I_o)$ against $[1/[Al^{3+}/I^-]$ as in the value of log K was calculated as $2.49x10^5$ having (R^2=0.99) for **C4SB**-Al^{3+} and **C4SB**-I^- $9.24x10^3$ with (R^2=0.98) complex respectively.

Job's Plot

The binding extent of probe was estimated by determining the stoichiometric ratio of the complexes. Therefore job's plot was used to evaluate the stoichiometry of **C4SB**-Al^{3+} and

C4SB-I^- complexes at 221 nm. The results are depicted in (Fig. S3 (a) and (b) supplementary information). The plot of absorbance against mole fractions indicate that maximum absorption values for both complexes touches 0.5. Which infers that probe **C4SB** forms 1:1 coordination with Al^{3+} and I^-. Furthermore, the complexes were analyzed by using ESI-MS (Fig. S6 and S7). The peak at 1163 m/z correspond the **C4SB [1 + H]**$^+$. While in the case of complexes both show 1540 and 1335 m/z for **C4SB**-Al^{3+} and **C4SB**-I^- complexes respectively.

Interference Study

Functional properties and selective nature of **C4SB** toward Al^{3+} was investigated in the presence of co-existing metal ions. Competitive experiments were carried out by using 10 equivalents of other metal ions with Al^{3+} separately. No significant spectral variations were noticed in absorption behavior. Similarly efficiency and potential application of **C4SB** for I^- also examined in the presence of foreign anions and there was no any prominent change observed in the presence of rest of the anions. Furthermore, interfering behavior for both metal and anions was envisioned by the change in ratiometric absorption behavior (A/A_0) by the incorporation of other guest ions as shown in (Fig. S4 and S5 Suplementary information). Representative ratiometric absorption change (A/A_0) clarifies that only Hg^{2+} show remarkable change among rest of the other metal ions for Al^{3+} selectivity. Because of Hg^{2+} interference (A/A_0) value of **C4SB-**Al^{3+} complex decreased slightly from 1 to 0.97 as shown in (Fig. S4).

Various parameters like compatible nature of binding sites for guest, ionic radii, electronegativity as well as HSAB theory are responsible for the selective complexation property of probe **C4SB** for Al^{3+} and I^-. Moreover, probe possess hard coordination site having N, O and C=N binding group imply the selective response to hard acid Al^{3+} which traditionally follow the

Pearson's HSAB theory [53]. Since probe **C4SB** is actually a Schiff base has nitrogen and oxygen-rich coordination environments for detection of hard-acid Al^{3+} and this reflects to some Al^{3+} selective Schiff bases reported in literature possessing similar binding sites [56-61]. As it discloses due to the presence of lone pair of electrons on nitrogen, oxygen and π electrons of imine (-C=N-) in the periphery of calix[4]arene moiety which favors the interaction with low polarizable hard acid Al^{3+} along with the conformity of ionic radii of metal with cavity size of calixarene framework. Slightly disturbance in the selective behavior for Al^{3+} by Hg^{2+} is because of binding sites as well as ionic cavity conformity. Beside this, presence of hydroxyl protons of naphthalene aromatic rings accessible for hydrogen bonding with I^- as well. Which reflects the selective nature of **C4SB** for I^-.

FT-IR Study

Since FT-IR spectroscopy helps to understand the functionalities and changes in structure after complexation. Selective response of **C4SB** toward Al^{3+} and I^- was further characterized by FT-IR spectroscopy. Free probe show its various characteristics peaks as shown in (Fig. 7 a). A broad but less intensive band from 3600-3400 cm^{-1} is due to υ(O-H) group stretching and small broad, sharp and weak bands from 3100–2800 cm^{-1} due to the symmetric and antisymmetric υ (C-H) stretching modes belongs to aliphatic as well as aromatic methyl and methylene groups. Additionally, bands at 1635 cm^{-1} indicate the υ (C=N) azide functional group, 1607 cm^{-1} υ(C=C) of aromatic rings, 1518 cm^{-1} υ(H-N=C),1481 cm^{-1} υ(C=C), 1457 cm^{-1} υ(C-O-H), 1361 cm^{-1} υ(O-H) bending, 1345 cm^{-1} and 1299 cm^{-1} for υ(C-N), 1262cm^{-1} and 1239cm^{-1} represents (C-O), 1201 cm^{-1} (C-N), 1124 cm^{-1}, 1108 cm^{-1} and 1038 cm^{-1} for υ(C-O-C) of calix[4]arene rings. After complexation, the spectrum of **C4SB** shows distinctive variations in terms of shifting, disappearance and appearance of new bands spectrum (Fig. 7 b). On complexation with Al^{3+} the band at 1635 cm^{-1} shifted to 1655 cm^{-1}. Besides this, the bands at 1391, 1299, 1262, 1240 and 1038 cm^{-1} disappeared and new band at 1286 cm^{-1}, 1128 and 1066 cm^{-1} appeared in the spectrum of **C4SB**-Al^{3+} complex. These changes are informative sign due to metal-nitrogen/oxygen stretching and bending vibrations gives clear indication for involvement of nitrogen and oxygen donor atoms with Al^{3+}. In the case of I$^-$ complexation some evidences show the strong interaction of **C4SB** with guest specie as in (Fig. 8 b). The band at 3492 cm^{-1} corresponds to the hydroxyl protons on complexation the intensity of this band increased along with band blue shifted to 3423 cm^{-1}. Due to the hydroxyl protons engaged in hydrogen bonding with I$^-$. The band at 1635 and 1607 cm^{-1} merged together and appeared as strongly single band at 1620 cm^{-1}. Other band at 1518 cm^{-1} decreased on complexation. Intensity of the band at 1345 cm^{-1} decreased to medium. Moreover, the band at 1042 cm^{-1} completely disappeared and new bands appeared at 1550, 1104 and 1066 cm^{-1}. Which indicate that on hydrogen bonding with I$^-$ the electronic cloud on hydroxyl oxygen changed and resulting the appearance of new bands. These spectral changes support the formation **C4SB**-I$^-$ complex. The selective chromogenic response of **C4SB** for Al^{3+} and I$^-$ is strongly evidenced for by shifting, disappearance and appearance of various bands of specific functional groups occurred as a result of guests introduction into receptor cavity.

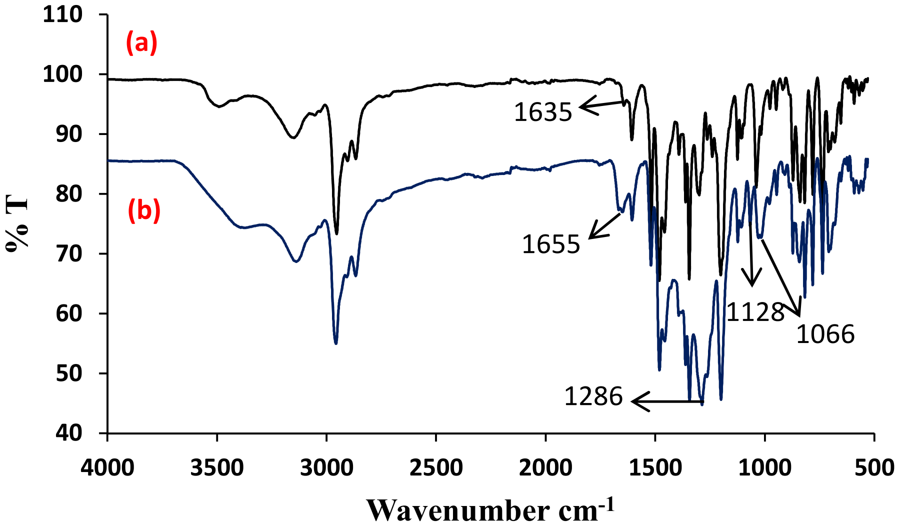


Figure 7 FT-IR spectra (a) **C4SB** and (b) **C4SB**-Al^{3+} complex.

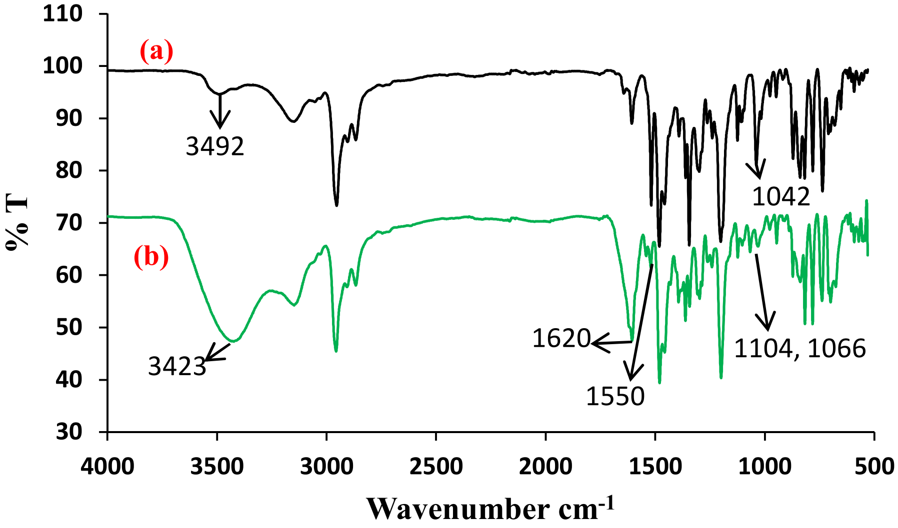


Figure 8 FT-IR spectra (a) **C4SB** and (b) **C4SB**-I$^-$ complex.

Conclusions

Fluoroionophoric behavior of 2-hydroxynaphthalimine functionalized calix[4]arene Schiff base, i. e. **C4SB** was explored toward series of selected different metals and anions. The probe displayed excellent selectivity for Al^{3+} as turn-on sensor over a broad range of tested metal ions with remarkably enhanced fluorescent intensity. Similarly probe exhibited high sensitivity toward I^- with turn-off fluorescence response. Experimental results clarify the selective sensing ability of **C4SB** toward Al^{3+} and I^- even in the presence of other competent ions. Only Hg^{2+} interferes in Al^{3+} detection. Stoichiometric ratio indicates that probe forms 1:1 complex with both Al^{3+} and I^-. Moreover complexes were characterized and confirmed by using FT-IR spectroscopy. Since the geometry and ideal binding sites containing N, O in **C4SB** possessing conformity in size, nature, and lodging with both Al^{3+} and I^-. Furthermore, selective response of probe for guests helps in supramolecular systems to detect and determine these toxic metal and anion in aqueous media.

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