



## Original Research Article

## Imidazoanthraquinone-triarylamines based Chromofluorogenic Chemosensors for Anion Sensing

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### ABSTRACT

In this report, imidazoanthraquinone-triarylamines fluorescent probe have examined for their coordination behaviour against tetrabutylammonium (TBA) salts of various anions in DMSO solvent. The anionic sensing ability of dyes was monitored by using colorimetric technique, UV-Vis absorption/emission spectroscopy. Among the various anions used, the probes were found selectively sensitive towards F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup> ions and show marked anion-induced colorimetric and optical response with red-shifted intramolecular charge transfer (ICT) absorption and emission band. The red shift in optical signal of all sensors established a deprotonation mechanism involving the -NH moiety of the imidazole ring. Besides, anion selectivity for probe-analyte interaction was found to be depended on the acidity/binding unit of sensor and basicity/hardness of anions (F<sup>-</sup> >CN<sup>-</sup> >OH<sup>-</sup>). Additionally, presence of electron donor or acceptor substituents on triarylamine also alters the chromogenic response or binding affinity of the sensors and found to be decreased with increase in ICT character. Further, low detection limit and high stability constant obtained from titration studies of ~10<sup>-6</sup> M sensors than previously reported ~10<sup>-5</sup> M imidazoanthraquinone sensors makes them strong selective and sensitive anionic-chemosensors.

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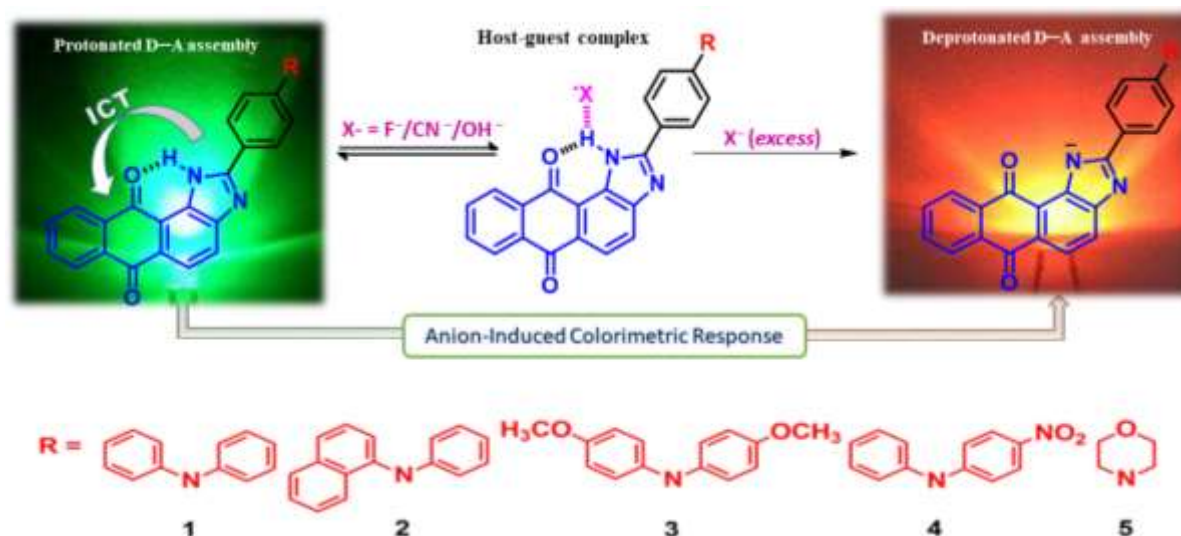
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## GRAPHICAL ABSTRACT



## 1. INTRODUCTION

Despite the crucial feature of ions in the environment, development of fluorescent sensors that can recognize ionic species with high selectivity, gain much attention in the area of chemical analysis, bio-imaging, and molecular electronics [1–6]. It requires low-cost, extensively accessible instrumentation to generate an optical signal from visible to the naked eye after a probe-analyte interaction [7,8]. Moreover, on equating cationic and anionic sensing, formulation of anionic receptors are quite challenging than the cationic due to its lower stability constants, complex pH-dependence, varied shapes and sizes, and microenvironment sensitivity [1,9–12]. Despite these shortcomings of anions, the sensors which are capable to show anion-induced color changes are of prime importance in nowadays as they offer highly sensitive response even at very low analyte concentration [13].

In that case, currently used colorimetric/fluorimetric sensing method became emerging tool for the recognition of

anions over the other previously used methods as it is simple, cost-effective, convenient, sensitive, selective and do not require expensive instruments for the 'naked-eye' detection of target ions [1,2,14–25]. Further, the development of methods for the selective detection of strong basic anions such as  $F^-$  and  $CN^-$  ions are in great demand as they play important roles in biological, environmental, clinical and industrial process [21,23,26,27]. The  $F^-$  ion has a hard Lewis base character with small ionic radius, high charge density and ability to interact with a suitable ionophore reversibly either through H-bonding interaction or deprotonation. Thus, electronegative nature of  $F^-$  ion and strong nucleophilic nature of  $CN^-$  can be easily accomplish sensing mechanism by naked eye detection after probe-analyte interaction. However, a sensor which can detect both anions are relatively less known [28–30]. Most of the past reports on  $F^-$  ion sensing are based upon colorimetric sensing method but some of them associated with quenching in

fluorescence [31–34] and few of them illustrate fluorescence enhancement study based on the ratiometric fluorescence which is still in demand [35,36].

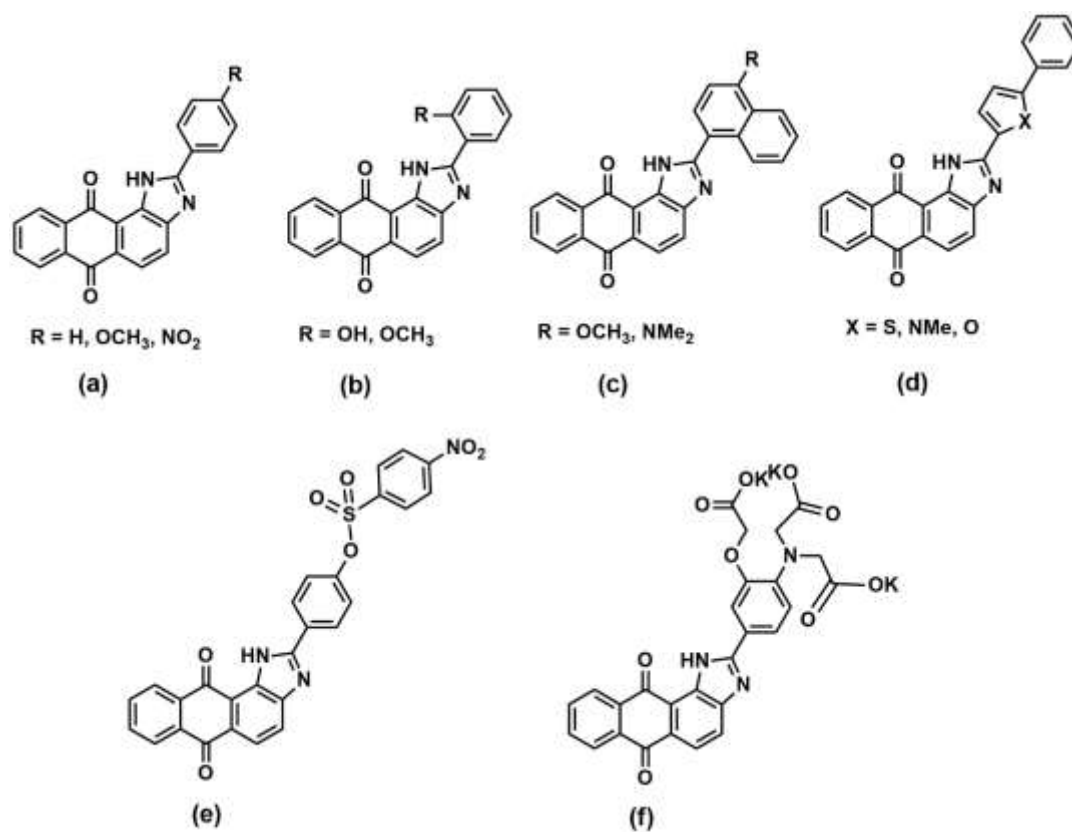
Further, for a development of successful fluorescent probe an appropriate sensing mechanism is required in addition with their critical properties i.e. excitation/emission wavelength, Stokes shifts, fluorescent quantum yields, solvatochromism. Majority of sensing mechanism based on photoinduced electron transfer (PET) or the modulation of luminescence processes involving metal ions and intramolecular charge transfer (ICT) are intensively studied and widely used for sensing purpose of ions [37–50]. However, in terms of specificity and sensitivity, PET based probe sensing associated with fluorescence quenching or emit in the UV range [51,52]. While metal centred probes usually emit in the visible region, but lack a straightforward tunability of their output frequencies over a broad spectral range. As a result, ICT based signalling mechanisms in which electronic transition takes place from electron donor (D) to electron acceptor (A) through the push-pull mechanism arouse significant attention towards the development of D–A molecules in ion-sensing field [13,53].

ICT mechanism, facilitate alteration in colour from visible to the naked eye with large shift in absorption/emission band which reflects the strength of the D–A interaction upon interaction with ions. Hence ICT characteristics could be advantageous for formulating the

desired spectral properties of a molecule by suitable selection of D–A receptor [54,55]. However, absence of ICT character in anionic sensor molecules leads to weak binding affinity towards the guests (anions) with feeble spectroscopic effects reflect upon complexation [56,57].

Numerous fluorophores were synthesized and reported as colorimetric anion sensors in the recent past having anthracene [58,59], dansyl [60], imidazole [61,62], anthraquinone [63], indole [64], nitrobenzene azo groups [65,66] and other  $\pi$ -conjugated moieties [2] as a signalling unit covalently attached to an anion receptor.

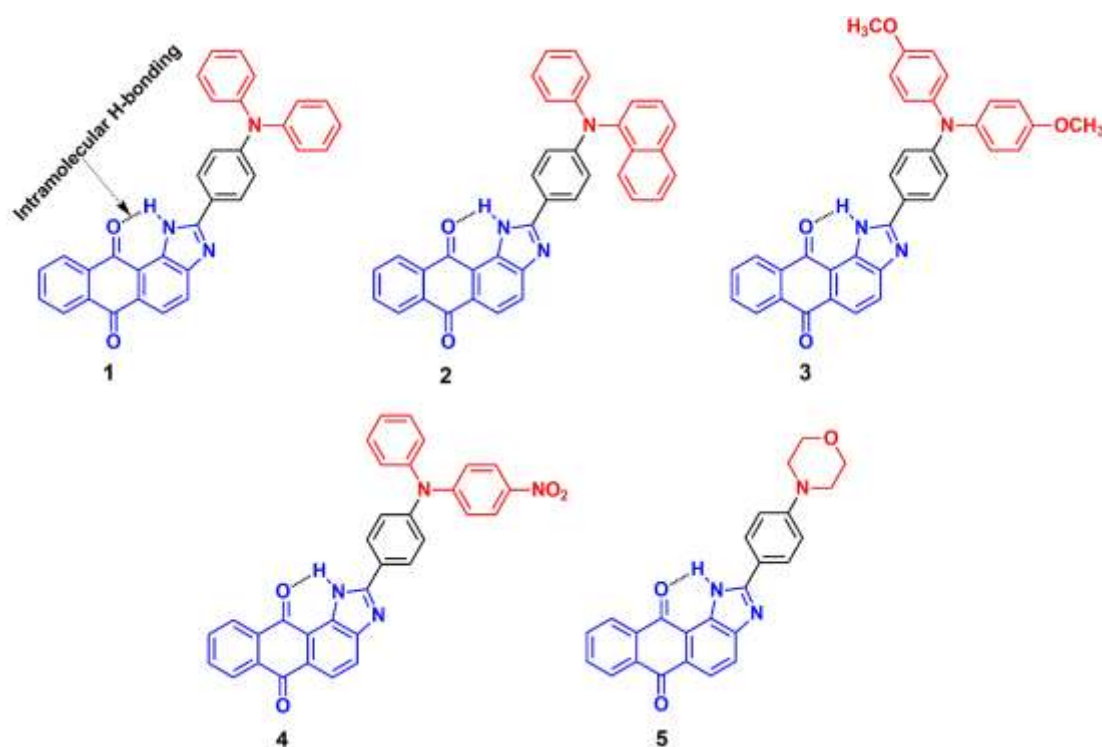
Among them imidazole is a five membered aromatic heterocyclic diazole compound having non-adjacent nitrogen atoms and when fused with anthraquinone ring it forms imidazoanthraquinone (IA). Past study on IA core and its derivatives suggest it has a distinct distribution of electron density and hence shows the D–A behaviour with prominent ICT character within it [67–80]. In addition, it possess an intramolecular hydrogen bonding between the –NH (hydrogen-bond donor) of the imidazole ring with the neighbouring quinone carbonyl group (hydrogen-bond acceptor), which can easily bind with basic anion through hydrogen bonding or proton transfer (PT) ground state process or through excited state proton transfer (ESPT) process, thereby make it an appropriate candidate as an anionic chemosensors [67–78].



**Chart 1.** Literature reported imidazoanthraquinone derivatives as chemosensing agents.

Earlier study on such framework (few of them disclosed in **Chart 1**), conceal the transfer of a proton via hydrogen bonds interaction can neutralize the charge separation which is reflected by shift in optical spectra with reduced energy of the ICT state [67–78]. In addition the acidity of the –NH proton of imidazole ring in anion-receptor D–A complex can be tuned by changing the electronic properties of the imidazole donor substituents [67–78]. Moreover, functionalization of triarylamine or amino subunit as signalling part is also one of the approach to design ICT based D–A chemosensors which can show receptor-ion interactions through intramolecular hydrogen bonding [71,81–84].

Bearing the above facts in mind, the anion induced sensing properties of triarylamine based imidazoanthraquinone chemoreceptors **1–5** (previously designed, characterized by our group and studied for their application in optoelectronic devices as n-type materials [80]) are investigated in this report. Sensibility of anion monitored by naked-eye colorimetric detection technique and through optical channel i.e. UV/Vis and fluorescence spectroscopy. In literature, various imidazoanthraquinone based moiety are reported as an ionic sensor till date [67–79]. However, in this report effect of various substituted donor triarylmines on sensing ability of imidazoanthraquinone (acceptor) are studied and discussed for the first time.



**Chart 2.** Molecular Structure of the Sensors 1–5.

Further, to check the selectivity-structure relationship or to access the PT or ESPT processes of ground or excited-state by tuning the acidity and the hydrogen-bond donor property of the –NH moiety with effect of electron donating (–OCH<sub>3</sub>) and withdrawing (–NO<sub>2</sub>) substituent on triphenylamine and rigidity of cyclic aliphatic amine (Morpholine), UV/Vis and fluorescence titration study was performed in organic solvent (DMSO). Molecular Structure of IA based anionic sensors 1–5 are shown in **Chart 2**.

## 2. EXPERIMENTAL

### Materials

All the chemicals and solvents used in the study were purchased from commercial sources of Sigma Aldrich and Alfa Aesar and were used without further purification unless stated. The organic solvents used were of analytical or spectroscopic grade. Before using, the solvents were dried and freshly distilled using the

standard procedures whenever anhydrous solvents were required.

### Synthesis of sensors 1–5

2-phenyl-anthra[1,2-*d*]imidazole-6,11-dione based triarylamines sensor 1–5 were prepared by Buchwald-Hartwig coupling amination reaction as specified in our previous report [80]. The Characterization (<sup>1</sup>H, <sup>13</sup>C NMR, IR, Maldi-tof and Elemental analysis) data of sensors 1–5 are found in our past report [80]. In this work, sensor/probe 1–5 were targeted for the study of their selective recognition and sensing ability of anions of different sizes and shapes i.e TBA salts of F<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, HNO<sub>2</sub><sup>-</sup>, OH<sup>-</sup> and HClO<sub>4</sub><sup>-</sup> anions.

### Methods and Instruments used for UV-vis and fluorescence sensing experiments

All UV-vis spectra were recorded in DMSO (spectroscopic grade) at 25 °C on a SHIMADZU UV-A114548 spectrometer after the addition of tetrabutylammonium (TBA) salts while keeping the sensor (1–5) concentration constant (1 ×

$10^{-6}$  M). Subsequently, all fluorescence spectra were recorded on a Horiba Fluorolog 3 spectrofluorometer at 25 °C upon the addition of TBA salts with the fixed concentration of sensor i.e.  $1 \times 10^{-6}$  M. TBA salts of  $F^-$ ,  $Br^-$ ,  $I^-$ ,  $CN^-$ ,  $BF_4^-$ ,  $HSO_4^-$ ,  $HNO_2^-$ ,  $OH^-$  and  $HClO_4^-$  anions were used for UV-vis and fluorescence experiments.

### 3. RESULTS AND DISCUSSION

#### *Photophysical study of sensors in DMSO solvent*

The absorption and emission properties of sensors **1–5** studied by UV-visible and fluorescence spectroscopy using dimethyl sulfoxide (DMSO) as solvent and the pertinent data obtained are summarized in **Table S1** (see supporting information (SI)). UV-Vis. spectral data of **1–5** recorded in  $2 \times 10^{-6}$  M DMSO solution show two type of transitions one in the UV range at 269–278 nm and 314–339 nm respectively assigned as  $n-\pi^*$  and  $\pi-\pi^*$  transitions which can be originated from entire molecule due to extension in conjugation by the introduction of triarylamine into imidazoanthraquinone core. However, second absorption band appeared in the visible range at 407–491 nm, which assigned to intramolecular charge transfer (ICT) transitions from electron-donor triarylamine subunit to electron-acceptor imidazoanthraquinone core and thus established D–A framework within a molecule [80]. On exciting the sensors (**1–5**) at 405 nm, they emit in green region with the emission maxima of 530–573 nm in DMSO solvent (see **Table S1** in SI) [80]. The corresponding shift in absorption and emission maxima were depend on the donating strength of triarylamine unit. Considerable stokes shift of around 2822–5702  $cm^{-1}$  was observed for **1–5** which further reveal the formation of a charge-transfer state within molecule (see **Table S1** in SI) [80].

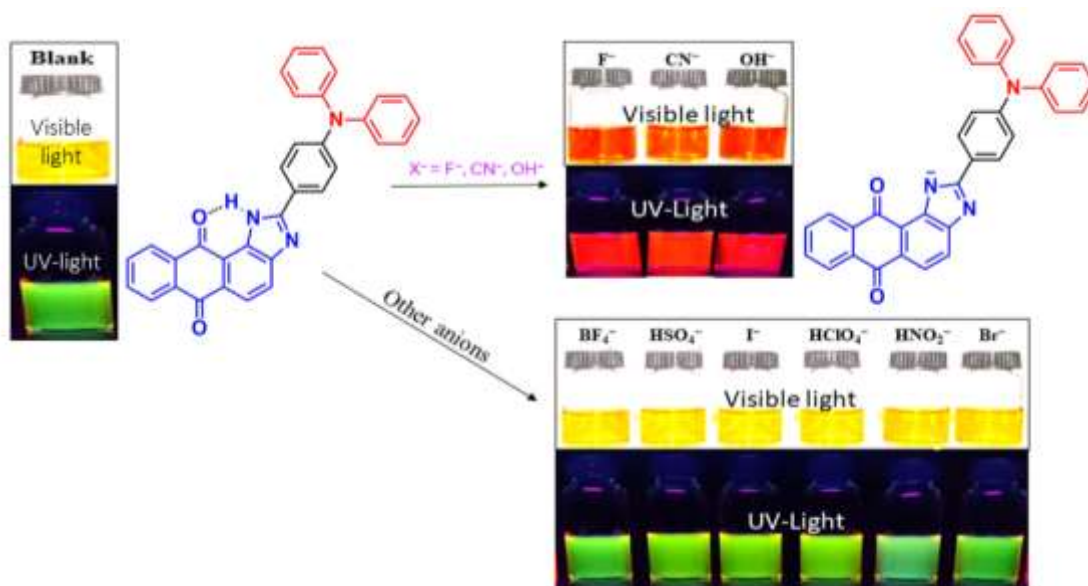
#### *Colorimetric analysis of Sensors with anions*

To investigate the chemical interaction between probe and anion, anionic solutions (50 equivalent) of various anions i.e. tetrabutylammonium (TBA) salts of  $F^-$ ,  $Br^-$ ,  $I^-$ ,  $CN^-$ ,  $BF_4^-$ ,  $HSO_4^-$ ,  $HNO_2^-$ ,  $OH^-$  and  $HClO_4^-$  ions, were added in  $1 \times 10^{-4}$  mol  $dm^{-3}$  DMSO solution of sensors at room temperature. Addition of strong basic anions such as  $F^-$ ,  $CN^-$  and  $OH^-$  ions (in contrast to other anions) in DMSO solution of each sensor (S), resulted into anion-inducing colour modulations that were visible to the naked eye (under visible lamp) or under UV light (lamp of  $\sim 365$  nm). As an example, interaction of sensor (host) with TBA salts of  $F^-$ ,  $CN^-$  and  $OH^-$  ions (guest) turn up the DMSO solution of **1** from yellow to orange coloured solution in visible light (**Figure 1**) may due to formation of host-guest assembly.

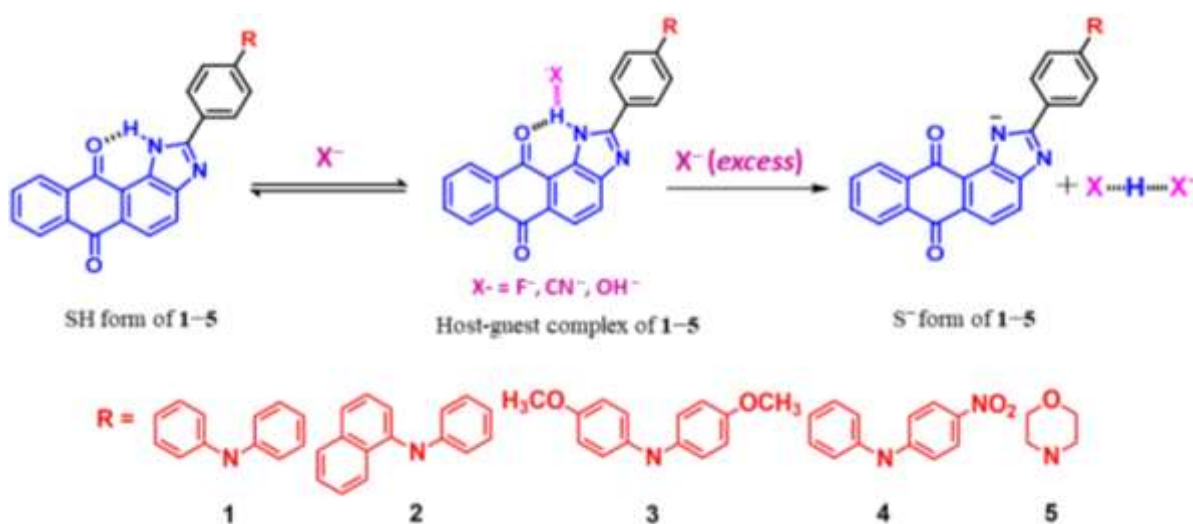
Similarly, DMSO solutions of **1** initially emit green colour under UV-lamp however after addition of 50 eq. anions (TBA salts of  $F^-$ ,  $CN^-$  and  $OH^-$  ions), emission of DMSO solution found in orange region (**Figure 1**).

These observed selective colorimetric response of sensor with anions especially  $F^-$ ,  $CN^-$  and  $OH^-$  ions is predicted due to strong H-bonding interaction between electronegative/basic nature of anions with electropositive acidic proton ( $-NH$ ) of imidazole ring in the sensor structure which leads to the deprotonation at the binding site of the sensor (PT process) (**Scheme 1**) [2,67–78].

However, other competitive anions such as  $Br^-$ ,  $I^-$ ,  $BF_4^-$ ,  $HSO_4^-$ ,  $HNO_2^-$  and  $HClO_4^-$  ions were unable to show effective colorimetric response in DMSO solution of sensors due to their weak basicity to deprotonate (**Figure 1**). Thus, corresponding result suggest the colorimetric response or binding affinities of anions is based on their differences in binding constants with proton ( $-NH$ ) group of receptor [85].



**Figure 1.** Colorimetric response of **1** ( $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) in DMSO solution after addition of 50 equivalent of anions.



**Scheme 1.** Mechanism of anion ( $\text{F}^-$ ,  $\text{CN}^-$  and  $\text{OH}^-$  ions) interaction with Sensor/Probe **1-5**.

#### Investigation of anion sensing of probes by UV-Vis and fluorescence spectroscopy

To confirm the colorimetric activities observed in the section above and effect of probe-analyte interaction on ICT wavelength, we have investigated anion recognition and sensing ability of **1-5** in DMSO solvent through optical channels such as visual, UV-Vis absorption and emission spectroscopy at 25 °C.

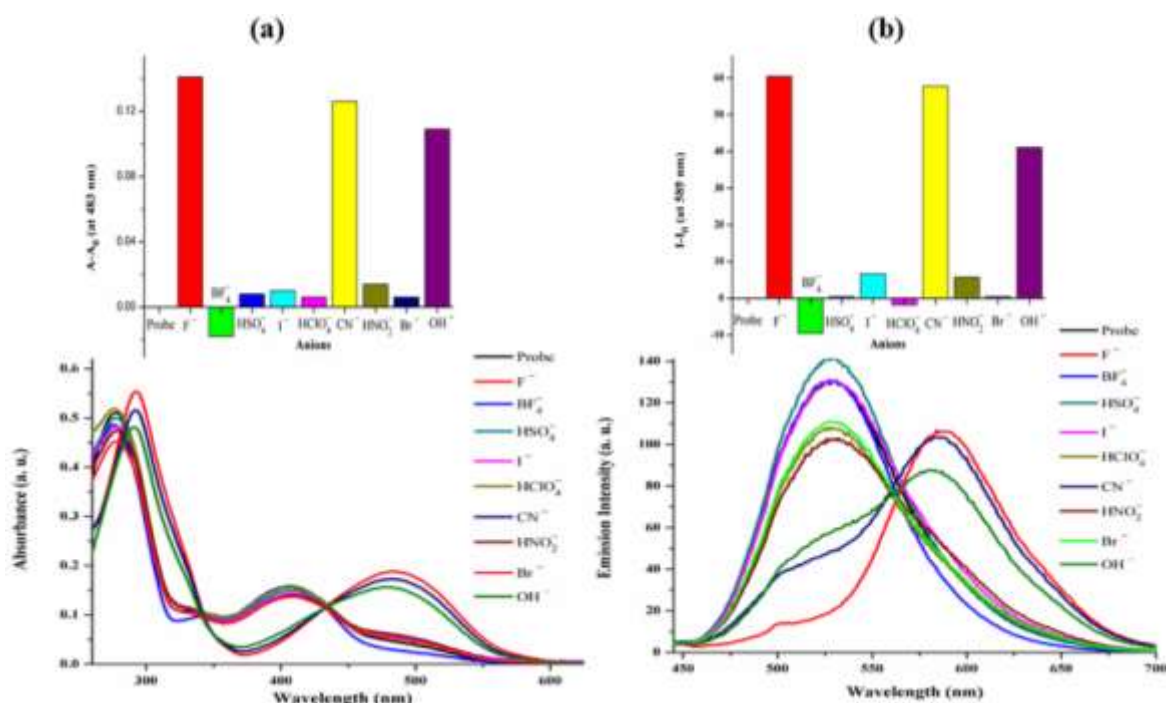
Anion sensing using optical spectroscopy study was performed in presence of anions of different sizes and shapes i.e. tetrabutylammonium (TBA) salts of  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{BF}_4^-$ ,  $\text{HSO}_4^-$ ,  $\text{HNO}_2^-$ ,  $\text{OH}^-$  and  $\text{HClO}_4^-$  ions. UV-vis absorption and emission response of **1** in DMSO after addition of 50 equivalent of different anions shown in **Figure 2** and pertaining change in spectral data for the

interaction of sensor **1–5** with  $F^-$ ,  $CN^-$  and  $OH^-$  ions presented in **Table 1**.

UV-vis absorption spectra of protonated form of sensors **1–5** in DMSO revealed the presence of an ICT band which were found to be red shifted with the increase in the donor strength of amines in sensor molecule (**Table 1** and SI **Table S1**). Maximum red shift was observed in case of electron donating substituted triarylamine based donor receptor i.e. **3** than other receptor in absence of any added ion (**Table 1** and SI **Table S1**) [80]. However, addition of TBA salt of different ions in DMSO solution of protonated sensor molecules **1–5** shift their corresponding ICT band towards longer wavelength could be due to anion-induced charge redistribution occurring in the “push-pull” system of deprotonated sensor molecules (**Table 1**) [70]. Interaction of negatively charged analyte/ions

with NH group of imidazole ring alter the protonated form of “D–A” moiety to deprotonated system through H-bonding interaction associated with PT mechanism (**Scheme 1**) which enhance the acidity of the hydrogen-bond donors and hence absorb at different wavelength than that of protonated species [67,68,70].

Moreover, extent of the deprotonation in each sensors molecule based on the enhancement in the increase of the acidity of the hydrogen bond donors and the basicity of the anions [68]. Further, negative charge on N atom of imidazole ring in deprotonated structure of sensors dispersed through  $\pi$ -conjugation present in acceptor core of **1–5** and stabilized the CT state of deprotonated species by lowering their energy [70].



**Figure 2.** (a) UV-visible and (b) emission responses of **1** ( $1 \mu M$ ) in DMSO after addition of 50 equivalent of anions. Inset show change in (a) absorbance at 483 nm and (b) emission at 589 nm after addition of anions.



**Table 1.** Spectroscopic data for the interaction of sensor **1–5** with anions (F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup>).

Sensor	Absorbance data			Fluorescence data				
	$\lambda_{\text{abs SH}}$ , (nm)	$\lambda_{\text{abs S}^-}$ , (nm)	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{ex SH}}$ (nm)	$\lambda_{\text{em SH}}$ (nm)	$\lambda_{\text{em S}^-}$ (nm)	$\lambda_{\text{em}}$ (nm)	Stokes shift (cm <sup>-1</sup> )
<b>1</b>	407	483	76	436	530	589	59	3726
<b>2</b>	407	483	76	436	530	589	59	4119
<b>3</b>	491	527	36	501	573	586	13	1910
<b>4</b>	436	510	74	--	--	--	--	--
<b>5</b>	465	512	47	--	--	--	--	--

Measured upon addition of 50 equivalent of anions in DMSO solution of sensors (S represent sensor).

Consequently, red shifted ICT band was observed upon addition of strongly basic F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup> ions in DMSO solution of **1–5** which propose partial negative charge transfer process in the anion-sensor complex (**Table 1**) [70]. Whereas other anion having least basicity show no significant effect on ICT maxima. Thus, it was observed that the chromogenic response of sensors depends on the hardness of the anions and found to follow the order of decreasing nature of hardness of anions as F<sup>-</sup> > CN<sup>-</sup> > OH<sup>-</sup> and thus receptor **1–5** were highly selective towards F<sup>-</sup> ion.

Additionally, maximum shift in wavelength ( $\lambda_{\text{abs}}$ ) was found in the deprotonated species of **1** and **2** ( $\lambda_{\text{abs}} = 76$  nm) as compared to other receptor on addition of F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup> ions in DMSO solution (**Table 1**). However, presence of electron donating -OCH<sub>3</sub> substituent on triphenylamine in **3** may enhance the electron density of the imidazole ring at -NH site as a result the acidity of the hydrogen-bond donors decreases which makes the deprotonation more difficult [67]. On the other hand, strong electron withdrawing -NO<sub>2</sub> substituent in deprotonated species **4** increases the acidity of hydrogen-bond donors by accumulating maximum negative charge density towards itself and

thereby show efficient anion-induced charge delocalization behaviour, which stabilizes the CT character [67]. Thus maximum ICT shift was observed in case of **4** ( $\lambda_{\text{abs}} = 74$  nm) than that of **3** ( $\lambda_{\text{abs}} = 36$  nm) after addition of ions (**Table 1**). While in case of receptor **5** after addition of ions maximum negative charge density is developed on the -CH<sub>2</sub> group of morpholine (cyclic) donor which reduces the basicity of imidazole ring at -NH site and leads to maximum red-shifted CT band ( $\lambda_{\text{abs}} = 47$  nm) than **3** (**Table 1**) [71]. As a result, corresponding shift in ICT wavelength in sensors were found to be based on strength of D-A unit with stabilization of CT state in sensor-analyte complex [71]. As the ICT nature in the dyes increases chromogenic response for the anions was observed to be decreased invariably with the presence of electron donor or acceptor substituents attached to the triarylamine subunit of the molecules. Thus, the shift in ICT ( $\lambda_{\text{abs}}$ ) and chromogenic response among the sensors was found to varied and follow the order **1**~**2**>**4**>**5**>**3** depending on the strength of ICT within the sensor molecule.

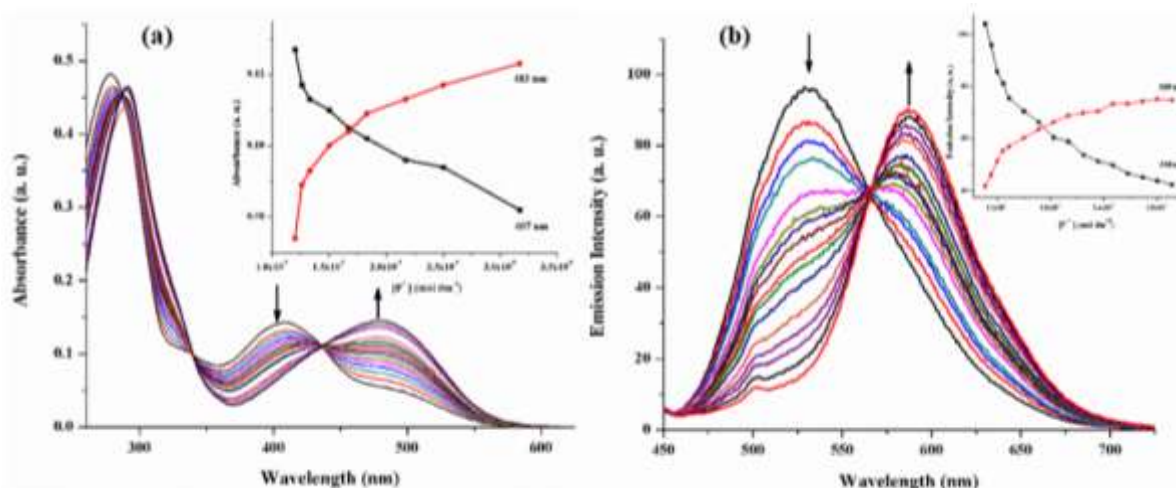
In addition to colorimetric response receptor **1**, **2** and **3** also exhibit strong fluorimetric sensing response on addition of F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup> ions. Further, anion-induced ESPT mechanism

in deprotonated form receptor of **1**, **2** and **3** was revealed by shift in corresponding emission wavelength ( $\lambda_{em}$ ) (**Table 1**) [67,70]. However, receptor **4** and **5** were unable to show fluorimetric response may be due to anion-induced quenching in emission associated with strong ICT character of probe-analyte complex on addition of  $F^-$ ,  $CN^-$  and  $OH^-$  ions. Nevertheless, detail quantitative aspects about the anions interaction with sensors **1–5** can be evaluated using the UV-vis. absorption and emission titration experiments.

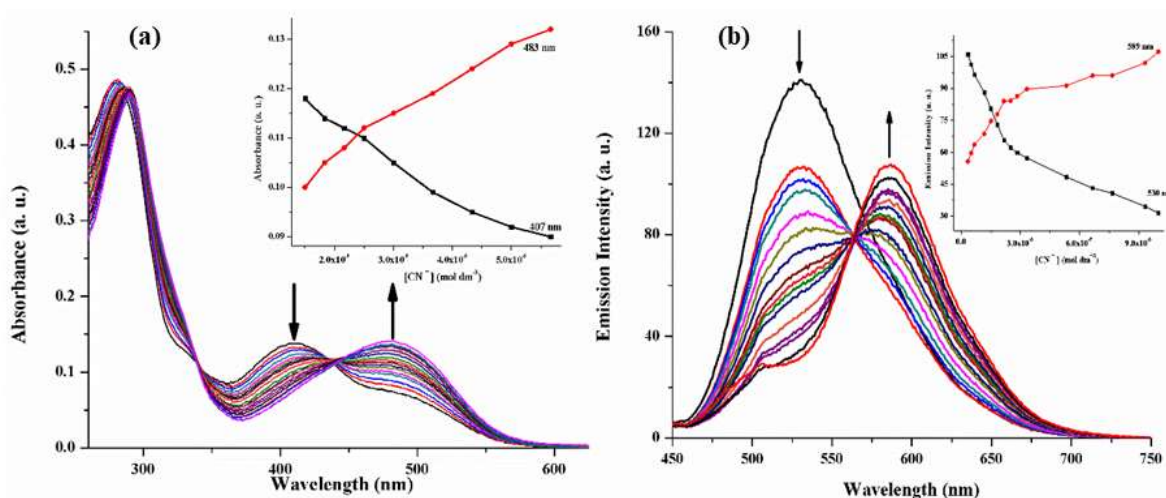
*Spectrophotometric and spectrofluorimetric titrations of sensors with anions*

In order to get quantitative aspects regarding the sensor-anions interaction, the UV-vis. absorption and emission titration experiments were assessed for sensor **1–5** with respect to the anions showing remarkable change in the spectral profile i.e.  $F^-$ ,  $CN^-$  and  $OH^-$  ion. During the UV-visible titration, incremental addition of  $F^-$ ,  $CN^-$  and  $OH^-$  ions in DMSO solution of **1** (**Figure 3 (a)**, **4 (a)** and **5 (a)**) and

**2** (**SI Figure S3 (left)**), the successive absorption curves pass through a well-defined isosbestic point at 436 nm evaluating a new red-shifted band at 483 nm whereas the original low energy absorption band at 407 nm seems to disappear gradually. The appearance of isosbestic points at 436 nm reveal that more than one species presents in the medium [68]. Further, titration absorption plot obtained for other sensors **3–5** also show presence of isosbestic point on incremental addition of  $F^-$ ,  $CN^-$  and  $OH^-$  in DMSO solution (**SI Figure S6 (left)**, **S9** and **S12**). However, the extent of shift in wavelength ( $\lambda_{abs}$ ) was found to be vary in accordance with their stabilization of CT state by the substituted amine strength in deprotonated receptor. Further, the emission titration of sensor **1** (**Figure 3 (b)**, **4 (b)** and **5 (b)**) and **2** (**SI Figure S3 (right)**) carried out in DMSO solutions with increase in concentration of  $F^-$ ,  $CN^-$  and  $OH^-$  ions using excitation wavelength ( $\lambda_{ex}$ ) = 436 nm.



**Figure 3.** Changes in (a) UV-vis absorption and (b) emission spectra of **1** in DMSO upon incremental addition of  $F^-$  ion. The insets to (a) and (b) show the change in wavelength as a function of  $F^-$  concentration for the experimental absorbance and luminescence data.



**Figure 4.** Changes in (a) UV-vis absorption and (b) emission spectra of **1** in DMSO upon incremental addition of  $\text{CN}^-$  ion. The insets to (a) and (b) show the change in wavelength as a function of  $\text{CN}^-$  concentration for the experimental absorbance and luminescence data.

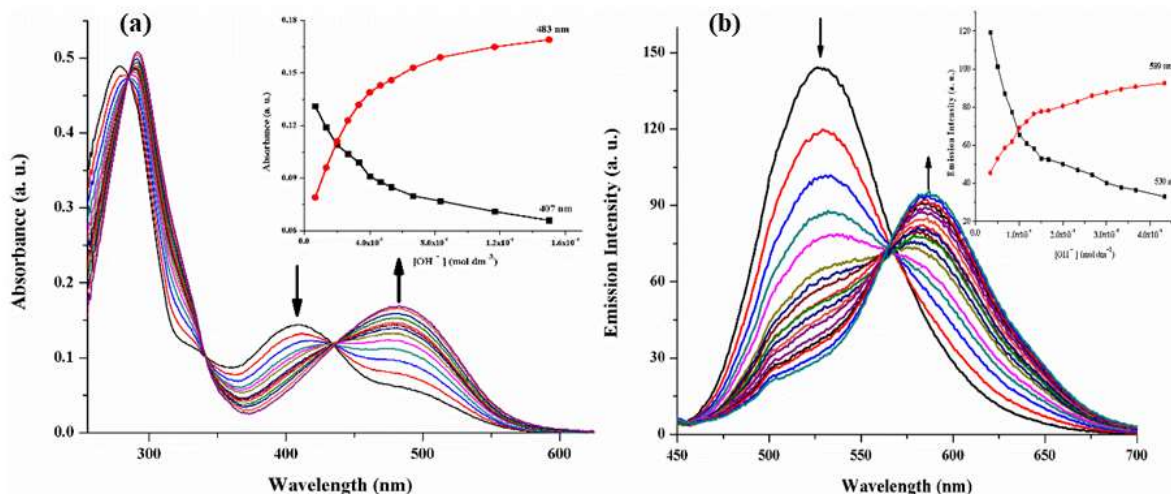
The emission titration plot of **1** (Figure 3 (b), 4 (b) and 5 (b)) and **2** (SI Figure S3 (right)) originally show a broad emission band at 530 nm ( $\lambda_{\text{ex}} = 436$  nm). The intensity of which gradually decreases and at its expense a progressive bathochromically shifted new emission band emerges at 589 nm on account of increasing  $\text{F}^-$ ,  $\text{CN}^-$  and  $\text{OH}^-$  anion concentration which gradually intensify upon increasing concentration of the ions. The successive emission spectrum passes through a clear isoemissive point at 565 nm as observed isosbestic point in the UV-visible titrations. However, in case of **3** incremental addition of  $\text{F}^-$ ,  $\text{CN}^-$  and  $\text{OH}^-$  ions in DMSO solution show switched on emission i.e. enhancement in fluorescence intensity (SI Figure S6 (right)) with bathochromic ( $\lambda_{\text{em}} = 13$  nm) shifted band (Table 1).

Moreover, the spectral behaviour of sensors toward  $\text{OH}^-$  ion show a smaller extent of change at lower concentration compared with that of  $\text{F}^-$  and  $\text{CN}^-$  ions. Which further explains the chromogenic responses of a sensors depending

on the hardness of the anions [67] and it is deflected in the binding constant of sensors for the specific anions (Table 2 and SI Table S2). The limit of detection of sensors **1–5** were calculated from the linear regression plots (Figure 7 (right), SI Figure S2, S5, S8, S11 and S14) for both absorption and emission titration data and found to lie in the order of  $10^{-7}$  M for  $\text{F}^-$ ,  $10^{-6}$  M for  $\text{CN}^-$  and  $10^{-5}$   $\text{OH}^-$  (Table 2 and SI Table S2).

Besides that, the Stokes shift of receptor **1** and **2** were high compared to the other sensors and found to be the order of  $3726\text{ cm}^{-1}$  and  $4119\text{ cm}^{-1}$  respectively (Table 1), supporting the strong ICT feature of the sensors. Fluorescent molecules featuring longer excitation/emission wavelength and larger Stokes shifts are desirable character for design of fluorescent chemosensors, because the longer excitation wavelength can help to suppress the background or the auto-fluorescence of bio-sample, which is beneficial for analytical

purpose, especially in vivo fluorescence bio-imaging [86].



**Figure 5.** Changes in (a) UV-vis absorption and (b) emission spectra of **1** in DMSO upon incremental addition of OH<sup>-</sup> ion. The insets to (a) and (b) show the change in wavelength as a function of OH<sup>-</sup> concentration for the experimental absorbance and luminescence data.

### Relay study

As discussed in above section, sensors **1–5** are highly selective towards F<sup>-</sup> ion as compared to other anions. While detailed concept of selective binding affinity of probes towards F<sup>-</sup> ion in presence of other anions in same media can be examined by a relay study using absorption and emission spectroscopy. Since, probe **1** was found highly selective receptor among the others (**2–5**) to show marked colorimetric response towards F<sup>-</sup> ion in DMSO solutions. Thus here we have chosen sensor **1** to check its selective sensing ability towards F<sup>-</sup> anion in presence other anions in same media. Interaction of sensor **1** with F<sup>-</sup> and BF<sub>4</sub><sup>-</sup> ions in the DMSO solutions using optical channel given in **Figure 6**.

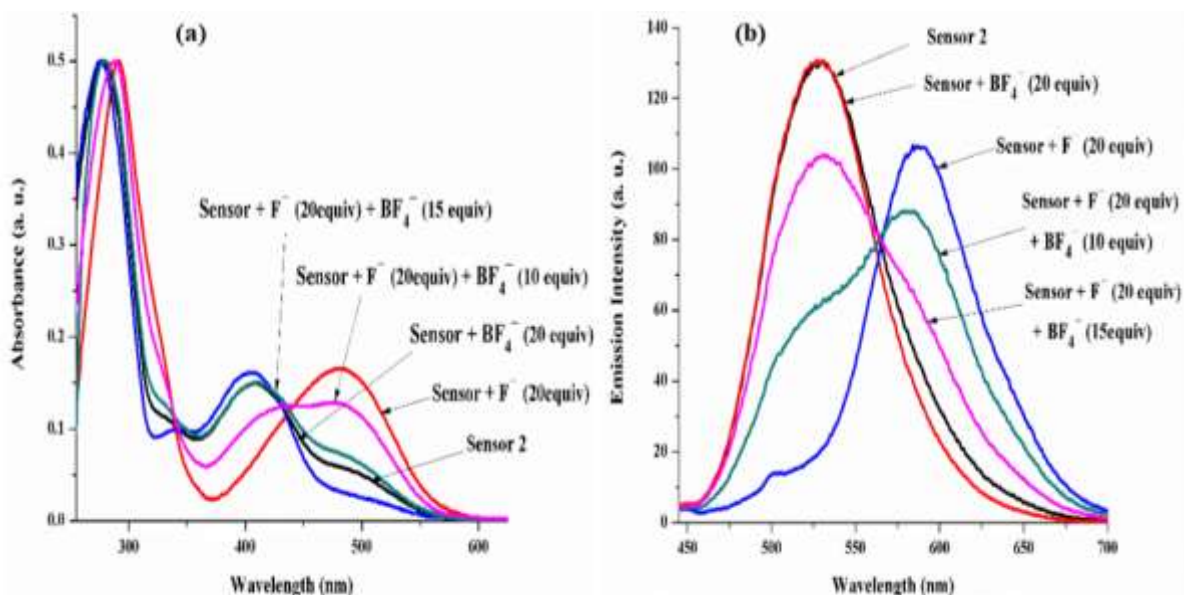
As selective sensitivity of various anion or formation of deprotonated species associated with PT process based on bathochromic shift in absorption and emission spectrum after addition of anion into the solution.

Consequently, selectivity of **1** towards F<sup>-</sup> was observed by red shifted ICT band (483 nm) after addition of 20 equiv. F<sup>-</sup> ion in DMSO solution of sensor **1** (10<sup>-6</sup> M) as compared to original CT band (407 nm) in absence of ion (**Figure 6 (a)**). While addition of BF<sub>4</sub><sup>-</sup> ion (20 equiv.) in DMSO solution may not show the PT mechanism due to their weak basic nature and show no effect in absorption spectra as compared to the original one (**Figure 6 (a)**).

Further relay study performed in a mixture of sensor with different anions in same media showed probe **1** was able to selectively detect the F<sup>-</sup> even in presence of CN<sup>-</sup> or OH<sup>-</sup> or other anion in the DMSO medium, except for BF<sub>4</sub><sup>-</sup> ion. Initially, addition of 10 equiv. BF<sub>4</sub><sup>-</sup> ion to a mixture of sensor **1** (10<sup>-6</sup> M) + F<sup>-</sup> (20 equiv.), broaden the CT absorption band from 407 to 483 nm with hypochromic shift. Further, on increasing the concentration of BF<sub>4</sub><sup>-</sup> (15 equiv.) ion and keeping the concentration of mixture

(sensor **1** ( $10^{-6}$  M) + F<sup>-</sup> (20 equiv.)) constant, the CT absorption band regain its original CT absorption state (**Figure 6 (a)**). Similar, result

was observed in emission spectral data on addition of BF<sub>4</sub><sup>-</sup> ion to a mixture of sensor **1** + F<sup>-</sup> (**Figure 6 (b)**).



**Figure 6.** Interaction study of Sensor **1** with F<sup>-</sup> and BF<sub>4</sub><sup>-</sup> ions in the DMSO solutions using UV-vis (a) and emission (b) data.

Insignificant changes in optical response after addition of BF<sub>4</sub><sup>-</sup> (15 equiv.) ion to a mixture of sensor **1** + F<sup>-</sup> (20 equiv.) can be justify by in accordance with Le Chatelier's principle

It suggests the addition of a common ion to same system at equilibrium shifts the reaction towards the left to decrease the stress and forming more reactants. Similarly, in this case when TBA salt of BF<sub>4</sub><sup>-</sup> and F<sup>-</sup> are dissolved in the same solution, they all ionize in the solution at a time and may contribute to the increase in concentration of the common F<sup>-</sup> ion. As a result deprotonation of **1** having acidic proton of imidazole ring prevented as much as it would without the added common ion. So, increase in concentration of F<sup>-</sup> ion driven the reaction to left by decreasing the [H<sup>+</sup>] i.e. prevent the PT process or deprotonation of acidic proton of imidazole ring of **1**. Hence, addition of BF<sub>4</sub><sup>-</sup> ion to the mixture of sensor **1** + F<sup>-</sup> increase the common ion effect which neutralizes the

colorimetric and optical response and show no shift in absorption and emission spectrum (**Figure 6**).

#### Determination of Stability Constants with Anions

The appearance of a new red shifted lower energy absorption and emission band with the suppression of initial absorption and emission peak for sensor **1-5** associated with proton transfer sensing mechanism that yielded the deprotonated species was quite analogous to previous reported related sensor moiety [67-78].

Interaction of sensors with anions may induced the loss of the proton of the imidazole N-H group from the sensor and forms weak HF hydrogen bonds, with the deprotonated receptor site (**Scheme 1**). This complex is quite unstable and thus results in deprotonation of the newly formed complex with removal of HF molecule, yielding the anionic form of the corresponding sensor which show shifted

absorption and emission band compared to that of original sensor molecule [67,70].

**Table 2.** Binding constant and limit of detection for **1** (1  $\mu$ M) with F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup> ion.

Anion	Absorbance data		Emission data	
	log K	Limits of detection	log K	Limits of detection
F <sup>-</sup>	5.11	4.23 x 10 <sup>-6</sup>	4.93	5.98 x 10 <sup>-7</sup>
CN <sup>-</sup>	4.78	5.95 x 10 <sup>-6</sup>	4.52	1.36 x 10 <sup>-6</sup>
OH <sup>-</sup>	4.88	1.01 x 10 <sup>-5</sup>	3.88	1.18 x 10 <sup>-5</sup>

**Table 3.** Binding constant and limit of detection for sensors **1–5** at 1 x 10<sup>-6</sup> mol dm<sup>-3</sup> of sensors in response of addition of F<sup>-</sup> ion.

Sensor	Absorbance data		Emission data	
	log K	Limits of detection	log K	Limits of detection
<b>1</b>	5.11	4.23 x 10 <sup>-6</sup>	4.93	5.98 x 10 <sup>-7</sup>
<b>2</b>	5.08	6.23 x 10 <sup>-7</sup>	4.78	2.26 x 10 <sup>-6</sup>
<b>3</b>	3.85	1.89 x 10 <sup>-5</sup>	4.91	8.02 x 10 <sup>-6</sup>
<b>4</b>	*5.43	6.23 x 10 <sup>-7</sup>	–	–
<b>5</b>	4.18	2.79 x 10 <sup>-6</sup>	–	–

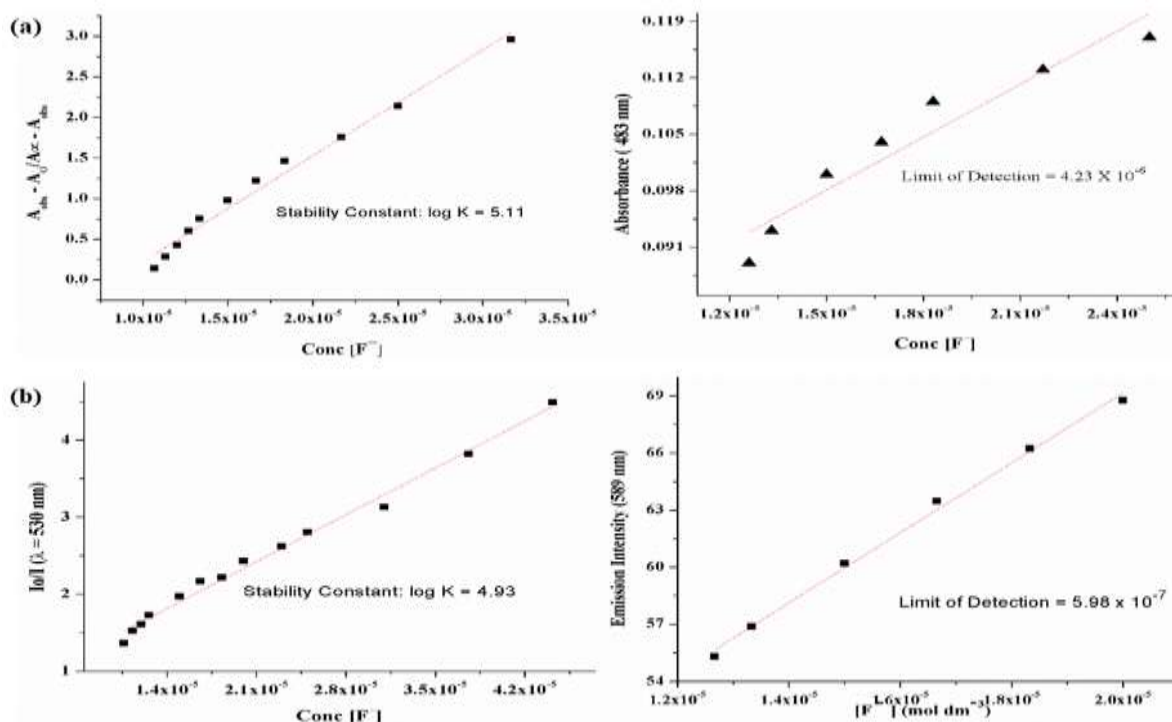
\*Calculated for sensor **4** at  $\sim 1 \times 10^{-4}$  mol dm<sup>-3</sup>

Consequently, to complete the characterization of the interaction among **1–5** with anions, the deprotonation process was further studied by evaluating the stability constants by both UV-vis absorption and fluorometric titrations data. Calculated binding constant and limit of detection values for sensor **1** with F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup> ions are shown in **Table 2** (For other sensor see SI **Table S2**) and for all sensor with F<sup>-</sup> ion is listed in **Table 3**. **Figure 7** shows stability constant and detection limit calculation plot with respect to F<sup>-</sup> ion for sensor **1** using absorption and emission data (for other anion see SI **Figure S1, S2** and for other sensor see SI **Figure S4, S5, S7, S8, S10, S11, S13** and

**S14**). The equilibrium constants from the absorbance data were evaluated using Benesi-Hildebrand equation [87–91] i.e.  $A_{obs} = (A_0 + A_{\infty}K[G]_T)/(1 + K[G]_T)$ ; Where  $A_{obs}$  is the observed absorbance,  $A_0$  is the absorbance of the free receptor,  $A_{\infty}$  is the maximum absorbance induced by the presence of a given anionic guest anion,  $[G]_T$  is the total concentration of the guest, and  $K$  is the equilibrium constant of the host-guest entity. Whereas, the equilibrium constant from emission data was evaluated using Stern Volmer equation [92–94] i.e.  $I_0/I_{obs} = 1 + K[G]$ ; Where  $I_{obs}$  is the observed absorbance,  $I_0$  is the absorbance of the free receptor,  $[G]$  is concentration of the guest anion,

and  $K$  is the equilibrium constant of the host-guest entity. However, in case of sensor **3** where only enhancement in emission was observed

were evaluated using modified Benesi-Hildebrand equation [90] i.e.  $(I_{\text{obs}} - I_0) / (I_{\infty} - I_{\text{obs}}) = 1 + K[G]$ ;



**Figure 7.** Calculated stability constant (**left**) and detection limit (**right**) with respect to F<sup>-</sup> ion for sensor **1** using (a) absorption and (b) emission data (for other anion see SI **Figure S1** and **S2**).

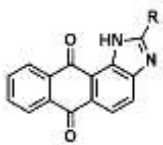
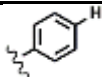
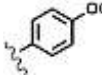
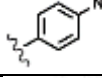
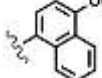
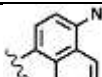
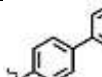
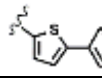
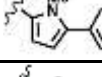
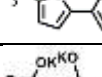
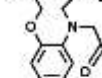
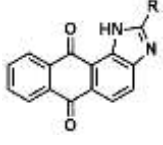
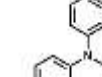
Where  $I_{\text{obs}}$  is the observed absorbance,  $I_0$  is the absorbance of the free receptor,  $I_{\infty}$  is the maximum absorbance induced by the presence of a given anionic guest anion,  $[G]$  is the total concentration of the guest, and  $K$  is the equilibrium constant of the host-guest entity. Limit of detection were calculated from the linear regression plots for both the absorption and emission data. The evaluated logarithms of stability constant ( $\log K$ ) for the sensors **1–5** for the interaction with F<sup>-</sup> ion (**Table 3**) was varying and found to depend on the substituents attached to the triarylamine moiety and the ICT character in the sensors. Maximum  $\log K$  value observed for the sensor **1** and **2** which suggest highly selective receptor

capability of these sensor towards F<sup>-</sup> ion over the other sensors. Stability constant was also found to be dependent on the hardness of the anions as shown in **Table 3** and SI **Table S2**. Stability constant for sensor **1** was found to decrease with the decrease in hardness of anions and it was observed maximum for the fluoride ion compared with that of cyanide and hydroxide anions. Despite this fact, the logarithms of the stability constants for the proton transfer for sensors **1–5** at sensor concentration of order  $\sim 10^{-6}$  M are of the same order but of slight greater magnitude to those reported for related compounds using sensor concentration of  $\sim 10^{-5}$  M [67,68,71,73,74,78]. Thus detailed study of colorimetric responses

by absorption and emission titration revealing a low limit of detection and high stability constant at lower concentration ( $\sim 10^{-6}$  mol dm<sup>-3</sup>) of sensor molecules **1-5** (especially **1**) as

compared with that of reported imidazoleanthraquinone derivatives ( $\sim 10^{-5}$  mol dm<sup>-3</sup>) (**Table 4**).

**Table 4.** Comparison of binding constant and limit of detection of sensor **1** ( $10^{-6}$  M) with literature reported imidazo-anthraquinone derivatives ( $10^{-5}$  M) in response to detection of F<sup>-</sup> ion.

Sensor Conc.	Sensor	R	Absorbance data		Emission data		Ref. No.	
			log K	Limits of detection	log K	Limits of detection		
$\sim 10^{-5}$ M			3.92	—	4.61	—	[67]	
			3.35	—	3.90	—		
			1.48	—	1.96	—		
		(Previously reported sensors for detection of F <sup>-</sup> ion)		4.14	$4.6 \times 10^{-6}$	—	—	[73]
				3.91	$4.6 \times 10^{-6}$	—	—	
				4.20	$10 \times 10^{-6}$	—	—	[74]
				3.30	$10 \times 10^{-6}$	—	—	
				3.81	$10 \times 10^{-6}$	—	—	
				3.38	$10 \times 10^{-6}$	—	—	
					4.52	—	—	—
$10^{-6}$ M		 Sensor <b>1</b>	5.11	$4.23 \times 10^{-6}$	4.93	$5.98 \times 10^{-7}$		



## CONCLUSION

A push-pull assembly of imidazoanthraquinone–triarylaminines were utilized to examine their selective and sensitive ability towards TBA salt of F<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, HNO<sub>2</sub><sup>-</sup>, OH<sup>-</sup> and HClO<sub>4</sub><sup>-</sup> anions at micro level in DMSO. The obtained colorimetric and optical response (red shifted ICT and emission band) suggest sensors were selectively sensitive towards the detection of F<sup>-</sup>, CN<sup>-</sup> and OH<sup>-</sup> ions, while other anion remain inactive due to their least basicity. Further, selectivity of anion is found varied as F<sup>-</sup> > CN<sup>-</sup> > OH<sup>-</sup> based on their hardness and stability constant (log K).

As, calculated log K value for each sensor in response of F<sup>-</sup> ion was found larger than CN<sup>-</sup> and OH<sup>-</sup> ion, thus sensors **1–5** are said to be highly selective towards the detection of F<sup>-</sup>. Besides sensitivity of receptor **1–5** in response of F<sup>-</sup> ions are found as **1** ≈ **2** > **4** > **5** > **3** on the basis of extent of shift in ICT ( $\lambda_{\text{abs}}$ ) and emission ( $\lambda_{\text{em}}$ ) band. Presence of strong withdrawing –NO<sub>2</sub> substituent on triphenylamine of **4** show high sensitivity towards F<sup>-</sup> over **3** having –OCH<sub>3</sub> electron donating group due to easy charge delocalization process aroused by accumulation of negative charge density on the donor site upon interaction with anion. Whereas on comparing the selective sensitivity of sensors towards the detection of F<sup>-</sup> amongst, sensor **1** was found highly sensitive than other receptors revealed from higher log K value. Also it has ability to selectively detect the F<sup>-</sup> even in presence of CN<sup>-</sup> or OH<sup>-</sup> or other anion in same medium, except for BF<sub>4</sub><sup>-</sup> ion due to common ion effect. Moreover, detailed study of colorimetric responses by absorption and emission titration of sensors **1–5** revealing a low limit of detection and high stability constant at lower concentration (10<sup>-6</sup> M) as compared with that of reported imidazoanthraquinone derivatives (~10<sup>-5</sup> M), thereby mark them good chromofluorogenic anion chemosensors even at micro level.

## Supplementary Information (SI)

Other additional information pertaining to photophysical characteristics and ion sensing experiment of sensor **1–5** in DMSO solvent, are given in the Supporting Information.

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## Conflicts of interest

There are no conflicts to declare.

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