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Colorimetric detection of fluoride ion by anthraimidazoledione based sensor in presence of Cu(II) ion†

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Anthraquinone based anion receptors have gained importance due to the colorimetric response on sensing a specific anion and the possibility of tuning this property by varying the conjugated moiety (the donor) to the diamine. In this work, we have synthesized and characterized four anthraimidazoledione compounds having 2,5-dihydroxy benzene, 4-(bis(2-chloroethyl)amino)benzene, imidazole and 4-methylthiazole moieties respectively (**1**-**4**). All of them were probed for their potential as anion sensor to study the effect of change in hydrogen bond donor-acceptor. The *p*-hydroquinone bound anthraimidazoledione (**1**) and thioimidazole bound anthraimidazoledione (**4**) were able to detect both F^- and CN^- in presence of other anions Cl^-, Br^-, I^-, $H_2PO_4^-$, OAc^-, NO_3^- and ClO_4^-. Both **1** and **4** could not differentiate F^- from CN^- and provided similar response to both. ^{1}H NMR studies of **1** and **4** with F^-, showed formation of $[HF_2]^-$ at 16.3 ppm and the ^{19}F NMR showed a sharp peak at -145 ppm in both cases. However, although there may be NMR evidence of $[HF_2]^-$ formation yet the F^- may not be detected colorimetrically if the CT band remains almost unchanged, as found for **3**. The results emphasize that the change of an hetero atom in the donor moiety of an anthraimidazoledione may render large difference in sensitivity. In case of **4** selective detection of F^- was possible in presence of 0.5 equivalent of Cu^{2+} with the exhibition of a distinct green colour with a $\Delta\lambda$ shift of ca. 50 nm in contrast to CN^- which showed orange colouration with a $\Delta\lambda$ shift of only 15 nm. In presence of Cu^{2+} the F^- detection limit was 0.038(5) ppm (below the WHO specified level) at a receptor concentration of 25 μM.

Introduction

Anion sensing has become a popular area of research due to its potential role in various biological processes and in environmental chemistry.[1-6] The well known advantages of a highly sensitive and selective anion sensor has led to a surge in research in this area, especially from the past decade.[7-8] Among various anionic analytes fluoride and cyanide seem to be of potential interest for their established roles in physiology.[9] The benefits of fluoride are well known in the treatments of osteoporosis, orthodontics, enamel demineralisation and as antidepressants.[10] However, excessive intake of fluoride often lead to fluorosis,[11-13] urolithiasis[9, 14] and even cancer.[9, 15] Cyanide the extremely toxic anion for mammals have extensive industrial applications including gold mining, electroplating, metallurgy, paper, textile and plastic industries.[16] The wide ranging use of cyanide may also be a major cause of contamination of various environmental sources spiking the cyanide amount beyond the safe limit. It is well known that cyanide inhibits cellular respiration by strong interaction with cytochrome a_3 of heme unit.[17] A very small amount of cyanide can be lethal to various metabolic functions including cardiac, renal, vascular, respiratory and central nervous systems.[18]

Hence contamination of water sources with cyanide and fluoride is a matter of concern.[19] According to World Health Organisation (WHO) and Environment Protection Agency (EPA) the permissible level of fluoride and cyanide in drinking water should be 1.5 and 0.2 ppm respectively.[20] Therefore, various methods have been developed for the detection of fluoride and cyanide among which colorimetric sensors have gained much importance due to its straight forward 'naked- eye' detection ability allowing it to be an inexpensive detection technique.[2, 21-34]

Three main approaches have been used to develop various anion sensors-

i) Anion binding to the hydrogen bond donor site due to which electronic properties of receptor is altered allowing the subsequent detection of anions.[5, 30, 35-46]
ii) Displacement assay, which involves formation of a complex between an indicator ion and receptor, followed by the displacement of the indicator by guest anions.[47-56] This creates change in the microenvironment of receptor resulting in alteration in colours or fluorescence properties.[5, 56-57]

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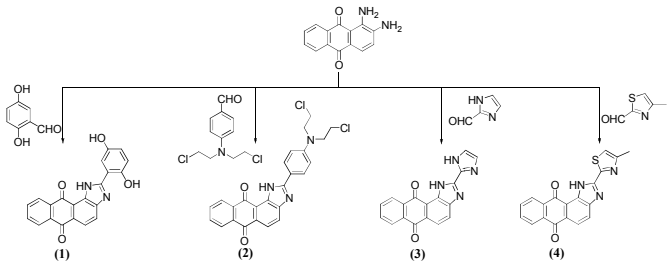
iii) Generation of new species with different properties upon chemical reaction between anionic species and receptor molecule called chemodosimeters.[58-63]

The hydrogen bond donating receptors include a wide range of molecules *viz* ureas,[35, 64-65] thioureas,[44, 66-68] imidazoles/ benzimidazoles,[21, 45, 69-75] amides/diamides,[76-78] indolocarbazoles,[30, 79-80] guanidinium derivatives,[81] azophenol,[31, 82] napthalimides,[83-87] pyrrole[88-89] and callixpyrrole[90-93] etc. The benzimidazole derivatives work via the deprotonation of N-H groups which results in either fluorescence quenching,[45, 94] photoinduced electron transfer (PET)[95-97] or intramolecular charge transfer processes (ICT).[21, 75, 98] The ICT process involves 'push-pull' mechanism between a donor (D) and an acceptor (A) moiety and binding of the negatively charged analyte to the electron deficient acceptor (A) moieties modulate the charge transfer character of D-A system.[21, 99-100] In colorimetric anthraquinone-imidazole based receptors the charge transfer band arises mainly from the $\pi_{imidazole} \rightarrow \pi^*_{anthraquinone}$. The Anthraquinone moieties serve as excellent acceptor due its electron deficient nature and conjugation with different electron rich aromatic donor moieties which help to modulate the charge transfer band that can be exploited for detection.[45, 101-106]

In this work, we varied the donor system with different aromatic systems including 2,5-dihydroxy benzene, 4-(bis(2-chloroethyl)amino)benzene, imidazole and 4-methylthiazole to prepare four compounds with potential as chemosensor (**1**-**4**). Our objective was to study how the variation of the donor type changes the compounds behaviour towards anions of choice viz. fluoride and cyanide. Our endeavour showed that among compound **1**-**4**, compound **1** and **4** detects F^- and CN^- with almost similar efficiency but could not exhibit any difference in recognition between F^- and CN^- separately. However, in presence of Cu^{2+} **4** could distinguish F^- from CN^- and hence compound **4** can act as a receptor for recognition of F^- with a detection limit of 0.038(5) ppm at a receptor concentration of 25 μM.



Scheme 1 Representative synthetic scheme for the preparation of **1**-**4**. Reaction condition applied: ethanol (100 mL), trifluoroacetic acid (catalytic amount), heated to reflux for 16-18 h.

Results and discussion

Syntheses

We have synthesized four anthraimidazoledione derivatives (**1**-**4**) with four different aldehydes as depicted in scheme 1. All the compounds were well characterized by ^{1}H NMR, ^{13}C NMR, CHN, IR as well as ESI-MS. The data obtained confirm the purity of the compounds. All compounds presented here are soluble in DMSO-d_6. The compounds are not soluble in any chlorinated solvent. Their solubility in polar protic solvents is good enough for the electronic spectral studies and anion recognition. All the compounds are insoluble in water.

Anion recognition without Cu^{2+} ion: colorimetry and spectrophotometry

The anion recognition properties of all the synthesized compounds were probed in acetonitrile and DMSO mixture (40:1) with the addition of various anions (F^-, Cl^-, Br^-, I^-, CN^-, NO_3^-, $H_2PO_4^-$, OAc^- and ClO_4^-) as tetrabutylammonium salts. Water was avoided due to poor solubility of the receptors. All of the four compounds exhibit charge transfer band around 409-499 nm (Fig. S1), which may be assigned to the $\pi_{imidazole} \rightarrow \pi^*_{anthraquinone}$ electronic transition.[20-21, 34, 97] Compounds **1** and **4** were found to be sensitive towards F^- and CN^- as per the results of UV-vis spectroscopic studies. However, **2** and **3** did not show any recognition capability in presence of the above mentioned anion using the same receptor concentration as **1** and **4** (i.e. 25 μM) (Fig. S2 and S3, ESI†).

Use of 25 μM of **1** and **4** showed that the ICT bands were red-shifted upon gradual addition of F^- and CN^- in contrast to other anions. Compound **1** have the 2,5-dihydroxy substituted aryl ring as the donor and the anthraquinone as the acceptor. **1** showed positive but similar colorimetric response in presence of either F^- or CN^-. They did not respond to other afore-mentioned common anions probed here (Fig. 1). The colour of the solution turned from yellow to bright orange when F^- and CN^- solutions were added to the solution of **1** (ACN:DMSO = 40:1) (Fig. 1). The charge transfer band at 425 nm showed bathochromic or red shift (Δλ = 59 nm) for both F^- and CN^-.

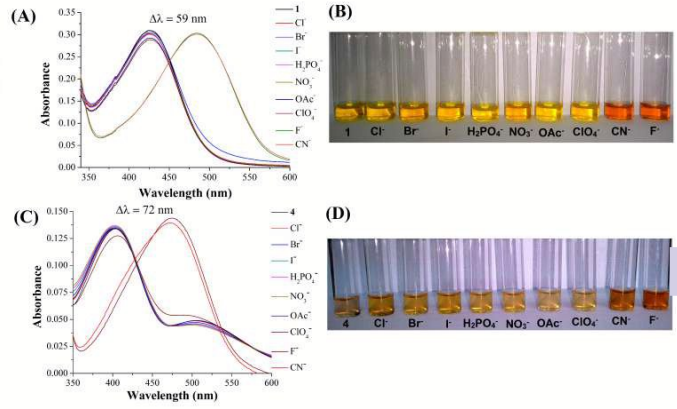


Fig. 1 (A) UV-vis of **1** (25 μM) in acetonitrile (2.5% DMSO) after addition of 6 equivalent anions, (B) colorimetric response of **1** in presence of different anions (6 equivalent), (C) UV-vis of **4** (25 μM) in acetonitrile (2.5% DMSO) after addition of 6 equivalent anions, (D) colorimetric response of **4** in presence of different anions (6 equivalent).

When **4** was used as the sensor the red shift of the band at 400 nm was more for both CN^- ($\Delta\lambda$ = 68 nm) and F^- ($\Delta\lambda$ = 72 nm) compared to **1**. The successive addition of F^- and CN^- ion to **1** showed gradual decrease in the absorption band at 425 nm and increase at 484 nm. The saturation limits were achieved with addition of 1.6 equivalent of F^- and 1.4 equivalents of CN^- ions. The titration curves for F^- and CN^- ions are shown in Fig. 2. Successive addition of F^- or CN^- solution to **4** showed gradual decrease in absorbance in the range of 401-404 nm along with a concomitant increase in the range 472-474 nm (Fig. 3). The saturation limit was achieved much earlier for CN^- (1.28 equiv, 32 μM) compared to F^- (2.48 equiv, 62 μM). The saturation achieved with low excess of the anions suggests that the sensitivity is high towards F^- or CN^-. The presence of isosbestic points, at 450 nm for **1** (Fig. 2) and 430 nm for **4** (Fig. 3), in case of either F^- or CN^-, indicates the presence of two different species at equilibrium. The presence of two different isosbestic point at 350 and 450 nm for **1** and 345 and 430 nm for **4** suggests that the binding stoichiometry may be 1:1. Hence we performed a Jobs plot for receptor **1** and **4** with F^- and CN^- and confirmed that the binding ratio is 1:1 (Fig. 4). The data showed that both **1** and **4** are not able to distinguish between F^- or CN^- and is detecting both of them. The above results signify that both F^- and CN^- are almost equally efficient in forming adduct with the –NH proton in **1** and **4** thereby leading to the deprotonation of –NH and decreasing the energy gap between the $\pi_{imidazole}$ and $\pi^*_{anthraquinone}$ rendering a bathochromic shift.

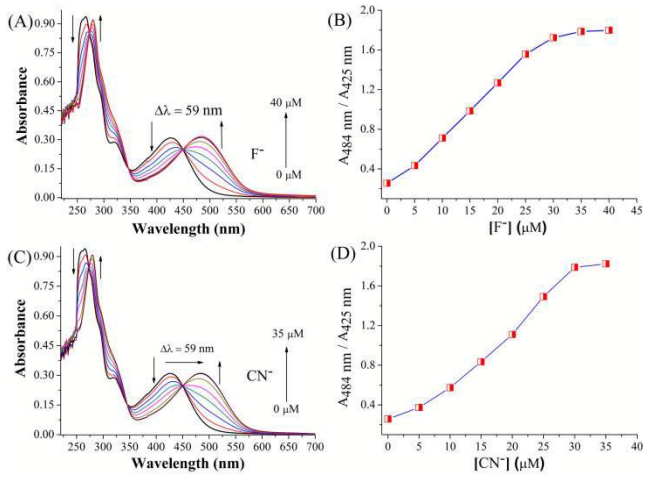


Fig. 2 UV-vis spectroscopic titration of **1** (25 μM) with (A) fluoride (0-40 μM) (B) ratiometric plot with fluoride (C) cyanide (0-35 μM) (D) ratiometric plot with cyanide.

As mentioned earlier **3** where two imidazole rings are present**,** did not show anion recognition in same receptor concentration level as of **1** and **4** (i.e 25 μM) (Fig. S3, S4, ESI†). With addition of upto 6 equivalent of anions (F^- and CN^-) and 2 equivalent of OH^-, **3** hardly shows any red shift of charge transfer band at 500 nm (Fig. S4, ESI†). Similar to **4** the imidazole protons in **3** are supposed to be susceptible to deprotonation and that should influence the CT band and yet we did not see any change in the spectra at concentrations similar to **1** and **4** so we increased the concentration of **3** to

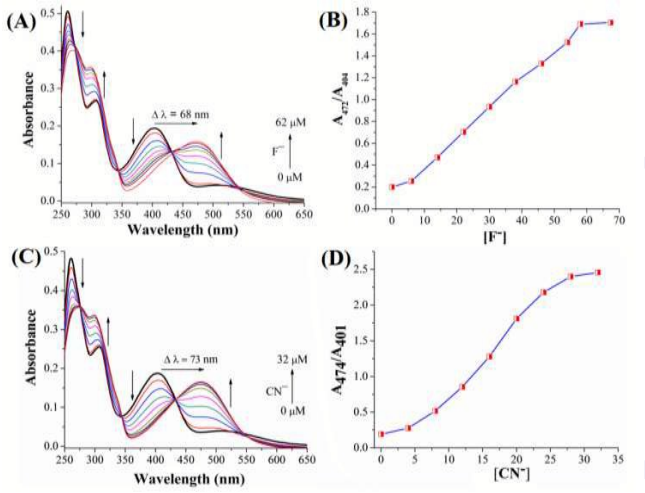


Fig. 3 UV-vis spectroscopic titration of **4** (25 μM) with (A) fluoride (0-62 μM) (B) ratiometric plot with fluoride (C) cyanide (0-32 μM) (D) ratiometric plot with cyanide.

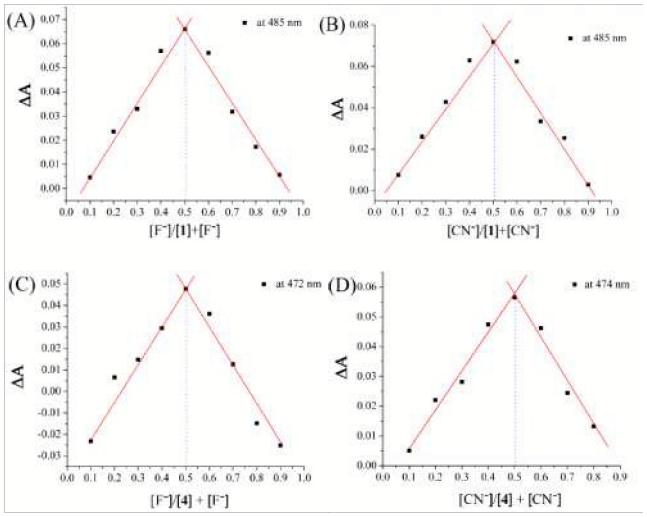


Fig. 4 Job's plot of receptor **1** and **4** where absorbance at 484 nm (for **1**) and at 472-474 nm (for **4**) were plotted as a function of the molar ratio of **1** and **4**. (A) **1** with F^-, (B) **1** with CN^-, (C) **4** with F^- and (D) **4** with CN^-

150 μM and went on adding TBAOH upto 1400 μM. In this case we were able to see a beginning of ca. 150 nm red shift after addition of ca. 7 equivalent OH^- which got saturated at ca. 9 equivalent. However, the colour change did not persist long and within 90 min the spectra goes back to its original position (Fig. S5A, ESI†). The results signify that the deprotonation of the imidazole hydrogen of **3** is difficult compared to **1** and **4** and it also corroborates well since in presence of base the colour change of the CT band takes place but after a while reverts back to original. We probed the behaviour of **3** with F^- and found that it is less sensitive to addition of F^- when compared with **1** and **4** and takes at least 110 equivalent of F^- to achieve a similar 50 nm shift, which is saturated at 230 equivalent of F^- (Fig. S5B, ESI†). The above phenomenon leads to a poor detection limit of F^- by **3** (259mM; 1054 ppm). In case of **2** the presence of the weak electron withdrawing *bis*(2-chloroethylamine) moiety decreases the acidity of the imidazole proton hence the F^- or the CN^- adduct is weaker and

unstable and **2** is not suitable for use as sensor of the probed anions.

The obtained differences in the results based on addition of TBAOH and TBAF/TBACN suggest the use of TBAOH for mechanistic purpose may be useful but the receptors may be much less sensitive to the anions viz. F^- and CN^- compared to the deprotonation by OH^- and hence the predicted mechanism is only an indication of the possible pathway. The binding stoichiometry for the receptors **1** and **4** were evaluated using Job's plot and it was found that they bind in 1:1 ratio as shown in Fig 4.

We calculated the detectable limit of fluoride and cyanide ions from the ratiometric plot of (A_{484nm}/A_{425nm} vs. [anion]).[107] The apparent association constants for anions were calculated from nonlinear regression analysis and the values are tabulated in Table 1. The apparent binding constants for F^- and CN^- are in the range of 10^3 to 10^4 M^{-1} showing relatively weak binding with the anions. The association constants in Table 1 show that without the influence of Cu^{2+}, CN^- has a higher affinity for receptor **1** and **4** signifying that under such conditions CN^- is more efficient in deprotonating the –NH. The UV-vis titrations also show that less CN^- is required to achieve saturation compared to the amount of F^-. The detection limits were calculated in parts per million (ppm) units. The calculations show that the detection limits are lower than the permitted limit set by WHO or EPA for both fluoride (1.5 ppm) and cyanides (0.2 ppm).[20, 108] We achieved lowest detection limit of ca. 0.07(6) ppm for F^- in case of **1** and 0.12(3) ppm for CN^- in case of **4**. However, it should be noted that **1** and **4** could not distinguish CN^- from F^- but we will see later that the presence of Cu^{2+} helps the selective detection of F^-.

Table 1. Apparent binding constants for **1** and **4**.[a]

Receptors	Anions	Δλ (nm)	K_{asso} (M^{-1})	Detection Limit (ppm)
1	F^-	59	$5.63(8) \times 10^3$	0.068(6)
	CN^-	59	$1.27(3) \times 10^4$	0.164(4)
4	F^-	68	$1.17(2) \times 10^4$	0.081(2)
	CN^-	73	$4.9(3) \times 10^4$	0.123(3)

[a]Experiments were carried out in triplicates. The values in parantheses shows standard error.

^{1}H titration experiment

The mechanism of F^- and CN^- detection was further explored through NMR using ^{1}H NMR titration experiments for the receptors **1** and **4** in DMSO-d_6. With the addition of TBAF solution to **1** we observed that the two singlet peak at 12.7 and 11.2 ppm for the two phenolic -OH were vanished signifying quick chemical exchange or possible deprotonation in presence of the anion and the singlet NH peak at 9.2 ppm was also broadened (Fig. 5). The broadening of NH peak suggests that the imidazole hydrogen may be experiencing hydrogen bonding interaction with F^-. After addition of 1.0 equivalent of TBAF the imidazole N-H signal vanished emphasizing that the F^- might have deprotonated the –NH group by interaction with the hydrogen trying to form $[HF_2]^-$ type of species. Indeed after the addition of 2.5 equivalent of F^- one triplet started to appear at ca. 16.3 ppm which is known to be due to the formation of the adduct $[HF_2]^-$ (Fig. 5). This adduct formation was also confirmed by ^{19}F NMR where we observed a sharp peak around -145 ppm for this same adduct formation (Fig. S6).[109] The deprotonation of imidazole -NH develops a negatively charged ring causing the upfield shift of protons of the anthraquinone moiety. Beside the triplet peak at 16.3 ppm for $[HF_2]^-$ adduct, one singlet peak at 14.5 ppm gradually increases at the same time and generation of this singlet peak might be due to the formation of $[N^{\delta-}\cdots H^{\delta+}\cdots O^{\delta-}]$ as shown in Fig. 5 since if it was due to the formation of $[O^{\delta-}\cdots H^{\delta+}\cdots F^{\delta-}]$ then it should have appeared as a doublet instead of the singlet, but we only get a singlet in the spectra (Fig. 5, inset A) which agrees well with similar observations in literature.[110] This peak of $[N^{\delta-}\cdots H^{\delta+}\cdots O^{\delta-}]$ arised due to the hydrogen bonding of an imidazole nitrogen with one of the –OH group of the hydroquinone upon deprotonation of the –NH in the imidazole ring.

Compound **4** also showed the generation of triplet peak for $[HF_2]^-$ at ca. 16.3 ppm with the successive addition of TBAF in the ^{1}H NMR (Fig. S7, inset A, ESI†). The imidazole -NH peak at 7.9 ppm also broadened and ultimately vanished after 1.25 equivalent of F^-. The ^{19}F NMR also confirms the deprotonation since we got sharp peak ca. -145 ppm for the $[HF_2]^-$ adduct formation (Fig. S8, ESI†). The deprotonation phenomenon was further confirmed from the results of the UV-vis experiment of **1** and **4** with the strong base viz. TBAOH. We observe similar red shift of ca. 57 nm and 72 nm respectively (Fig. S9, ESI†) comparable to that obtained for F^- and CN^- using the same receptors.

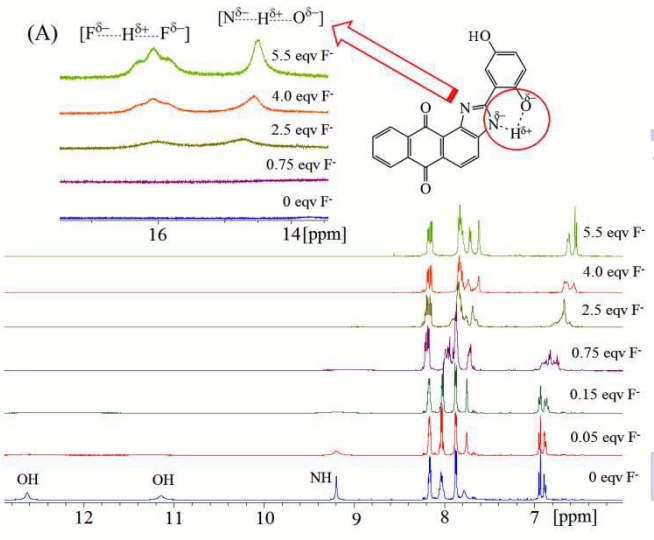


Fig. 5 Partial ^{1}H NMR spectra of **1** (4.96×10^{-2} M) in DMSO-d_6 in presence of TBAF (0-5.5 equivalent). Inset: (A) Expansion of the region 14-17 ppm in presence of 2.5 – 5.5 equivalent TBAF.

To study the effect of cyanide addition ^{1}H NMR titration were performed with **1** and **4** with TBACN. We could observe the -NH and –OH signals vanished upon addition of 0.4 - 1.0 equivalent of TBACN for both **1** and **4** (Fig. S10, S11) and the

same colour change suggests speciation similar to F^- for receptors **1** and **4**. Hence, the electronic spectroscopy studies could not distinguish between the fluoride and cyanide.

We also probed ^1H and ^{19}F titration for **3** using 5.4×10^{-2} M receptor concentration which is close to that taken for NMR studies of **1** and **4** (4.96×10^{-2} M for **1** and 9.9×10^{-2} M for **4**). We found the deprotonation of the imidazole hydrogen and the formation of $[HF_2]^-$ adduct both in ^1H (triplet at c.a 16.1 ppm) and ^{19}F NMR (doublet at -143 ppm) (Fig. S12-S14). However, as mentioned earlier there is no F^- recognition by **3** at concentrations similar to **1** and **4** and even at higher concentrations (1.4×10^{-3} M) at least 110 equivalent excess concentration of F^- is required for recognition (Fig. S5B, ESI†).

In order to achieve recognizable difference in the UV-vis spectra due to change in interaction we used Cu^{2+}. Since Cu^{2+} is known to have stronger interaction with CN^- we thought that this will help us based on the numerous literatures available with Cu^{2+} enabling cyanide sensing in presence of ligand.[56, 111-114] When we probed, we found that instead of cyanide the F^- sensing improved in presence of Cu^{2+} as discussed in the next section.

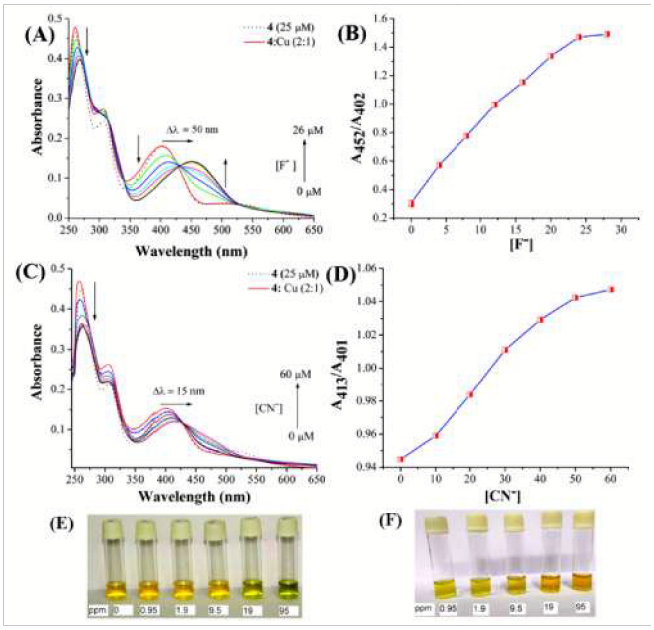


Fig. 6 UV-vis spectroscopic titration of **4** (25 μM) with (A) fluoride (0-26 μM) (B) ratiometric plot with fluoride (C) cyanide (0-60 μM) (D) ratiometric plot with cyanide. (E) colorimetric response of **4** (25 μM) in presence Cu^{2+} (12.5 μM) with the addition og different concentration of fluoride solution. (F) visual colorimetric response of **4** (25 μM) in presence Cu^{2+} (12.5 μM) with the addition of different concentration of cyanide solution. (Fluoride and cyanide solution: 0.95, 1.9, 9.5, 19 and 95 ppm)

In presence of Cu^{2+} ion

The spectral pattern of the CT band in **4** in presence of Cu^{2+} showed distinct effect and we could achieve specific recognition of F^-. The successive addition of F^- and CN^- ion to **4** in presence of 0.5 equivalent of Cu^{2+} is displayed in Fig. 6. We have added upto 60 μM (2.4 equivalent) of CN^- to get only 15 nm red shift. We did not find the 15 nm shift in presence of CN^- to be enough for a good detection so we did not attempt studies on detection of cyanide with **4**. The change in Δλ for F^- showed a difference of 50 nm compared to that of ca. 15 nm for CN^- (Fig. 6 and Fig. S15, ESI†). On addition of approx. half equivalent of Cu^{2+} with respect to the sensor **4**, the yellow solution turns to orange for all the anions probed except for F^-. Addition of upto ca. 5.6 equivalent of Cu^{2+} alone did not render any considerable change in the CT band (λ_{max} = 400 nm) (Fig. S16A, ESI†). However, in presence of only 0.5 equivalent Cu^{2+} **4** could sense F^- specifically as the CT band shifts by 50 nm.

In order to probe if deprotonation is one of the causes for recognition even in presence of Cu^{2+}, we carried out UV-vis titration with up to ca. 1.2 equivalent TBAOH instead of 1 equivalent F^-. A similar 51 nm red shift was observed. The above data suggests that the deprotonation phenomenon is also acting in presence of Cu^{2+} ion (Figure S16B, ESI†). JOB's plot for F^- sensing for **4** in presence of Cu^{2+} also indicates 1:1 ratio (Fig. S17, ESI†). Comparatively **1** hardly showed any significant change usable for detection purpose by shift in charge transfer band on addition of the other afore-mentioned anions in presence of Cu^{2+} (Fig. S18 and S19, ESI†).

We found that with successive addition of F^- to **4** in presence of Cu^{2+} a gradual decrease in the absorption band at 401 nm was observed with a concomitant increase at 451 nm. The saturation limits were achieved with addition of just 1 equivalent of F^-. Apparent association constant of **4** for F^- and CN^- in presence of Cu^{2+} was found to be $1.37(2) \times 10^5$ M^{-1} and the detection limit was achieved to be 0.038(5) ppm in case of F^- (Table 2).

Table 2. Apparent binding constants for **4** in presence of Cu^{2+}.[a]

Receptor	Anions	Δλ (nm)	K_{asso} (M^{-1})	Detection Limit (ppm)
4	F^-	50	$1.37(2) \times 10^5$	0.038(5)
	CN^-	15	$1.19(4) \times 10^4$	0.237(3)

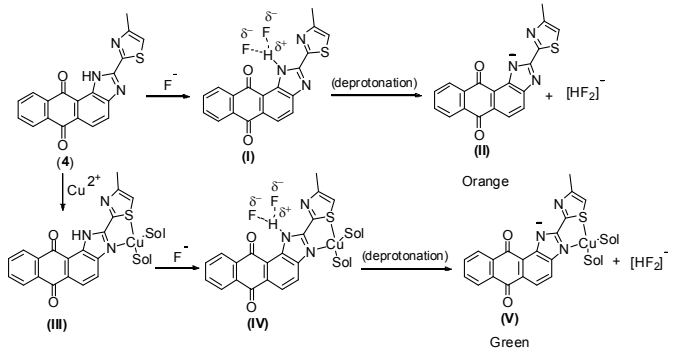
[a]Experiments were carried out in triplicates. The values in parantheses shows standard error.

Compound **1** - **4** have anthraquinone in common but the pendant moieties attached to the imidazole ring fused with anthraquinone are different. We found that **2** and **3** does not exhibit distinct recognition for any of the probed anions but **1** and **4** recognizes F^- and CN^-. In case of **1** the proton of the imidazole moiety, is released in presence of F^- and CN^- which renders a spectral change leading to the recognition of the fluoride or cyanide. Since both F^- and CN^- are equally efficient in interacting with the proton of the imidazole hence they cannot be distinguished from each other by **1**.

The titration experiments of **1**-**4** with OH^- shows that **4** is the easiest one to deprotonate as seen from the UV spectral changes (Fig. S20D, ESI†) followed by **1** (Fig. S20A, ESI†) which is also pretty similar in terms of stoichiometry needed to observe the change in CT band which may be assigned to the deprotonation of the benzimidazole nitrogen. Compound **2** and **3** however require higher stoichiometries of OH^- to observe the bathochromic shift of the CT band as seen in Fig.

S20B & S20C, (ESI†). Receptor **2** requires at least 9 molar equivalent of OH^- to initiate the prominent spectral change of the CT band and **3** requires at least 7 molar equivalent of OH^- for the same (Fig. S20B, S20C, ESI†). In contrast for **1** and **4** the saturation for the shift in Charge transfer band is achieved within 1.0 molar equivalent of OH^-. The above results signify that the benzimidazole –NH has low acidity in **2** and **3** compared to **1** and **4.** Hence, **2** and **3** are not useful as sensors to recognize any of the probed anions including F^- and CN^-.

The NMR studies showed that HF_2^- is formed in **3** similar to that reported in literature and found by us for **1** and **4**. However, the NMR studies are done in greater concentrations and prominent changes are observed with higher equivalent of F^- compared to the UV-vis studies. Hence, formation of HF_2^- should not be considered as a sufficient indication. Hence the visible colour change to the CT band, rendered by the interaction of the anion to the receptor is necessary for the recognition which is also dependent on the acidity of the –NH proton. The presence of the sulphur atom in **4** is clearly advantageous to render the colour change of the CT band upon interaction of the F^- with **4** since it helps the recognition with Cu^{2+}. The presence of Cu^{2+} should lead interaction between the receptor and the Cu^{2+} although we did not observe any colour change upon addition of Cu^{2+} to the receptor **1** or **4** (Fig. 6 and Fig. S12, ESI†) but in presence of F^- and Cu^{2+} in case of **4** the change becomes significant which is in contrast to other anions including CN^-.



Scheme 2. Mechanistic proposal of fluoride sensing by **4** in absence and in presence of Cu^{2+}.

In most cases the probable species formed which renders the colour is not commented upon since it is understood that the uncertainties are high. However, based on the evidences obtained we propose a plausible speciation for the F^- detection by **4** (Scheme 2). We strongly feel that prediction may help gain better insight and prediction of more accurate speciation in future. The above speciation is based on the following- (i) We have seen that in presence of TBAOH and in presence of F^- the colour change is the same using similar concentrations of the anions. Hence, deprotonation may be occurring in both cases leading to the formation of HF_2^- which supports that species (**II**) may be forming in solution rendering the colouration. (ii) The position of HF_2^- is almost same in both the cases of **1** and **4** suggesting that they may not be influenced by other atoms of **1** and **4** i.e. the formed HF_2^- may be independent species which renders the anion of the receptor and helps recognition supporting formation of **II** (scheme 2). (iii) In presence of Cu^{2+} added to the solution of **1** or **4** we do not see much shift in the native CT-band but when F^- is added to **4** there is a similar shift as that observed in presence of TBAOH and Cu^{2+}. Hence here (**V**) may be the species forming in solution rendering the colouration. The small shift of 15 nm for the CT band in case of addition of CN^- in presence of Cu^{2+} show that the interaction of CN^- in presence of Cu^{2+} in **4** is weaker than F^- which is supported by the obtained association constant (Table 2). Based on the results, **4** is not suitable for CN^- recognition.

The structural difference of receptor **1** renders a different speciation in presence of Cu^{2+}, which does not increase the acidity of the –NH proton of the benzimidazole sufficient enough such that it may be deprotonated by F^- or CN^-. However, due to the stronger deprotonation ability of TBAOH the CT band of **1** shows a shift (Fig. S16, S19, ESI†) similar to that in case of **4** (in presence of F^- and Cu^{2+}). The data also shows that higher concentration of OH^- is required in **1** to observe changes in the CT band similar to **4** suggesting that the F^- may not be able to form the anion of **1** diminishing its recognition capability.

Our preliminary computational studies by DFT level of theory with B3LYP function and 6-31G(d) basis set showed that the charge transfer bands are indeed from $\pi_{imidazole} \rightarrow \pi^*_{anthraquinone}$ (Fig. S21 and Table S1, ESI†) as assigned earlier in literature[20-21, 34, 97] and the bathochromic shift in the CT band upon recognition of F^- and CN^- is due to deprotonation of the benzimidazole –NH, as found from the TDDFT calculations of the deprotonated optimized structure of **1** and **4** (Fig. S22, ESI†).

Experimental

Materials and methods

All chemicals and solvents were purchased from commercial sources. 1,2-diamnioanthraquinone and other reagents were purchased from Sigma-Aldrich and Spectrochem. Solvents are of spectroscopic and GC grade and purchased from Merck. Melting points for the compounds were measured in a SECOR India melting point apparatus and the uncorrected values are reported. UV-visible measurements were done using Perkin Elmer lambda 35 spectrophotometer. FT-IR spectra were recorded using Perkin-Elmer SPECTRUM RX I spectrometer in KBr pellets. ^1H & proton decoupled ^{13}C NMR spectra were measured using either JEOL ECS 400MHz or Bruker Avance III 500MHz spectrometer at room temperature and the chemical shifts are reported in parts per million (ppm). Elemental analyses were performed on a Perkin-Elmer 2400 series II CHNS/O series. ESI-MS spectra were recorded using micromass Q-Tof micro™ (Waters) in ESI +ve mode electrospray ionization. The isolated yields were reported for analytically pure compounds.

Syntheses and characterization

General synthetic method to prepare anthraimidazolediones

1,2-diaminoanthraquinone (1.0 mmol) and different aldehydes (1.0 mmol) were suspended in 60 mL ethanol. Catalytic amount of trifluoroacetic acid were added to the reaction mixture and heated to reflux for 16 h.[20-21, 94] After completion of the reaction, the reaction mixtures were cooled down to room temperature followed by addition of diethyl ether which led to precipitation of the desired compounds. The precipitations were collected by filtration and washed several times with diethyl ether. Finally the precipitations were collected after drying over P_2O_5.

2-(2,5-dihydroxyphenyl)-1H-anthra[1,2-*d*]imidazole-6,11-dione (1). Dark red solid; Yield 76%; m.p. 235-245°C (dec). Anal. Calc. for $C_{21}H_{12}N_2O_4$: C, 70.78; H, 3.39; N, 7.86%. Found C, 70.13; H, 3.33; N, 7.91%. ^{1}H-NMR (500 MHz, DMSO-d_6) δ 12.66 (s, 1H, OH), 11.17 (s, 1H, OH), 9.21 (s, 1H, NH), 8.19 (m, 2H, ArH), 8.08 (m, 2H, ArH), 7.89 (d, 2H, J = 3 Hz, ArH), 7.88 (d, 1H, J = 3 Hz, ArH), 6.96 (dd, 1H, J = 5 Hz, ArH), 6.88 (m, 1H, ArH) (Fig. S37, ESI†) ^{13}C-NMR (125 MHz, DMSO-d_6) δ 183.8 (CO), 182.1 (CO) 156.0 (ArC), 150.3 (ArC), 149.5 (ArC), 147.9 (ArC), 134.5 (ArC), 134.2 (ArC), 133.3 (ArC), 132.9 (ArC), 131.8 (ArC), 129.8 (ArC), 127.5 (ArC), 126.8 (ArC), 126.3 (ArC), 124.4 (ArC), 123.3 (ArC), 121.1 (ArC), 120.5 (ArC), 117.9 (ArC), 113.9 (ArC) (Fig. S38, ESI†); UV-vis λ_{max} /nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_3CN-DMSO (50:1) 266 (44068), 319 (13530), 424 (12692). IR (KBr, cm^{-1}) 3391 (s), 2358 (s), 1668 (s), 1495 (s), 1330 (s), 1294 (s), 1261 (s), 1218 (m), 717 (s); ESI-MS (CH_3OH), m/z (calc.): 379.21(379.07) $[M+Na]^+$.

2-(4-(bis(2-chloroethyl)amino)phenyl)-1H-anthra[1,2-*d*]imidazole-6,11-dione (2). Red solid; Yield 68%; mp. 260-265°C (dec). Anal. Calc. for $C_{25}H_{19}N_3O_2Cl_2$: C, 64.66; H, 4.12; N, 9.05%. Found C, 64.79; H, 4.15; N, 9.12%. ^{1}H-NMR (500 MHz, DMSO-d_6) δ 12.71 (s, 1H NH), 8.27 (m, 2H, ArH), 8.19 (m, 2H, ArH), 8.01 (m, 2H, ArH), 7.91 (m, 2H, ArH), 6.91 (d, J = 8.5 Hz, 2H, ArH), 3.84 (m, 8H, $C\underline{H}_2C\underline{H}_2Cl$) (Fig. S39, ESI†); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 183.2 (CO), 182.1 (CO), 158.2 (ArC), 149.9 (ArC), 148.7 (ArC), 134.3 (ArC), 134.1 (ArC), 133.2 (ArC), 133.1 (ArC), 132.9 (ArC), 129.8 (ArC), 129.7 (ArC), 127.0 (ArC), 126.7 (ArC), 126.1 (ArC), 123.8 (ArC), 123.3 (ArC), 120.9 (ArC), 117.8 (ArC), 116.8 (ArC), 111.5 (ArC), 51.8 (CH_2Cl), 41.1 ($\underline{C}H_2CH_2Cl$) (Fig. S40, ESI†); UV-vis λ_{max} /nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_3CN-DMSO (50:1) 266 (34550), 315 (29520), 462 (20190); IR (KBr, cm^{-1}) 3444 (s), 2922 (w), 1660 (s), 1607 (s), 1489 (s), 1326 (s), 1294 (s), 1184 (m), 1008 (w), 719 (s); ESI-MS (CH_3OH), m/z (calc.): 464.33 (464.09) $[M+H]^+$.

2-(1H-imidazol-2-yl)-1H-anthra[1,2-*d*]imidazole-6,11-dione (3). Dark brown solid; Yield 75%; mp. 221-229°C (dec). Anal. Calc. for $C_{18}H_{10}N_4O_2$: C, 68.79; H, 3.21; N, 17.83%. Found C, 68.88; H, 3.24; N, 17.91%. ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.20 (m, 1H, ArH), 8.11 (m, 1H, ArH), 7.95 (br s, 2H, NH), 7.82 (m, 2H, ArH), 7.48 (d, J = 8 Hz, 1H, ArH), 6.79 (d, J = 8 Hz, 1H, ArH), 6.34 (s, 2H, ArH) (Fig. S41, ESI†); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 184.6 (ArC), 180.2 (ArC), 143.6 (ArC), 139.8 (ArC), 134.5 (ArC), 133.6 (ArC), 131.1 (ArC), 126.2 (ArC), 125.9 (ArC), 121.2 (ArC), 120.3 (ArC), 114.1 (ArC), 111.2 (ArC) (Fig. S42, ESI†) ; UV-vis λ_{max} /nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_3CN-DMSO (50:1) 260 (36575), 499 (7574). IR (KBr, cm^{-1}) 3416 (s), 3368 (s), 1667 (s), 1624 (s), 1588 (s), 1531 (s), 1441 (s), 1329 (s), 1301 (s), 1165 (w), 840 (m), 715 (s); ESI-MS (CH_3OH), m/z (calc.): 315.56 (315.09) $[M+H]^+$.

2-(4-methylthiazol-2-yl)-1H-anthra[1,2-*d*]imidazole-6,11-dione (4). Blackish brown solid; Yield 62%; mp. 270-275°C (dec). Anal. Calc. for $C_{19}H_{11}N_3O_2S$: C, 66.07; H, 3.21; N, 12.17%. Found C, 66.35; H, 3.28; N, 12.11%. IR (KBr, cm^{-1}) ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.20 (d, J = 7 Hz, 1H, ArH), 8.10 (d, J = 7 Hz, 1H, ArH), 7.93 (br s, 1H, NH), 7.81 (t, J = 6.5 Hz 2H, ArH), 7.48 (d, J = 8.5 Hz, 1H, ArH), 6.79 (d, J = 9 Hz, 1H, ArH), 6.33 (br s, 1H, ArH), CH_3 protons obscure in DMSO-d_6 (Fig. S43, ESI†); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 184.5 (ArC), 180.1 (ArC), 143.5 (ArC), 139.7 (ArC), 134.5 (ArC), 133.6 (ArC), 131.2 (ArC), 126.2 (ArC), 126.0 (ArC), 121.5 (ArC), 120.2 (ArC), 114.1 (ArC), 111.7 (ArC) (Fig. S44, ESI†); UV-vis λ_{max} /nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_3CN-DMSO (50:1) 260 (22400), 406 (5600), 504 (3100). IR (KBr, cm^{-1}) 3433 (s), 2373 (s), 1665 (s), 1583 (s), 1328 (s), 1293 (s), 1216 (s), 1048 (w), 1005 (m), 714 (s); ESI-MS (CH_3OH), m/z (calc.): 346.17(346.06) $[M+H]^+$.

UV-vis titration of 1 and 4 with F^- and CN^-

20 µL of DMSO solution of **1** and **4** (10^{-2} M) were added in 800 µL acetonitrile solution to make final concentration 25 µM. Acetonitrile solution of tetrabutylammonium fluoride (TBAF) and tetrabutylammonium cyanide (TBACN) (10^{-3} µM) were added to the solution of **1** and **4** successively. After 2 minutes the UV-vis spectral data has been recorded in room temperature.

Determination of binding ratio (Jobs' plot)

1 and **4** and were prepared in DMSO mixture (40:1) to achieve 10^{-2} µM concentration. Likewise TBAF and TBACN solution were prepared in the same concentration (10^{-2} µM) in acetonitrile. Nine sets of sample solution containing receptor **1** and **4** with F^- and CN^- were prepared in vials varying the mole fraction of **1** or **4** from 0.1 to 0.9. Thus different volume of receptor (**1** or **4**) and analyte solution (TBAF or TBACN) were added to vary the mole fraction from 0.1 to 0.9 keeping the total volume same in each case. After shaking the vials for a few minutes, the UV-vis spectra were recorded. The Job's plots were obtained by plotting ΔA *vs*. mole fraction of **1** or **4**.

^{1}H and ^{19}F NMR titrations

Receptor **1** (10.6 mg, 0.01 mmol) was dissolved in DMSO-d_6 (600 µL) and TBAF (1 M) in DMSO-d_6 was added into the solution of receptor **1**. After shaking them for a minute, ^{1}H NMR spectra were obtained at room temperature. For compound **3** and **4** same methods were followed.

Conclusions

The results emphasize that in detection of F^- and CN^- using anthraimidazolediones the deprotonation of the benzimidazole –NH in presence of the anion renders the recognition due to the shift of the CT band. We have seen that variation of the donor arm regulates the deprotonation and hence the recognition ability. When the donor arm has thioimidazole or p-hydroquinone it was possible to detect F^-

and CN^-. However, selectivity for F^- increased in presence of Cu^{2+} due to its coordinating ability to the receptor and the influence on the deprotonation of the benzimidazole -NH. The detection limit of 0.038 ppm and selectivity for F^- in case of **4** is encouraging. The results signify that although the NMR studies reveal the formation of HF_2^- in the case of **1**, **3** and **4** yet **3** cannot recognize F^- at concentrations similar to **1** and **4**. The UV-vis spectral studies with OH^- to probe the acidity of the benzimidazole –NH shows that benzimidazole –NH is most acidic in **4** followed by **1** and relatively much less acidic in **2** and **3**. It should be noted that formation of HF_2^- may be a good evidence to predict the mechanism but does not necessarily comment on the recognition sensitivity. The presence of sulphur in the heterocyclic ring influences the anion recognition property in a positive fashion at lower concentrations. In fact when we compare the activity of **4** with the rest in the series we also see that the presence of S in the heterocycle helps distinct recognition of F^- from CN^- in presence of Cu^{2+}.

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Table of contents graphic

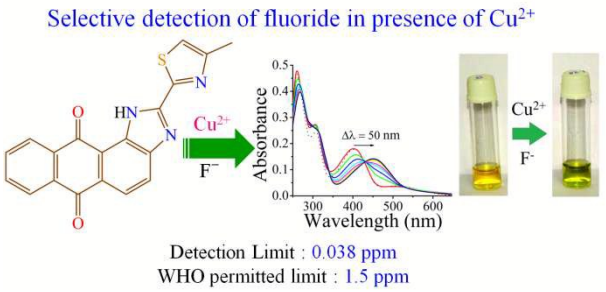

Table of contents abstract:

A thioimidazole bearing anthraimidazoledione detects fluoride selectively in presence of Cu^{2+} with a detection limit of 0.04 ppm. Results show change of thioimidazole to imidazole leads to no detection.