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Chromofluorescent Probes for Selective Detection of Fluoride and Acetate Ions

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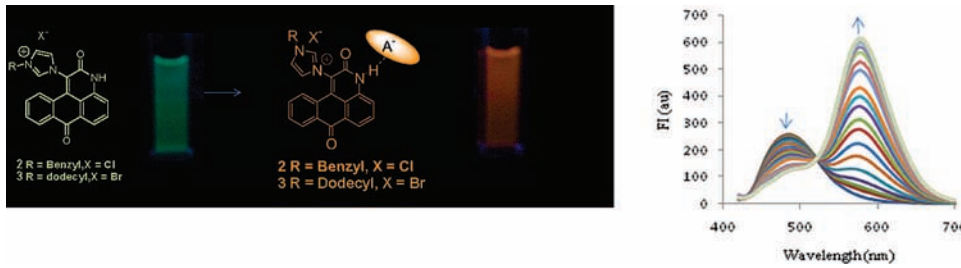
ABSTRACT



Chromofluorescent probe 2 has been developed for selective and ratiometric estimation of F^- (CH_3CN) ions. The presence of a lipophilic dodecyl appendage at imidazolium nitrogen in 3 successfully allows the selective determination of AcO^- ions in protic ($CHCl_3$−MeOH, 1:1) solvent.

The development of artificial optical receptors for selective anion recognition has attained significant interest, as anions play a fundamental role in a wide range of chemical and biological processes.[1] Recently, considerable efforts have been made to develop colorimetric[2] and fluorescent[3] molecular probes for the recognition of anions. The colorimetric probes have been attracted for their "naked eye" detection of target species and offer qualitative and quantitative information using inexpensive equipment.[4] The emission-based chemosensors are particularly attractive as fluorimetric techniques, in general exhibit a high degree of specificity (via choice of excitation and emission wavelengths), and enable access to a wealth of information (e.g., spectral and intensity changes, fluorescence lifetime, etc.) in a rather straightforward manner and fast measurement protocols. Especially, the probes with visible region excitation and emission have attained significance for their reduced scattering and low background emissions. However, only scarce examples of metal ion probes with red emission have been reported,[5] and to the best of our knowledge, anion probes with red emission are not known.

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In molecular probes, the binding affinity and thus the selectivity between an anion and the host is attributed to hydrogen bonding and/or electrostatic interactions and is also significantly affected by the topology of the ligating sites,[6] viz.,

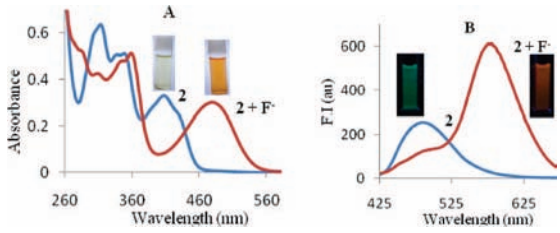


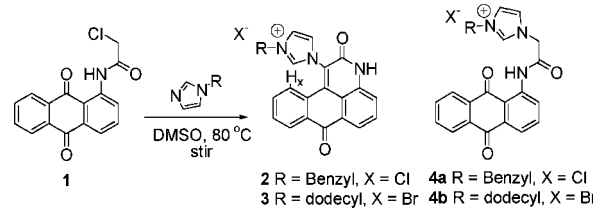
Figure 1. (A) UV−vis spectra of **2** (50 μM) in CH_3CN−DMSO (20:1) and **2** + F^- (100 μM). (B) Fluorescence spectra of **2** (10 μM) and **2** + F^- (20 μM). The inset shows the color changes on addition of fluoride ions under (A) visible light and (B) irradiation of UV light. See Figure S10 in Supporting Information for **3**.

that of the anion (size and spherical, trigonal, or tetrahedral geometries). In contrast to ammonium and guanidinium[7] based anion probes, quaternary ammonium,[8,12c] imidazolium,[9] benzimidazolium,[10] pyridinium,[11] etc. salts based anion probes remain unaffected by the pH of the medium and so can find applicability under physiological conditions.

Our work aims[12] at the design and synthesis of molecular probes with colorimetric and fluorimetric assays to selectively detect the presence of a target anion over the wide range of other interfering anions. Here, we have developed new *N*-aryl imidazolium based probes **2** and **3**, which enable naked eye and dual channel (absorption and fluorescence) detection of F^- and AcO^- ions, respectively. Significantly, in these probes, the appearance of absorption and emission maxima due to free probe (λ_{abs} 405 nm, $\varepsilon = 6600\ M^{-1}\ cm^{-1}$; λ_{em} 475 nm; $\varphi = 0.11$) and their complexes with the anion (λ_{abs} = 480 nm, $\varepsilon = 6000\ M^{-1}\ cm^{-1}$; λ_{em} = 580 nm, φ = 0.38) at different wavelengths has enabled elaboration of ratiometric approach (Figure 1). The probes **2** and **3** constitute the first examples where *N*-arylimidazoilium[9] salts have found application as anion sensors.

1-(Chloroacetylamido)-anthracene-9,10-dione (**1**)[13] on heating with 1-benzylimidazole and 1-dodecylimidazole in DMSO for 4−5 h gave respective chemosensors **2** (80%, mp > 300 °C, M^+ *m*/*z* 404) and **3** (78%, mp > 300 °C, M^+ *m*/*z* 482 for cation); for spectral data see Figures S1−S8 in Supporting Information. Evidently, the initially formed imidazolium salts **4a** and **4b** undergo intramolecular condensation at the anthraquinone carbonyl group to form respective compounds **2** and **3**. The appearance of upfield 1H doublet at δ 6.68 in **2** and at δ 6.58 in **3** demonstrates that the H_x proton (Scheme 1) faces

Scheme 1. Synthesis of Chemosensor **2** and **3**



the ring currents of imidazolium ring. The proximity of this CH with imidazolium ring has been ascertained by X-ray crystal structure of PF_6 salt of **2** (Figure S9, Supporting Information).

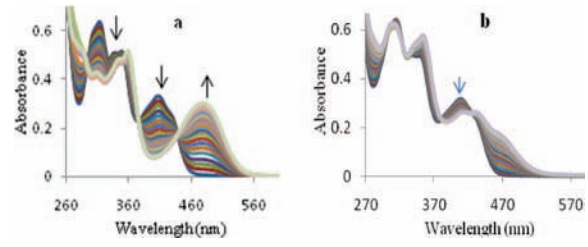


Figure 2. (a) Effect of incremental addition of fluoride ions on the UV−vis spectrum of **2** (50 μM) in CH_3CN−DMSO (20:1). (b) Effect of incremental addition of acetate ions on the UV−vis spectrum of **3** (50 μM) in $CHCl_3$−MeOH(1:1).

The chemosensor **2** (50 μM, CH_3CN−DMSO (20:1)) exhibited absorption bands at λ_{max} 308 nm (ε 8200) and 405 nm

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(ε 6600). On addition of tetrabutylammonium fluoride (TBA F) (100 μM) to a solution of **2**, the color of the solution changed from light yellow to orange. The addition of acetate (100 equiv) and dihydrogen phosphate (500 equiv) to the chemosensor **2** showed significantly smaller changes than that observed for 2 equiv of F^- anion (Figure S11, Supporting Information). The other anions, e.g., Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, CN^-, and ClO_4^-, caused no significant change in the absorption spectrum of **2**.

On gradual addition of TBAF to a solution of **2** (50 μM, $CH_3CN-DMSO$ (20:1), the absorbance at 405 nm underwent gradual decrease in its intensity with concomitant increase at 480 nm with isobestic point at 440 nm (Figure 2a). This red shift by 75 nm points to the significant stabilization of the intramolecular charge transfer the excited state achieved through interaction of **2** with fluoride anions. On addition of water, the reversal in spectral changes indicated both the reversibility of the process and poor complexation of **2** with F^- ion. Evidently, the solvation of fluoride ions in protic solvent decreased its binding with chemosensor **2**.

The addition of tetrabutylammonium hydroxide (TBA OH) to the solution of chemosensor **2** gave the similar change in its UV−vis spectrum (Figure S12, Supporting Information) as that observed with the TBAF and points to the fluoride ion induced deprotonation[14] of amide NH responsible for the spectral and visible color changes.

The plot of absorbance of **2** at 308 and 480 nm against concentration of fluoride ions shows a straight line that attains a plateau after addition of 100 μM (2 equiv) of fluoride ions.

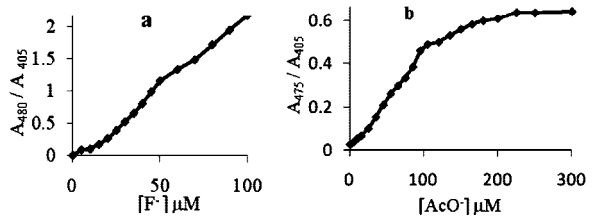

Figure 3. (a) Absorbance ratiometric (50 μM) responses (A_{480}/A_{405}) of chemosensor **2** and (b) **3** (A_{475}/A_{405}) upon incremental addition of fluoride and acetate ions respectively.

The spectral fitting (Figure S13, Supporting Information) of these absorbance data shows the formation of 1:1 and 1:2 (**2**:F) stoichiometric complexes [$\log \beta_{LF2} = 8.45 \pm 0.34$ and $\log \beta_{LF} = 5.19 \pm 0.12$].

The chemosensor **3** (50 μM, CH_3CN) on addition of fluoride and acetate ions gave similar UV−vis changes as observed in the case of **2** with only fluoride ions. The spectral information obtained from titration of **3** with fluoride and acetate ions (Figures S14 −S17, Supporting Information) on nonlinear regression analysis using specfit 32 gave complexation constants[15] $\log \beta_{LF} = 6.2 \pm 0.3$, $\log \beta_{LF2} = 12.0 \pm 0.4$; $\log \beta_{L2AcO} = 11.4 \pm 0.2$, $\log \beta_{LAcO} = 5.7 \pm 0.1$; $\log \beta_{LAcO2} = 10.7 \pm 0.2$. This shows that among 1:1 complexes of **3** with F^- and AcO^- ions, the F^- ions are associated only five times better than AcO^- ions. Also, probe **3** exhibits nearly 10 times stronger association with F^- ions than that observed for probe **2**. Therefore, the presence of the lipophilic dodecyl appendage in **3** increases its binding capacity toward F^- and AcO^- anions.

To evaluate the role of the dodecyl chain in **3** on its association with anions in the presence of protic solvents,[16] we studied the effect of different amounts of MeOH on spectra of **3**-F^- and **3**-AcO^- complexes in chloroform. We have found that a $CHCl_3-MeOH$ (1:1) solution of **3** does not show any spectral or color change on addition of F^- ions, but on addition of AcO^- ions, a new absorption band at 475 nm is observed that is hypsochromically shifted by only 10 nm in comparison to that observed in pure $CHCl_3$. On gradual addition of TBA OAc to a solution of **3** (50 μM, $CHCl_3-MeOH$; 1:1), the absorbance at 405 nm underwent gradual decrease in its intensity with concomitant increase at 475 nm, and the spectral fitting of these absorbance data (Figure 2b, Figure S18, Supporting Information) revealed the formation of 1:1, 1:2, and 1:3 (**3**:AcO^-) stoichiometric complexes with stability constants $\log \beta_{LAcO} = 5.15 \pm 0.2$, $\log \beta_{LAcO2} = 10.6 \pm 0.2$, and $\log \beta_{LAcO3} = 14.4 \pm 0.2$. Therefore, **3** can be used as a probe for selective estimation of AcO^- ions. Probably, due to greater solvation of fluoride ions in protic solvent, the association of F^- ions is completely inhibited, but AcO^- ion shows reasonable complexation with **3**.

The "OFF−ON" switching behavior on addition of F^- ions to a solution of **2** at 405 and 480 nm and on addition of acetate ions to **3** provides dual absorption channel for elaborating a ratiometric approach[17] that permits signal rationing and allows the estimation of analyte independent of the concentration of the receptor (Figure 3a). Chemosensor **2** (CH_3CN) can be used for estimation of fluoride ions between 5 and 100 μM, and chemosensor **3** ($CH_3CN-MeOH$, 1:1) for the estimation of acetate ions between 2 and 200 μM (Figure 3b).

Chemosensor **2** (10 μM, $CH_3CN-DMSO$ (20:1)) on excitation at 410 nm exhibited an emission band at λ_{em} 480 nm. The addition of Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, HSO_4^-, $H_2PO_4^-$, and ClO_4^- anions (0.01 M) to a solution of **2** caused insignificant changes in its fluorescence spectrum. Interestingly, on addition of fluoride ions (20 μM), the fluorescence intensity at 480 nm (green emission) was turned off and simultaneously a new red-shifted fluorescence emission band at 580 nm appeared ($\Delta\lambda_{max}$ 100 nm) (Figure 4a). The color of this solution under UV−vis radiation appears red due to the 580 nm emission band. The nonlinear regression analysis of the spectral data obtained on titration of solution of **2** with fluoride ions shows the formation of 2:1, 1:1, and 1:2 (**2**:F)

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(15) As receptors **2** and **3** on addition of anions undergo deprotonation, it is not a strict binding phenomenon and so the log β values need to be taken with caution.

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stoichiometric complexes [log $\beta_{L2F} = 11.5 \pm 0.4$, log $\beta_{LF} = 6.22 \pm 0.24$, and log $\beta_{LF2} = 11.37 \pm 0.32$].

The chemosensor **3** (10 μM, CH_3CN) upon excitation at 410 nm gave similar emission changes on addition of fluoride and acetate ions (40 μM) (Figures S19 and S20, Supporting Information) as observed in the case of **2** with only fluoride ions. On

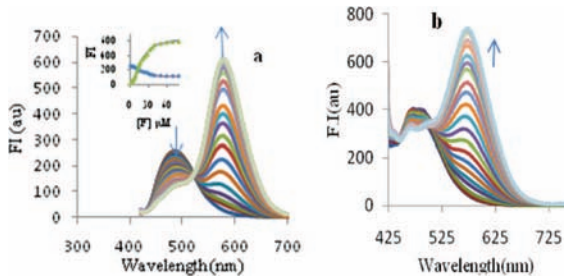

Figure 4. (a) Effect of incremental addition of fluoride ions on the fluorescence spectrum of **2** (10 μM) in CH_3CN. Inset shows plot of fluorescence intensity versus [F^-] (points show the experimental results and line is curve fit). (b) Effect of incremental addition of acetate ions on fluorescence spectrum of **3** (10 μM) in $CHCl_3$−MeOH (1:1).

shifting from aprotic (CH_3CN) to protic solvent $CHCl_3$−MeOH (1:1), the chemosensor **3** selectively showed red emission with AcO^- ions only. On addition of acetate ions the fluorescence intensity at 480 nm (green emission) was turned off and simultaneously a new red-shifted fluorescence emission band at 580 nm appeared ($\Delta\lambda_{max}$ 100 nm) (Figure 4b). The additon of F^- and other anions did not cause any significant change in the fluorescence spectrum of **3**. The spectral fitting of the fluorescence data obtained by titration (Figure 4b) of solution of **3** with acetate ions shows the formation of 2:1, 1:1, and 1:2 (**3**:AcO^-) stoichiometric complexes [log $\beta_{L2AcO} = 11.5 \pm 0.4$, log $\beta_{LAcO} = 6.22 \pm 0.24$, and log $\beta_{LAcO2} = 11.37 \pm 0.32$].

The "OFF-ON" switching behavior at 480 and 580 nm on addition of F^- to a solution of **2** and acetate ions to a solution of **3** provides a dual emission channel for elaborating a ratiometric approach (Figure 5a). The ratio of emission intensities (I_{580}/I_{480}) of **2** (CH_3CN) varies from 0.09 to 5.3 on gradual addition of fluoride ions, showing 60-fold emission ratio change and can be used to estimate F^- ions between 2 and 40 μM. In the case of chemosensor **3** ($CHCl_3$−MeOH, 1:1), the ratio of emission intensities varies from 0.1 to 2.3 on gradual addition of AcO^- ions, indicating a 23-fold emission ratio change, and can be used to estimate acetate ions between 2 and 25 μM (Figure 5b).

We have further evaluated the selectivity of probes **2** and **3** for estimation of the fluoride and acetate ions in the competitive media of other anions. For these studies the number of solutions of chemosensor **2** (CH_3CN) having a different concentration of fluoride ions and 500 μM other anions (Cl^-, Br^-, AcO^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, CN^-, and ClO_4^-) were prepared. The fluorescence intensity of each solution was measured at 580 nm, and the result showed that the intensity of the fluorescence was almost identical to that obtained in the absence of anions (Figure S21, Supporting Information). Similarly, probe **3** could be used to estimate acetate ions in $CHCl_3$−MeOH (1:1) without any interference by other anions (Figure S22, Supporting Information).

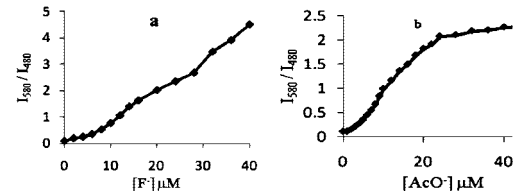

Figure 5. (a) Fluorescence ratiometric (10 μM) responses (I_{580}/I_{480}) of **2** and (b) **3** upon incremental addition of fluoride ions and acetate ions, respectively.

^{1}H NMR titration experiments were performed to understand the character of the receptor−anion interactions. The ^{1}H NMR (DMSO-d_6) spectrum of **2** on addition of fluoride ions showed upfield shift of protons of nitrogen bearing ring of anthrone moiety. This upfield shift clearly points to the generation of negative charge on nitrogen on addition of fluoride ions (Figure 6). Similar ^{1}H NMR spectral changes

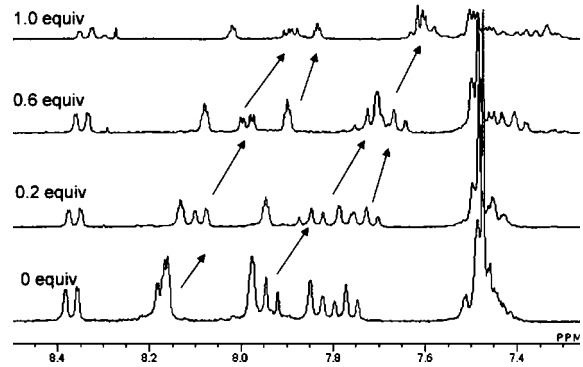

Figure 6. ^{1}H NMR spectra of chemosensor **2** on addition of TBA F in DMSO-d_6.

have been observed on addition of F^- or AcO^- anions to **3** (Figures S23−S24, Supporting Information), pointing to similar anion−receptor interactions in both **2** and **3**. These interactions are in consonance with stabilization of the intramolecular charge transfer excited state responsible for red-shifted absorption bands.

Thus, we have synthesized *N*-arylimidazolium based chromofluorescent probes where the presence of lipophilic dodecyl appendage on imidazolium nitrogen tuned the selectivity for AcO^- ions in protic solvents. Further effect of substituents on imidazolium ring on the anion sensing behavior is under investigation.

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Supporting Information Available: Synthesis and spectral data of chemosensors **2** and **3**, X-ray structure of **2**. PF_6 and selected UV−vis, fluorescence, and ^{1}H NMR titrations data.This material is available free of charge via the Internet at http://pubs.acs.org.

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