

Pyrene Based Chemosensor for Selective Sensing of Fluoride in Aprotic and Protic Environment

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Abstract A new aromatic hydrazone based on pyrene-1-aldehyde was synthesized and characterized by ¹H NMR and mass spectrometric analyses. The sensing properties of the hydrazone were studied by absorption and fluorescence studies in the aprotic solvent DMSO. It was capable of visual and fluorescent detection of fluoride over competitive ions (Cl⁻, Br⁻, H₂PO₄⁻, AcO⁻). Moreover, the in-situ prepared iron(III) complex of the hydrazone was investigated as a turn off fluorescent fluoride sensor in aqueous medium by displacement mechanism.

Keywords Pyrene-1-aldehyde · Chromogenic and fluorescent sensor · Fluoride sensor · Displacement mechanism

Introduction

Inorganic anions are responsible for various vital processes in our life. In biological systems it may be essential as

phosphate ion, major constituent of DNA or as an acute toxicant like cyanide ion. Hence in environment inorganic anions can act as a nutrient or as a contaminant depending on its concentration and availability. In this context fluoride is of special interest as it is essential for development of teeth and bones whereas excess fluoride intake can cause fluorosis, urolithiasis, or even cancer [1, 2]. It is well known that fluoride is capable of forming strongest hydrogen bonds, thus most of reported fluoride sensors utilizes this property for selective detection. Although these sensors suffer from two major disadvantages firstly they are not suitable in protic medium since fluoride is highly solvated, secondly other H-bonding anions like AcO⁻ or PO₄³⁻ can substantially interfere with the detection of fluoride even in aprotic solvents [3, 4]. However, there are several fluoride chemosensors that utilizes high affinity of fluoride towards boron and/or silicon [5–7]. Unfortunately these types of chemosensors generally involve difficult synthetic procedures and some of them are not suitable for spontaneous detection. Another relatively less explored method is to use the metal as an active center for fluoride detection where fluoride displaces metal chelated fluorescent neutral ligands resulting alteration of the fluorescence output. Several fluorescent fluoride sensors were reported utilizing zirconium, iron, aluminium as metal center [3, 4, 8–10]. Pyrene-containing molecular systems have been studied extensively because they exhibit a distinctive excimer emission. Various pyrene systems capable of showing the metal-induced excimer enhancement or quenching have been reported earlier [11, 12]. Taking into account our interest in the development of sensors for anions and inspired by our previous work on the use of hydrazones [13], we report herein the synthesis and characterization of new heteroaromatic conjugated system consisting of pyridyl-N, imine-N and pyrene ring. This

Highlights

- Pyrene-1-aldehyde based hydrazone was investigated as a chromogenic and fluorescent sensor for fluoride in DMSO medium. The in-situ prepared iron(III) complex of the sensor shows selectivity towards fluoride in aqueous medium through fluorescence turn-off process.
- No significant interference was observed for other anions.
- The sensor and its iron(III) complex exhibit low detection limit for fluoride in aprotic and protic medium respectively.

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sensor was investigated as a chemosensor for fluoride in aprotic medium and its insitu prepared iron(III) complex was utilized as fluoride sensor in aqueous medium.

Experimental

Materials and Method

All chemicals were purchased from sigma-Aldrich and used as received without further purification unless otherwise stated. A Perkin Elmer 2400 C Elemental Analyzer was used to collect microanalytical data (C, H, N). FTIR data were collected with the help of Spectrum One FT-IR Spectrometer. The NMR spectra were recorded on a Bruker DRX-400 spectrometer with TMS as the internal standard in DMSO- d_6 . Absorption spectra were measured on a Shimadzu UV-1700 spectrophotometer. Fluorescence measurements were performed on a Hitachi F7000 spectrofluorimeter. Mass spectra measurement was carried out by Waters Xevo G2-S QToF Mass Spectrometer. The stock solution of anions for spectroscopic studies were prepared by dissolving tetrabutylammonium (TBA) salts of F^- , Cl^- , Br^- , $H_2PO_4^-$, OAc^- in DMSO.

Synthesis

The receptor L (pyrene-1-carbaldehyde-2-pyridylhydrazone) was synthesized by following a published method [14].

L: The receptor was prepared by condensation between pyrene -1- aldehyde (0.03 gm, 0.02 mM) and 2-hydrazinopyridine (0.02 gm, 0.02 mM) in methanol. Yield: 85 %. 1H NMR (400 MHz, DMSO d_6) δ : 11.3 (s, H), 9.21 (s, H), 8.72–8.62 (m, H), 8.49–8.48 (m, 4H), 8.40–8.38 (m, 2H), 8.30–8.28 (m, H), 8.22–8.41 (m, H), 8.13–8.09 (m, H), 7.79–7.59 (m, H), 7.43–7.41 (m, H), 6.88–6.85 (m, H). EIMS (m/z): calculated for $C_{22}H_{15}N_3$, 321.37; found, 322.13 (MH^+). Elemental Anal. Calc. for $C_{22}H_{15}N_3$ (L) C, 82.22; H, 4.70; N, 13.08. Found: C, 82.20; H, 4.74; N, 13.06. FTIR (KBr pellets, cm^{-1}): 3003, 1651, 1606, 1568, 1545, 1460, 1445, 1323, 1284, 1164, 1143, 1089, 990, 897, 836, 765, 750, 708, 677.

Determination of Association Constants, Quantum Yields (Φ) and Limit of Detection (L.D) for Receptors

The association constants for L with fluoride anion in DMSO medium were calculated from UV–Vis (K_{ass}) and fluorescence ($K_{ass}^{\#}$) studies by the linear Benesi–Hildebrand expression [15],

$$\frac{1}{F1-F10} = \frac{1}{F1\infty-F10} \left[\frac{1}{K_{ass}[F^-]_0} + 1 \right]$$

$F1_0$ is the fluorescence intensity of free receptor, $F1_{\infty}$ is the fluorescence intensity measured with an excess amount of F^- , $F1$ is the fluorescence intensity with F^- , K_{ass} is the association constant (M^{-1}), and $[F^-]_0$ is the concentration of F^- added. The same equation was followed for absorption studies also.

The association constant for Fe-L complex in aqueous (4:1 MeCN: H_2O) medium was calculated based on the fluorescence titration by a nonlinear least squares fitting of the data using the following equation [16, 17], where X represents the fluorescence intensity, X_{lim} represents the

$$X = X_0 + (X_{lim}-X_0)/2C_0 \left\{ C_H + C_G + 1/K_{ass} - \left[(C_H + C_G + 1/K_{ass})^2 - 4C_H C_G \right]^{1/2} \right\}$$

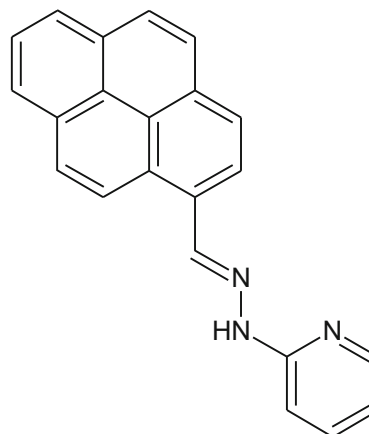
fluorescence intensity at full complexation, C_0 is the initial concentration of the ligand, C_H and C_G are the corresponding concentrations of the ligand and metal ion during titration.

Fluorescence quantum yields of fluoride-receptor complexes were measured against quinine sulphate as standard [18]. The limit of detection (L.D) of L for F^- was calculated from the calibration curves. (Table 1).

Results and Discussion

Synthesis

The receptor L was synthesized by the Schiff base condensation reaction between pyrene -1- aldehyde and 2-hydrazinopyridine in methanol and characterized by mass and 1H NMR spectrometric studies.

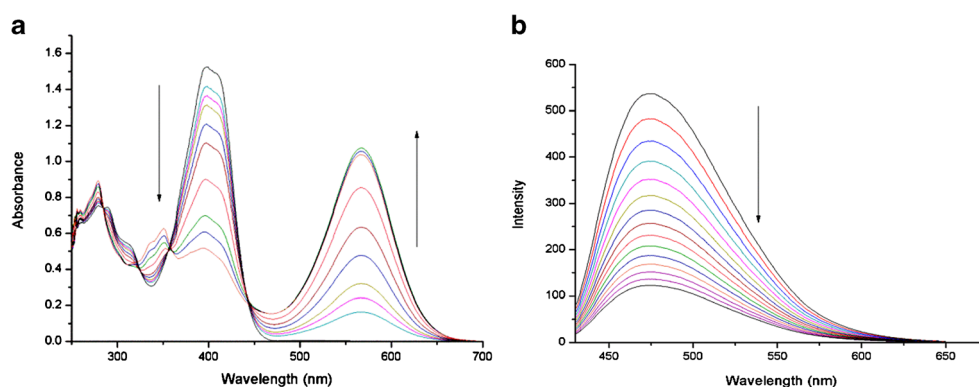


L

Table 1 The association constants, quantum yield (Φ) and limit of detection (L.D) for receptors

	$K_{\text{abs}}(\text{F}^-)(\text{M}^{-1})$	$K_{\text{fl}}(\text{F}^-)(\text{M}^{-1})$	Φ	L.D (M)
L			0.006 (DMSO)	
L-F ⁻	2.94×10^3	3.5×10^3	–	8.9×10^{-7} (UV) 1.7×10^{-6} (Fl)
FeL		2.4×10^4	0.028 (MeCN:H ₂ O) 4:1	
FeL-F ⁻			0.006 (MeCN:H ₂ O) 4:1	6.7×10^{-6} (Fl)

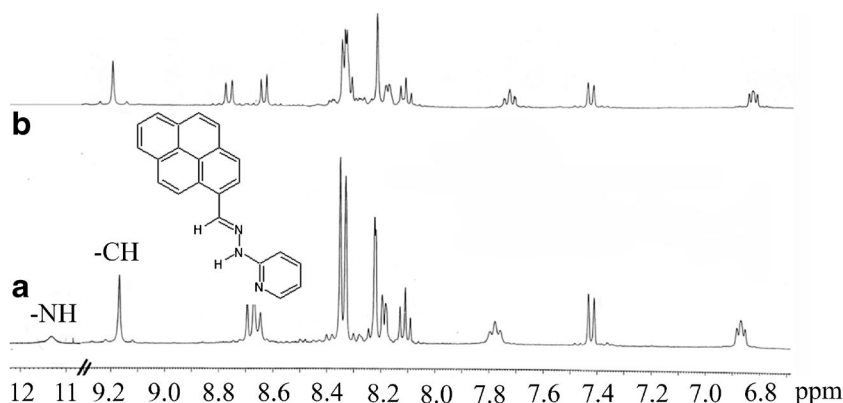
These results indicated that the receptor L can be used for selective sensing of F⁻ based on the distinct color changes

Fig. 1 (a) UV–Vis titration of L (5×10^{-5} M in DMSO) upon successive addition of 0–20 equivalents of TBAF. (b) Fluorescence titrations of L (5.0×10^{-5} M) with TBAF (0–20 equivalents) in DMSO

Fluorescence and Absorption Studies of Receptor L Towards Various Anions in Aprotic Medium

The UV–Vis and emission spectra of L was studied in DMSO in presence of various anions as TBA salts (F⁻, Cl⁻, Br⁻, H₂PO₄⁻, OAc⁻). Addition of F⁻ to the solution of L, respectively, resulted in a prominent change in the UV–visible absorption spectra, as shown in Fig. 1. The absorption band at

398 nm disappeared and a new absorption band at 563 nm was developed. This phenomenon may be attributed to the fluoride induced deprotonation of hydrazine N–H proton and resulting better delocalized charge transfer from pyrene to pyridine moiety [19–21], it is further supported from NMR experiment provided in Fig. 2. The Benesi–Hildebrand plot of L with F⁻ shows a linear relationship, indicating that the receptor associates with F⁻ in a 1:1 stoichiometry (Fig. 3). However, other

**Fig. 2** ¹H NMR (400 MHz) spectra of L in DMSO-d₆; (a) in the absence of TBAF and (b) in the presence of 2 equivalents of TBAF

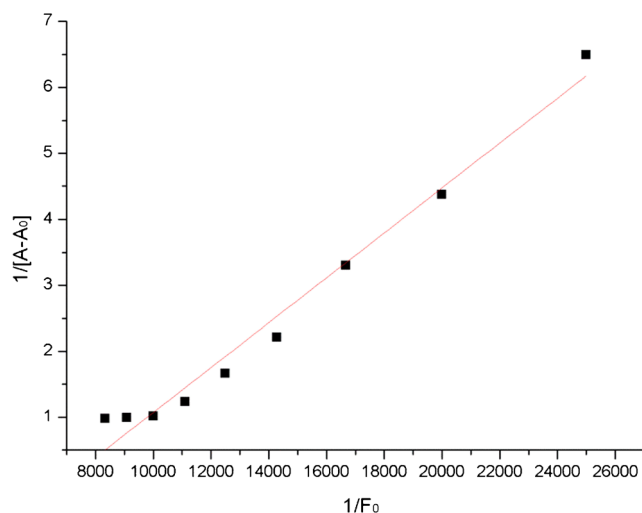


Fig. 3 Benesi–Hildebrand plot of L with F[−] from absorption studies

anions such as Cl[−], Br[−], H₂PO₄[−], AcO[−] did not show any significant changes in their UV–visible absorption spectra. Meanwhile, the solution of L, showed a dramatic color change from yellow to violet which could easily be detected by the naked-eye (Figs. 4 and 5).

The fluorescence behavior of L was studied in DMSO. Upon excitation at 400 nm the receptor L weakly emits in

the blue region at 446 nm (Fig. 1). Upon addition of F[−] upto 20 equivalents this emission peak gradually decreased in intensity probably due to photoinduced electron transfer (PET) enhanced quenching process resulting from deprotonation of imine proton [21]. No significant spectral change was observed after addition of other TBA salts (Br[−], Cl[−], OAc[−] and H₂PO₄[−], 0–20 equivalents) (Fig. 4). Thus the receptor L exhibits high selectivity towards the F[−] anion in the DMSO medium (Fig. 3).

Fluorescence Studies of In-Situ Prepared Fe-L Complex Toward Various Anions in Protic Medium

The interaction of L with Fe³⁺ ion was studied fluorimetrically in MeCN: H₂O (4:1) medium by titrating L with MeCN solution of FeCl₃. Job's plot indicated a 1:2 complexation stoichiometry of Fe-L as obtained from emission studies and the binding constants were measured by a nonlinear least squares fitting of the data (Table 1). On excitation at 400 nm the receptor L weakly emits at 475 nm (Fig. 6). Upon addition of Fe³⁺, the 3 fold increment in the emission intensity was observed with slight red shift to 484 nm. This increase of emission intensity can be attributed to the chelation enhanced fluorescence [22, 23].

The recognition capability of the in-situ prepared Fe-L complex was studied in MeCN:H₂O (4:1) medium.

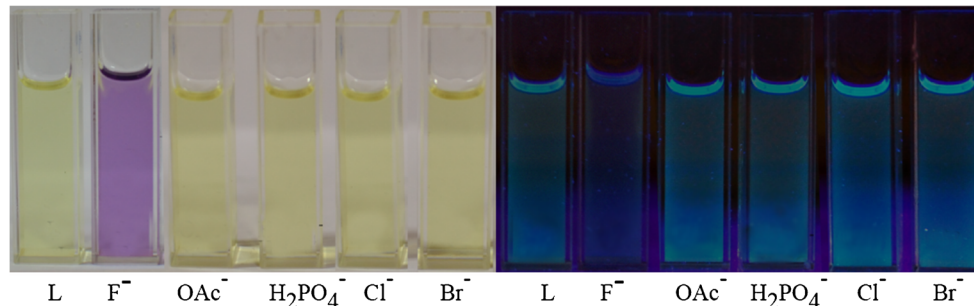


Fig. 4 Color changes under visible and UV radiation (300 nm) upon addition of 20 equivalents of various anions in 0.05 mM DMSO solution of the receptor L

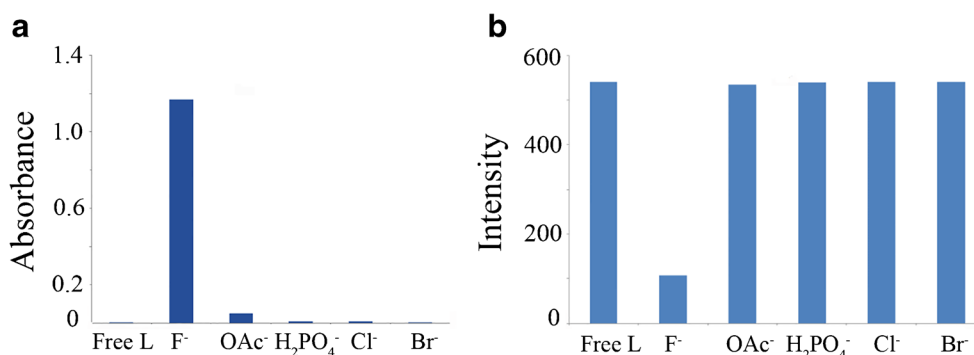


Fig. 5 (a) Absorption changes at 563 nm of L (5.0×10^{-5} M) in DMSO upon addition of 20 equivalents of TBAF and other TBA salts, respectively. (b) Emission changes at 446 nm of L (5.0×10^{-5} M) in DMSO upon addition of 20 equivalents of TBAF and other TBA salts, respectively

Fig. 6 Fluorescence titration of L (5.0×10^{-5} M) with Fe^{3+} (0–2 equivalents) in MeCN: H_2O (4:1)

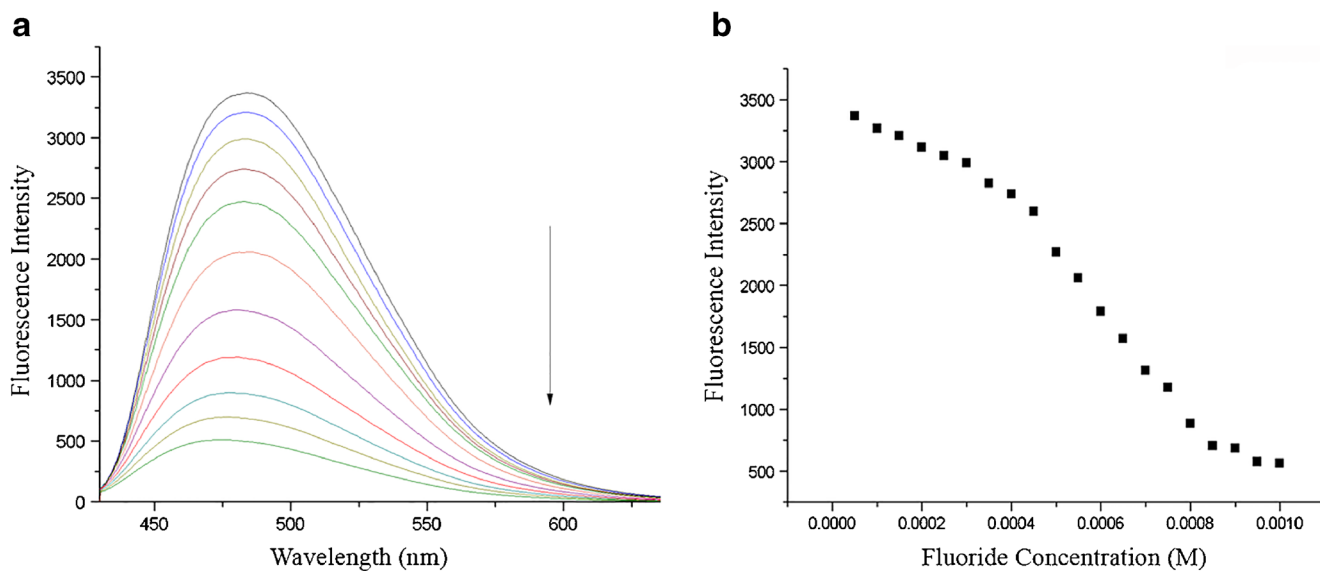
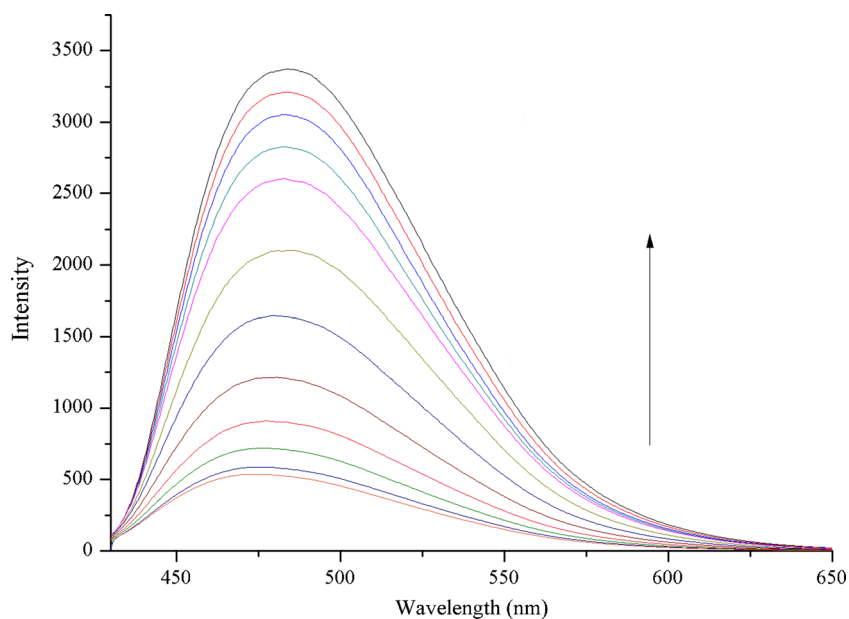


Fig. 7 (a) Fluorescence titration of Fe-L complex (5.0×10^{-5} M) with TBAF (0–20 equivalents) in MeCN: H_2O (4:1). (b) Change in emission intensity at 485 nm upon successive addition of TBAF

Scheme 1 Proposed mode of sensing

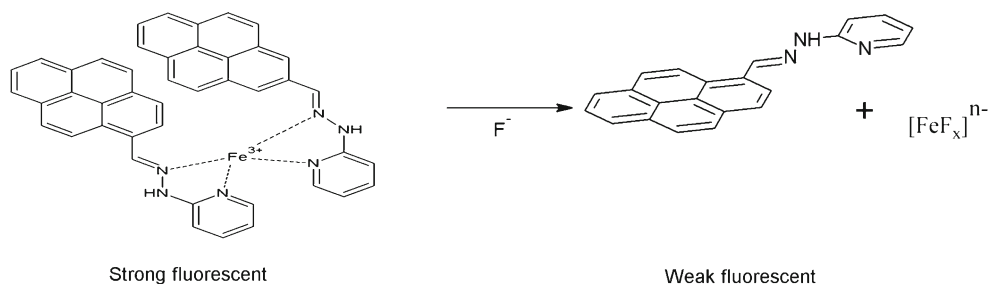
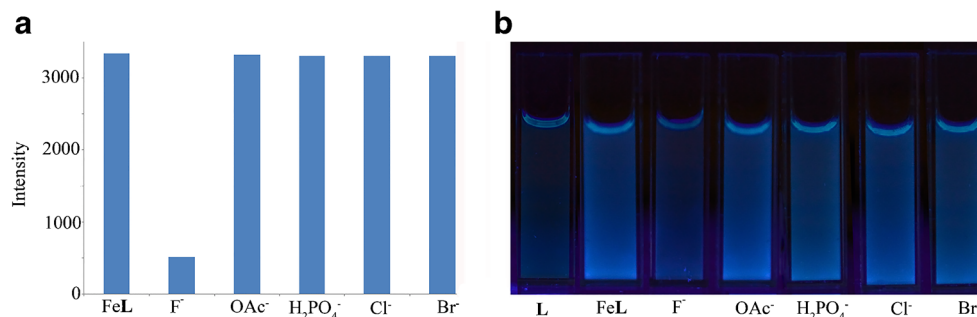


Fig. 8 (a) Emission changes at 485 nm of for L upon addition of 20 equivalents of TBAF and other TBA salts. (b) Color changes under UV radiation upon addition of 20 equivalents of various anions in 0.05 mM DMSO solution of L



Remarkably the addition 20 equivalents of F^- causes gradual decrease in emission intensity at 484 nm (Fig. 7) with a slight blue shift to 475 nm due to the replacement of neutral L by hard anion F^- and the proposed mode of binding of the insitu prepared iron(III) complex is given in Scheme 1. However, no significant changes were found in presence of other anions like Cl^- , Br^- , $H_2PO_4^-$, OAc^- (Fig. 8).

Hence, the sensors reported here offer the attractive opportunity for sensing fluoride in both aprotic and protic medium in the concentration range of 10^{-6} M. This pyrene base receptor has a potential for practical application, which is currently being investigated.

Conclusion

In summary, herein we have synthesized and characterized a hydrazone containing pyrene as an active fluorophore unit. Molecular structure was determined by NMR and mass spectrometric studies. The receptor was investigated as chromogenic and fluorescent sensors for selective detection of fluoride ion in DMSO medium. The association constants were calculated from UV–vis and fluorescence studies by the linear Benesi–Hildebrand expression revealing 1:1 stoichiometry for the sensor and fluoride. The in-situ prepared iron(III) complex exhibits selectivity towards fluoride in aqueous medium through turn-off process. No significant interference was observed for OAc^- , $H_2PO_4^-$ and other anions.

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