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Fe^{3+}-ensemble of triazole appended pentacenequinone derivative for "turn-on" detection of fluoride ions

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ABSTRACT

Triazole appended pentacenequinone derivative **6** has been synthesized by Suzuki–Miyaura coupling protocol. Compound **6** exhibits selective response towards Fe^{3+} ions. Interestingly **6.Fe^{3+}** ensemble exhibits "turn-on" response towards fluoride ions and thus, makes the **6.Fe^{3+}** ensemble a novel probe for the selective detection of fluoride ions. Further, derivative **6** coated test strip can detect traces of Fe^{3+} and F^- ions and provide a simple, portable and low cost method for detection of Fe^{3+} and F^- ions in aqueous solution.

1. Introduction

Anion recognition is an area of great interest due to its wide applications in environmental, clinical, chemical, and biological systems [1–11]. Among the various important anions, fluoride has received great interest due to its role in preventing dental caries and osteoporosis [12,13]. Excess of fluoride ions can cause dental or skeletal fluorosis [14], and they are also associated with kidney failure and nephrolithiasis [15,16]. In view of the importance of fluoride ions in day-to-day life, considerable effort has been devoted to the development of techniques for detection and monitoring of fluoride ions. Fluorescence signaling is one of the best choices due to its high detection sensitivity and simplicity [17]. The usual approach to design a fluorescent sensor involves the covalent linking of a fluorescent fragment to a receptor, which displays specific binding tendency towards a given analyte. On the other hand, 'Chemosensing ensemble method' is a kind of competitive approach to the design of fluorescent chemosensors [18]. Recently, metals such as Hg^{2+}, Cu^{2+}, and Ca^{2+} that act as a quencher were used as the receptor in a chemosensing ensemble method for the detection of specific amino acids and anions [19–25]. Most of the reports based on ensemble system are for the detection of CN^- ions [26–34]. There are few reports in the literature for the detection of F^- ions [35] based on this technique. Our research work involves the molecular recognition and sensing of novel artificial receptors for the selective sensing of soft metal ions [36–38] and inorganic anions [39,40]. Recently, we reported terphenyl based mercury ensemble for selective detection of acetate ions over fluoride ions in a blood plasma like system [41]. In addition we also reported a triphenylene based copper ensemble which shows selective sensing of cyanide ions and responds to CN^- ions even in the presence of bovine serum albumin and in blood serum milieu [42]. In continuation of this work, in the present manuscript, we have now developed a new ensemble system based on pentacenequinone scaffold for the selective detection of fluoride ions which respond to even in the presence of blood serum milieu. As practical applications, we also utilized the derivative **6** coated test strip for trace detection of Fe^{3+} and F^- ions which provides a simple, portable and low cost method for the detection of Fe^{3+} and F^- ions in aqueous solution. The pentacenequinone motif has gained considerable attention due to its usage in the synthesis of pentacene derivative as pentacene derivatives have wide applications in electronic devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and film-making characteristics [43–46]. However, their utility as a fluorescent sensor has not been explored. To the best of our knowledge, this is the first report where a pentacenequinone based ensemble has been used for selective sensing of fluoride ions even in the presence of blood serum milieu.

2. Experimental

2.1. General information

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and

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benzophenone and kept over molecular sieves overnight before use. The ^1H and ^{13}C NMR spectra were recorded on a JEOL 300 MHz spectrometer using TMS as the internal standard and $CDCl_3$ as the solvent. The UV/vis and fluorescence spectra were recorded with Shimdzu UV-2450 spectrophotometer and Shimadzu RF-5301(PC) spectrofluorophotometer, respectively. Stock solutions (0.1 M) of metal perchlorate salts and tetrabutylammonium salts were prepared in THF/H_2O (9.5/0.5, v/v). Stock solution (0.1 mM) of compound **6** was prepared in THF/H_20 (9.5/0.5, v/v). For all measurements of fluorescence spectra, excitation wavelength was 352 nm. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s=singlet, d=doublet, br=broad singlet m=multiplet), coupling constants J (Hz), integration, and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography.

2.2. Experimental

2.2.1. Synthesis of compound 2

To a solution of 4-bromophenol (2.0 g, 11.56 mmol) in dry DMF (15 mL) was added K_2CO_3 (6.38 g, 46.24 mmol), and mixture was stirred at room temperature for 10–15 min. Then propargyl bromide (2.75 g, 23.12 mmol) was added drop-wise. The resulting mixture was heated at 60–70 °C overnight. The mixture was then diluted with dichloromethane and washed with water. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure to get the crude product. The crude product was purified by column chromatography, eluting with hexane to give compound **2** in 75% yield. ^1H NMR δ (300 MHz, $CDCl_3$): 2.53 (*t*, 1H, J=2.4 Hz, CH), 4.66 (*d*, 2H, 2.4 Hz, OCH_2), 6.86 (*d*, 2H, J=9.0 Hz, ArH), 7.39 (*d*, 2H, J=9.3 Hz, ArH); ^{13}C-NMR δ (75.45 MHz, $CDCl_3$): 55.60, 75.84, 77.98, 113.51, 116.44, 132.00, 156.24; MS (ESI) *m*/*z*: 254 $(M+K+H)^+$ Elemental analysis: calcd. for C_9H_7BrO: C, 51.22; H, 3.34; Found: C 51.16, H 3.35.

2.2.2. Synthesis of compound 3

To a solution of compound **2** (2 g, 9.48 mmol) and hexylazide (1.93 g, 15.16 mmol) in dry DMF, was added Cu(I) (0.9 g, 4.74 mmol) and the resulting reaction mixture was heated at 90 °C for overnight. The mixture was then diluted with water and extracted with dichloromethane. The organic layer was separated, and dried over anhydrous $NaSO_4$. The solvent was then evaporated under reduced pressure to get the crude product. The crude product was purified by column chromatography using Hexane/Ethylacetate (7:3) as an eluent to give the compound **3** in 58% yield. ^1H NMR δ (300 MHz, $CDCl_3$): 0.87 (t, 3H, J=6.9 Hz, N–CH $_2CH_2(CH_2)_3CH_3$), 1.31 (s, 6H, N–CH $_2CH_2(CH_2)_3CH_3$), 1.90 (t, 2H, J=7.2 Hz, N–CH $_2CH_2(CH_2)_3CH_3$), 4.34 (t, 2H, J=7.2, $N–CH_2CH_2(CH_2)_3CH_3$), 5.18 (s, 2H, OCH_2), 6.87 (*d*, 2H, J=9.0 Hz, ArH), 7.37 (*d*, 2H, J=9.0 Hz, ArH), 7.56 (s, 1H, ArH); ^{13}C-NMR δ (75.45 MHz, $CDCl_3$): 13.78, 22.23, 25.96, 30.03, 30.94, 50.35, 62.14, 113.25, 116.53, 122.48, 132.16, 143.53, 157.19; MS (ESI) *m*/*z*: 338 $(M+1)^+$; Elemental analysis: calcd. for $C_{15}H_{20}BrN_3O$: C, 53.26; H, 5.96; N, 12.42; Found: C 53.20, H 5.90, N 12.36.

2.2.3. Synthesis of compound 4

To a suspension of $[PdCl_2(PPh_3)_2]$ (0.083 g, 0.118 mmol) in 1,4-dioxane (15 mL) were added compound **3** (1.0 g, 2.96 mmol), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.14 g, 8.88 mmol), and triethylamine (0.896 g, 8.88 mmol) under nitrogen. After stirring for 5 h at 80 °C, the 1,4-dioxane was removed under vacuum and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The organic layer was evaporated and the compound was purified by column chromatography using dichloromethane as an eluent to give compound **4** in 75% yields. ^1H NMR δ (300 MHz, $CDCl_3$): 0.87 (s, 3H, N–CH $_2CH_2(CH_2)_3CH_3$), 1.25 (s, 6H, N–CH $_2CH_2(CH_2)_3CH_3$), 1.33 (s, 12, CH_3) 1.88 (s, 2H, N–CH $_2CH_2(CH_2)_3CH_3$), 4.33 (t, 2H, J=7.05 Hz, $N–CH_2CH_2(CH_2)_3CH_3$), 5.23 (s, 2H, OCH_2), 6.97 (*d*, 2H, J=8.1 Hz, ArH), 7.60 (s, 1H, ArH), 7.75 (*d*, 2H, J=8.4 Hz, ArH); ^{13}C-NMR δ (75.45 MHz, $CDCl_3$): 13.45, 21.88, 24.32, 25.55, 29.66, 30.59, 49.87, 66.44, 113.58, 122.49, 129.00, 136.10, 143.11, 160.30; MS (ESI) *m*/*z*: 386.2 $(M+1)^+$; Elemental analysis: calcd. for $C_{21}H_{32}BN_3O_3$: C, 65.46; H, 8.37; N, 10.91; Found: C 65.40, H 8.30, N 10.80.

2.2.4. Synthesis of compound 6

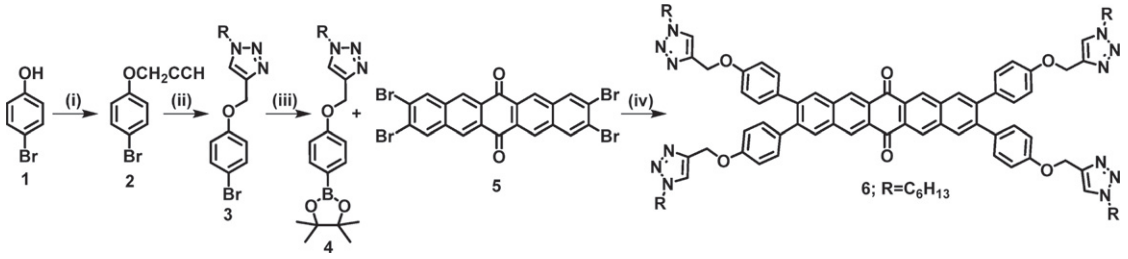
To a mixture of 2,3,9,10-tetrabromopentacenequinone **5** (0.578 g, 0.927 mmol) and $[Pd(PPh_3)_4]$ (0.236 g, 0.203 mmol) in 1,4-dioxane (20 mL) was added a suspension of compound **4** (1.5 g, 3.89 mmol) in 1,4-dioxane (5.0 mL) and 2 M aqueous solution of K_2CO_3 (1.02 g, 7.41 mmol). The reaction mixture was degassed and purged with N_2 for 15 min. The mixture was then refluxed overnight. After that the reaction mixture was allowed to cool to room temperature. The mixture was then diluted with water and extracted with dichloromethane. The organic layer was separated, and dried over anhydrous $NaSO_4$. The solvent was then evaporated under reduced pressure to get the crude product. The crude product was purified by column chromatography using chloroform/Methanol (9.5:0.5) as an eluent to give the compound **6** in 50% yield: ^1H NMR δ (300 MHz, $CDCl_3$): 0.89 (s, 12H, N–CH $_2CH_2(CH_2)_3CH_3$), 1.33 (s, 24H, N–CH $_2CH_2(CH_2)_3CH_3$), 1.93 (s, 8H, N–CH $_2CH_2(CH_2)_3CH_3$), 4.38 (t, 8H, J=7.05 Hz, $N–CH_2CH_2(CH_2)_3CH_3$), 5.22 (s, 8H, OCH_2), 6.92 (*d*, 8H, J=8.7 Hz, ArH), 7.17 (*d*, 8H, J=8.4 Hz, ArH), 7.63 (s, 4H, ArH), 8.10 (s, 4H, ArH), 8.94 (s, 4H, ArH); ^{13}C-NMR δ (75.45 MHz, $CDCl_3$): 13.96, 22.43, 26.16, 30.26, 31.14, 50.62, 62.04, 114. 94, 122.68, 129.47, 130.80, 131.08, 133.35, 135.86, 141.25, 142.46, 143.86, 148.72, 157.73; MS (MALDI) *m*/*z*: 1338.9 $(M+1)^+$; Elemental analysis: calcd. for $C_{82}H_{88}N_{12}O_6$: C, 73.63; H, 6.63; N, 12.57; Found: C 73.60, H 6.55, N 12.50.

3. Results and discussions

3.1. Synthesis of compound 6

Synthesis of compound **6** involves the reaction of 4-bromophenol **1** with propargyl bromide in the presence of potassium carbonate to give compound **2**, which on reaction with hexylazide using "click reaction" furnished compound **3**. Further, reaction of compound **3** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane in the presence of triethylamine gave compound **4**. Finally, fourfold Suzuki–Miyaura coupling of 2,3,9,10-tetrabromopentacenequinone **5** [47] with respective boronic esters **4** gave compound **6** in 50% yield (Scheme 1).

The structures of compounds **2, 3, 4** and **6** were confirmed from their spectroscopic and analytical data (See Supporting Fig. S9–S20). The ^1H NMR spectrum of compound **6** showed three singlets (12H, 32H, 8H) for alkyl chain appended to the triazole group, one singlet (8H) for OCH_2 group, one triplet (8H) for NCH_2, three singlets (4H, 4H, 4H) and two doublets (8H, 8H) for aromatic protons. The mass spectrum of compound **6** showed a parent ion peak at *m*/*z* 1338.9 $(M+1)^+$. These spectroscopic data corroborate structure **6** for this compound (See Supporting Fig. S18-S20).



(i) DMF(dry), Propargyl Bromide, K_2CO_3, 80-90 ^{O}C; (ii) Hexylazide, CuI, DMF (dry), 70-80 ^{O}C; (iii) $PdCl_2(PPh_3)_2$, Et_3N, 1,4-dioxane, 4,4,5,5-tetramethyl-1,3,2 dioxaborolane, 80-90 ^{O}C; (iv) $Pd(PPh_3)_4$, K_2CO_3 (2 M), 1,4-dioxane, 80-90 ^{O}C

Scheme 1. Synthesis of compound **6**.

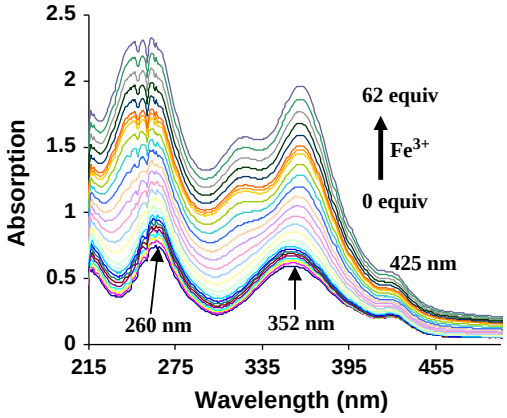


Fig. 1. UV–vis spectra of compound **6** (10.0 μM) upon various additions of Fe^{3+} (0–62 equiv.) in 5% aqueous THF, buffered with HEPES, pH=7.0.

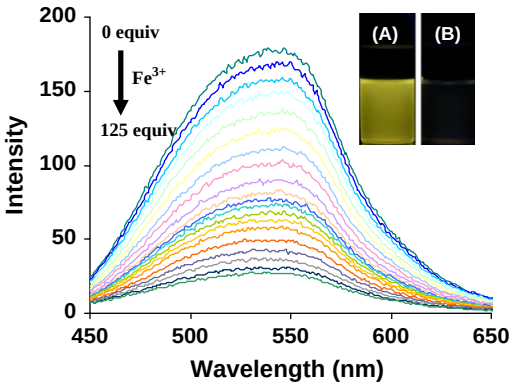


Fig. 2. Fluorescence emission spectra of compound **6** (5.0 μM) upon various additions of Fe^{3+} (0–125 equiv.) in 5% aqueous THF, buffered with HEPES, pH=7.0. An inset photograph shows the fluorescence intensity changes upon addition of Fe^{3+} from (A) 0 to (B) 125 equiv.

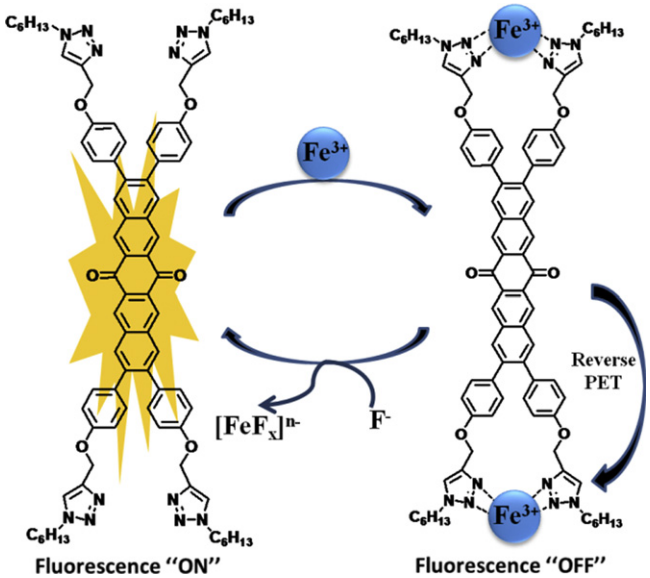
3.2. Binding behavior

Presence of triazole groups at the periphery of the pentacenequinone derivative **6** prompted us to investigate its behavior towards different metal ions. To evaluate binding ability of compound **6** toward different metal ions, we carried out UV–vis and fluorescence experiments in THF/H_2O (9.5/0.5) by adding aliquots of different metal ions (Cu^{2+}, Fe^{3+}, Hg^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Mg^{2+}, K^{+}, Na^{+}, and Li^{+}) as their perchlorate salts. The absorption spectrum of compound **6** (1×10^{-5} M) is characterized by the presence of a typical absorption band at 352 nm (Fig. 1).

Of the various metal ions tested, the addition of increasing amounts of Fe^{3+} ion (1.0–62 equiv.) results in an increase in absorption at λ 260, 352 and 425 nm, which indicates the interaction between ferric ions and compound **6** (Fig. 1). No change in the absorption spectra was observed in the presence of any other cations (See Supporting Fig. S1).

The fluorescence spectrum of compound **6** (5.0 μM) in THF/water (9.5/0.5) exhibits emission band at 542 nm when excited at 352 nm (Fig. 2). The fluorescence behavior of compound **6** was investigated toward different metal ions and showed high selectivity towards Fe^{3+} ions among all the metal ions tested. Addition of increasing amounts of Fe^{3+} ions (0.01–125 equiv.) to the solution of compound **6** (5 μM) resulted in significant quenching in fluorescence emission (Fig. 2), which is clearly visible to naked eye under the illumination of 365 nm (Fig. 2, inset).

We believe that due to interactions between Fe^{3+} ions and nitrogen atoms of triazole moieties of derivative **6**, electron density on triazole moieties is decreased which lead to reverse photo-induced electron transfer (reverse PET) from pentacenequinone unit to triazole units (Scheme 2) [48,49].



Scheme 2. Schematic representation of Fe^{3+} and F^{-} sensors based on the fluorescence "turn-off" and "turn-on" of the pentacenequinone derivative **6**.

The fluorescence quantum yield [50] (See Supporting Fig. S5) of compound **6** in the free and **6.Fe^{3+}** ensemble was found to be 0.25 and 0.02 respectively. This substantial decrease in the quantum yield of compound **6** in the presence of Fe^{3+} ions shows its high affinity towards Fe^{3+} ions. The binding of Fe^{3+} ions with compound **6** is also proved by mass spectroscopy (See Supporting Fig. S8). The mass spectrum showed a peak at m/z 242.32 cor-

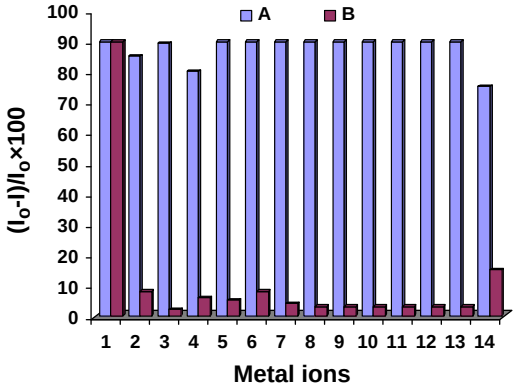


Fig. 3. Fluorescence response of **6** (5 μM) to various cations (125 equiv.) in THF/water (9.5/0.5). buffered used HEPES, pH=7.0; λ_{ex}=352 nm. Bars represent the emission intensity ratio $(I_o-I)/I_0)\times100$ (I_o=initial fluorescence intensity at 542 nm; I=final fluorescence intensity at 542 nm after the addition of 125 equiv. of various cations). 1=Fe^{3+},2=Hg^{2+},3=Ni^{2+},4=Cu^{2+},5=Cd^{2+},6=Pb^{2+},7=Zn^{2+},8=Ba^{2+},9=Na^{+}, 10=K^{+},11=Li^{+},12=Co^{2+},13=Mg^{2+},14=Ag^{+} (B) The brown bars represent the addition of individual metal ions, (A) the sky blue bars represent the change in the emission that occurs upon the subsequent addition of Fe^{3+} (125 equiv.) to the above solution.

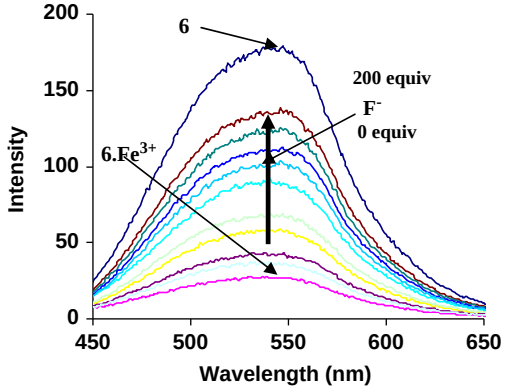


Fig. 4. Fluorescence emission spectra of compound **6.Fe^{3+}** (5.0 μM) complex upon addition of fluoride in 5% aqueous THF, buffered with HEPES, pH=7.0.

responding to the $[6.2Fe]^{6+}$ complex, which not only confirms the binding of Fe^{3+} ions with compound **6** but also proves the 1:2 stoichiometry of the host and guest species.

Under the same conditions as those used above for Fe^{3+}, we also tested the fluorescence response of compound **6** to other metal ions, no significant fluorescence change in compound **6** occurred in the presence of (125 equiv.) these cations (Fig. 3B). Fitting the changes in the fluorescence spectra of **6** with Fe^{3+} ions using the nonlinear regression analysis program SPECFIT [51] gave the best fit and demonstrated that a 1:2 stoichiometry of the host and guest (Fe^{3+}) was the most stable species in the solution with binding constants (log β)^{1,2} of 7.5 ± 0.02 M^{-1}. The method of continuous variation (Job's plot) was also used to prove the 1:2 stoichiometry (Host:Guest) (See Supporting Fig. S2).

The detection limit for Fe^{3+} ions was found to be 3 μM (See Supporting Fig. S5). To check the practical applicability of compound **6** as Fe^{3+} sensor, competitive studies were carried out in the presence of Fe^{3+} at 125 equiv. mixed with other metal ions, no significant change was observed by comparison with or without the other metal ions (Fig. 3A).

Having done this, we were interested in studying the behavior of Fe^{3+} ensemble of compound **6** toward different anions. It was found that this **6.Fe^{3+}** ensemble has pronounced selectivity towards fluoride ion (Fig. 4). The addition of increasing amounts of fluoride ions to the solution of the **6.Fe^{3+}** ensemble results in a revival of fluorescence emission which indicate that Fe^{3+} is being completely removed from the **6.Fe^{3+}** ensemble by fluoride ions (Fig. 4).

We also carried out the UV–vis studies of **6.Fe^{3+}** ensemble with F^- ions. The UV–vis spectral of compound **6** changes upon the addition of 62 equiv. of ferric perchlorate. Interestingly, with gradual addition of tetrabutylammonium fluoride (TBAF) to **6.Fe^{3+}** ensemble complete recovery of absorption bands corresponding to the free receptor **6** is observed (See Supporting Fig. S3).

The revival of absorbance and fluorescence intensity with the addition of F^- ions is due to a higher affinity of Fe^{3+} ions for F^- ions than with the compound **6**. We propose that in the presence of Fe^{3+} ions, derivative **6** forms non-fluorescent **6.Fe^{3+}** complex however, in the presence of fluoride ions demetallation of **6.Fe^{3+}** complex takes place due to the formation of stable $[FeF_x]^{n-}$ species which restores the original emission of derivative **6** (Scheme 2).

The fluorescence quantum yield of **6.Fe^{3+}** and after the addition of fluoride ions was found to be 0.02 and 0.22 respectively. This large increase in the quantum yield of compound **6.Fe^{3+}** in the presence of F^- ions showed its credibility as good fluoride sensor. We also tested the fluorescence response of compound **6.Fe^{3+}** in the presence of other anions like Cl^-, Br^-, I^-, OAc^-, CN^-, HSO_4^-, $H_2PO_4^-$, NO_3^- besides F^-, no significant fluorescence change in **6.Fe^{3+}** ensemble occurred in the presence of these anions (Fig. 5A). Unique feature of the present

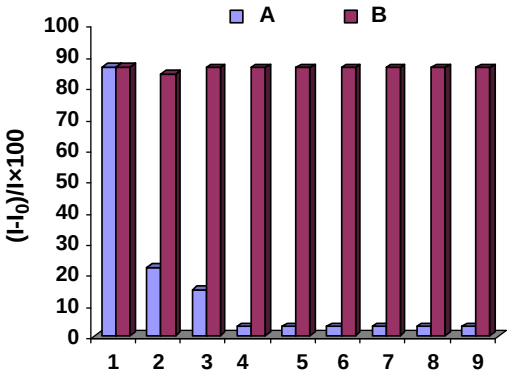


Fig. 5. (**A**) Sky blue bars represents selectivity of **6.Fe^{3+}** ensemble (5.0 μM) towards F^- ion upon addition of various anion, *X*-axis 1=**6.Fe^{3+}**+F^- 2=**6.Fe^{3+}**+OAc^- 3=**6.Fe^{3+}**+CN^- 4=**6.Fe^{3+}**+Cl^- 5=**6.Fe^{3+}**+Br^- 6=**6.Fe^{3+}**+I^- 7=**6.Fe^{3+}**+NO_3^- 8=**6.Fe^{3+}**+HSO_4^- 9=**6.Fe^{3+}**+$H_2PO_4^-$, and (**B**) Brown bars represents competitive selectivity graph of ensemble **6.Fe^{3+}** (5 μM) toward F^- ions in the presence of 200 equiv. of various anions. *X*-axis 1=**6.Fe^{3+}**+F^- 2=**6.Fe^{3+}**+OAc^-+F^- 3=**6.Fe^{3+}**+CN^-+F^- 4=**6.Fe^{3+}**+Cl^-+F^- 5=**6.Fe^{3+}**+Br^-+F^- 6=**6.Fe^{3+}**+I^-+F^- 7=**6.Fe^{3+}**+NO_3^-+F^- 8=**6.Fe^{3+}**+HSO_4^-+F^- 9=**6.Fe^{3+}**+$H_2PO_4^-$+F^- in 5% aqueous THF, buffered with HEPES, pH=7.0. (I_0=initial fluorescence intensity at 542 nm; I=final fluorescence intensity at 542 nm after the addition of 200 equiv. of various anions)

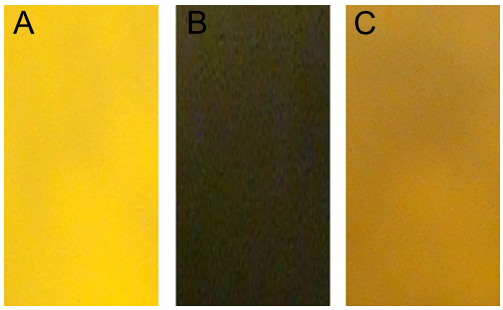


Fig. 6. Photographs of compound **6** (under 365 nm UV light) on test strips (A) before and (B) after dipping into aqueous solutions of Fe^{3+} (C) revival in fluorescence after dipping the test strip into aqueous solution of KF (test strip dried under vacuum).

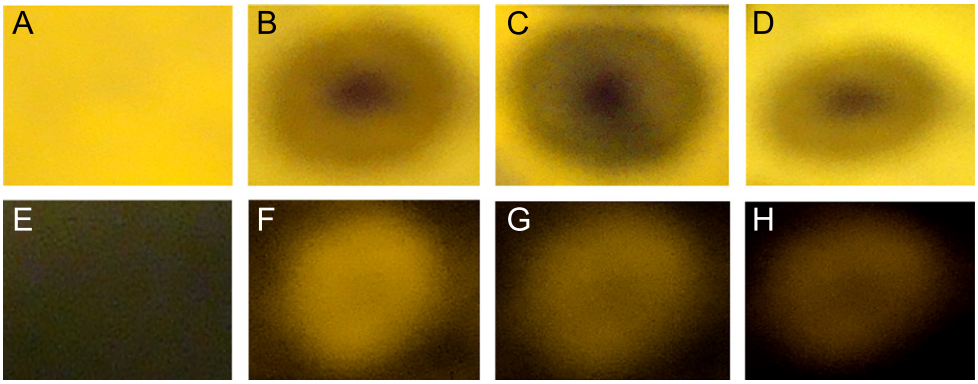


Fig. 7. Photographs (under 365 nm UV-light) fluorescence quenching of compound **6** on test strips for the visual detection of small amount of Fe^{3+} ions (A) test strip of compound **6**; Fe^{3+} ions of different concentration (B) 10^{-3} M (C) 10^{-5} M (D) 10^{-7} M on compound **6** test strip. Revival in fluorescence of ensemble **6.Fe^{3+}** on test strips for the visual detection of small amount of F^- ions (E) test strip of **6.Fe^{3+}** ensemble; F^- ions of different concentration (F) 10^{-3} M (G) 10^{-4} M (H) 10^{-6} M on **6.Fe^{3+}** ensemble test strips.

investigation is the discrimination between F^- and carboxylate anions (such as CH_3COO^-), which is rarely seen in the early reported receptors for fluoride and acetate anions [52,53].

Further, the detection limit of **6.Fe^{3+}** for F^- ions was found to be 4 μM (See Supporting Fig. S6) which is sufficiently low for the detection of maximum contaminant level defined by the US Environmental Protection Agency (4.0 mg/L, 211 μM [54]. To further examine the F^- ions as selective sensor, we also examined the possible interference from co-existing related anions. The competitive experiments showed that most of negatively charged species (Cl^-, Br^-, I^-, OAc^-, CN^-, HSO_4^-, $H_2PO_4^-$, NO_3^-), do not produce considerable interference to the fluoride sensing (Fig. 5B). The fluorescence was quenched again when Fe^{3+} was titrated to the solution of the **6.Fe^{3+}.F$^-$** ensemble, indicating that the compound **6** showed an interesting reversible "On-Off-On" switchable behavior with Fe^{3+} and F^- ions (See Supporting Fig. S4).

3.3. Detection of Fe^{3+} and F^- ions in contact mode

We also carried out the detection of Fe^{3+} and F^- ions on paper strip. For this we prepared the test strips of compound **6** by dip-coating into THF/H_2O (9.5/0.5) solution of compound **6** on Whatman filter paper followed by drying the strips under vacuum. The strong fluorescence of compound **6** was completely quenched upon dipping the test strips into saturated aqueous solution of Fe^{3+}. However, revival in the fluorescence was observed after dipping this test strip into aqueous solution of potassium fluoride (KF) (Fig. 6). This revival in the fluorescence would be the practical application of this chemosensor for the detection of Fe^{3+} and F^- ions.

For detection of very small amounts of Fe^{3+} and F^- ions, we prepared the aqueous solutions of $Fe(ClO_4)_3$ and KF of different concentrations and 3 μL of Fe^{3+} solution were placed on compound **6** test strip. The visual detection response of Fe^{3+} ions at different concentrations is shown (Fig. 7A–D).

The minimum amount of Fe^{3+} ions, detectable by naked eye was upto 1×10^{-7} M level. For detection of small amounts of F^- ions we prepared the test strip by dip-coating the compound **6** test strip into aqueous solution of Fe^{3+} ions and 3 μL of KF solution were placed on test strip. The visual detection response of F^- ions at different concentrations is shown (Fig. 7E–H). The minimum amount of F^- ions, detectable by naked eye was upto ppm level.

Biological applicability of **6.Fe^{3+}** ensemble for F^- ions was checked by carrying out the fluorescence titration of *in situ* prepared **6.Fe^{3+}** complex with F^- ions in the presence of different concentrations of blood serum [55]. Upon addition of blood serum to the solution of **6.Fe^{3+}** ensemble, no change in the fluorescence emission of **6.Fe^{3+}** ensemble was observed (Fig. 8A). However, revival in fluorescence emission of **6.Fe^{3+}** ensemble having blood serum solution was observed with the addition of varying concentrations of F^- ions (Fig. 8B). These results show that *in situ* prepared **6.Fe^{3+}** ensemble can detect F^- ions in the presence of blood serum.

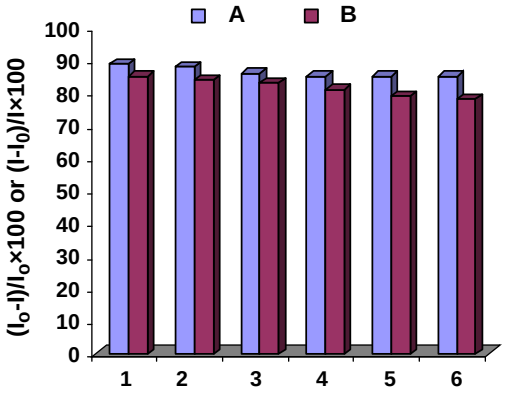


Fig. 8. (**A**) Sky blue bars represents competitive selectivity of **6** toward Fe^{3+} ions in the presence of different concentrations of blood serum (BS), *X*-axis 1=**6**+0 μL BS+Fe^{3+}, 2=**6**+20 μL BS+Fe^{3+}, 3=**6**+40 μL BS+Fe^{3+}, 4=**6**+60 μL BS+Fe^{3+}, 5=**6**+80 μL BS+Fe^{3+}, 6=**6**+100 μL BS+Fe^{3+} and (**B**) brown bars represents competitive selectivity of **6.Fe^{3+}** ensemble towards F^- ion in the presence of different concentrations of blood serum, *X*-axis 1=**6**+0 μL BS+Fe^{3+}+F^-, 2=**6**+20 μL BS+Fe^{3+}+F^-, 3=**6**+40 μL BS+Fe^{3+}+F^-, 4=**6**+60 μL BS+Fe^{3+}+F^-, 5=**6**+80 μL BS+Fe^{3+}+F^-, 6=**6**+100 μL BS+Fe^{3+}+F^- in 5% aqueous THF, buffered with HEPES, pH=7.0, *Y*-axis for (**A**) $(I_0-I)/I_0\times100$, and for (**B**) $(I-I_0)/I\times100$.

Further, we used the **6.Fe^{3+}** ensemble for the detection of fluoride ions from solution of KF in tap water. For this purpose we titrated the **6.Fe^{3+}** ensemble with variable amounts of KF. We found that on addition of F^- ions (200 equiv.), the fluorescence of **6** was recovered (see supporting Fig. S7). This result clearly indicates that **6.Fe^{3+}** ensemble can be used for the detection of fluoride ions in tap water.

4. Conclusions

We have developed a simple and efficient method for selective recognition and rapid detection of fluoride anion based on ferric-ensemble of compound **6**. The recognition of this 'off-on' type sensory system is based on the receptor's good affinity for ferric ions and the selective response of *in situ* formed **6.Fe^{3+}** ensemble

toward F^- ions. This **6.Fe^{3+}** ensemble can also detect F^- ions in the presence of different concentration of blood serum. Further, **6.Fe^{3+}** ensemble has been used for the detection of KF in tap water. We carried out the detection of Fe^{3+} and F^- ions on paper strips and this provide a simple, portable and low cost method for the detection of Fe^{3+} and F^- ions in aqueous solution.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.11.044.

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