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Off-On fluorescent polyanthracene for recognition of ferric and fluoride ions in aqueous acidic media: Application to pharmaceutical and environmental analysis

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Abstract

Fluorescent polyanthracene prepared by chemical oxidative route was shown to sense ferric ions (Fe^{3+}) from aqueous acidic solution. The fluorescence titration indicates that intensity of fluorescence of polyanthracene (PAT) was quenched gradually by successive addition of Fe^{3+} ion solution ('Off-fluorescence'). The fluorescence quenching data fits well into conventional Stern-Volmer relation. The mechanism of Photoinduced Electron Transfer (PET) is proposed to explain observed 'Off fluorescence' state of PAT. Based on the strong affinity of Fe^{3+} to F^- ion, the mixture of polyanthracene- F^- ions exhibiting 'On fluorescence', could behave as fluorescence 'On type probe'. Thus a method using single probe for detection of both Fe^{3+} and F^- ion is developed using fluorescence 'Off-On' approach and applied successfully for determination of these ions from the commercial samples.

Key words: Off-On fluorescence, polyanthracene (PAT), ferric ion, fluoride ion, Photoinduced Electron Transfer (PET).

Introduction

Fluorescence sensing is most promising technique to recognize and detect analyte species from environmental^{1,2} and pharmaceutical samples.^{3,4} The technique uses various types of fluorescent probes like low molecular weight organic compounds,⁵ inorganic compounds,⁶ supramolecules,⁷ crown ethers,⁸ co-ordinate compounds,⁹ organic nanoparticles,¹⁰ inorganic nanoparticles,¹¹ inorganic quantum dots,¹² doped fluorescent polymers¹³ and functionalized polymers.¹⁴ Currently, though quantum dots and nanoparticle probes are of interest, they suffer from the drawbacks of complicated and long time synthesis route and polydispersity.^{15, 16} The dye doped polymers are also known to act as probe in the same manner as low molecular weight fluorescent probes.¹⁷ However, very few analyte molecules absorb in the region of dye emission. Designing and synthesis of novel fluorescent conjugated polymer (CP) probe to sense and recognize metal ions in terms of Off –On signal realization have emerged as an important class of sensory materials for chemical and biological targets.¹⁸⁻¹⁹

More attention is being paid to polymers synthesized from monomers of polycyclic aromatic hydrocarbons such as polyanthracene,²⁰ polynaphthalene,²¹ polyfluorene,²² polyphenanthracene²³ and polypyrene²⁴ because of their unique optical properties due to a continuous pattern of unsaturated conjugated π - bonds which are suitable for application in photoluminescent devices and chemical sensors even without receptor. A linear polymer of anthracene with repeating units can be considered as one dimensional box due to the extended π -electron system.²⁵ The polyanthracene solution emits strong blue fluorescence at 440 nm wavelength and found to be quenched selectively (Turn Off) by ferric ion solution. Based on ‘Turn Off’ fluorescence strategy (method), polyanthracene suits for detection of iron (Fe^{3+}) which is of health concerned. Iron has important role in the different biosystems such as

haemoglobin, myoglobin, and hem enzyme activities as well as in oxygen transport. It has also harmful effects on the various biological systems either alone or in combined state. Due to deficiency of iron anaemia is usually diagnosed, and excess of iron can also cause many health concern problems such as cancer, heart problems and other illnesses known as hemochromatosis.²⁶

Fluoride is a natural mineral found throughout the earth's crust and widely distributed in nature. Some foods and water supplies contain fluoride. American scientists in the 1930s found that people living in towns using higher levels of fluoride in the water experienced less tooth decay than people living in areas with much lower levels of fluoride.²⁷ In case of excess fluoride ion over a lifetime may lead to increased likelihood of bone fractures in adults, and may result in effects on bone leading to pain and tenderness.²⁸ Fluoride is also known as hard base and more inclined with hard acid like ferric (Fe^{3+}) ion due to selective coordination reaction of Fe^{3+} with F^- ion.²⁹ Hence, the gradual addition of F^- ion in the mixture of polyanthracene and Fe^{3+} ions releases polyanthracene, and shown fluorescence enhancement i. e 'Turn On' fluorescence. Present paper deals with development of single probe sensory system using as prepared and characterized PAT to detect both cation Fe^{3+} and anion F^- from aqueous acidic solution. The present sensing strategy proved to be more selective and superior to those developed so far for F^- detection using conjugated polymers with traditional receptors providing sites for F^- binding.³⁰⁻³²

Experimental

Materials

Anthracene (scintillation grade) purchased from Sisco Research Lab. Pvt. Ltd., Mumbai (India) was recrystallized four times from its saturated solution in chloroform. All solvents such as nitrobenzene, *n*-hexane and chloroform were procured from Merck India Ltd., Mumbai, Runa Chemicals Pvt. Ltd., Dombivali (India) and Sisco Research Lab. Pvt. Ltd., Mumbai (India) respectively and were used after distillation. Anhydrous ferric chloride (FeCl_3) obtained from Thomas Baker Pvt. Ltd., Mumbai (India) and Tetrabutylammonium iodide (TBAI, 95%) obtained from Acros Organics, Mumbai (India) were used as received.

Preparation of polyanthracene (PAT) by oxidative polymerization of anthracene with

FeCl_3 : A chemical route

A 4.0 mmole solution of anthracene in 30 mL *n*-hexane was prepared and warmed up to 80°C . FeCl_3 solution containing 6.250 gm in 30 mL nitrobenzene warmed to the same temperature was added drop wise into anthracene solution with constant stirring for about 24 hours. The observation of change of color of reaction mixture changing from white to black indicated polymerization of anthracene. The polymerization was terminated with the addition of 20 mL ethanol. The whole reaction mixture is centrifuged to obtain the sediment. The sediment was washed with water until washing showed absence of Fe^{3+} , Fe^{2+} , Cl^- ions when tested by their confirmatory test.^{33,34} Similarly, unpolymerized anthracene monomer and low molecular weight polymer was removed by washing sediment with ethanol repeatedly for 3 times until wash out showed no color. To eliminate Fe^{3+} or Fe^{2+} contaminants, the resulting polymer was added into 20 mL 1M HCl , stirred for a day, centrifuged and sediment collected was washed

with water. The treatment using 30 mL 0.2M NH_3 solution was then given to remove HCl . The polyanthracene (PAT) obtained is brown colored powder and the yield is 78.0%.

Preparation of standard solution of polyanthracene (PAT)

A 0.1 g/L stock solution of polyanthracene (PAT) was prepared in concentrated sulphuric acid. Then 0.5 mL of this solution was diluted to 10 mL with double distilled water in volumetric flask to obtain 0.005 g/L aqueous acidic solution of PAT and was undertaken for

Characterization of Polyanthracene (PAT)

FT-IR spectra of polyanthracene (PAT) and anthracene with KBr disk in the range from 4000 to 450 cm^{-1} was recorded on a Shimadzu IR-470 FT-IR spectrophotometer. FT-Raman spectra were recorded on a Bruker FT-Raman spectrophotometer (Multi Ram, Germany). Nuclear Magnetic Resonance spectra were taken in DMSO on a Bruker Avanced III-300-MHz Spectrometer using tetra-methyl silane (TMS) as an internal standard. Molecular weight of polyanthracene was determined using Gel Permeation Chromatography (GPC) analysis at a flow rate of 1 $mL\ min^{-1}$ in chloroform at 30 °C (Thermo separation products) equipped with spectra series UV 100 and spectra system RI 150 detectors. The sample concentration was 2 to 3 $mg\ mL^{-1}$. HPLC grade chloroform was used as an eluent. Polystyrene was used as the calibration standard. X-ray diffraction pattern of polyanthracene (PAT) and anthracene were recorded with the help of Philips diffractometer (model PW-3710, Holland) with filtered $CuK\alpha$ (1.54\AA) while Thermogravimetric analysis was performed on Thermal Analyser (TG-DTA-DSC) TA Inc. SDT-2790 using heating rate $10^\circ C$ per minute in nitrogen atmosphere. The size and surface morphology of PAT was examined on Malvern Zetasizer (nano ZS-90) equipped with a 4 mW,

633 nm He-Ne Laser (U.K.) at 25° C under fixed angle of 90° in disposable polystyrene cuvettes and on Scanning Electron Microscope (SEM), JEOL model JSM-6360, Japan with 10 kV accelerating voltage in vacuum respectively. The UV-Visible absorption spectra and the steady state excitation and fluorescence spectra were recorded on UV-VIS-NIR spectrophotometer [Shimadzu UV-3600] and PC-based spectrofluorimeter JASCO, Japan (Model FP-750). The fluorescence life time was obtained from the decay profile under the conditions of $\lambda_{\text{ex}} / \lambda_{\text{em}} = 370 \text{ nm} / 440 \text{ nm}$ recorded on Time-correlated single photon counting (TCSPC) spectrometer (Horiba, Japan).

Results and discussion

Spectral characterization of polyanthracene (PAT)

The characteristic FT-IR spectra of anthracene and chemically synthesized polyanthracene (PAT) are shown in Fig.1. The characteristic absorption bands seen at 882, 808, 770, and 730 cm^{-1} in the spectrum of polyanthracene (PAT) are assigned to out-of-plane carbon-hydrogen vibration for one, three, and four adjacent hydrogen atoms of benzene ring, respectively.³⁵ The absorption band at 2922 cm^{-1} assigned to the C-H stretching vibrations seen more pronounced and red shifted when compared to the similar band of anthracene monomer is an indication of presence of linear hydrocarbon units in the polymer structure.³⁶ The absorption bands at 1750 and 1630 cm^{-1} in the spectrum of the polymer are highly intense and red shifted from corresponding bands in the spectrum of monomer because of the high conjugation and strong bonding structure of polymer. In addition the strong absorption band at 883 cm^{-1} in the spectrum of monomer assigned to the vibration of C-H single bonds at the 9- and 10- positions is

seen to be disappeared in the spectrum of the polymer.³⁴ These observations led to conclude that the majority of chain growth of the polymer is at 9 and 10 position of phenyl ring.³⁷

The typical Raman spectra of anthracene and polyanthracene (PAT) are shown in Fig.2. The sharp bands appeared at 756, 1013, 1186, 1258, 1397.80,1484,1553 and 3060 cm^{-1} in Fig. 2A of anthracene are not seen in the spectrum of PAT in Fig. 2B. This observation suggests that the anthracene monomer from the reaction mixture is converted into polyanthracene (PAT).³⁷ The broad absorption band of PAT is in support of loss of crystallinity and high chain distribution of the polymer.

The ^1H NMR spectrum of polyanthracene (PAT) taken in DMSO d_6 after 24 hours reaction time of the soluble division of PAT is shown in Fig. 3. The ^1H NMR spectrum of PAT displayed complex signals at $\delta = 7.30\text{-}7.90$ and $8.13\text{-}8.30$ ppm corresponding to protons of (2, 3, 6, 7) and (1, 4, 5, 8), respectively. The absence of the peak at 8.50 ppm which corresponds the protons of C_9 and C_{10} of anthracene suggests that anthracene molecules are linked at the 9, 10 position during polymerization.³⁸

Determination of molecular weight by Gel permeation chromatography

Molecular weight of dissolved part of PAT in chloroform was estimated by GPC. Molecular weights M_n (number average molecular weight) and M_w (average molecular weight) of polyanthracene are summarized in Table 1. From weight average molecular weight (M_w) and number average molecular weight (M_n) the polydispersity index was calculated. The PDI value less than 2 indicates uniform and one length of polymer was obtained in our preparation method.³⁹

Size, morphology and structure of polyanthracene (PAT) powder

The particle size distribution of polyanthracene (PAT) suspended in water determined by Dynamic light scattering (DLS) instrument is shown in Fig. 4 A. The size distribution of the particles seen in the figure is remarkably narrow and the average diameter of the particles is 200 nm. The SEM photomicrograph of polyanthracene (PAT) presented in Fig. 4B reveals globular nature of particles.³⁷ The particles are aggregating into spongy structure having average diameter of 300 nm. Comparatively large particle size seen from SEM is because of aggregation of particles during the sample preparation.

The X-ray diffraction profiles of anthracene monomer and that of polyanthracene (PAT) are shown in Fig. 5. The sharp and distinct diffraction peaks in the 2θ region from 15° to 35° reported in XRD profile of anthracene eventually became broad band due to lack of distinct separate planes responsible for diffraction of X-ray which might have undergone coupling with each other during chain growth.^{37, 40, 41} From the nature of XRD profiles it is clear that original crystallinity of monomer is lost during polymerization and as expected amorphous nature of polymer is revealed. The large broad diffraction peak seen in the 2θ region of 20° - 35° indicates that large content of the anthracene repeating units are involved in polymer structure.^{42, 43} Absence of broad diffraction peaks in the 2θ region of 35 - 50° suggests that the present preparation method of polymerization does not add into the product of the graphite content.^{44, 45}

Thermal stability of polyanthracene (PAT)

Thermal stability of polyanthracene (PAT) examined by TGA-DTA is shown in Fig.6. The figure reveals weight loss of 42.56% (char residue) at 1000°C by three consequent steps. The initial weight loss in first step is 5.07% in the temperature range of 25 - 80°C owing to evaporation

of water which was physically absorbed. The estimated weight loss of 4.8% at second step in the temperature range of 80-250°C is observed due to some oligomers in the reaction mixture. The third step indicating rapid decrease in weight loss is due to the decomposition of conjugated PAT.⁴¹ The DTA curve of polyanthracene (PAT) shows endotherm in the range of temperature 400-1000°C. The decomposition temperature 799°C noted from the curve is higher than decomposition temperature of anthracene 216°C.⁴⁶ This observation indicates that the strong intramolecular bonding will tend PAT to withstand high temperatures.

Photophysical properties of polyanthracene (PAT)

Photophysical properties such as fluorescence and absorption were examined to test the suitability of polyanthracene (PAT) as a probe for sensing application. The UV-Visible absorption spectrum of polyanthracene (PAT) in aqueous solution of H_2SO_4 presented in Fig. 7 shows broad and red shift at maximum wavelength 275, 400 and 450 nm in contrast to the structured spectrum of anthracene. From the figure it is observed that absorption at maximum wavelength 275 nm is due to aggregation of monomers while other absorptions at maximum wavelength 400 and 450 nm is due to extended conjugation of polymer chains. Fluorescence and fluorescence excitation spectra of polyanthracene (PAT) in aqueous H_2SO_4 solution are shown in Fig. 8. The excitation and emission spectra of anthracene in chloroform are shown in the same figure for the sake of comparison. Anthracene in aqueous H_2SO_4 solution forms a red dye and hence its dilute solution in chloroform is used. It is seen that the excitation and emission spectra of anthracene in chloroform are structured and exhibits mirror image relationship with negligible Stokes shift. However, a spectrum of PAT in aqueous H_2SO_4 solution is a broad and structureless band with maximum emission at 440 nm and exhibits significant Stokes shift of

3382.38 cm^{-1} . The observed Stoke's shift is in support of the linear conjugation of anthracene units during polymerization.⁴⁷

Results and discussion

Selective fluorescence 'Turn-Off' of polyanthracene (PAT) by Fe^{3+} ions

Conjugated polymers have ability to recognize or bind with various metal ions due to presence of wiring molecular recognition sites.⁴⁸ Therefore, the metal ion recognition behavior of polyanthracene (PAT) was evaluated from changes in the fluorescence intensity upon addition of different metal ions. The fluorescence response of PAT containing each of 160 μM solutions of the metal ions like Ca^{2+} , Mg^{2+} , Fe^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , Cu^{2+} , Ag^+ and Fe^{3+} is shown in Fig. 9. Figure reveals remarkable fluorescence quenching in the composite holding with Fe^{3+} ion solution as compared with other metal ions. In the case of other metal ions, it appears that the addition of most common metal ions like Ca^{2+} , Mg^{2+} and Fe^{2+} slightly enhances the fluorescence inspite of quenching and the presence of other metal ions like Cd^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , Cu^{2+} and Ag^+ quenches the fluorescence to very small extent. In comparison, Fe^{3+} ions only induce a sizable quenching effect. Therefore, to explore the use of PAT as a probe for quantitative determination of Fe^{3+} ions, a fluorescence titration was carried out by adding incremental amounts of Fe^{3+} ion solution in the concentration range 0-160 μM . It is observed that the fluorescence intensity of a fixed concentration of PAT at 440 nm decreases gradually with increasing Fe^{3+} ion solution without any spectral modification as shown in Fig. 10. The fluorescence quenching efficiency was calculated by relation $(1 - F/F_0)$ and maximum quenching upto 50.54% was obtained when concentration of Fe^{3+} was 160 μM . The large

quenching efficiency largely ‘Turn Off’ the fluorescence of PAT to greater extends and also provides an optimal ‘Off-State’ for sensitive ‘Turn On’ quantitative analysis. This fluorescence quenching is because of binding interaction of Fe^{3+} with excited PAT.

The quenching results fit into the conventional linear Stern-Volmer equation given below.

$$\frac{F_0}{F} = 1 + K_{sv}[Q] \quad [1]$$

where F and F_0 are the fluorescence intensities of PAT at given ferric ion concentration and in a ferric ion-free solution respectively. Fig. 11 represents Stern-Volmer quenching line describing F/F_0 as a linear function of ferric ion concentration is linear. From the graph, linear fit obtained is 0.976 and quenching rate constant K_{sv} was found to $5.8 \times 10^3 \text{ M}^{-1}$.

Mechanism of binding interaction:

The selectivity observed for Fe^{3+} ions over to other ions is remarkably high. Evidently, the coexistence of other ions did not interfere with the fluorescence detection of Fe^{3+} ions. The absorption spectra of PAT in absence and presence of different metal ions in aqueous acidic solution are shown in Fig. 12. The characteristic absorption band of PAT remains unchanged after the treatment with most of the metal ions such as Ca^{2+} , Mg^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , Cu^{2+} , Ag^+ and Fe^{2+} . In contrast, the absorption band of PAT at 280 nm attributed to conjugated backbone is red shifted to 300 nm and increased significantly upon in presence of Fe^{3+} ions mostly due to electron density induced in the backbone of PAT by Fe^{3+} ions. It is thus reasonable to consider that the Fe^{3+} ion undergo complexation with PAT due to the electron density variation on the main chain and may generate trap level below the Lower Unoccupied

Molecular Orbital (LUMO) of PAT. As the addition of Fe^{3+} solution quenches intensity of fluorescence of PAT without any spectral shift, the mechanism of photoinduced electron transfer (PET) from excited PAT to Fe^{3+} is most effective in the present complexation system and is further supported by excited state life time measurement of PAT in presence of Fe^{3+} . Fig. 13 shows fluorescence decay profile of PAT in presence of Fe^{3+} . The life time estimate from the decay profile of 0.834 ns and seen to be decreased to 0.640 ns and then to 0.390 ns when 80 μ M and 160 μ M solution of Fe^{3+} ions was added respectively. The observed decrease in the excited state life time of PAT with Fe^{3+} ion concentration suggest that the static process contribute to the quenching of fluorescence of PAT.⁴⁹ Conjugated polymers involve binding of entire main chain not only through saturated sigma bonds but also by a continuous pattern of saturated π -bonds which creates a molecular wire between each repeating units. The resultant coalescing of molecular orbitals give a semiconductor band structure including a valence band (VB) filled with electrons and a conduction band (CB) devoid of electrons as shown by band diagram in Fig. 14. The binding of Fe^{3+} generates trap level in the band gap region which will be a lowest unoccupied molecular orbital (LUMO) of Fe^{3+} . Excitation of PAT by low energy UV photon causes promotion of an electron to the CB which is now of much higher energy and creates a hole in the VB. The low lying LUMO of Fe^{3+} can then in an exergonic process, accept electron from the excited state of PAT. This in effect destroys the polymer based excited state and fluorescence of PAT is decreased. The final step of reverse electron transfer from Fe^{3+} to the VB of PAT is nonradiative process and satisfies the hole in the VB as shown in Fig.14.

Application of proposed method for quantitative detection of ferric ions from ferrous succinate in pharmaceutical capsules

The proposed method of fluorescence quenching of polyanthracene (PAT) by Fe^{3+} was applied for the determination of ferrous succinate oxidizing by Fe^{2+} contained in pharmaceutical tablet namely Tonoferon-SF capsules available commercially in the market by East India pharmaceuticals Ltd. Kolkata, West Bengal (India). After carefully peeling off the coat, tablet was ground into fine powder. The powder was dissolved in appropriate amount of aquaregia and then heated to dryness to oxidize Fe^{2+} ions to Fe^{3+} ions.⁴⁵ After being cooled; it was transferred into calibrated flask and diluted to 10 mL with water, then filtered and undertaken for determination. The standard addition method was used and Fe^{3+} was estimated from the analysis of three parallel samples. The results listed in Table No. 2 are in good agreement with certified value of the iron in the capsules. The fluorescence quenching method has good repeatability and relative standard deviation is 0.56 %. The average recovery is 97.1%. The limit of detection defined by equation, $LOD = 3\sigma/k$, where σ is the standard deviation of the y-intercepts of the regression lines and k is the slope of the calibration graph.⁵¹ The estimated LOD limit is 54.89 μ M. The detection limit is better than that of ordinary methods for the detection of Fe^{3+} like volumetric determination and titrimetric analysis. Therefore, the proposed method is a successful application of determination of Fe^{3+} from pharmaceutical samples in aqueous solution.

Polyanthracene (PAT) as a selective fluorescence ‘Turn-On’ optoprobe for F^- ions

The approach used to design ‘Turn-On’ sensor with operating principle based on the removal of CP-attached Fe^{3+} quencher through the interaction with anion.²⁵ The competitive experiment was done for various anions such as HCO_3^- , CH_3COO^- , HPO_4^- , HSO_4^- , NO_3^- , SO_3^- , Br^- , Cl^- and F^- . Fig.15 shows the fluorescence spectra of probe containing several

anions each of concentration 160 μM monitored at the excitation wavelength of PAT ($\lambda_{\text{ex}} = 383$ nm). It is observed that only F^- anions induces remarkable fluorescence enhancement. The carboxylate (CH_3COO^-) anion instead of quenching a slight fluorescence enhancement due to its basicity being same as that of F^- .⁵² The other anions such as HCO_3^- and HSO_4^- produces precipitate with ferric ions, by which fluorescence is slightly enhanced due to release PAT from complex. From these observations, it is concluded that the mixture of polyanthracene- Fe^{3+} could be selective for recognition of F^- ions over to other anions. To investigate practical application to sense F^- ions, a fluorescence titration was carried out by adding its incremental amounts into mixture of PAT and Fe^{3+} taken in some definite proportion and results are presented in Fig. 16. From the fluorescence spectra it is observed that the fluorescence intensity of PAT is enhanced gradually with increased F^- ion solution without any spectral modification. These results indicate that the F^- ion undergoes an interaction with Fe^{3+} and does not permit it to complex with PAT and thus prevent PET. The sensing of F^- was further supported by fluorescence life time of PAT decreased by Fe^{3+} solution to 0.390 ns was again increased to 0.814 ns when F^- solution of concentration 160 μM was added into the mixture of PAT and Fe^{3+} solutions.

A calibration curve constructed by plotting ΔF (increase in fluorescence intensity) Vs concentration of F^- ions is presented in Fig.17. The increase in 'Turn On' fluorescence (ΔF) is a linear function of F^- ion concentration with correlation coefficient equal to 0.9654. According to universal method for calculating the detection limit, the F^- ion in the of concentration range of 0-160 μM is 1.72593 μM , which is lower than the enforceable drinking water standard for fluoride of 4 mg/L (221 μM) laid by the United State Environmental Protection Agency (USEPA).

Selectivity of probe for F^- and fluorescence ‘Turn On’ mechanism :

The usefulness of fluorescence ‘Turn On’ method by using of mixture of PAT and Fe^{3+} for F^- ions recognition in aqueous acidic solution was explored by measuring the changes in fluorescence intensity of the mixture in the presence of co-existing anions such as HCO_3^- , CH_3COO^- , HPO_4^- , HSO_4^- , NO_3^- , SO_3^- , Br^- , Cl^- and F^- each of 160 μM concentrations. The results presented in Fig. 15 (red bar histogram) reveal a remarkable fluorescence enhancement response only in the presence of F^- ion solution and no other anions caused noticeable enhancement in these experiments. It is therefore concluded that the Fe^{3+} complexed with PAT is more inclined towards hard base F^- ion to form stable $[FeF_x]^{n-}$ complex and thus release of PAT increased its fluorescence with addition of F^- ions exhibiting fluorescence ‘Turn On’.

Application of proposed method for quantitative detection of F^- from environmental water samples

The proposed fluorescence ‘Turn Off -Turn On’ of polyanthracene (PAT) was applied for the determination of F^- ions from environmental water samples. The water samples collected were portable drinking water, lake and river water from local area (Kolhapur, Maharashtra state, India). Impurities and suspended matters from water samples were removed by filtration process using Whatmann filter paper No. 41 and then boiled for 5 minutes to remove dissolved gaseous. Then water samples were spiked with standard F^- at two different concentration levels, and were diluted with double distilled water within the working range of 0-160 μM of F^- ions. These samples were analyzed for F^- content with polyanthracene- Fe^{3+} fluorescence ‘Turn On’ method. The accuracy and reliability of the method was further ascertained by recovery studies

using standard addition method and percent recovery was found in between 98.93 to 102.87%. The results summarized in Table 3, show good agreement with spiked F^- ion concentrations and demonstrate that the polyanthracene (PAT) is effective probe for sensing and estimation of F^- ions from environmental water samples.

Conclusion

Polyanthracene (PAT) prepared by facile chemical oxidative route using anthracene was shown to be a selective optoprobe to sense Fe^{3+} and F^- ions from aqueous acidic solution as compared to other conventional fluorescent probes. The detection method is based on fluorescence ‘Turn Off’ and ‘Turn On’ mechanism exhibiting by PAT in presence of Fe^{3+} and then in F^- ion solution. This single probe has potential application for the detection of Fe^{3+} in the pharmaceutical tablets and fluoride ions in the environmental water samples. The present analytical method is more selective, simple, less expensive, quick method and requires no any prior separation of analytes using expensive chromatography, extractions methods etc.

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Graphical Abstract

Off-On fluorescent polyanthracene for recognition of ferric and fluoride ions in aqueous acidic media: Application to pharmaceutical and environmental analysis

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Fluorescent polyanthracene (PAT) prepared by chemical oxidative route shown to recognize Fe^{3+} and F^- ions in aqueous acidic solutions using fluorescence 'Turn Off' and 'Turn On' approach. The sensing mechanism of PAT as fluorescent probe is illustrated using band diagram and the spectral results as given below.

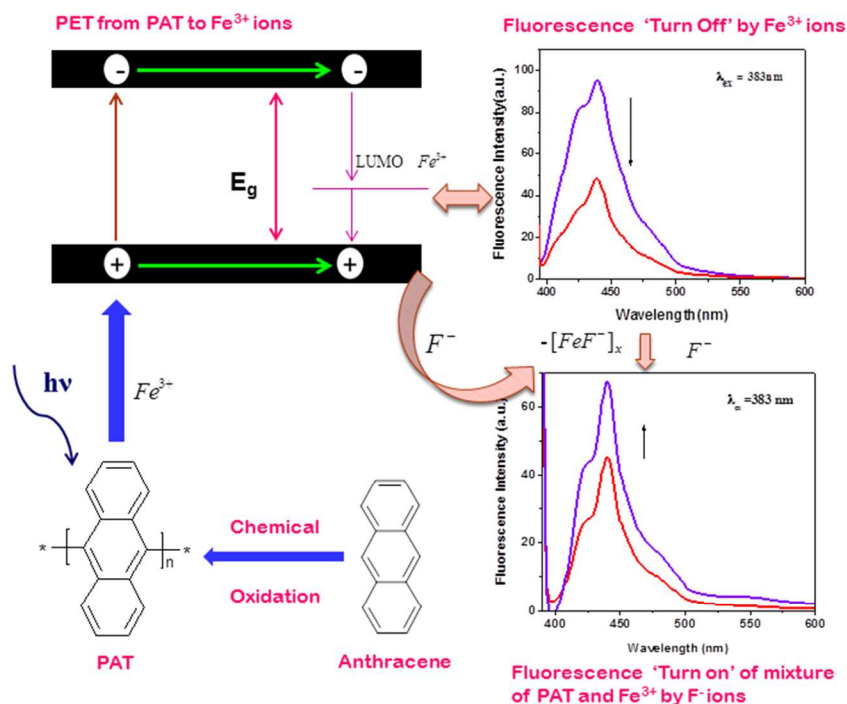


Figure captions

Fig. 1 IR spectra of anthracene monomer (A) and polyanthracene (PAT) (B).

Fig. 2 FT-Raman spectra of solid powdered anthracene (A) and polyanthracene (PAT) (B).

Fig. 3 ^1H NMR spectra polyanthracene (PAT) in DMSO-d_6 as a solvent.

Fig. 4 A) Particle size distribution of polyanthracene (PAT) particles suspended in water (DLS analysis) and (B) SEM photomicrograph of polyanthracene (PAT) powder.

Fig. 5 X-ray diffraction profiles of anthracene (A) and polyanthracene (PAT) (B).

Fig. 6 TGA and DTA curve of polyanthracene (PAT).

Fig. 7 UV-Visible absorption spectrum of 0.25 mg/L polyanthracene (PAT) in aqueous acidic solution of H_2SO_4 (A) and spectrum of 0.1 mg/L anthracene solution in chloroform (B).

Fig. 8 Normalized excitation and fluorescence spectra of anthracene in chloroform and polyanthracene (PAT) in aqueous acidic solution of H_2SO_4 .

Fig. 9 Fluorescence Intensity response (F_0-F) at excitation wavelength 383 nm in absence and presence of the Fe^{3+} ions and several coexisting cations like Mg^{2+} , Ag^+ , Ca^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Co^{2+} , Hg^{2+} , and Fe^{2+} each of concentration 160 μM in aqueous acidic media.

Fig. 10 Fluorescence response of polyanthracene (PAT) (0.25 mg/L) in aqueous acidic solution at varied concentration of Fe^{3+} ions solution in the range of 0-160 μM (excitation wavelength of 383 nm).

Fig. 11 Stern-Volmer plot of polyanthracene (PAT) fluorescence quenched by Fe^{3+} ions in aqueous acidic solution.

Fig. 12 UV-Visible absorption spectra of polyanthracene (PAT) (0.25 mg/L) in aqueous acidic solution containing different metal ions solution each of 160 μM concentration.

Fig. 13 Fluorescence life time spectra of polyanthracene (PAT) (0.25 mg/L) in aqueous acidic solution containing different concentration of Fe^{3+} ions, A) 0 μM (without Fe^{3+} ions), B) 80 μM and C) 160 μM Fe^{3+} .

Fig. 14 Band diagram illustrating exciton transport in polyanthracene (PAT) and electron transfer resulting in fluorescence quenching.

Fig. 15 Fluorescence Intensity response (F_0-F) of mixture of polyanthracene (PAT) and Fe(III) solution in the presence and absence of the F^- ion solution and several coexisting anions like HCO_3^- , CH_3COO^- , HPO_4^- , HSO_4^- , NO_3^- , SO_3^- , F^- , Br^- , Cl^- each of concentration 160 μM in aqueous acidic media.

Fig.16 Fluorescence spectra of mixture as polyanthracene (PAT) (0.25 mg/L) and Fe^{3+} solution of 160 μM concentrations in aqueous acidic solution with varying concentration of F^- ions in the concentration range 0-160 μM monitored at excitation wavelength of 383 nm.

Fig.17 Calibration curve of fluorescence 'Turn On' of polyanthracene (PAT) at varied concentration of F^- ion solution.

Fig.1

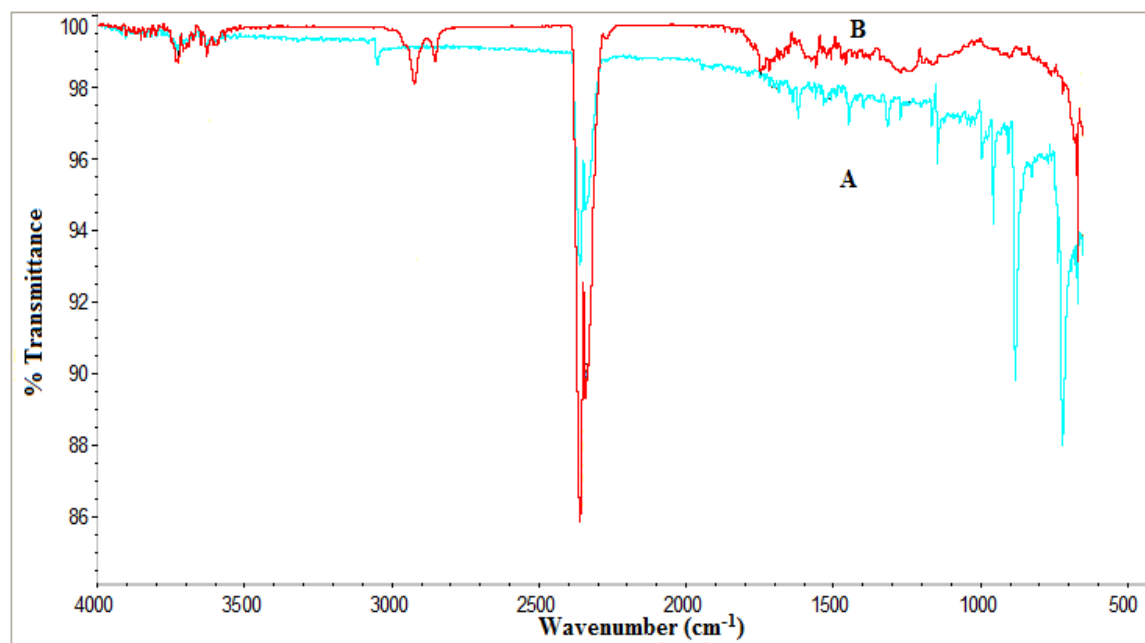


Fig.2

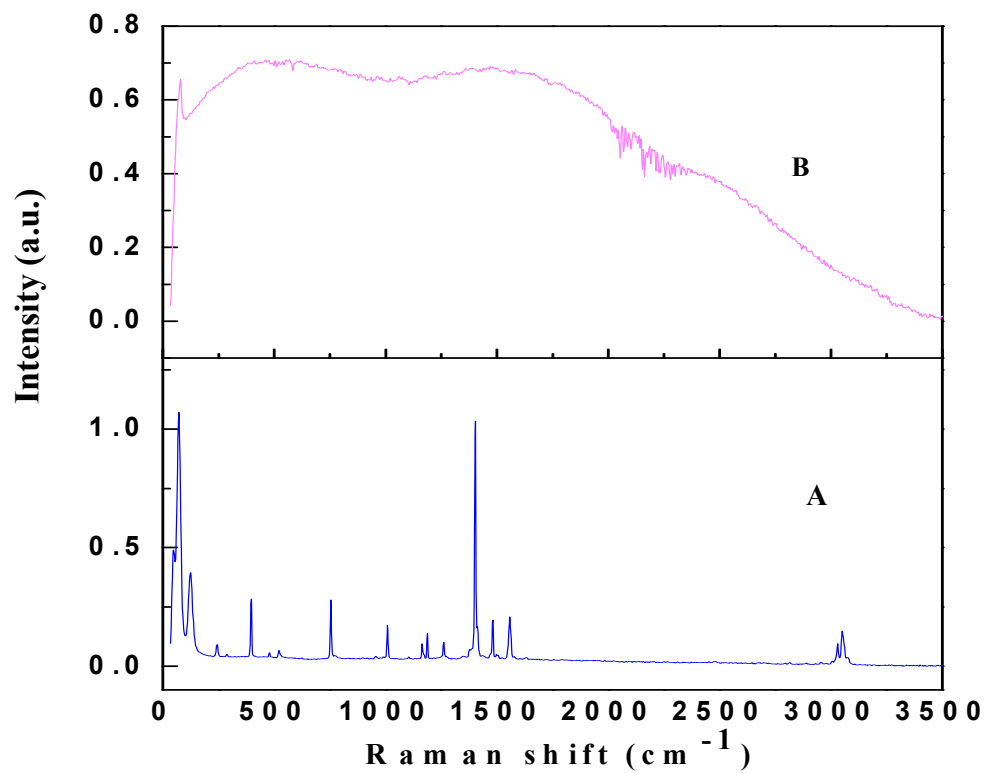


Fig.3

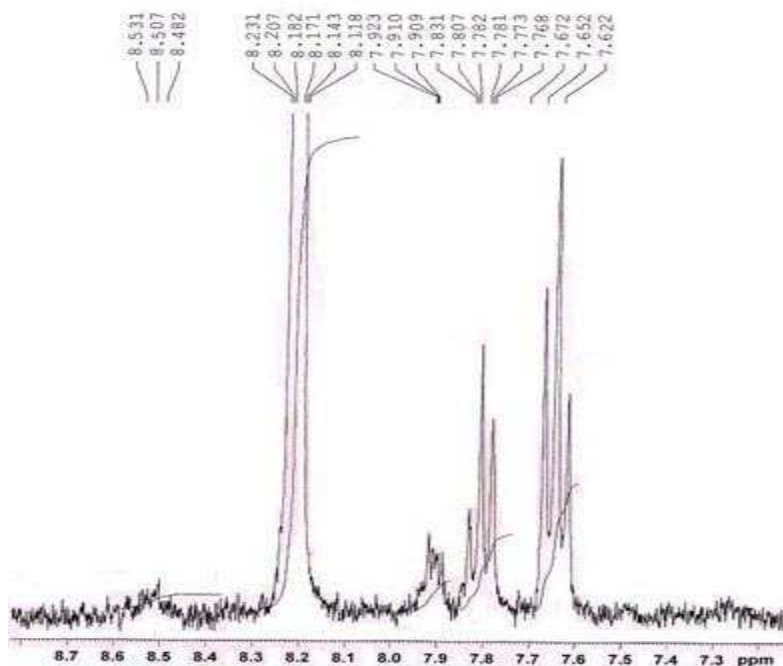


Fig.4

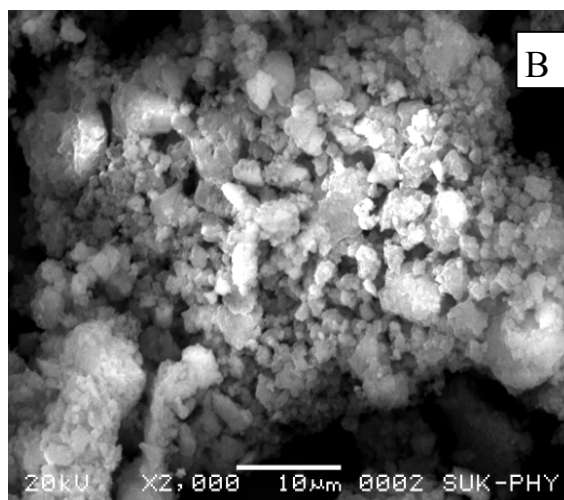
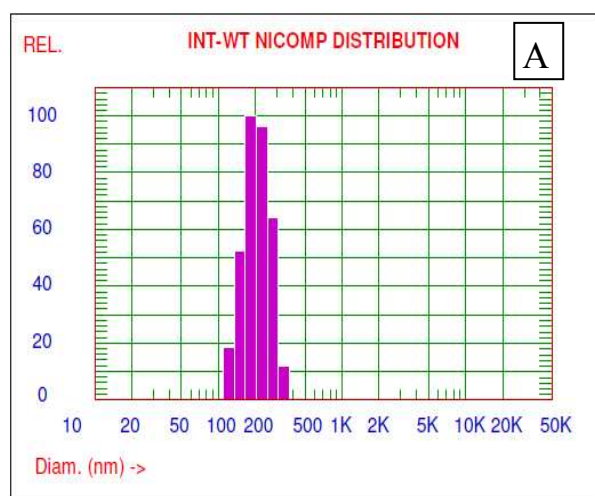


Fig. 5

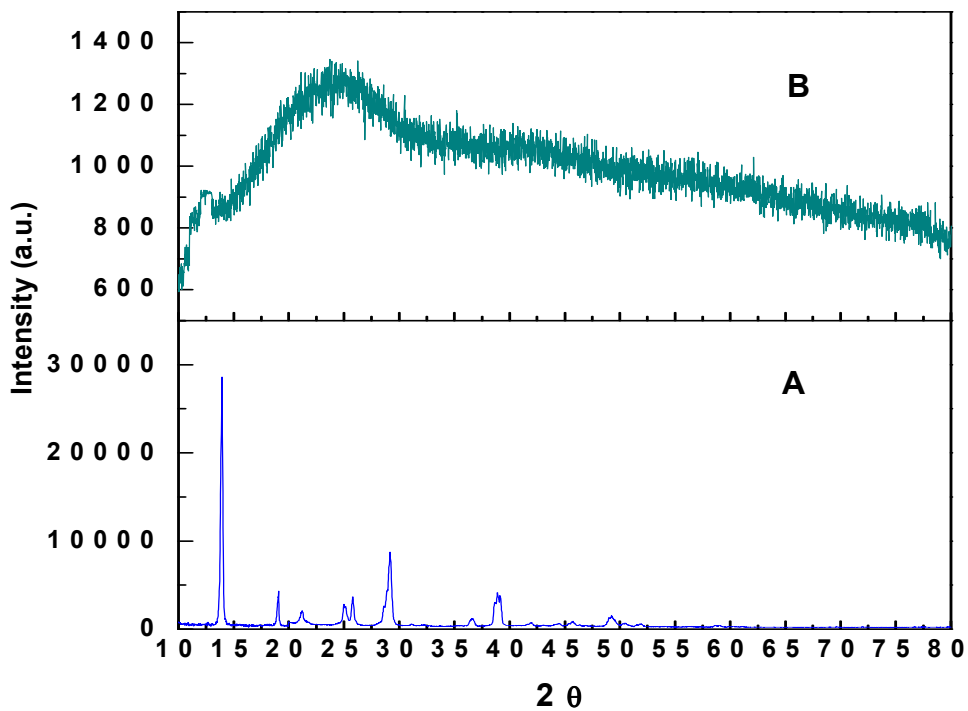


Fig.6

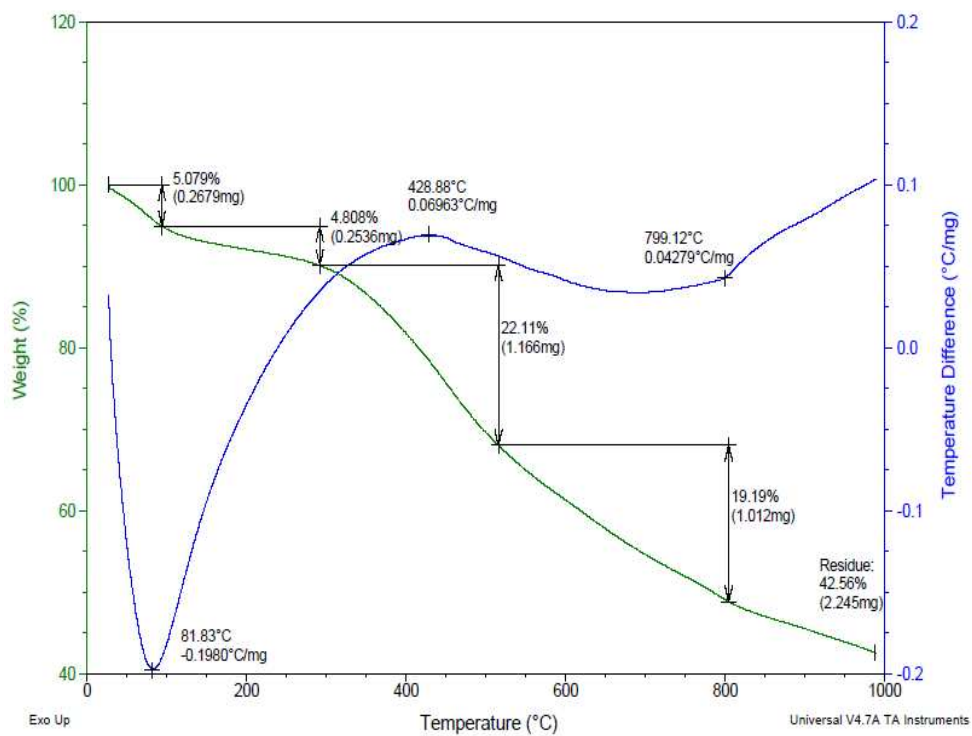


Fig.7

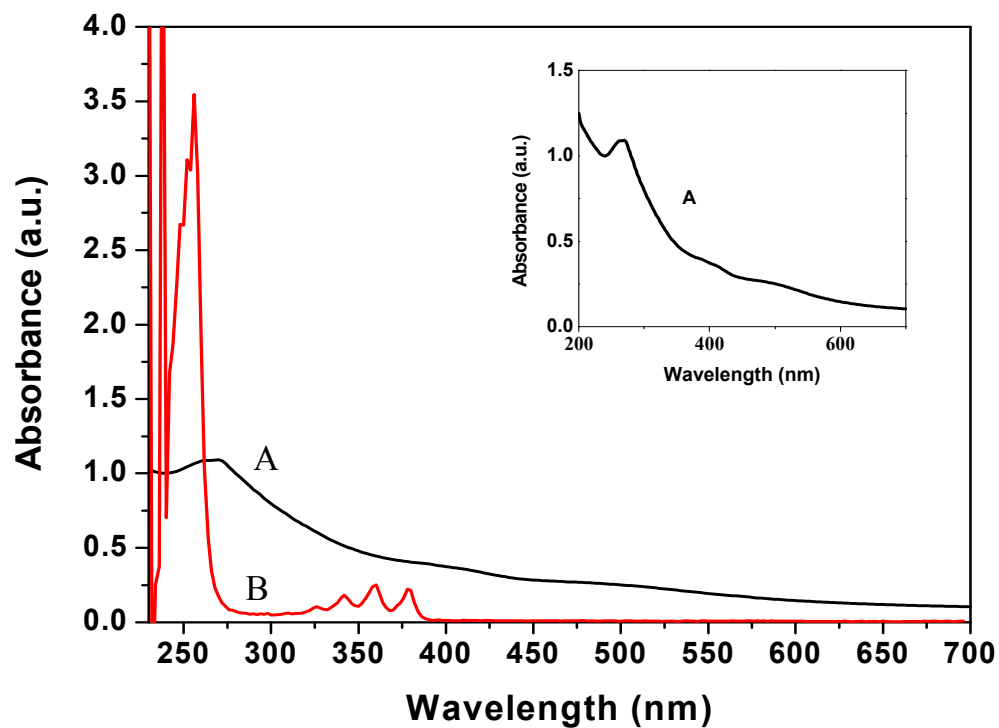


Fig.8

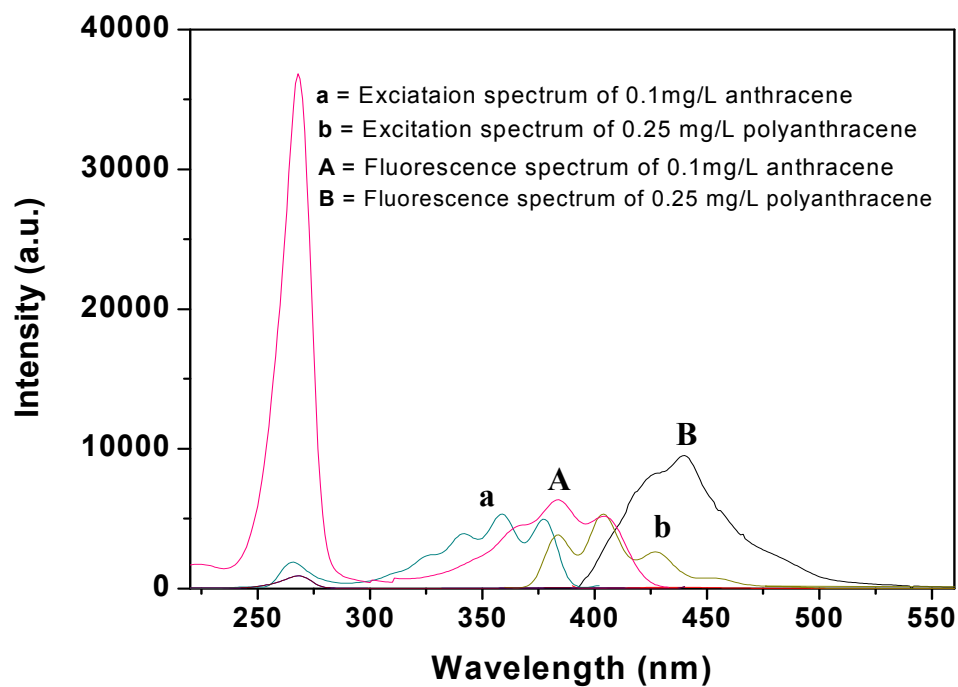


Fig.9

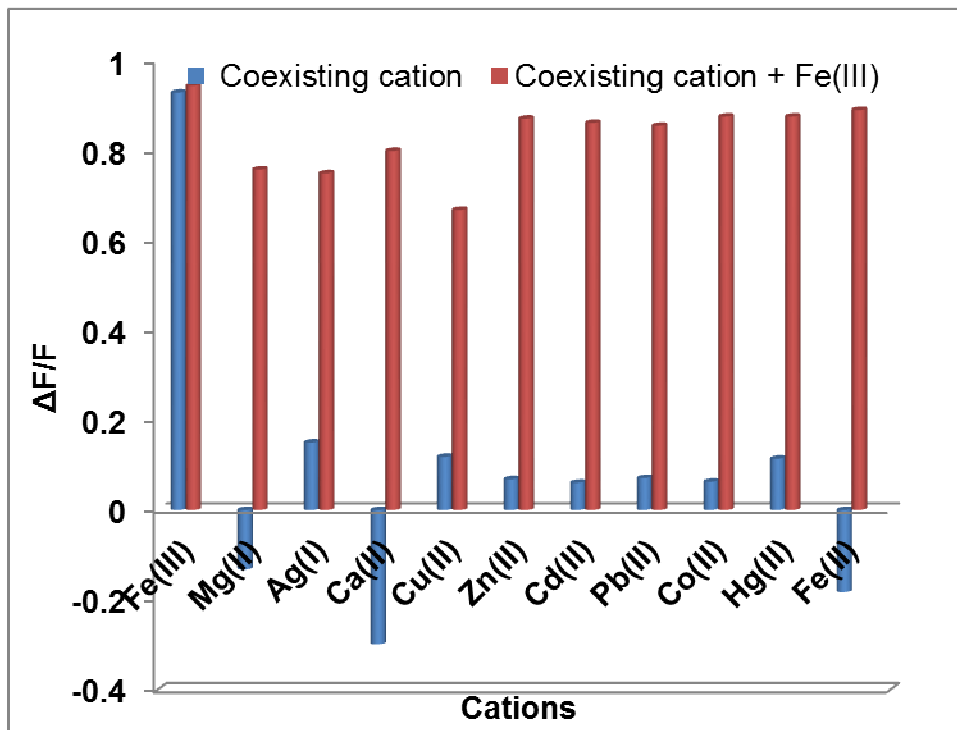


Fig.10

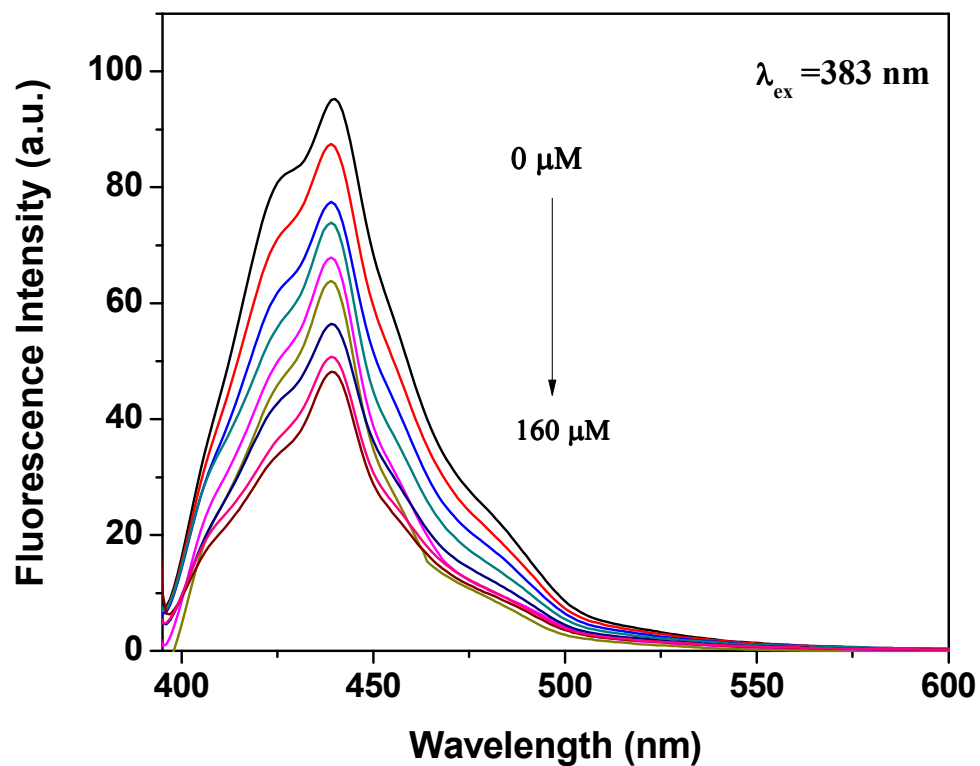


Fig. 11

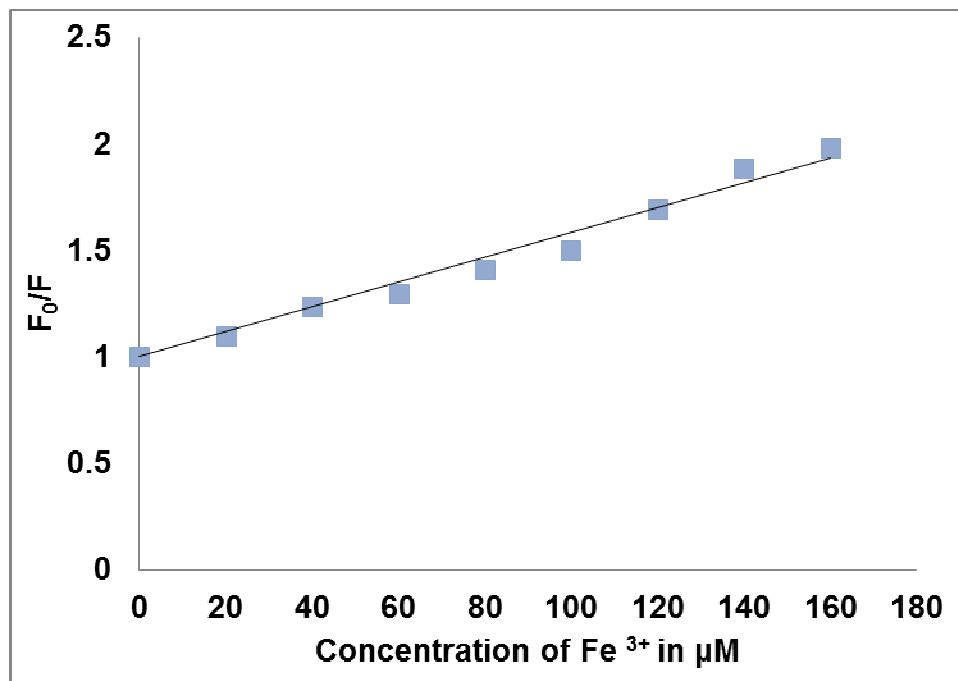


Fig.12

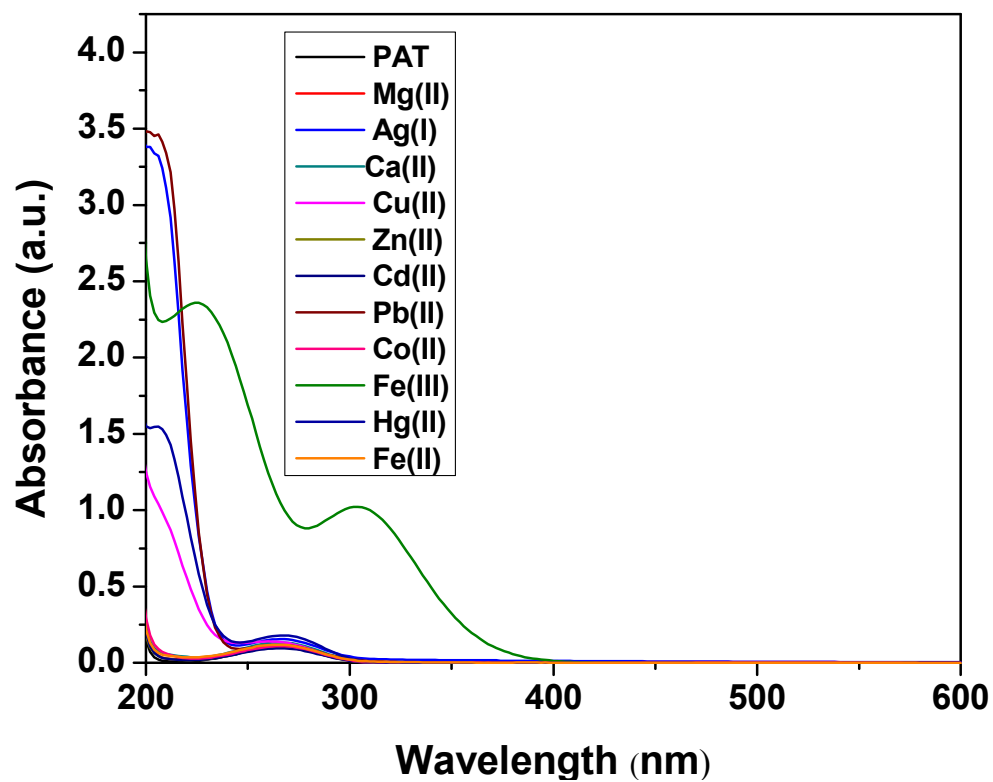


Fig.13

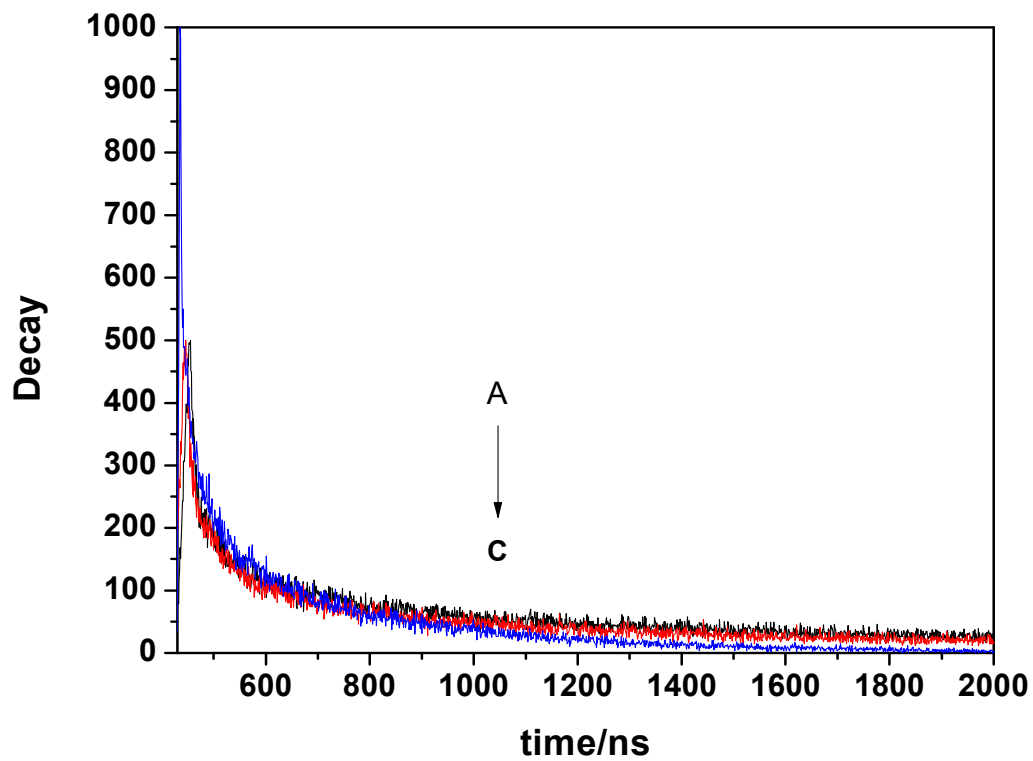


Fig.14

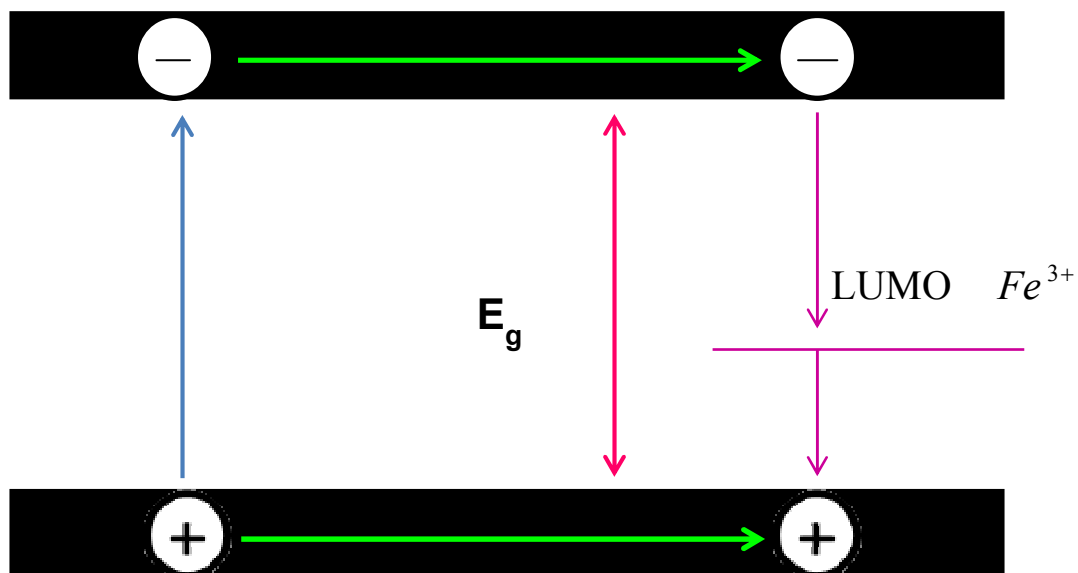


Fig.15

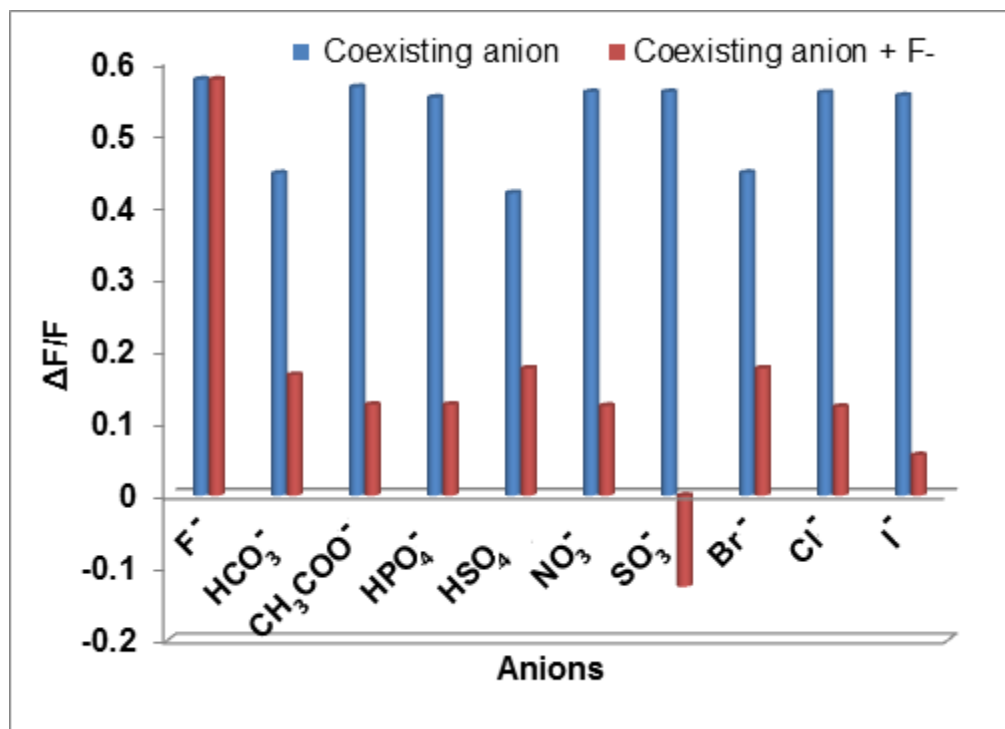


Fig.16

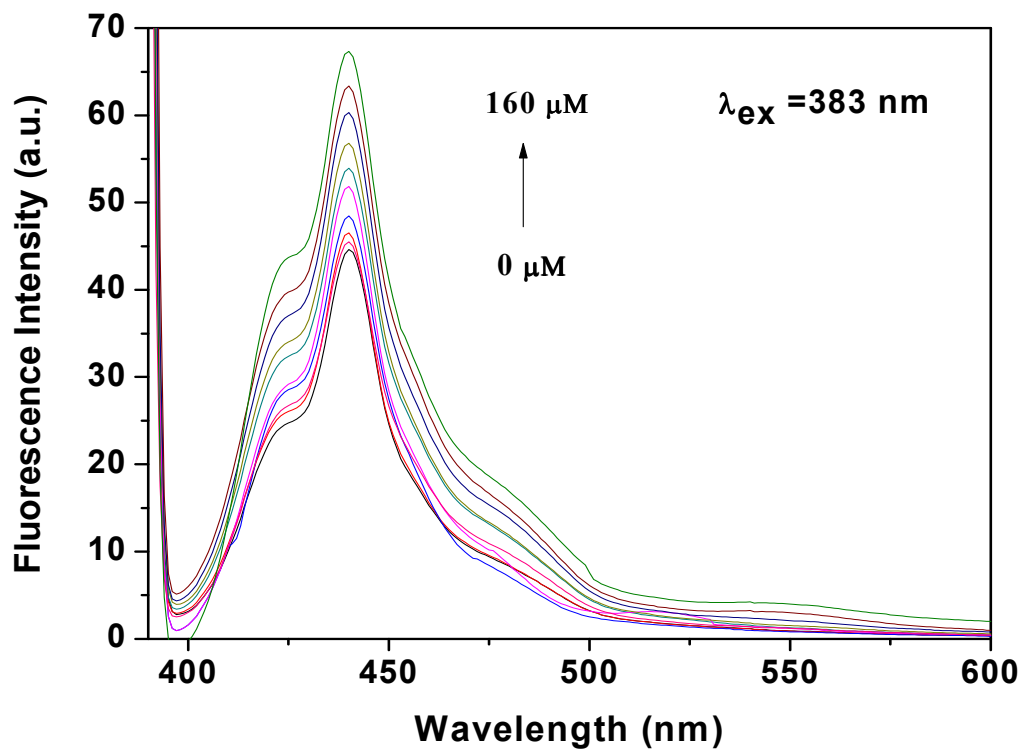


Fig.17

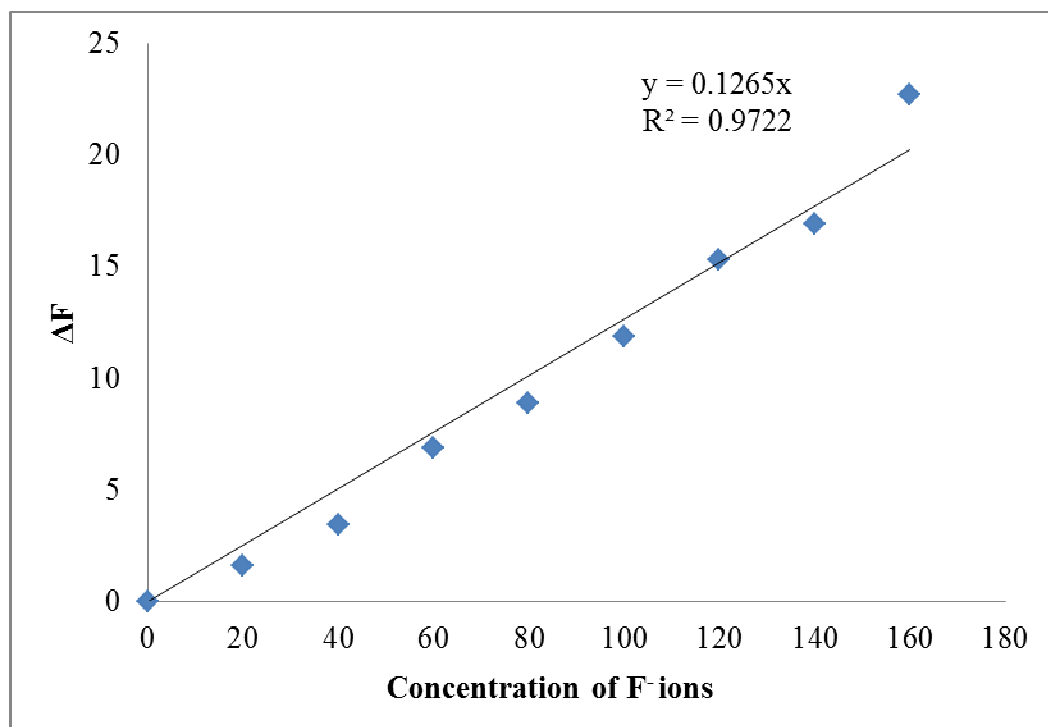


Table captions

Table No. 1 GPC data for polyanthracene

Table No. 2 Determination of ferric ions from ferrous succinate containing pharmaceutical capsules

Table No. 3 Determination of F^- ions in water samples from different water sources by standard addition method ($n = 3$).

Table No.1

Polymer	Molecular weight		Polydispersity index	Degree
	g/mol		(PDI)	Polymerization
	M_n	M_w	M_w/M_n^a	(DP)
Polyanthracene	1724	2321	1.34	13

^a Measured on GPC in chloroform; polystyrene was used as the calibration standard.

Table No.2

Sample source of Fe	Composition	Amount of ferric			
		Certified Value	Found ^a	Recovery	RSD
Tonnoferon-SF Capsule East India pharmaceutical works Limited Kolkata, West Bengal (India)	Ferrous Succinate 200 mg (Equivalent to elemental Iron 70 mg) Folic Acid (Vit B9) 400 µg Succinic Acid 210 mg	70 mg (per tablet)	68 mg (per tablet)	97.1%	0.56%

^a Estimated value of ferric is average of five determinations

Table No.3

Resources of Water samples	Amount of F ⁻ added (μM)	Amounts of F ⁻ Found ^a (μM)	Recovery of F ⁻ (%)	RSD (%)	Relative error (%)
Drinking water	60.00	59.798	99.663	2.146	0.337
(Department of Chemistry, Shivaji University Kolhapur, Maharashtra state, India)	100.00	98.938	98.938	1.073	-1.062
Rajaram Lake	60.00	61.002	101.67	0.786	-1.67
(Kolhapur, Maharashtra state, India)	100.00	101.24	101.24	2.014	-1.246
Panchganga River	60.00	61.453	102.421	0.065	-2.421
(Kolhapur, Maharashtra state, India)	100.00	102.878	102.878	1.307	-2.878

^aEstimated value of fluoride is average of three determinations