



# A Selective Turn off Fluorescence Sensor Based on Propranolol-SDS Assemblies for Fe<sup>3+</sup> Detection

Varsha Gujar<sup>1</sup> · Vijay Sangale<sup>1</sup> · Divya Othoor<sup>1</sup>

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## Abstract

A fluorophore modulation with sodium dodecyl sulphate (SDS) assemblies for the selective and sensitive sensing of Fe<sup>3+</sup> ions in aqueous solution is illustrated in this work. Emission spectral characteristics of fluorescent molecule, propranolol (PPH) was intact in presence of metal ions. While on modulation with SDS assemblies, PPH was transformed into a tuneable sensor for Fe<sup>3+</sup> ions. This sensor ensemble was not only highly sensitive towards Fe<sup>3+</sup> ions in aqueous solution with detection limits lower than 3 μM but also possess high discriminating efficiency in presence of other metal ions like Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup>, Hg<sup>2+</sup> and Mn<sup>2+</sup>. The electrostatic interaction of the anionic group of surfactants with the metal cations significantly increases the communication between metal ions and PPH moiety which results in the quenching of PPH fluorescence. We have employed fluorescence steady state and lifetime studies to understand the metal sensing behaviour of the PPH-SDS sensor system. Principal component analysis (PCA) was used to evaluate the discriminative ability of the developed sensor system towards Fe<sup>3+</sup> ions.

**Keywords** Propranolol · SDS · Fluorescence quenching · Tuneable sensor · Selective detection Fe<sup>3+</sup> ions

## Introduction

Presence of various metal ions in wide range of environmental and biological processes insists their recognition and the development of sensors for their detection [1, 2]. Optical sensing has been an advantageous method of metal ion detection due to their relatively lower cost, high selectivity and sensitivity compared to other instrumental methods [3]. Therefore, recent studies on metal ions sensing are focused on the development of selective, sensitive and reversible ion sensors using spectral methods [4]. Spectrofluorimetric sensing methods are generally based on fluorescence turn on or turn off of fluorophore which along with the various fluorescence parameters can be utilized for developing sensor design strategies.

Metal ions can modify either the electronic structure or the molecular structure of the fluorophore which can probably cause a change in the intensity of fluorescence, shift in

wavelength maximum, modification of the orientation or distance between the donor acceptor pair of fluorophores. Fluorosensor for metal ions is generally composed of a receptor (for binding metals ions) linked to a fluorophore which acts as transducer (for signal output to report the sensing process). The specific interactions between the receptor and the metal ions induce the high selectivity and sensitivity to the sensor system [5].

Exploration of alternative strategies for the development of aqueous based fluorosensors for metal ions is highly required as most of the synthesised fluorophores of sensor system are soluble in organic solvents or having poor solubility in water. In this context, amphiphilic surfactants have shown great potential in the modification of sensing behaviour of fluorophores by acting as a receptor for analytes especially metal ions. Surfactant not only enhances the solubility of fluorophore but also enhances its quantum yield by incorporating it to the micellar phase by providing them hydrophobic environment [6]. These properties of surfactant assemblies have been widely used in developing and modulating fluorosensor systems for metal ions sensing [7–9]. Anionic surfactants are used as a receptor in the sensor system for the metal ions such as Zn<sup>2+</sup>, Hg<sup>2+</sup>, Cu<sup>2+</sup> etc [10, 11], while

✉ Divya Othoor  
divya@chem.unipune.ac.in

<sup>1</sup> Department of Chemistry, Savitribai Phule Pune University, Ganeshkhind Road, Pune 411007, India

cationic surfactants are used as a receptor for the sensing of anionic ions  $S^{2-}$ ,  $F^-$ ,  $CN^-$  *etc* [12–14]. Pyrene derivative-SDS assemblies and  $Cu^{2+}$  based ternary sensor system was used for the fast detection of arginine and lysine in aqueous solution [15]. Foldamer-based fluorosensor system which is modulated by surfactant is used by Yan Zhao and co-workers for  $Hg^{2+}$  ions sensing [9]. In our previous work, we have explored the sensing behaviour of Amiloride (AMI) for the metal ions in presence of different surfactants and developed AMI-SDS sensor system for metal ions [10, 16]. CTAB was employed by Matteo Berton and co-workers to develop a self-assembled chemosensor with lipophilic ligand *N*-decyl-glycylglycine which is selective towards  $Cu^{2+}$  ions [17]. Fluorescence on-off sensing system that is selective towards  $Ni^{2+}$  and  $Cu^{2+}$  was developed using non-ionic Triton X-100 surfactant with lipophilised diamino–diamido ligand [18]. A new strategy has been introduced by Das et al., which demonstrates the transformation of a cationic fluorophore in to an efficient sensor for copper ions detection by the use of anionic surfactant of proper hydrophobic chain length and concentration [2].

Iron is the most abundant transition metal in biological systems among all other metal ions. It is widely distributed in environmental and biological materials. Iron plays many crucial roles in processes like oxygen uptake, oxygen metabolism, electron transfer, and transcriptional regulation. Deficiency or excess of iron with respect to the standard permissible limit can cause serious disorders like, hepatitis, various cancers, hemochromatosis, alzheimer's disease, parkinson's disease and dysfunction of heart, liver, and pancreas *etc* [19, 20]. Despite of widespread application of  $Fe^{3+}$ , sensitive and selective fluorescent sensors are relatively less than other heavy and transition metal ions [21, 22], such as,  $Hg^+$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  [23–26]. Therefore, exploration of new fluorosensor systems for  $Fe^{3+}$  ions with high selectivity, cost effectiveness and easy availability is highly recommended.

In this work we have selected propranolol hydrochloride [(RS)-1-Isopropyl n-3-(1-naphthoxy) propan-2-ol hydrochloride] (PPH), a naphthol derivative, for the study of its sensing behaviour towards metal ions (Fig. 1). The interaction of fluorophore with various surfactants was carried out and the PPH-SDS system was used further for sensing different metal ions. It shows a selective sensing for  $Fe^{3+}$  ions with good detection limits. The presence of other metal ions did not exhibit any interference on the sensing of  $Fe^{3+}$  ions. Fluorescence lifetime (TCSPC) and chemometric data analysis results are in good agreement with the spectrofluorimetric results.

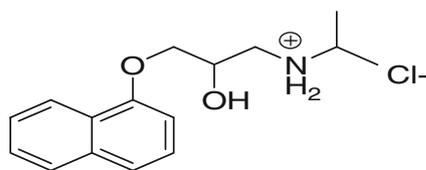


Fig. 1 Structure of propranolol hydrochloride

## Experimental

### Materials

Propranolol (PPH) and sodium dodecyl sulphate (SDS) were purchased from Sigma-Aldrich and used as received without further purification. Metal solutions were prepared from their respective sulphate or nitrate salt. Copper was prepared from  $CuSO_4 \cdot 7H_2O$ , lead from  $Pb(NO_3)_2$ , zinc from  $ZnSO_4 \cdot 7H_2O$ , nickel from  $NiSO_4 \cdot 6H_2O$ , iron(II) from  $Fe(SO_4)_3 \cdot 7H_2O$ , cadmium from  $CdSO_4 \cdot 8H_2O$ , cobalt from  $CoSO_4 \cdot 7H_2O$ , aluminium from  $Al_2(SO_4)_3 \cdot 16H_2O$ , magnesium from  $Mg(SO_4) \cdot 7H_2O$ , iron(III) from  $Fe_2(SO_4)_3 \cdot H_2O$ , manganese from  $MnSO_4 \cdot H_2O$ , mercury from  $HgSO_4$ . All the metal salts used are A.R. grade and were purchased from S.D. fine chemicals and used as received without further purification.

Stock solutions were prepared in higher concentrations and diluted as per the required concentrations. The concentration of PPH was kept constant at  $5 \times 10^{-6}$  M for the steady state fluorescence emission study. Surfactants concentrations were varied from their respective pre-micellar to micellar concentrations. All metal ions were maintained at 1 ppm concentrations. For ferric ions, a series of concentrations ranging from 0.1–1 ppm were prepared. To attain equilibrium, all the solutions were kept for 24 h at room temperature. Reproducibility in the results was achieved by performing the experiments in triplicates.

### Method

#### Steady State Fluorescence

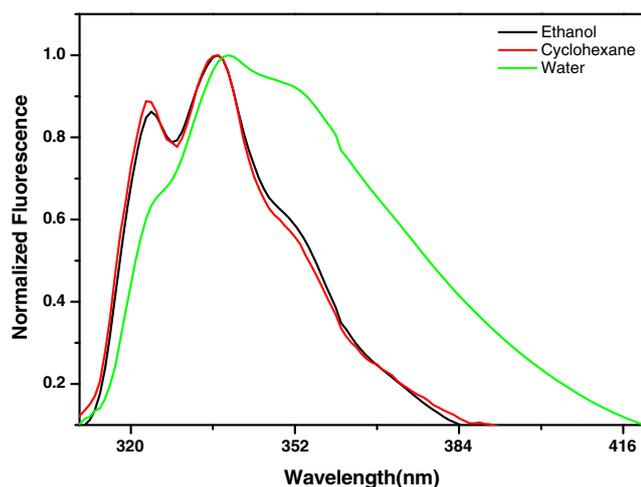
JASCO FP 8300 spectrofluorimeter was used to record steady state fluorescence emission. All measurements were recorded with scan speed of  $1000 \text{ nm s}^{-1}$ . The slit width of 2.5 nm was kept for both the excitation and emission. Excitation wavelength for PPH was kept at 288 nm and the emission was measured from 298 nm to 500 nm wavelength range.

#### Time Correlated Single Photon Counting (TCSPC)

Horiba Jobin Yvon IBH equipped with picosecond laser diodes as excitation source was employed for the fluorescence life time measurements. IBH-DAS6 software was used for the fitting of decay curves. The lifetime decays were fitted using minimum number of exponential. Fitting of decay curves were evaluated by  $\chi^2$  values and residual plots.

#### Principal Component Analysis (PCA)

PCA analysis was performed to understand the pattern of sensing of PPH-SDS system with metal ions. Logarithm of fluorescence intensity variation of metal-PPH-SDS system



**Fig. 2** Fluorescence spectra of PPH ( $5 \times 10^{-6}$  M) in ethanol, cyclohexane and water

with PPH-SDS system ( $\log(I/I_0)$ ; where  $I$  and  $I_0$  are the fluorescence intensity in the presence and absence of metal ions), was calculated and used for the analysis. PCA of the spectral data was performed using SOLO software (version: SOLO+MIA 7.8) of Eigenvector Research Inc.

## Results and Discussion

### Steady State Fluorescence Spectra of PPH in Ethanol, Cyclohexane and Water

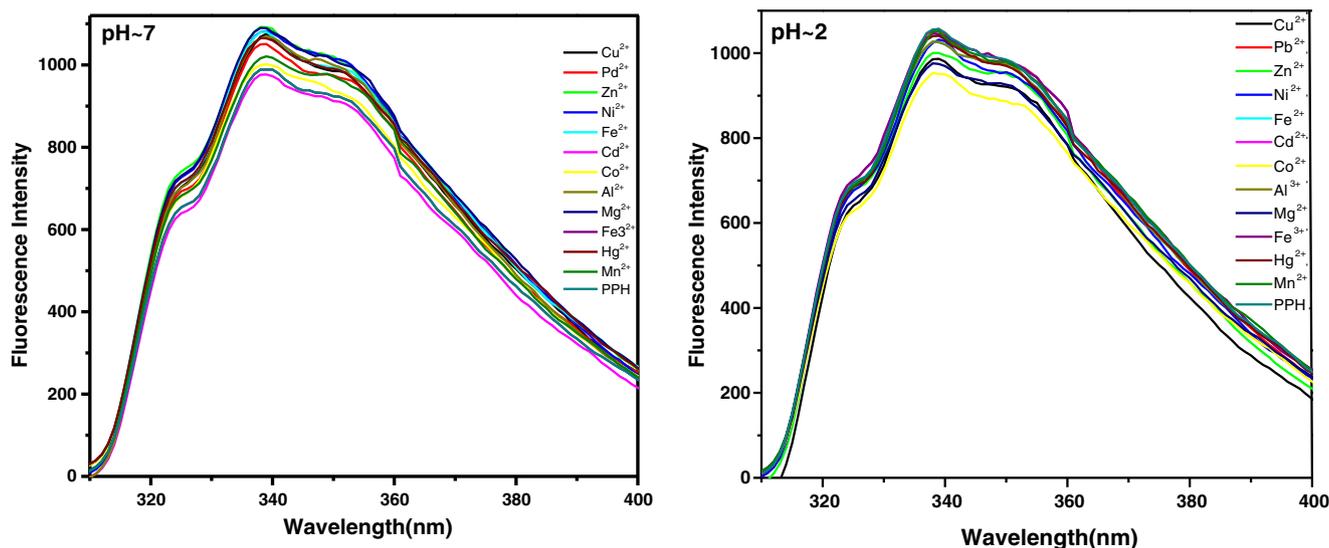
As evident from Fig. 2, the fluorescence spectra of PPH vary with solvent [27, 28]. In ethanol and cyclohexane, PPH shows a structured emission with peaks at  $\sim 325$ ,  $\sim 337$  and  $\sim 351$  nm and in water the spectral features get broadened with a slight

red shift. The broad band which is observed at longer wavelength indicates the possibility of hydrogen bond with water. This further induces a charge transfer between the naphthalene ring and the side chain in PPH.

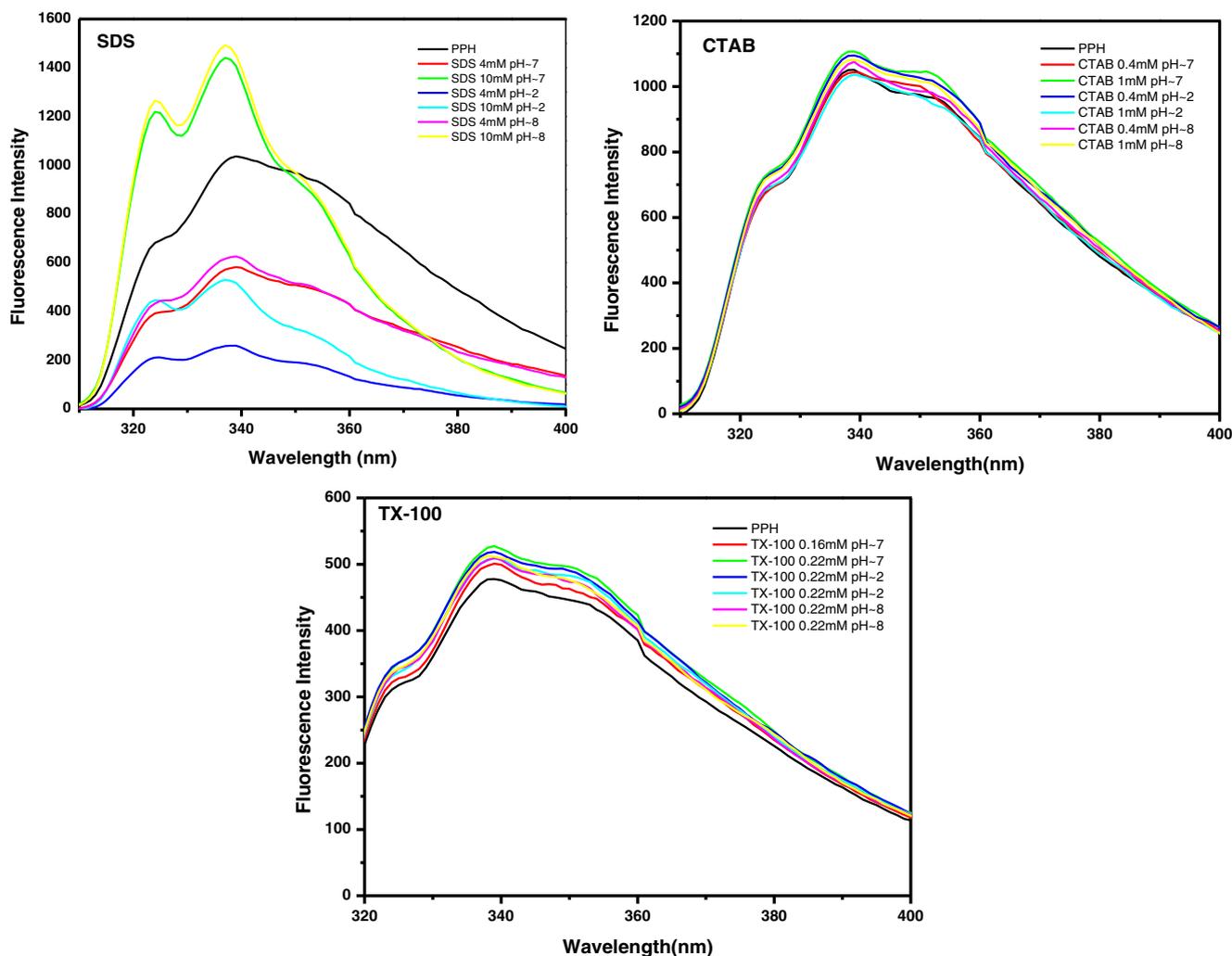
### Steady State Fluorescence Response of PPH towards Different Metal Ions

The fluorescence sensing behaviour of PPH for the various metal ions,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$  and  $\text{Mn}^{2+}$  has been studied at  $\text{pH} \sim 7$  and  $\text{pH} \sim 2$  (Fig. 3). The PPH fluorescence spectra show maximum emission at  $\sim 337$  nm when excited at 288 nm. Addition of metal ions show either no change or slight change in the fluorescence intensity of PPH.

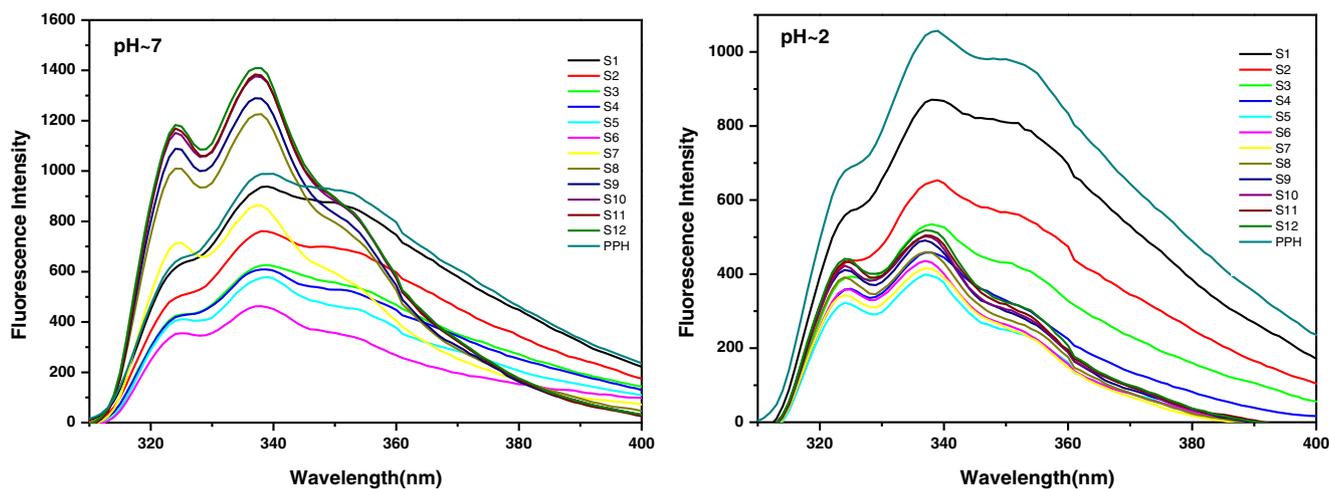
At  $\text{pH} \sim 7$ , PPH exists as cationic species; therefore metal ions could not communicate with PPH and alter its fluorescence response. Cationic fluorophores are generally not good candidates for metal ion detection due to electrostatic repulsion [24]. However, modification of fluorophore with a receptor is possible in such a way that the receptor performs the molecular recognition of the analyte species and fluorophore receives the signals of the recognition process. Based on the nature of receptor group and its interaction with analyte, modification occurs to the spectral characteristics of the fluorophore. Surfactant systems can act as good receptors in fluorosensing methods due to their versatile properties. They can modulate the performance of sensor system by simply adjusting the surfactant concentrations and by varying pH [21]. In this work, we have employed three types of surfactants such as SDS, CTAB and TX-100 as receptor systems and the change in PPH response in presence of various metal ions are monitored.



**Fig. 3** Fluorescence spectra of PPH ( $5 \times 10^{-6}$  M) with different metal ions (1 ppm)  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$  and  $\text{Mn}^{2+}$  at  $\text{pH} \sim 7$  and  $\text{pH} \sim 2$



**Fig. 4** Fluorescence emission spectra of PPH ( $5 \times 10^{-6}$  M) in presence of surfactants; anionic SDS (a) (4, 10 mM), cationic CTAB (b) (0.4, 1 mM) and non-ionic TX-100 (c) (0.16, 0.2 mM) at pH-7 and pH-2



**Fig. 5** Fluorescence emission of PPH ( $5 \times 10^{-6}$  M) in SDS (1–12 mM) at (a) pH-7 and (b) pH-2

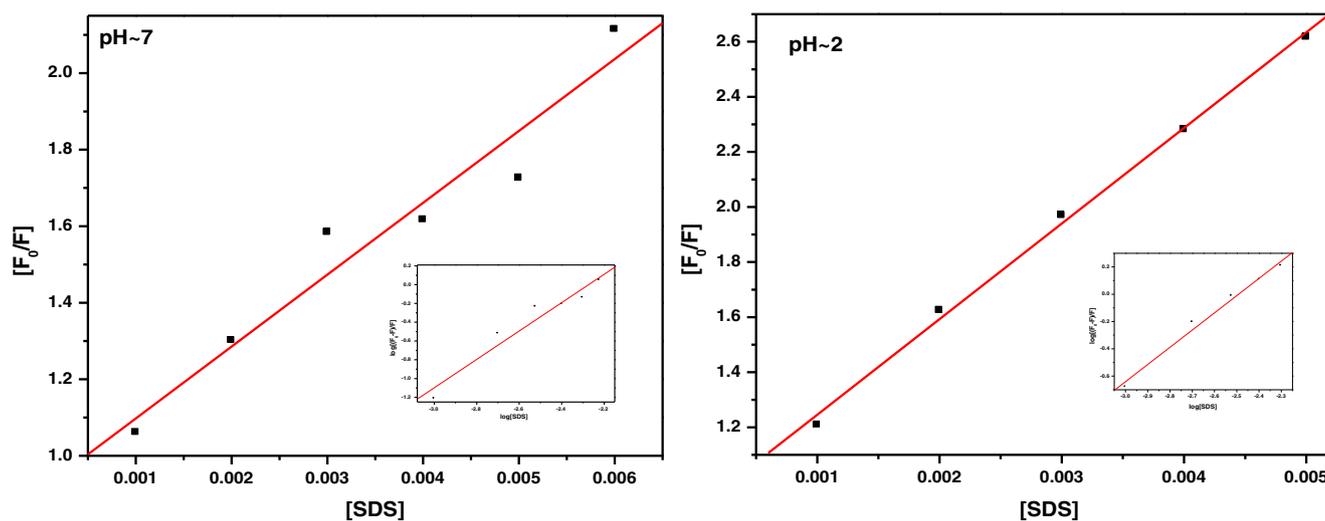


Fig. 6 Stern-Volmer quenching and binding constant plots (inset) of PPH in presence of SDS

### Fluorescence Response of PPH with Different Surfactants

Fluorescence studies of PPH in various surfactants have been carried out using their micellar and pre-micellar concentrations at pH~7, pH~2 and pH~8. Various charged surfactants like, anionic SDS (4,10 mM), cationic CTAB (0.4, 1 mM), non-ionic TX-100 (0.16, 0.22 mM) were used for the study at their respective pre-micellar and micellar concentrations.

Electrostatic interactions play a vital role here also; only anionic surfactant (SDS) has altered the fluorescence of PPH. Fluorescence spectra of PPH in presence of SDS shows (Fig. 4a). distinct change in intensity at the critical micelle concentration (10 mM) in pH~7 and pH~8. At pre-micellar conditions, the fluorescence intensity is reduced compared to PPH fluorescence. At pH~2, the fluorescence intensity is drastically reduced both at micellar and pre-micellar conditions.

Naphthalene ring of PPH molecule can partition spontaneously into the micellar core which switches the fluorophore environment from aqueous to hydrophobic. Due to its incorporation into the hydrophobic

interior of micelles, thus preventing all non-radiative processes, an enhancement of fluorescence intensity was observed at CMC concentration of SDS. Fluorescence spectra of PPH with SDS show a distinct change at the CMC concentration with the absence of charge transfer band. Pre-micellar spectra are similar to the spectra shown in water with the charge transfer band. These results demonstrate the association between PPH and SDS micelle, where the naphthalene ring of PPH is well inside the micellar hydrophobic environment which is completely shielded from water. At pH~2, due to the formation of ion pair complex the fluorescence intensity is quenched at both micellar and pre-micellar conditions.

The cationic micelle, CTAB could not interact with the cationic PPH due to electrostatic repulsion. Therefore noticeable changes were not observed in fluorescence spectra of PPH-CTAB system (Fig. 4b). PPH-TX-100 emission spectra remained unaltered due to the lack of any electrostatic attraction (Fig. 4c).

This explains the key role of anionic head group of SDS which changes the fluorescence response of PPH through electrostatic interactions (Fig. 4c). Hence; the interaction of SDS with PPH was studied further in detail, by varying SDS concentrations at different pH.

**Table 1** Quenching and binding constants of PPH-SDS system at different pH

PPH + SDS	Quenching constant $K_{SV}$ ( $LM^{-1}$ )	Binding Constant ( $K_b$ )	No. of Binding sites
pH~7	187.8	$2.73 \times 10^3$	1.51
pH~2	358.9	$1.52 \times 10^3$	1.27

### Effect of SDS on PPH Fluorescence

At pH~7, linear decrease in fluorescence intensity of PPH was observed from 1 mM to 6 mM SDS concentration; further higher concentration of SDS leads to increase in fluorescence (Fig. 5a). The variations in SDS aggregates were likely to affect the geometry and environment of PPH as strong

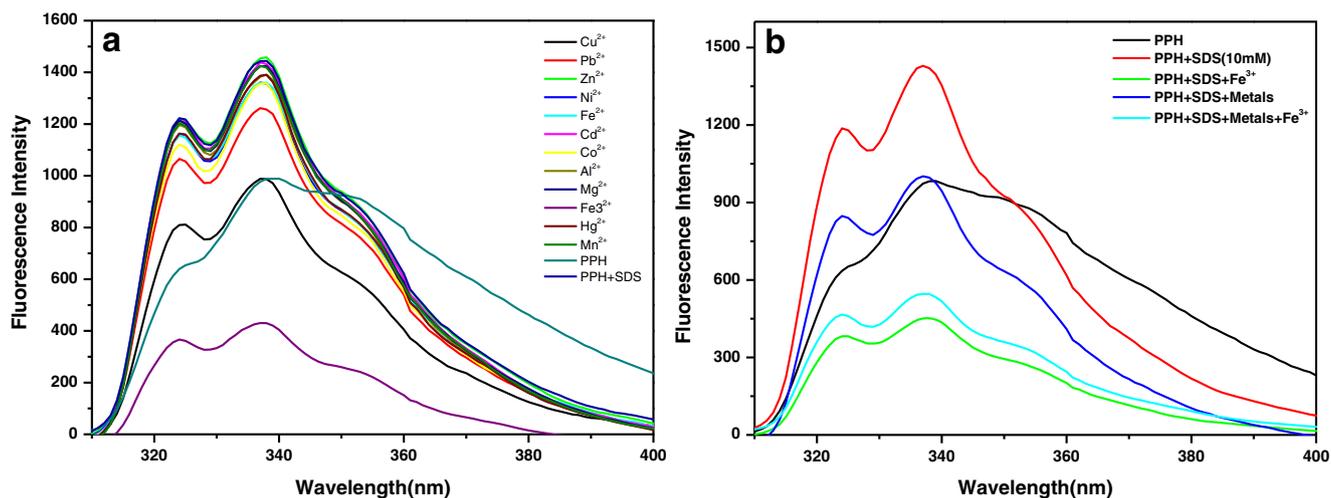


Fig. 7 Steady State fluorescence spectra of PPH-SDS (10 mM) system for different metal ions (1 ppm)

electrostatic interactions are present [29]. SDS at its low concentration will be able to form ion-pair complex with cationic fluorophores [30, 31]. However, at critical micellar concentration, micellation generally overpowers the ion pair formation. Monomers of SDS start aggregating at higher concentrations of SDS to form micelles which incorporates the naphthalene moiety into the micellar core. The probe which is in aqueous environment is now shifted to restricted hydrophobic environment of SDS micelles. This switching of the environment of PPH induce the reduction in non-radiative processes (collisional quenching and energy transfer) in excited state of PPH, which in turn enhances the fluorescence intensity of PPH. At and above the CMC of SDS, the fluorescence spectra show the lack of the charge transfer band.

The interaction pattern observed is different when study is carried out at pH~2. From 1 to 5 mM concentration of SDS, linear decrease in fluorescence of PPH was observed; higher concentrations of SDS could not enhance the fluorescence of PPH (Fig. 5b). PPH is remained in ion-pair complex with SDS at micellar concentration. As PPH has higher cationic charge density at pH~2 it forms strong non-ion pair complex with SDS micelles.

This higher cationic charge density on PPH overpowers the micellation of SDS monomers and remains intact with PPH, therefore on micellation also enhancement was not observed. This is also evident from the presence of charge transfer band in the fluorescence spectra. The strong binding of PPH with SDS in pH~2 also supported from Stern-Volmer quenching

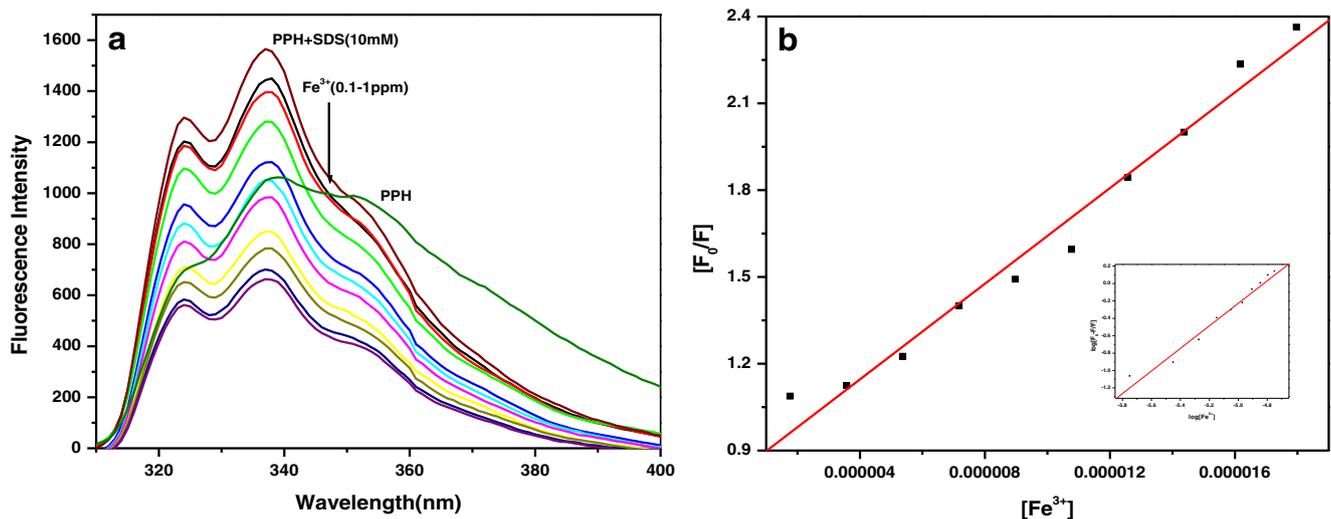


Fig. 8 a Steady state fluorescence spectra of PPH-SDS (10 mM) system for  $\text{Fe}^{3+}$  ions, b Stern-Volmer quenching and binding constant plots (inset) of PPH-SDS system for  $\text{Fe}^{3+}$  ions

**Table 2** Quenching and binding constants of PPH-SDS system by Fe<sup>3+</sup> ions

Quenching constant K <sup>SV</sup> (M <sup>-1</sup> )	Detection limit (M)	Binding constant K <sub>b</sub>	Number of binding sites N	Bimolecular quenching constant (M <sup>-1</sup> s <sup>-1</sup> ) k <sub>q</sub>
8.27 X10 <sup>4</sup>	2.70 X10 <sup>-6</sup>	1.43 X10 <sup>7</sup>	1.34	5.23 X10 <sup>12</sup>

(Eq. 1) and binding constant (Eq. 2) plots which are higher in pH~2 than in pH~7.(Fig. 6, Table 1).

### Stern-Volmer Quenching and Binding Constant

Plot of F<sub>0</sub>/F against the quencher concentration [Q], gives K<sub>SV</sub> i.e. Stern Volmer quenching constant as slope as per Eq.1 [32, 33].

$$\frac{F_0}{F} = 1 + K_{SV}[Q] \tag{1}$$

F<sub>0</sub> and F are the fluorescence intensities of PPH in the absence and in the presence of quencher respectively.

A modification of Stern-Volmer equation (Eq. 2) provides K<sub>b</sub> which is the binding constant [32, 33],

$$\log \frac{F_0 - F}{F} = \log K_b + n \log [Q] \tag{2}$$

Slope n is the number of binding sites and antilog of intercept K<sub>b</sub> is the binding constant.

k<sub>q</sub> is the bimolecular quenching constant and can be determined using the Eq. 3, where τ<sub>0</sub> is the fluorescence lifetime of the molecule in the absence quencher.

$$k_q = \frac{K_{SV}}{\tau_0} \tag{3}$$

Due to electrostatic attraction, anionic surfactant systems act as a receptor for binding with the metal ions. These counter

**Table 3** Fluorescence lifetime of PPH, PPH-SDS system in the absence and presence of metal ions with Fe<sup>3+</sup> ions

System	Fluorescence Lifetime (ns)	
	τ1	τ2
PPH	10.3	–
PPH + SDS	15.8	–
PPH + SDS + Fe <sup>3+</sup> (1 ppm)	6.59 (68.01%)	3.90 (31.99%)
PPH + SDS + Fe <sup>3+</sup> (1 ppm) + Metals	6.66 (66.99%)	3.70 (33.01%)

charged SDS assemblies can be used to modulate fluorescence response of probe towards metal ions. For a more detailed understanding, SDS is used at its micellar concentration i.e. 10 mM for the metal ions sensing with PPH.

### Effect of Micellar Concentration of SDS (10 mM) on Sensing Performance of PPH for Metal Ions (1 Ppm) at pH~7

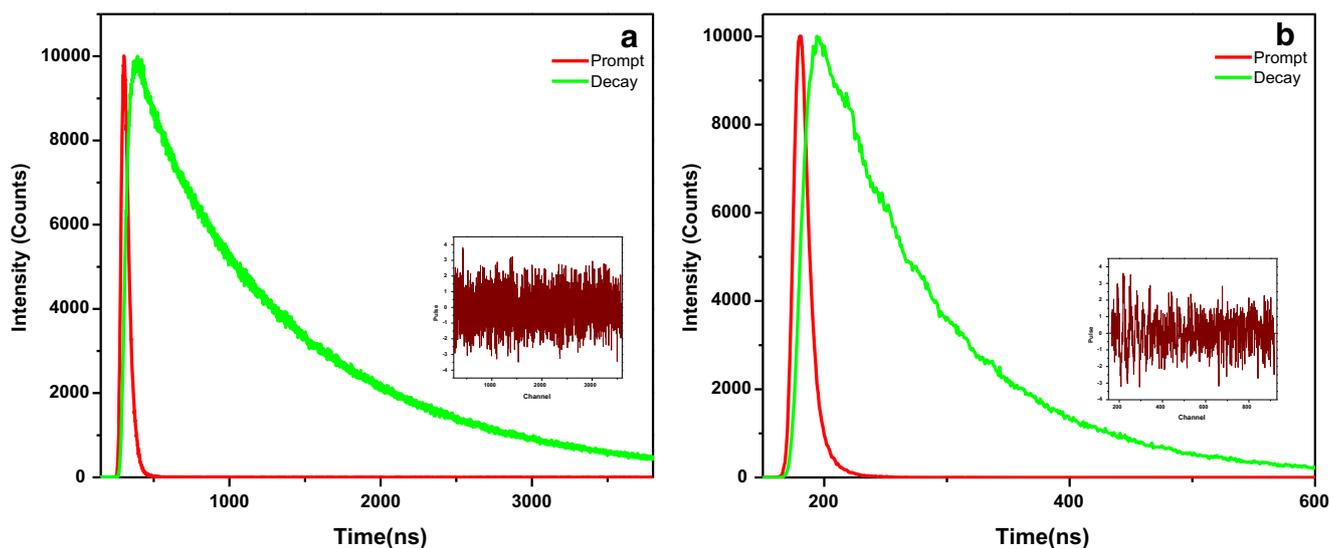
It can be understood that Fe<sup>3+</sup> ions quenches the PPH-SDS system more predominantly over other metal ions from Fig. 7a. To confirm the selectivity of Fe<sup>3+</sup> ions over other metal ions, we have compared the results obtained in absence and presence of other metal ions. Figure 7b represents the fluorescence spectra of PPH alone, PPH-SDS, PPH-SDS-Fe<sup>3+</sup>, PPH-SDS-Other metal ions, and PPH-SDS-other metal ions-Fe<sup>3+</sup>. From the results it has been confirmed that metal ions in the absence of Fe<sup>3+</sup> ions could not show significant change in PPH fluorescence and the quenching observed is only due to Fe<sup>3+</sup> ions. Therefore Fe<sup>3+</sup> ions have been studied comprehensively to determine its quenching, binding, bimolecular quenching constant as well as to determine the detection limits with PPH-SDS system.

Enhancement in fluorescence of PPH on addition of SDS (10 mM) (Fig. 8a). is due to its incorporation into the micellar core thereby reducing the possible non radiative processes. PPH-SDS system shows linear turn off of fluorescence for added Fe<sup>3+</sup> ions (0.1-1 ppm). This is due to the enhanced interaction driven by the receptor i.e. SDS, which on one hand interacts with PPH and enhances its fluorescence and on other hand by electrostatic interactions strongly binds metal ions to the sensor system. Fluorescence quenching of PPH-SDS system could be due to the increase in the local concentration of the metal ion at the anionic micellar surface of SDS through ion exchange with Na<sup>+</sup> and hydronium. Linear Stern Volmer plot shows (Fig. 8b) strong quenching and binding values (Table 2). Detection limit of PPH-SDS (10 mM) was found to be 2.7 μM with high selectivity for Fe<sup>3+</sup> ions. Detailed sensing performance of PPH-SDS system towards Fe<sup>3+</sup> ions has been also studied by fluorescence lifetime studies (TCSPC), explained in section 3.7.

The k<sub>q</sub> value obtained indicates the presence of static quenching component also along with collisional quenching as the value exceeds the diffusion controlled quenching process i.e. 10<sup>10</sup>M<sup>-1</sup>s<sup>-1</sup>.

### Fluorescence Lifetime Analysis

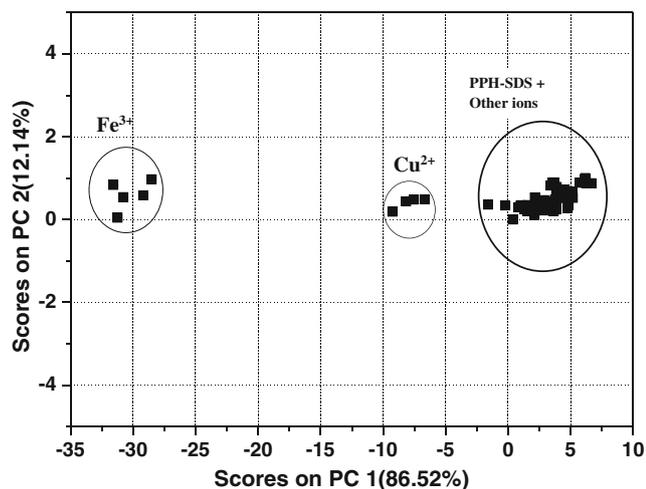
Table 3 shows the fluorescence life time values of PPH-SDS system for Fe<sup>3+</sup> ions with and without metal ions. Fluorescence lifetime of PPH was found to be in nano second



**Fig. 9** **a** Fluorescence decay profile of PPH-SDS (10 mM) system (mono exponential) and **b** Fluorescence decay profile of PPH-SDS (10 mM)-Fe<sup>3+</sup> system (bi exponential)

time scale (10.3 ns). PPH in the SDS (10 mM) micelle showed increased lifetime (15.8 ns) (Fig. 9a) due to the incorporation of naphthalene moiety into hydrophobic micellar interface from the aqueous environment. Shift in the environment of PPH results in the reduction in non radiative processes which in turn enhances the fluorescence emission as well as fluorescence lifetime of PPH.

Addition of Fe<sup>3+</sup> ions to PPH-SDS system shows the existence of bimolecular species (Fig. 9b) with the average lifetime of 5.73 ns. The PPH molecule which is very close to the interfacial region experiences effective quenching due to the high accessibility for metal ions which reduces the fluorescence lifetime to 3.90 ns. The longer lifetime of 6.59 ns was exhibited by the PPH species which is well inside the hydrophobic core thus less accessible for the metal ions.



**Fig. 10** Two dimensional Scores plot of Principal Component Analysis. (Other ions: Principal Component Analysis (PCA))

These results validates the observations obtained from steady state fluorescence studies which shows enhanced communication between Fe<sup>3+</sup> ions and PPH at micellar interface. To ensure the selectivity of Fe<sup>3+</sup> ions over other metal ions we have measured the fluorescence life time of PPH-SDS-other metal ions system in presence of Fe<sup>3+</sup>. Results obtained for all metal ions with Fe<sup>3+</sup> ions are similar to that of PPH-SDS-Fe<sup>3+</sup> system. These results clearly indicate that the PPH-SDS system is highly selective towards Fe<sup>3+</sup> ions.

### Principal Component Analysis (PCA)

It is evident from the fluorescence quenching studies that the PPH-SDS system efficiently senses ferric ions over all the other metal ions studied. This discriminative power of PPH-SDS ensemble for ferric ions is evaluated using principal component analysis. The evaluation was conducted for 12 different metal ions at the same concentration. For each metal ion 5 replicate samples were prepared and the fluorescence responses were measured. The fluorescence intensity data of PPH-SDS system and PPH-SDS-Metal ions system is taken as  $F_0$  and  $F$  respectively. The parameter,  $\log [F_0 / F]$  was calculated and used for PCA analysis. PCA is a statistical method used for the classification and reinterpretation of multidimensional datasets. PCA captures the most significant variations within the dataset by the calculation of orthogonal eigenvectors or principal components. Highest source of variance will be captured by PC1 and other PCs capture the rest of the variance in the decreasing order. The distance between the data points on a PCA scores plot differentiate the sample from one another.

The two dimensional PCA score plots of  $\log[F_0 / F]$  dataset of 12 metal ions with 5 replication are shown in Fig. 10. The first component, PC1, along the horizontal axis captured 86.52% variance, and the second PC captured 12.14%. The first two PCs captured 98.66% variance together, which signifies that the maximum variance is captured by the first two PCs without missing much information. From the scores plot it is evident that  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions are effectively separated along the PC1 axis from the other 10 metal ions and PPH-SDS itself. Five different ferric ions are grouped together and well separated from the cluster formed by PPH-SDS and PPH-SDS with other metal ions. Cluster belongs to copper ions are also separated from the main cluster, but the distance of separation is not significant. This pattern recognition can easily differentiate the sensing of PPH-SDS system by ferric and cupric ions from the rest of the ions.

## Conclusion

In summary, we have modulated a non-sensor fluorophore, PPH into selective and sensitive tunable sensor using SDS assemblies for  $\text{Fe}^{3+}$  ions in aqueous solution. SDS act as a receptor for metal ions and also enhances the fluorescence quantum yield of PPH. Ion-pair complex is formed between PPH and SDS at pre-micellar concentration of SDS which causes fluorescence quenching. In micellar concentration of SDS, enhancement in fluorescence intensity of PPH at  $\text{pH} \sim 7$  was observed due to the change in environment around PPH from aqueous to restricted hydrophobic environment. PPH-SDS ensemble have shown fluorescence quenching i.e. fluorescence turn off type sensing response for added  $\text{Fe}^{3+}$  ions. Fluorescence quenching of PPH can be attributed to intramolecular photoinduced electron transfer (PET) process due to the paramagnetic nature of  $\text{Fe}^{3+}$  ions; giving rise to fluorescence ‘turn-off’ type of sensing response by PPH-SDS sensing array. The quenching mechanism is also supported by fluorescence lifetime and chemometric studies. Static as well as dynamic mechanism is involved in the quenching of PPH-SDS system by  $\text{Fe}^{3+}$  ions which is confirmed by the fluorescence lifetime studies. Principle component analysis study validates the discrimination of  $\text{Fe}^{3+}$  ions sensing over the other metal ions. PPH-SDS system is selective towards  $\text{Fe}^{3+}$  ions in presence of other metal ions with detection limit of  $\sim 2.7 \mu\text{M}$ .

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## References

- Hossain Z, Brennan J (2011)  $\beta$ -Galactosidase-based colorimetric paper sensor for determination of heavy metals. *Anal Chem* 83: 8772–8778. <https://doi.org/10.1021/ac202290d>
- Das P, Mallick A, Sarkar D, Chattopadhyay N (2008) Application of anionic micelle for dramatic enhancement in the quenching-based metal ion fluorosensing. *J Colloid Interface Sci* 320:9–14. <https://doi.org/10.1016/j.jcis.2007.12.026>
- Wolfbeis O (1993) Fluorescence spectroscopy: new methods and applications. Springer-Verlag, New York <https://www.springer.com/in/book/9783642773747>
- Santos H, Pedras B, Tamayo A, Casabo J, Escribe L, Covelo B, Capelo J, Lodeiro C (2009) New chemosensors based on thiomacrocyclic-containing coumarin-343 fluoroionophore: X-ray structures and previous results on the effect of cation binding on the photophysical properties. *Inorg Chem Commun* 12:1128–1134. <https://doi.org/10.1016/j.inoche.2009.09.005>
- Prasanna S, Nimal GHQ, Thorfinnur G, Allen JMH, Colin PM, Jude TR, Terence ER (1997) Signaling recognition events with fluorescent sensors and switches. *Chem Rev* 97:1515–1566. <https://doi.org/10.1021/cr960386p>
- Acharya S, Rebery B (2009) Fluorescence spectrometric study of eosin yellow dye-surfactant interactions. *Arab J Chem* 2:7–12. <https://doi.org/10.1016/j.arabjc.2009.07.010>
- Ding L, Wang S, Liu Y, Cao J, Fang Y (2013) Bispyrene/surfactant assemblies as fluorescent sensor platform: detection and identification of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  in aqueous solution. *J Mater Chem A* 1: 8866–8875. <https://doi.org/10.1039/c3ta10453b>
- Shihuai W, Ding L, Fan J, Wang Z, Fang Y (2014) Bispyrene/surfactant-assembly-based fluorescent sensor Array for discriminating lanthanide ions in aqueous solution. *ACS Appl Mater Interfaces* 6:16156–16165. <https://doi.org/10.1021/am504208a>
- Zhao Y, Zhong Z (2006) Detection of  $\text{Hg}^{2+}$  in aqueous solutions with a foldamer-based fluorescent sensor modulated by surfactant micelles. *Org Lett* 8:4715–4717. <https://doi.org/10.1021/ol061735x>
- Gujar V, Pundge V, Ottoo D (2015) Interaction of antihypertensive drug amiloride with metal ions in micellar medium using fluorescence spectroscopy. *J Lumin* 161:87–94. <https://doi.org/10.1016/j.jlumin.2014.12.047>
- Subhendu SB, Rajen K, Sangita T (2012) Fluorometric sensing of  $\text{Cu}^{2+}$  ion with smart fluorescence light-up probe, triazolylpyrene (TNDMPy). *Tetrahedron Lett* 53:5875–5879. <https://doi.org/10.1016/j.tetlet.2012.08.074>
- Jamkratoke M, Tumcharern G, Tuntulani T, Tomapatanaget B (2011) A selective spectrofluorometric determination of micromolar level of cyanide in water using naphthoquinone imidazole boronic-based sensors and a surfactant cationic CTAB micellar system. *J Fluoresc* 21:1179–1187. <https://doi.org/10.1007/s10895-010-0796-9>
- Jamkratoke M, Ruangpornvisuti V, Tumcharern G, Tuntulani T, Tomapatanaget B (2009) A-D-A sensors based on naphthoimidazole-dione and boronic acid as turn-on cyanide probes in water. *J Org Chem* 74:3919–3922. <https://doi.org/10.1021/jo900170r>
- Tian H, Qian J, Bai H, Sun Q, Zhang L, Zhang W (2013) Micelle-induced multiple performance improvement of fluorescent probes for  $\text{H}_2\text{S}$  detection. *Anal Chim Acta* 768:136–142. <https://doi.org/10.1016/j.aca.2013.01.030>
- Cao J, Ding L, Zhang Y, Wang S, Fang Y (2016) A ternary sensor system based on pyrene derivative-SDS assemblies- $\text{Cu}^{2+}$  displaying dual responsive signals for fast detection of arginine and lysine in aqueous solution. *J Photochem Photobiol A Chem* 314:66–74. <https://doi.org/10.1016/j.jphotochem.2015.08.017>

16. Gujar V, Othoor D (2017) Medium dependent dual turn on/turn off fluorescence sensing of Cu<sup>2+</sup> ions using AMI/SDS assemblies. *Spectrochim Acta A Mol Biomol Spectrosc* 173:666–674. <https://doi.org/10.1016/j.saa.2016.10.024>
17. Berton M, Mancin F, Stocchero G, Tecilla P (2001) Self- assembling in surfactant aggregates: an alternative way to the realization of fluorescence chemosensors for cu(II) ions. *Langmuir* 17:7521–7528. <https://doi.org/10.1021/la015502k>
18. Fernandez Y, Gramatges A, Amendola V, Foti F, Mangano C, Pallavicini P, Patroni S (2004) Using micelles for a new approach to fluorescent sensors for metal cations. *Chem Commun*:1650–1651. <https://doi.org/10.1039/b404543b>
19. Brugnara C (2003) Iron deficiency and erythropoiesis: new diagnostic approaches. *Clin Chem* 49:1573–1578. <https://doi.org/10.1373/49.10.1573>
20. Beutler E, Felitti V, Gelbart T, Ho N (2001) Genetics of iron storage and hemochromatosis. *Drug Metab Dispos* 29:495–499 <http://dmd.aspetjournals.org/content/46/8>
21. Xiang Y, Tong A (2006) A new rhodamine-based chemosensor exhibiting selective Fe III-amplified fluorescence. *Org Lett* 8: 1549–1552. <https://doi.org/10.1021/ol060001h>
22. Said N, Burhan K, Muhammad RS, Mehmet AO (2015) Synthesis of novel bisphenol-Biphenanthroline-based molecular tweezers. *Mugla J of Sci and Tech* 1:1–5. <https://doi.org/10.1021/ol070017n>
23. Zhang X, Shiraishi Y, Hirai T (2008) A reversible Hg<sup>2+</sup>-selective fluorescent chemosensor based on a thioether linked bis-rhodamine. *Tetrahedron Lett* 49:4178–4183. <https://doi.org/10.1039/C3RA43675F>
24. Maksim R, Zhaohua D, James WC (2005) Ratiometric displacement approach to cu(II) sensing by fluorescence. *J Am Chem Soc* 127:1612–1613. <https://doi.org/10.1021/ja0431051>
25. Ayyappanpillai A, Priya C, Sivaramapanicker S (2005) A Ratiometric fluorescence probe for selective visual sensing of Zn<sup>2+</sup>. *J Am Chem Soc* 127:14962–14963. <https://doi.org/10.1021/ja054149s>
26. Liu HM, Parthiban V, Wu SP (2014) A sensitive and selective fluorescent sensor for zinc(II) and its application to living cell imaging. *Sensors Actuators B Chem* 203:719–725. <https://doi.org/10.1016/j.snb.2014.07.049>
27. Surewicz WK, Leyko W (1981) Interaction of propranolol with model phospholipids membranes. *Biochim Biophys Acta* 643: 387–397. [https://doi.org/10.1016/0005-2736\(81\)90083-3](https://doi.org/10.1016/0005-2736(81)90083-3)
28. Bisby RH, Botchway SW, Crisostomo AG, Karolin J, Parker AW, Schröder L (2010) Interactions of the  $\beta$ -blocker drug, propranolol, with detergents,  $\beta$ -cyclodextrin and living cells studied using fluorescence spectroscopy and imaging. *Spectroscopy* 24:137–142. <https://doi.org/10.3233/SPE-2010-0415>
29. Adina RP, Elena AR, Cosmina AL, Nicoleta LO, Aurelia M, Maria M (2016) Specific interactions within micelle microenvironment in different charged dye/surfactant systems. *Arab J Chem* 9:9–17. <https://doi.org/10.1016/j.arabjc.2015.09.009>
30. Joshi S, Pant D (2014) Steady state and time-resolved fluorescence spectroscopy of quinine sulfate dication bound to sodium dodecylsulfate micelles: fluorescent complex formation. *J Lumin* 145:224–231. <https://doi.org/10.1016/j.jlumin.2013.07.060>
31. Gawandi VB, Guha SN, Priyadarsini KI, Mohan H (2001) Steady-state and time-resolved studies on spectral and redox properties of dye–surfactant interactions. *J Colloid Interface Sci* 242:220–229. <https://doi.org/10.1006/jcis.2001.7753>
32. Lakowicz J (2006) Principles of fluorescence spectroscopy. 3rd edn. Springer, pp 17–20 <https://www.springer.com/in/book/9780387312781>
33. Rohatgi-Mukherjee KK (1997) Fundamentals of photochemistry. New age international (P) limited, Publishers, New Delhi, pp 171–174 <https://www.scribd.com/document/246279535>