Analytical Methods

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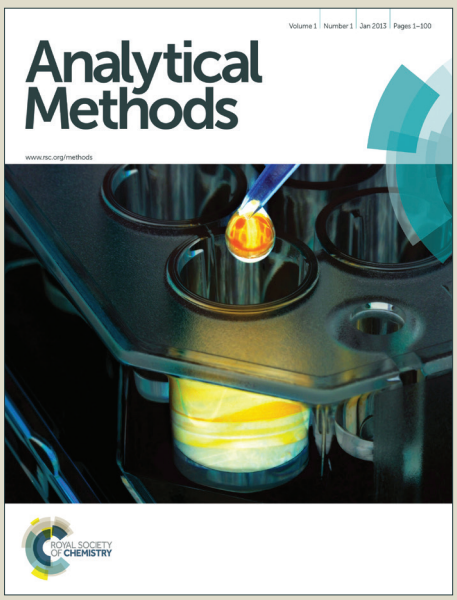

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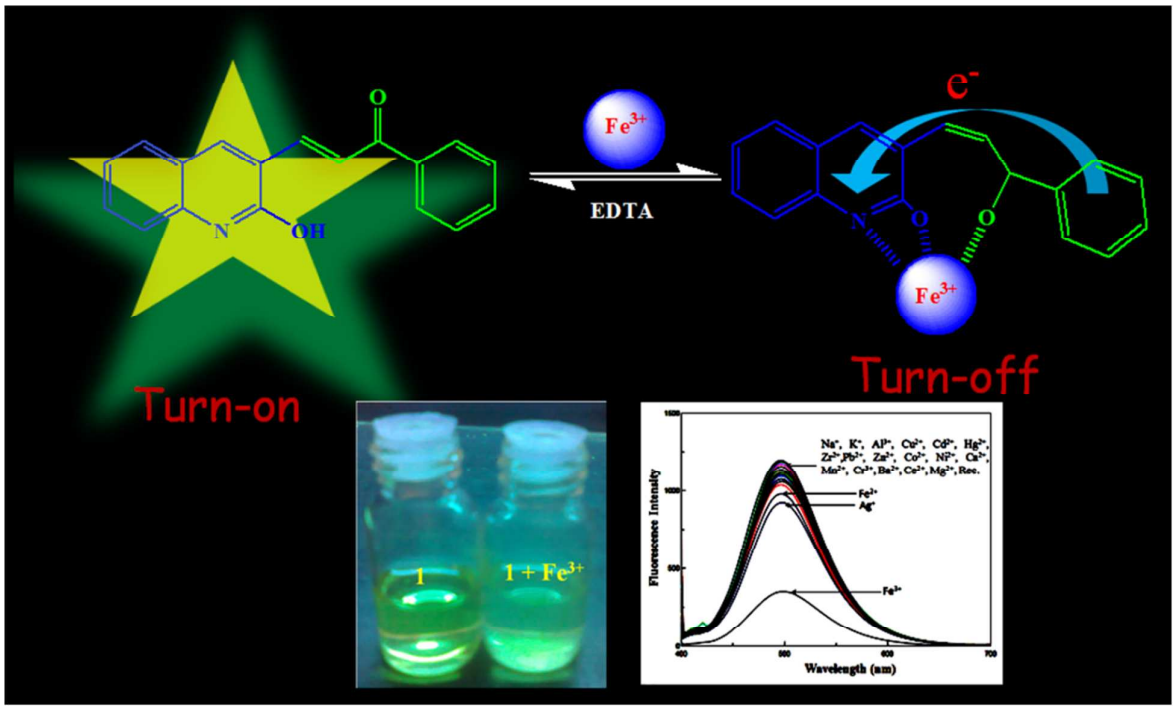
A simple chalcone based fluorescent chemosensor for the detection and removal of Fe^{3+}-ion using membrane separation method

K. Velmurugan[a], J. Prabhu[a], Lijun Tang[b,*] T. Chidambaram[c], M. Noel[c], S. Radhakrishnan[d], and R. Nandhakumar[a,*]

Graphical abstract



A simple chalcone based fluorescent chemosensor for the detection and removal of Fe^{3+}-ion using membrane separation method

K. Velmurugan[a], J. Prabhu[a], Lijun Tang[b,*] T. Chidambaram[c], M. Noel[c], S. Radhakrishnan[d], and R. Nandhakumar[a,*]

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Abstract

A simple chalcone based fluorescent chemosensor **1** capable of detecting Fe^{3+} in aqueous media has been designed and synthesized by the condensation of 3-formyl-2-hydroxyquinoline and acetophenone. The Fe^{3+} recognition processes are proven to be hardly influenced by other coexisting metal ions and found to be a reversible processes with EDTA. Moreover, the sensor is applied in the Fe^{3+} removal process from environmental water samples by using the membrane separation method.

Keywords: Chemosensor, Chalcone, Reversible PET, Iron detection, Iron removal

Introduction

In the recent research of highly selective and sensitive organic fluorescent probes for metal ion recognition has gained tremendous importance in environmental and biological area.[1-4] *Hemoglobin (Hgb), the iron-containing respiratory protein in red blood cells, is essential for transporting oxygen from the lungs to the rest of the body. Hemoglobin levels indicate the blood's ability to carry oxygen and iron.* Iron is the most abundant vital trace element in the human body and provides the oxygen carrying capacity of heme and acts as a cofactor in many enzymatic reactions. It plays an essential role in many biological processes at the cellular level ranging from oxygen metabolism to DNA and RNA synthesis.[5-9] The deficiency or excess of iron is toxic and causes various pathological disorders in human.[10-13] In well-nourished people the total iron content is 4 g (70% in Hgb, 25% in storage). The main role of iron in human and animal health became obvious during the past century with identification of Fe^{3+} as a body constituent and realization of the relationship between adequate Fe^{3+} intake and prevention of certain diseases.[14-16]

Among the several analytical methods available, fluorescence technique is a great tool due to its high sensitivity, and relatively simple instrumentation.[17,18] It also allows a real-time, non-destructive detection and quantification of chemical species. Significant exploration of fluorescent molecular sensors and switches which focus on the selective and sensitive detection of transition metal ions; e.g., detection of Cu^{2+}, Pb^{2+}, Zn^{2+}, and

Hg^{2+} have been reported.[19-24] Surprisingly, the reported Fe^{3+}-selective fluorescent sensors are relatively rare[25-29] due to the fluorescent quenching of the Fe^{3+}.

Therefore, we are encouraged to design and synthesize a novel molecular system which can sense Fe^{3+} against environmental and biological samples. As an important fluorophore, 8-hydroxyquinoline (8-HQ) has attracted wide research interests in the construction of various fluorescent sensors for many important metal ions.[30-32] To the best of our knowledge, no work has been done on 2-hydroxyqinoline (2-HQ). Herein, we report for the first time, a chalcone based fluorescence sensor containing 2-hydroxyquinoline (2-HQ) which quenches the fluorescence on addition of Fe^{3+} due to the reversible photo induced electron transfer (PET) process. Simple variation of the hydroxyl group from 8 to 2-position selectively detects Fe^{3+}-ion based on the "turn on-off" process in neutral pH value.

2. Experimental section

2.1. Materials

2-hydroxy-4-methylquinoline purchased from sigma Aldrich and all other commercially available chemicals were of Merck grade and all the organic solvents were used as HPLC grade and without further purification.

2.2. Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker 400 MHz spectrometer, solution DMSO with TMS as internal standard. LC-MS were determined on a LC-MSD-Trap-XCT Plus based on infusion methods. Absorption spectra were made on a

Shimadzu UV-240 spectrophotometer. Fluorescence measurements were performed on a Jasco FP-8200 spectrofluorimeter equipped with quartz curettes of 4 cm path length. The excitation and emission slit widths were 5.0 nm. All emission spectra were recorded at 24 ±1 ^{0}C. Stock solutions for analysis were prepared (2 x 10^{-3}M for compound **1** (DMSO/H_2O (1:1), HEPES=50 mM, pH=7.0) immediately before the experiments. The solutions of metal ions were prepared from nitrate salts of Na^{+}, K^{+}, Al^{3+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Zr^{2+},Pb^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Ce^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and Ag^{+}.

2.1. Synthesis of receptor 1

Aqueous sodium hydroxide (4 ml, 10%) was added to a mixture of 3-formyl-2-hydroxy quinoline 1.0 g (5.78 mmol), acetophenone 0.69 g (5.78 mmol) and 25 ml of methanol. The reaction mixture was stirred at room temperature for 24 h. The resulting precipitate was collected by filtration, washed with more methanol and recrystallized from DMF. The resulting product was afford 1.3 g (81%) of compound **1**(E)-3-(2-hydroxyquinolin-3-yl)-1-phenylprop-2-en-1-one) as yellow solid M.p.180-181^{0}C, ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.57 (s, 1H), 8.27-8.31(d, J= 16 Hz, 1H), 8.04-8.06 (d, J=8 Hz, 1H), 7.55-7.81 (m, 7H), 7.34-7.36 (d, J=16 Hz, 1H), 7.22-7.26 (t, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ =190.1, 161.6, 141.7, 139.7, 138.1, 133.5, 132.2, 129.3, 129.1, 128.7, 126.3, 124.3, 122.6, 119.6, 115.8, 40.5, 40.3, 40.1. Elemental Analysis: $C_{18}H_{13}NO_2$; calc ; C, 78.53; H, 4.76; N, 5.09. Found; C, 78.40; H, 4.61; N, 5.17. LC-MS: m/z= 274.2 [M^{+}-H].

2.2. Membrane Preparation

Polyvinylene fluoride (PVDF) (17 wt %) was dissolved in N, N-Dimethylformamide in a round bottom flask under continuous stirring with a stir bar for 6 h at 30^0 C.[41] Before casting, the PVDF solution was degassed for 1 hour at vacuum condition to remove trapped bubbles. To form the membrane, the PVDF solution was cast using an automatic film applicator (Elcometer 4340 Motorised, Elcometer, UK). Subsequently the nascent membrane was immersed in a coagulation bath consisting of a mixture of Sodium Dodecyl Sulfate (NaDS) (0.03%) with deionized water. The formed membrane was kept in 1% formalin solution for controlling biological growth.

2.3. Binding studies

The studies on the binding properties of **1** & **2** were carried out in solution (DMSO/H_2O, 1:1 (v/v), HEPES=50 mM, pH=7.0). The different metal ion solutions (100 equiv.) were prepared by dissolving the desired amount of metal salts in solution (DMSO/H_2O, 1:1 (v/v), HEPES=50 mM, pH=7.0). The fluorescence titration was performed with a series of 4 x 10^{-5} M solutions of **1** containing various equivalents of Fe^{3+}-ions (λex= 390 nm). Binding studies were confirmed by job's plot and non linear curve fitting methods.

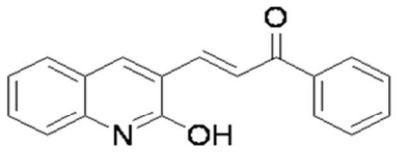
3. Results and Discussion

3.1. Synthesis and Structural Characteristics of Receptor

The fluorescent receptor **1** was synthesized in excellent yield from 2-hydroxy-3-formyl-quinoline **3** and acetophenone by a simple methodology of aldol condensation (Scheme

1). The structure of the final receptor **1** was confirmed by NMR (^{1}H and ^{13}C) and mass spectrometry. Compound **2** was purchased and directly used for binding studies and compared with **1**.

Scheme 1



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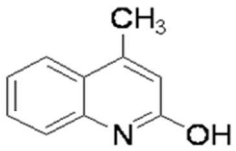

2

3.2. Evaluation of Selectivity

The selectivity of the fluorescent sensor **1** and **2**, was evaluated by complexation studies with different metal ions, i.e. Na^{+}, K^{+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Ag^{+}, Cu^{2+}, Co^{2+}, Cd^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zr^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+} and Ce^{2+}. The results showed that the receptor **1** retains excellent selectivity towards Fe^{3+}-ions. However, compound **2** does not show any selectivity with these common environmental and biological metal ions (Fig. 1 & Fig. 2). The above study indicates that the additional acyl ring with an oxygen atom plays a vital role towards the selectivity for Fe^{3+}-ions in sensor **1**.

Figure. 1

Figure. 2

Competition experiments were also carried out to test the practical applicability of the sensor **1** for Fe^{3+} detection. A fixed concentration of 100 equiv. was used for Fe^{3+} by adding same concentration of other metal ions to the solution of **1** and the results are shown in Fig. 3. No significant variation in fluorescence intensity was found, which

indicates that the signalling of Fe^{3+} by **1** is hardly affected by these common coexistent metal ions. These results suggested that receptor **1** could be used as Fe^{3+} selective fluorescent chemosensor.

Figure. 3

3.3. Stoichiometry and Binding Mode studies

The sensor **1** exhibited a strong fluorescence signal at 498 nm in DMSO/H_2O (1:1 (v/v), HEPES=50 mM, pH=7.0) (Fig. 4). However, addition of Fe^{3+} to the solution of **1** markedly diminished the fluorescence intensities. As the Fe^{3+} concentration (0-100 equiv.) increases, the fluorescence intensity decreases to 9.9 % .

Figure. 4

For a homogeneous medium that has only a single component exponential decay, the concentration of the quencher can be calculated using the Stern-Volmer equation.[33] The spectral titration data obtained by fluorescence spectrum were used in Benesi-Hildebrand equations.[34] The equation for 1:1 complex is given below

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K[I - I_0][Fe^{3+}]}$$

The calibration plot of $1/I\text{-}I_o$ versus $1/[Fe^{3+}]$ showed a good linear relationship (R=0.998) for Fe^{3+} -ion concentration (Fig. 5).

Figure. 5

The detection limit of **1** is found to be 3.49×10^{-6} M^{-1}, which is calculated using 3δ/S, where δ is the standard deviation of the blank signal, and S is the slope of the linear calibration plot.[35] The Job's plot (Fig. 6), which is extensively used to find out the complexation mode in the host (**1**)–guest (Fe^{3+}) interactions, showed a maximum mole fraction of **1** is 0.5 M at 498 nm. It is clearly indicative of a 1:1 (**1**:Fe^{3+}) binding stoichiometry.[36] The binding constant (Ka) is determined to be 3.38×10^{3} M^{-1} by the standard algorithm for competitive binding of **1** with Fe^{3+} in DMSO-H_2O (1:1 (v/v), HEPES=50 mM, pH=7.0) at 25°C.

Figure. 6

3.4. Mechanism of binding studies with the complex

The possible binding mechanism of **1** with Fe^{3+} that led to the fluorescence changes is shown in Scheme 2. Based on the earlier proposed mechanism of some quinoline-based chemosensors[37,38] reported so far, it may be that Fe^{3+} coordinates with the corresponding oxygen and nitrogen atoms of sensor **1** and induces the fluorescence changes. The possible fluorescence quenching caused by Fe^{3+} can be explained by the intramolecular reverse photoinduced electron transfer (PET) process which is due to the paramagnetic nature of Fe^{3+} transition metal ion. The free electron easily participates in the electron transfer processes with the quinoline and benzene moiety by opening a non-radiative deactivation channel.[30,31]

Scheme 2

Furthermore, for a chemosensor, the recognition reversibility is an important requirement. We examined the reversibility of the binding between **1** and Fe^{3+} (DMSO/H_2O, 1:1 (v/v), HEPES= 50 mM, pH=7.0) in the presence of Fe^{3+} & EDTA (100

equiv.) excited at 390 nm. Accordingly, upon the addition of EDTA (100 equiv.) to the solution of **1** containing Fe^{3+} led to the disappearance of the fluorescence signals of **1**-Fe^{3+}, indicating that the chelation process is reversible as shown in Fig. 7. The binding constant of EDTA-Fe^{3+} is 1.11 x 10^3 M^{-1} and the completion of reversible process between Fe^{3+} with EDTA is 10 minutes.

Figure. 7

NMR and IR Analysis for Fe^{3+} Complexes

^1H NMR titration analysis was performed to get some insight into the coordination modes for **1** in a D_2O/DMSO mixture (1/3 v/v) with and without Fe^{3+} (0-30 equiv)(Fig. S8). Even though the exact binding mode cannot be easily predicted, we could confirm the presence of iron binding with **1** as the NMR peaks of the sensor **1** become broadening on the addition of 10, 20, 30 etc., equivalents of iron. Addition of 10 eq. of Fe^{3+} leads to not only the considerable shift in aromatic protons but protons splitting patterns are disturbed and the O-H proton signal of host **1** is observed as a broad singlet at δ 12.07 ppm. This was further confirmed by the ^1H–^1H COSY analysis (Fig. S4 & S5). On comparison with the sensor **2**, which showed no selectivity towards any of the metal ion, there is a possibility for the acyl oxygen atom in sensor **1** to be involved in coordination with iron.

IR spectral studies

The IR spectral studies of sensor **1** with and without Fe^{3+} were recorded in D_2O/DMSO mixture (1/3 v/v) (Fig. S9). Accordingly, the IR spectrum of **1** alone shows an absorption band at 1651 cm^{-1} & 2142 cm^{-1} assigned to the acyl carbonyl and –NH-C=O stretching

frequencies. On addition of Fe^{3+} to the solution **1**, there is a noticeable shift in its absorption bands towards 1655 cm^{-1} & 2138 cm^{-1}.[39,40] This band shift is probably due to the Fe^{3+} coordination with the acetophenone C=O and quinoline –NH-C=O moieties. Ultimately, the NMR and IR results indicate that Fe^{3+} complex coordinate with quinoline –NH-C=O and acetophenone C=O groups. Based on the above results a possible mechanism is shown is scheme 2.

4. Removal of Fe^{3+}-ion from environmental water samples with influence of 1 by membrane separation methods

4.1. Removal of Fe^{3+}-ion by membrane separation method

To validate the sensor for its practical applicability, the removal of Fe^{3+} from membrane separation method was experimented. Accordingly, we collected one ground water sample (Sample-A) from karunya Nagar, Coimbatore, India and one River water sample (Sample-B) from Siruvani river, Karunya Nagar, Coimbatore, India were used for studies. 4 and 8 ppm of Ferric chloride salt was added to the water samples and the samples were subjected to membrane separation before and after adding of **1** (1×10^{-5} M). The separation was carried out by using stirred cell (STERLITECH- HP4750 UK) with 14.6 $\times10^{-4}$ m^2 effective area of synthetic membrane (PVDF) under very low operating pressure (10 psi) at room temperature (25±1°C). The concentrations of the Iron in permeate and blank solution was analyzed by spectrophotometric method.

The PVDF membrane exhibits significant rejection of Fe^{3+} even without addition of **1**. The rejection was found to be around 72% for both contaminated ground water (Samples-

A) and River water (Samples-B) containing 4ppm Fe^{3+}. The rejection increases to 85±1 % for samples containing 8 ppm Fe^{3+}. However, addition of **1** was found to be enhancing Fe^{3+} rejection to more than 99% in all four cases as reported in Table.1. These results clearly indicate that **1** has excellent binding capacity for Fe^{3+} leading to its complete removal from the contaminated river water as well as ground water.

Table.1.

Conclusion

In conclusion, a novel fluorescent chemosensor **1** was designed and synthesized by the condensation of 3-formyl-2-hydroxyquinoline and acetophenone. Studies showed that **1** exhibited highly selective and sensitive to Fe^{3+} over other metal ions through a fluorescence "turn on-off" process with low detection limit. Meanwhile, common metal ions showed negligible detection interference with **1**and Fe^{3+}-ion. Practical applicability of the sensor is shown as Fe^{3+}-ion can be completely removed from environmental water samples with the help of **1** and membrane by using the membrane separation method. Further works are underway is our laboratory towards the modification of sensor **1,** which could be operated to remove Fe^{3+} in 100 % aqueous solution for environmental and biological application.

Acknowledgement

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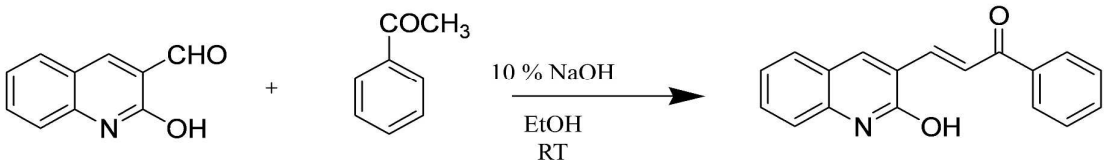
Figures and Schemes



3 **1**

Scheme 1: Synthesis of Receptor 1

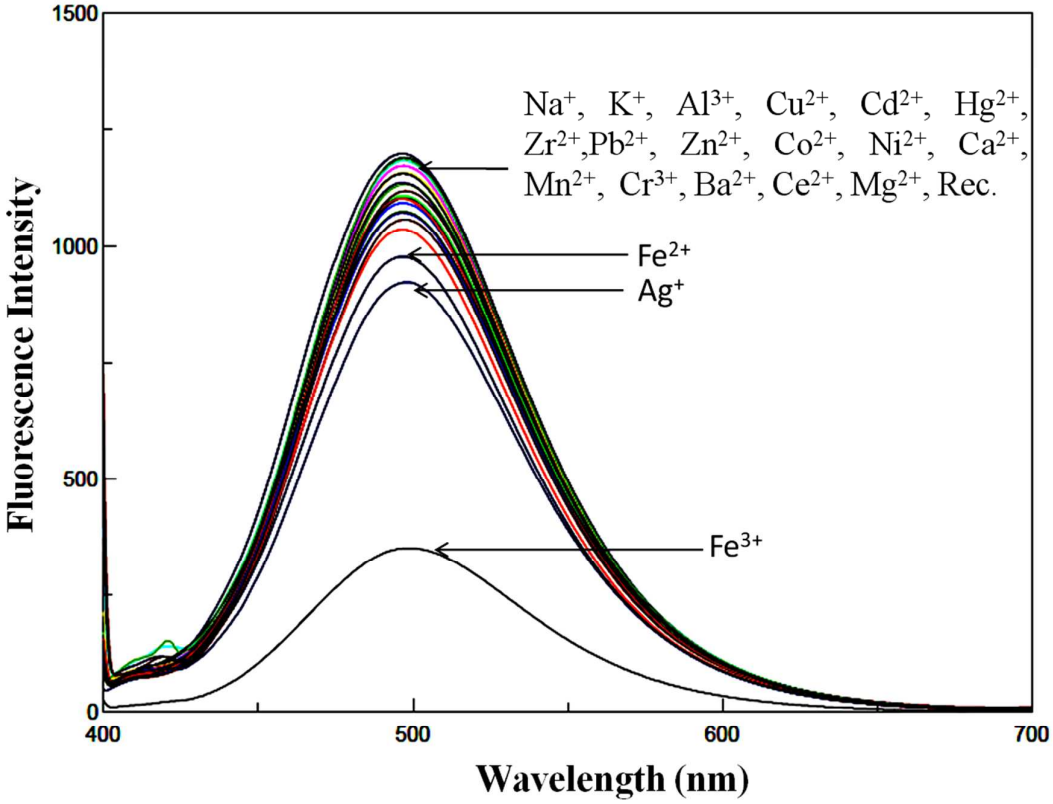


Fig. 1. Metal ions selectivity spectrum of **1** (4×10^{-5}M) solution (DMSO/H_2O, 1:1 (v/v), HEPES=50 mM, pH=7.0) in the presence of various metal ions (100 equiv. of each, excited at 390 nm)

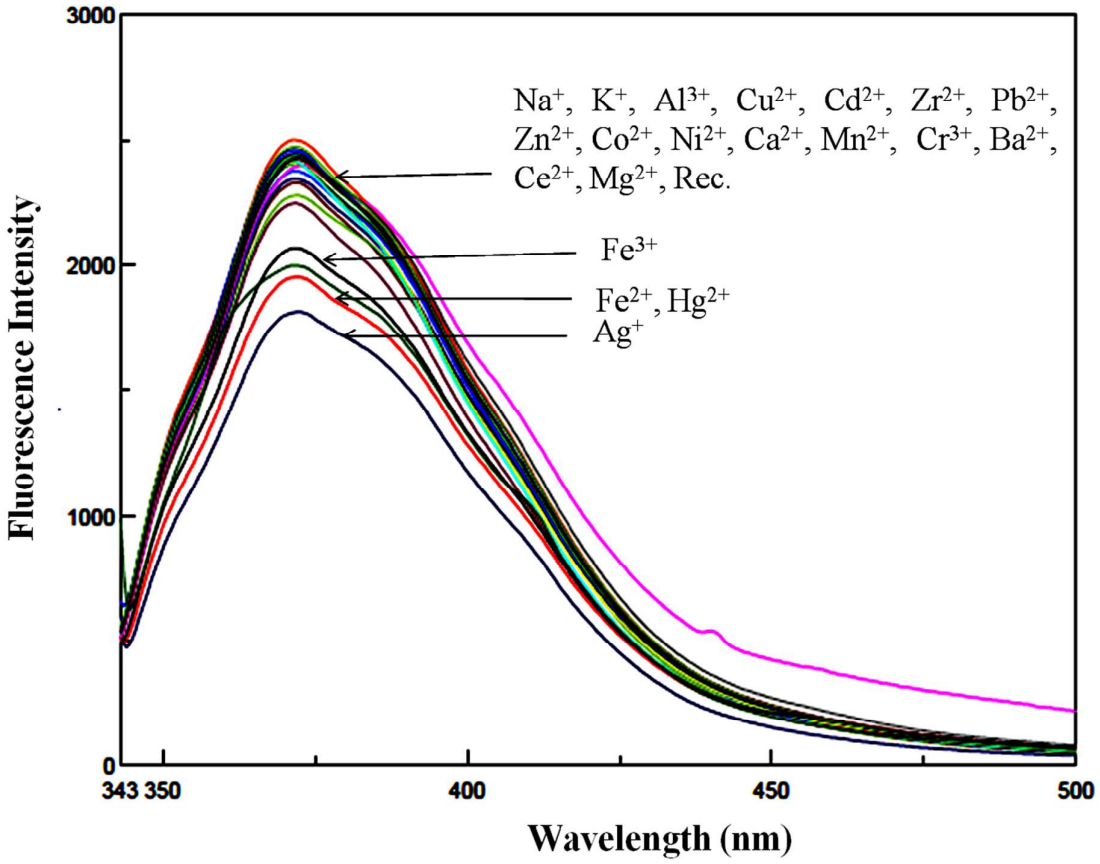


Fig. 2. Metal ions selectivity spectrum of **2** (4×10^{-5}M) solution (DMSO/H_2O, 1:1 (v/v), HEPES=50 mM, pH=7.0) in the presence of various metal ions (100 equiv. of each, excited at 390 nm)

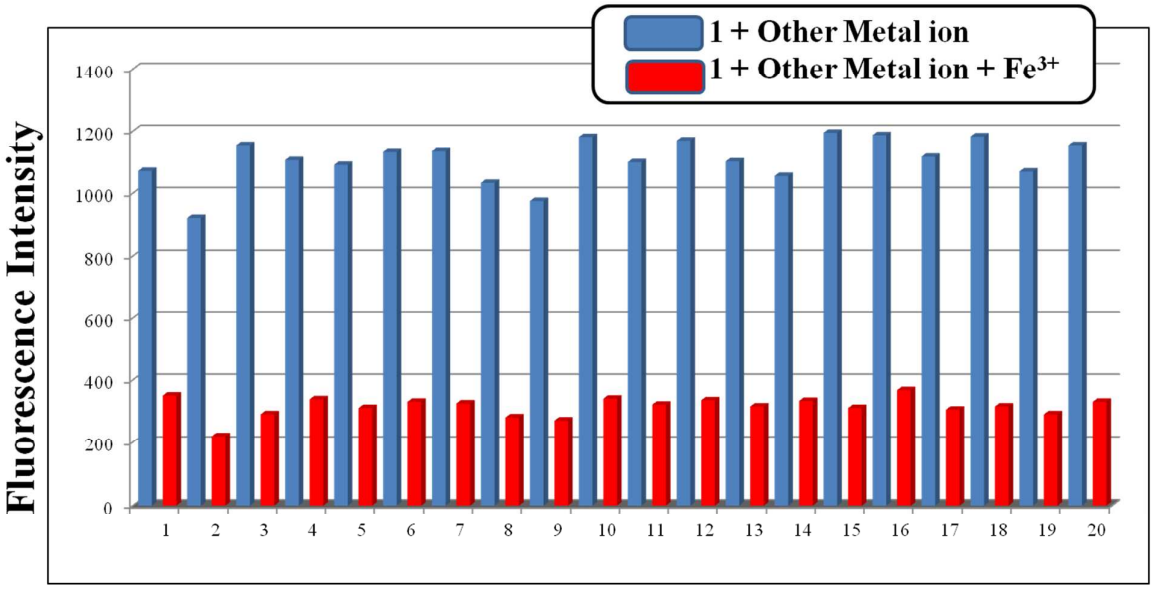


Fig. 3. Metal ions competition analysis of **1** (4×10^{-5} M) in DMSO/H_2O, 1:1 v/v, HEPES = 50 mM, pH = 7.0. The blue bars represent the fluorescence emission of **1** and 100 equiv. of other metal ions. The red bars represent the fluorescence changes that occur upon addition of 100 equiv. of other metal ions to the solution containing **1** and Fe^{3+} (100 equiv.). 1. Rec., 2. Ag^{+}, 3. Fe^{2+}, 4. Cu^{2+}, 5. Na^{+}, 6. Ca^{2+}, 7. Ce^{2+}, 8. Ba^{2+}, 9. Cd^{2+}, 10. Mn^{2+}, 11. Co^{2+}, 12. Ni^{2+}, 13. Zr^{2+}, 14. Cr^{3+}, 15. Al^{3+}, 16. Hg^{2+}, 17. Zn^{2+}, 18. Mg^{2+}, 19. Pb^{2+}, 20. K^{+}.

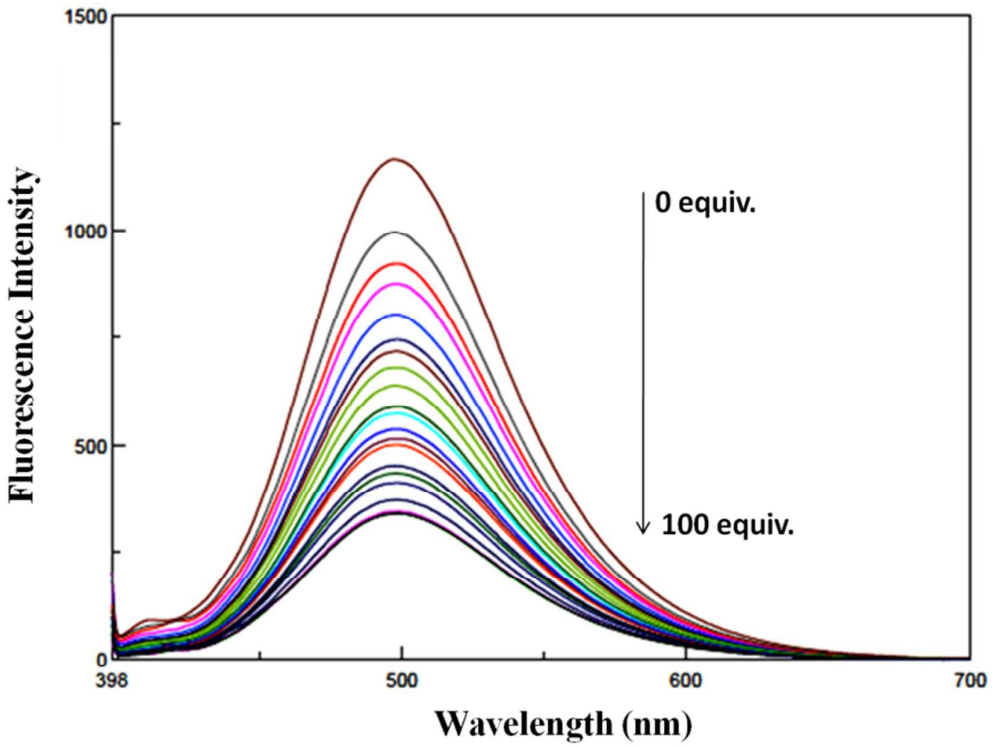


Fig. 4. Fluorescence titration spectrum of **1** (4×10^{-5} M) solution (DMSO/H_2O, 1:1 (v/v), HEPES= 50 mM, pH=7.0) in the presence of different concentrations of Fe^{3+} (0-100 equiv.) excited at 390 nm).

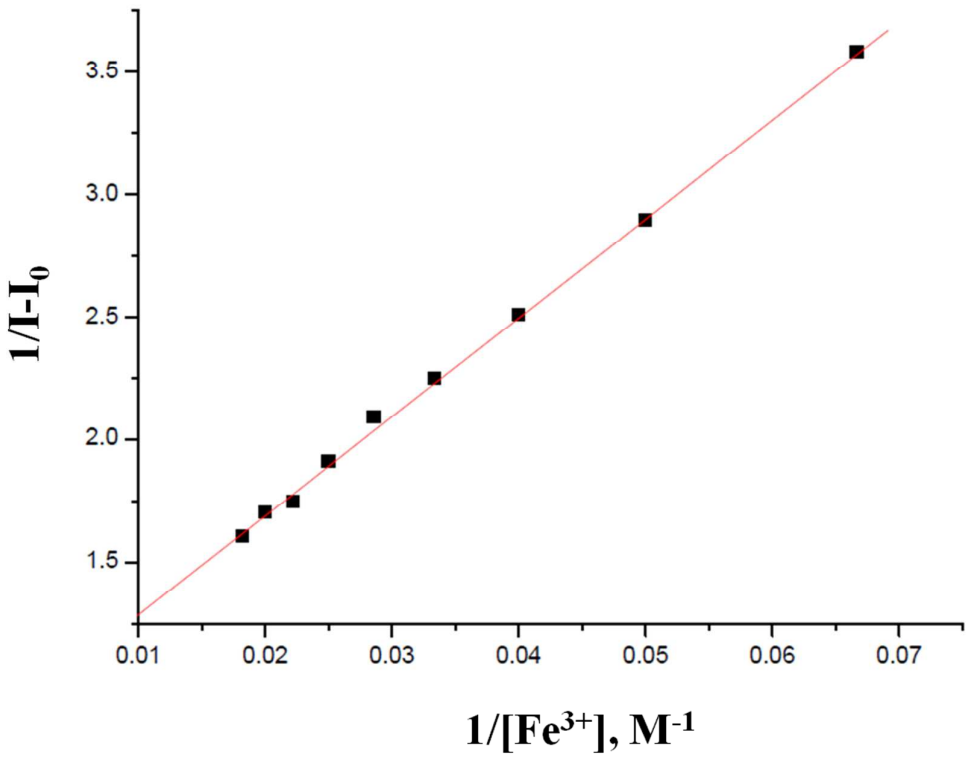


Fig. 5. Benesi–Hildebrand plot (emission 498 nm) of **1** using Eq. (1), assuming 1:1 stoichiometry for association between **1** and Fe^{3+}.

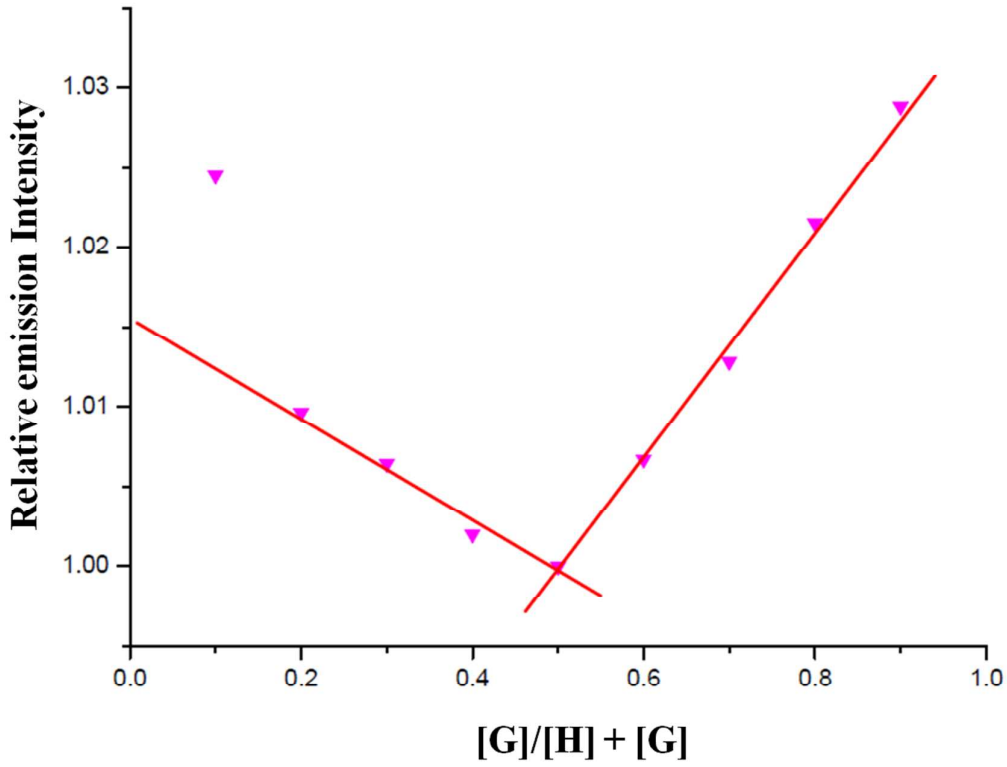


Fig. 6. Job's plot for probe **1** in (DMSO/H_2O, 1:1 (v/v), HEPES= 50 mM, pH=7.0).

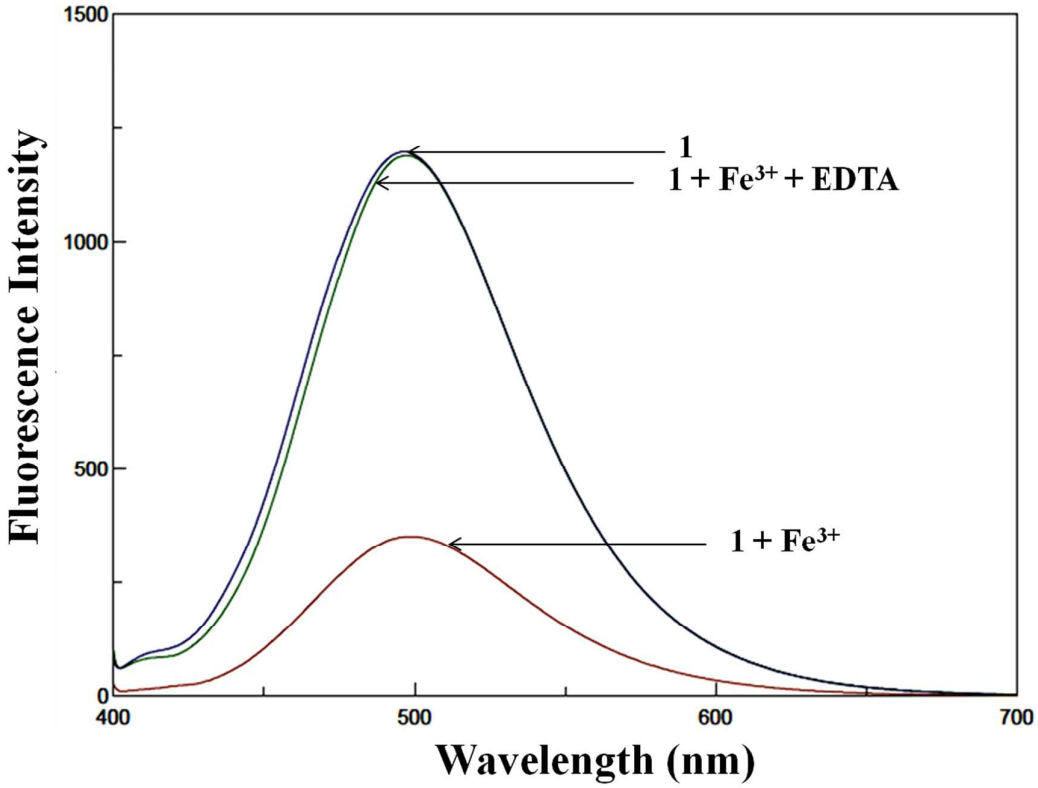
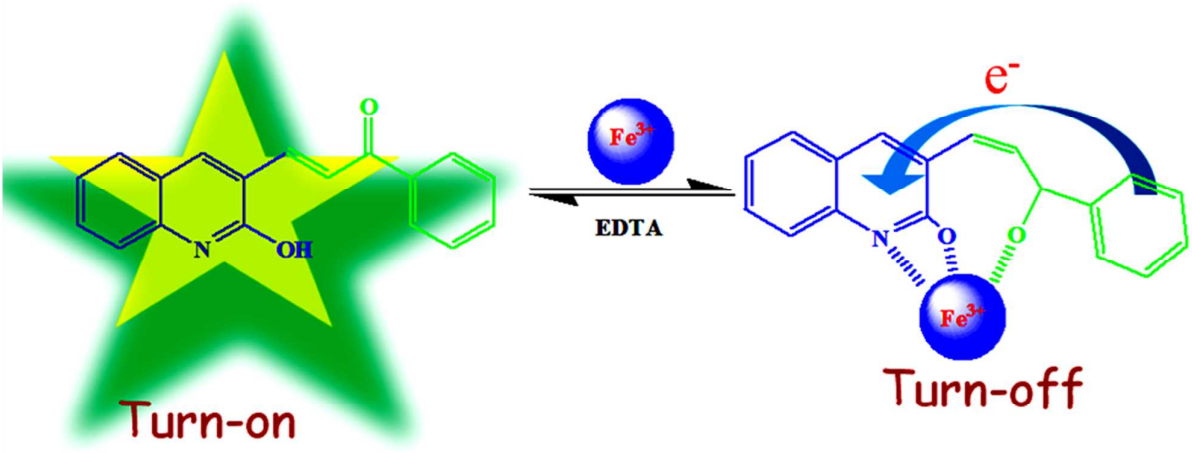


Fig. 7. Changes in Fluorescence spectra of **1** (4×10^{-5}M) solution (DMSO/H_2O, 1:1 (v/v), HEPES= 50 mM, pH=7.0) in the presence of Fe^{3+} & EDTA (100 equiv.) excited at 390 nm).



Scheme 2. Proposed binding mode of **1** with Fe^{3+}

Table.1. Fe^{3+}- ion removal in PVDF membrane with **1** (1 x 10^{-5} M)

Samples	Amount of Fe^{3+} present in blank (ppm)	Amount of Fe^{3+} present in Permeate (ppm)		Rejection (%)	
		Before adding of 1	After adding of 1	Before adding of 1	After adding of 1
Sample-A	8	1.2	0.05	84	99
Sample-A	4	1.15	0.04	71	99
Sample-B	8	1.18	0.05	86	99
Sample-B	4	1.12	0.04	72	99