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A highly sensitive “Off-On” optical and fluorescent chemodosimeter for detecting Iron (III) and its application in practical samples: An investigation of Fe^{3+} induced oxidation by mass spectrometry

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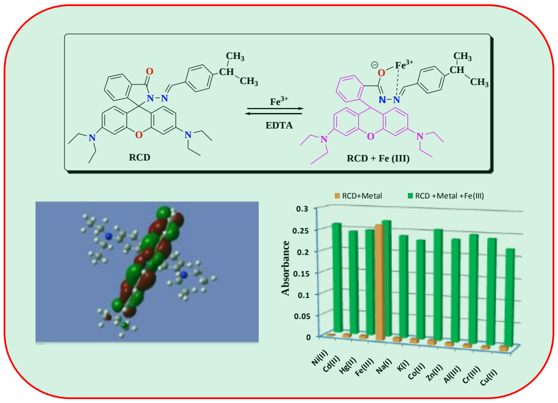
Graphical abstract:



Highlights:

- New Rhodamine-based colorimetric and fluorescent reversible chemodosimeter was developed for detecting Fe^{3+}
- The probe could be serve as a 'naked eye' chemosensor for Fe^{3+} and exhibits greater emission response with 48-fold fluorescence enhancement
- The probe is insensitive to pH under normal conditions(5-8) therefore can be applicable for biological and environmental samples
- The probe exhibits greater sensitivity and specificity for Fe^{3+} over other biologically important metals tested with low LOD and high association constant values.
- The high recoveries and low RSD % indicates that RCD can acts as a potential probe for the accurate recognition of Fe^{3+} in water samples.

Abstract

We describe a highly sensitive turn on colorimetric and fluorescent probe for trivalent iron ions (Fe^{3+}). The newly synthesized compound (RCD) was characterized by FTIR, NMR and mass spectral studies. Competitive experiments reveal that probe RCD exhibits greater sensitivity and specificity towards Fe^{3+} among other biologically important metals. Binding of Fe^{3+} to RCD triggers spirolactum ring opening of rhodamine and evokes a 48-fold fluorescence enhancement accompanied by color variation from colorless to pink. The formation of 1:1 complex between RCD and Fe^{3+} was supported by Job's plot, DFT and Mass spectral studies. The detection limit for RCD is found to be 5.05μM even lowers than the permissible [Fe^{3+}] in drinking water as per WHO standard. The high recoveries and low RSD % indicates that RCD can acts as a potential probe for the accurate recognition of Fe^{3+} in water samples. Moreover, the probe is insensitive to pH 5-8 therefore can be applied for biological and environmental samples.

Key words: Naked eye sensor**,** Fluorescent, Reversible, DFT study, Turn on, Rhodamine

1. Introduction

Fluorometric and colorimetric chemodosimeters are powerful tools for the recognition of biometals because of their simplicity, high specificity and great sensitivity [1]. In past decades, various analytical techniques like anodic stripping vol-tammetry, atomic emission spectrometry (AAS), atomic absorption spectrometry (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) have been explored for the detection of environmentally and biologically important ions [2]. Despite their numerous applications, the limitations such as huge maintenance cost, long analysis time and operational difficulties associated with these techniques hinder their widespread utility [3]. Hence, there is a considerable need for the emergence of new techniques to determine the analytes present in the chemical, biological and environmental systems. Recently, photo physical methods have been attracted significant interest to researchers due to their high selectivity and low-cost instrumentation.

Iron is the most versatile transition metal performing different biological functions in living systems [4]. Among them, physiological processes such as electron transfer, oxygen metabolism and transportation could not occur without Iron [5]. Furthermore, Iron participates in transcriptional regulation and structural enhancement of red blood proteins. Even though, Iron is an essential dietary mineral, under overloading conditions this metal can cause Alzheimer’s disease, cancer and fatal damage to the liver and brain [6].Whilst Iron deficiency lead to anemia. As a consequence, detection and quantification of Iron has become a major concern in biomedical analysis. Literature is enriched with significant number fluorescent probes for iron ion sensing such as calcein derivatives, anthracene analogues, coumarin and fluorescein derivatives [7-9].The success accomplished by previous rhodamine turn-on sensors in intracellular Zn (II) and Cu (II) detection has led to the investigation of novel candidates for other biologically important metals. Schiffbase derivatives have been extensively studied in the fields of inorganic and analytical chemistry as chemosensors because of their chelating ability [10-11]

Currently, rhodamine fluorophores have gained tremendous interest in the field of biosensors because of their advantages such as greater photo stability, longer emission wavelength, high fluorescence coefficient and quantum yields [12]. In general, rhodamine derivatives with spirocyclic form are non fluorescent and colorless, interestingly upon binding with protons and metals they become fluorescent and produce intense color because of ring-opened structure [13]. Owing to their structural property, rhodamine derivatives would serve as ideal candidates for constructing off-on fluorometric and colorimetric sensors. Construction of probes on the basis of rhodamine spirolactum facilitates both absorbance and emission enhancement and “naked eye” detection [14]. Therefore, rhodamine derivatives have been intensively studied as colorimetric, fluorometric and ratiometric sensors.

Recently, we explored a novel rhodamine appended conjugate as a selective and sensitive probe for Fe^{3+} in which, rhodamine spirolactum ring-opening process led to a “turn-on” emission signal and colorimetric change toward Fe^{3+} [15]. As we anticipated in the development of efficient probes for Fe^{3+} ions, herein we report a new conjugate base on rhodamine as a dual responsive molecular probe for Fe^{3+}.

2. Experimental

2.1. Reagents and Equipments

The reagents used for synthesis were procured from commercial suppliers and used without further treatment. Deionized water was used throughout the experiment. The metal salts used were chloride salts of Hg^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, K^{+}, and Cd^{2+}. The progress of the reaction was checked by means of TLC (Thin layer chromatography) with detection by UV. Absorbance experiments were accomplished on Perkin Elmer Lamda 40 UV-vis. spectrophotometer. Fluorescence titrations were done on Jobin-Yvon Fluorolog 3-22 spectrofluorometer. FTIR spectra were obtained on Perkin Elmer Spectrum RXI-IR Instrument. Mass spectral analysis performed using MALDI MS-ABI Sciex 5800 TOF/TOF System with LC-MALDI.

2.2. Preparation of Rhodamine B hydrazide (RBH):

Rhodamine B hydrazide (RBH) was prepared using earlier procedure [16].The analytical data for structural characterization of RBH is presented in supporting information.

2.3. Synthesis of chemosensor RCD

The presented probe RCD was facilely synthesized in single step condensation between RBH and cuminaldehyde in methanol solvent. Methanolic solution of Rhodamine B hydrazide (20 mL) was added to ethanolic solution of Cuminaldehyde. The resulting mixture was stirred with reflux for 12 h. On cooling the reaction mixture, a white precipitate was generated which filtered and washed with cold ethanol and dried under vacuum.

Yield: 66 %; white solid; TOF MS ES$^+$: m/z 587.29; IR υ_{max}(cm^{-1}): 1710 υ(C=O), 1571 υ(CH=N), 693 υ(Ar-CH); ^{1}H-NMR (300 MHz, $CDCl_3$), δ_H : 1.124-1.147 (t, J =6.9 Hz, 12H, NCH_2CH_3), 1.192-1.214 (d, J = .6.6 Hz, 6H, $CH(CH_3)_2$)), 2.777-2.865 (m, 1H, $CH(CH_3)_2$), 2.889-3.346 (q, J = 6.6 Hz, 8H, NCH_2CH_3,), 6.203-6.241 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 2H, Xanthene-H,), 6.426-6.433 (d, J = 2.1 Hz, 2H, Xanthene-H), 6.506-6.535 (d, J = 8.7 Hz, 2H, Xanthene-H), 7.088-7.097(d, J = 2.7 Hz,1H, Phen-H), 7.116-7.143 (d, J = 8.1 Hz, 2H, Ar-H), 7.412-7.424 (d, J = 3.6 Hz, 1H, Phen-H), 7.452-7.463 (d, J_1 = 3.3 Hz, 2H, Phen-H,), 7.471-7.498(d, J = 8.1 Hz, 2H, Ar-H), 7.972-7.994(d, J = 6.6 Hz,1H, Phen-H), 8.620 (s, 1H, CH=N); ^{13}C-NMR (75 MHz ,$CDCl_3$) δ_C: 12.86, 24.02, 33.78, 44.10, 65.93, 97.77, 106.09, 108.43, 123.38, 124.25, 127.19, 127.28, 128.06, 129.20, 129.51, 132.78, 134.17, 148.46, 148.91, 151.36, 151.47, 153.19, 164.06;

2.4. Absorbance and fluorescence spectral experiments

The absorbance and fluorescence measurements were performed at room temperature in CH_3CN- aq. HEPES buffer. (5:5, v/v; pH = 7.2) The selectivity and sensitivity of probe RCD against various metal ions like Ni^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+}, K^+, Na^+,Cr^{3+} and Al^{3+}were investigated. The metal salts were dissolved in the mixture of distilled water. The absorbance and fluorescence spectra of RCD were recorded with and without metal ions. All the solutions were mixed and equilibrated for 10 min before the spectra were taken.

Based on spectro photometric and spectro fluorometric data detection limit and binding constant values were calculated. The interaction capacity of RCD toward Fe^{3+} was determined by Benesi-Hildebrand equation [17].

$$1/ (I - I_0) = 1/K (I_{max} - I_0) [Mn^{+}] + 1/ (I_{max} - I_0) \qquad (1)$$

Where I_0 is the emission intensity of probe RCD, I refers to the emission intensity at a given concentration and I_{max}, corresponding to the maximum fluorescence in the presence of Fe^{3+} at 585 nm respectively. The equation which used to calculate detection limit is as follows [18].

$$\text{Detection limit}=3SD/S \qquad (2)$$

Where SD and S refers to standard deviation and slope of the calibration line.

2.5. **DFT** *Study*

Density functional theory (DFT) is found to be an excellent tool to predict the various key properties like: geometrical and opto-electronic of enormous class of organic, inorganic and their metal complexes [19, 20]. Moreover, DFT has been developed as a mutual contrivance in first-principles calculations intended to predict and describe the characteristic properties of molecular and condensed matter schemes. Quantum chemical calculations for probe RCD were performed using Gaussian 09program at the B3LYP/6-31G* level. The optimized structures of the ligand and its metal complex were visualized by Gauss view 5 programs. The ground state molecular geometry of RCD and its Fe^{3+}complex are shown in fig and data of HOMO, LUMO bond energies were compiled in Table 1.

3. Results and Discussion

The synthetic procedure for title compound is given in scheme 1. The condensation of RBH with cumminaldehyde in the presence of methanol produces RCD. The solution of RCD in buffered solution is colorless suggesting the formation of spirocyclic form. Structural elucidation of synthesized compound was carried out by means of UV, FTIR, Mass and NMR spectroscopy.

3.1 spectral characteristics

The FTIR spectrum of compound RBH exhibited a sharp signal at 3362 cm^{-1} ascribed to NH vibrations (Fig S1). The disappearance of this band and emergence of strong band at 1571 cm^{-1} in the FTIR spectrum of RCD indicate the formation of azomethine moiety. The bands corresponding to C=O vibrations were appeared at 1710 cm^{-1}. At 1121cm^{-1}, a medium intense band was appeared due to C-O-C stretching vibrations. However, the bending vibrations corresponding to aromatic CH bending bond were found at 693 cm^{-1} respectively**.**

The NMR spectra of RCD are given in Fig. 1 and Fig. 2. The broad peak observed at 3.61 ppm in the NMR spectra of RBH attributed to amine group suggesting the formation of rhodamine B hydrazide (Fig. S2). However this peak was disappeared in the ^{1}H NMR spectra of RCD indicating the condensation of amine group with cuminaldehyde. Moreover, the appearance of a sharp signal at 8.62 ppm due to azomethine proton further confirms the schiff base formation. The proton signals related to xanthenes were observed between 6.42 and 6.53 ppm whereas aromatic protons were appeared between 7.08 and 7.99 ppm respectively. A sharp signal at 65 ppm in the ^{13}C NMR spectra of RCD further provides evidence for the formation of spirolactum ring form [21]. The peak appeared at 148 ppm was attributed to azomethine moiety.

3.2. Absorbance response of probe RCD to metal ions

The binding capacity of compound RCD was investigated towards diverse metal ions (Ni^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+}, K^{+}, Na^{+},Cr^{3+} and Al^{3+}) by absorption and fluorescence spectroscopy. The absorption spectrum of RCD exhibited absorption bands at 350 nm, but no bands were observed over 500 nm which might be due to the closed spirolactam form of RCD [22]. The metal ions except Fe^{3+} induce minute or no changes in the absorption spectra of RCD. On the addition of 5 equivalents of Fe^{3+}, RCD exhibited a band at 550 nm implying that the test compound exhibiting selectivity towards Fe^{3+} among other metal ions (Fig. 3a). Besides the color change of the solution from colorless to pink indicating that RCD could serve as “naked-eye” chemo sensor for Fe^{3+} (Fig. 4) [23]. The emergence of new band at 550 nm is because of the existence of ring-opened amide form of title compound (Fig. 3b). Job’s plot experiments were also carried out in order to find out the binding stoichiometry between probe RCD and Fe^{3+}. As illustrated in the Fig. 3b maximum absorbance was appeared at the ratio of 0.5 suggesting the 1:1 complex formation between RCD and Fe^{3+}. [24]

3.3. Fluorescence response of probe RCD to metal ions

The fluorescence responses of probe RCD towards different metal ions are illustrated in Fig. 5a. As depicted in the figure only Fe^{3+} cause a 48-fold fluorescence emission enhancement where as other metal ions induce mild or no apparent changes in the fluorescence intensity of probe RCD. As the concentration of Fe^{3+} increased, the fluorescence intensity at 585 nm was significantly enhanced due to the increased concentration of Fe^{3+}-RCD complex (Fig. 5b). Furthermore, competitive binding experiments were also performed to investigate the sensitivity and practical applicability of probe RCD as a Fe^{3+} selective fluorescent chemosensor [25]. The fluorescence intensity of probe RCD to Fe^{3+} complex is unaffected by other metal ions indicate that proposed probe could applicable for practical applications (Fig. 9). The detection limit and association constant of probe RCD to the receptor is found to be $5.05 \text{ X } 10^{-6}$M and $3.42 \text{ X}10^{4}M^{-1}$ (Table 2).

3.4. pH responses of RCD

The absorbance and fluorescence response of probe RCD was also investigated under various pH conditions. As the pH decreases the absorbance and fluorescence intensity of RCD increases which could be ascribed to the spirolactum ring opening of test compounds due to the strong protonation [26]. While at pH 4, the enhanced absorbance and fluorescence intensity was gradually reduced. The disappearance of absorbance (at 550 nm) and fluorescence (at 585 nm) was observed between pH 5-8. The experimental results reveal that the newly synthesized probe is insensitive to pH 5-8 therefore practically applicable under physiological conditions. These results indicated that, the probe RCD can be applied for environmental and biological samples.

3.5. Proposed sensing mechanism by FTIR and Mass spectral analysis

In order to intend the sensing mechanism FTIR and mass spectral analysis were done for RCD with and without Fe^{3+} ions. The IR spectrum of RCD showed a sharp signal at 1710 Cm^{-1} corresponding to carbonyl vibrations. However this band shifted to 1681Cm^{-1} (lower frequency) suggesting the involvement of C=O group in complexation with Fe^{3+} ions (Fig. 6).

The reaction products of probe RCD with Fe^{3+} were subjected to mass spectral analysis in order to scrutinize sensing mechanism. A plausible mechanism is proposed on the basis of intermediates formed in the reaction (scheme 2). As shown in the Fig. 7a, the apparent peak observed at m/z value 587 is corresponding to newly synthesized probe RCD. However, upon addition of five equivalents of Fe^{3+} to the solution, intense peaks were obtained at m/z values of 471 and 443(Fig. 7b). The fragment peak detected at 471 is attributed to an intermediate 1 which subsequently oxidized to rhodamine B characterized by an intense pink color [27]. The results indicate that interaction of Fe^{3+} to RCD lead to Fe (III) induced oxidation reaction where 1 formed as an initial product which is unstable and further hydrolyzed to Rhodamine B(2) as a final product.

3.6. Theoretical investigations

Quantum chemical calculations were also performed to scrutinize the binding pattern of RCD with Fe^{3+} and to resolve the geometry of RCD- Fe^{3+}complex. The spatial distribution and energies of HOMO and LUMO were determined by means of DFT calculations. As illustrated in the Fig. 8, the oxygen atom form the amide group of RCD and nitrogen atom of azomethine moiety is involved in the complexation with Fe^{3+}. In case of compound RCD the electron density in HOMO is distributed over the phenylene and cumunaldehyde moieties while LUMO it is localized on the xanthene moiety. On the other hand the HOMO and LUMO of RDFB-Fe^{3+} complex were spread over the half of xanthane and spirolactum ring and central metal ion. The energy gap between HOMO and LUMO for probe RCD is calculated to be 3.76 eV. Whereas for RCD-Fe^{3+} complex it is found to be 0.841 eV respectively demonstrating that binding of RCD to Fe^{3+} decreases the HOMO-LUMO energy gap of RCD-Fe^{3+} complex and stabilizes the system. As results indicated the cleavage of spirocyclic C-N bond occur in order to facilitate the interaction of Fe^{3+} to oxygen atom of amide moiety of RCD [28].

3.7. Determination of Fe^{3+} in practical samples

Furthermore to check the practical applicability, RCD was employed for the determination of Fe^{3+} in drinking, distilled and tap water samples. Initially, the analyzed samples contain no Fe^{3+}, indicating the absence of ferric ions in these samples. Then the water samples were spiked with known concentrations of Fe^{3+} and subjected to recovery studies. For each spike sample three replicate determinations were done and the results were reported in Table 3.An excellent harmonization was observed between added and determined values which validate our proposed sensing method. In addition, the high recoveries and low RSD % indicate that RCD could acts as a potential probe for the accurate detection of Fe^{3+} in practical samples.

4. Conclusions

We synthesized a novel dual responsive colorimetric and fluorescent chemodosimeter which showed greater sensitivity towards Fe^{3+} ions over other tested metal ions. The presented probe displayed remarkable absorbance enhancement accompanied with a color change from colorless to pink upon interaction to Fe^{3+}. In addition to that probe RCD exhibited 48-fold fluorescence enhancements suggesting the high potential of this compound to serve as an effective “Off-On” switch for Fe^{3+}. A job plot and mass spectral analysis confirmed the 1:1 binding mode between synthesized probe and Fe^{3+}. DFT studies and FTIR spectral analysis provided the evidence of involvement of oxygen and nitrogen atoms of RCD in complexation with Fe^{3+}. The detection limit for RCD (5.05µM) is found to be lowers than the permissible [Fe^{3+}] in drinking water as per WHO standard. The low RSD % high and recoveries demonstrates that RCD can serve as a potential sensor for the detection of Fe^{3+} in water samples. Moreover, this probe is insensitive to pH between 5-8 which property makes it practically applicable for biological samples under physiological conditions.

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Figures

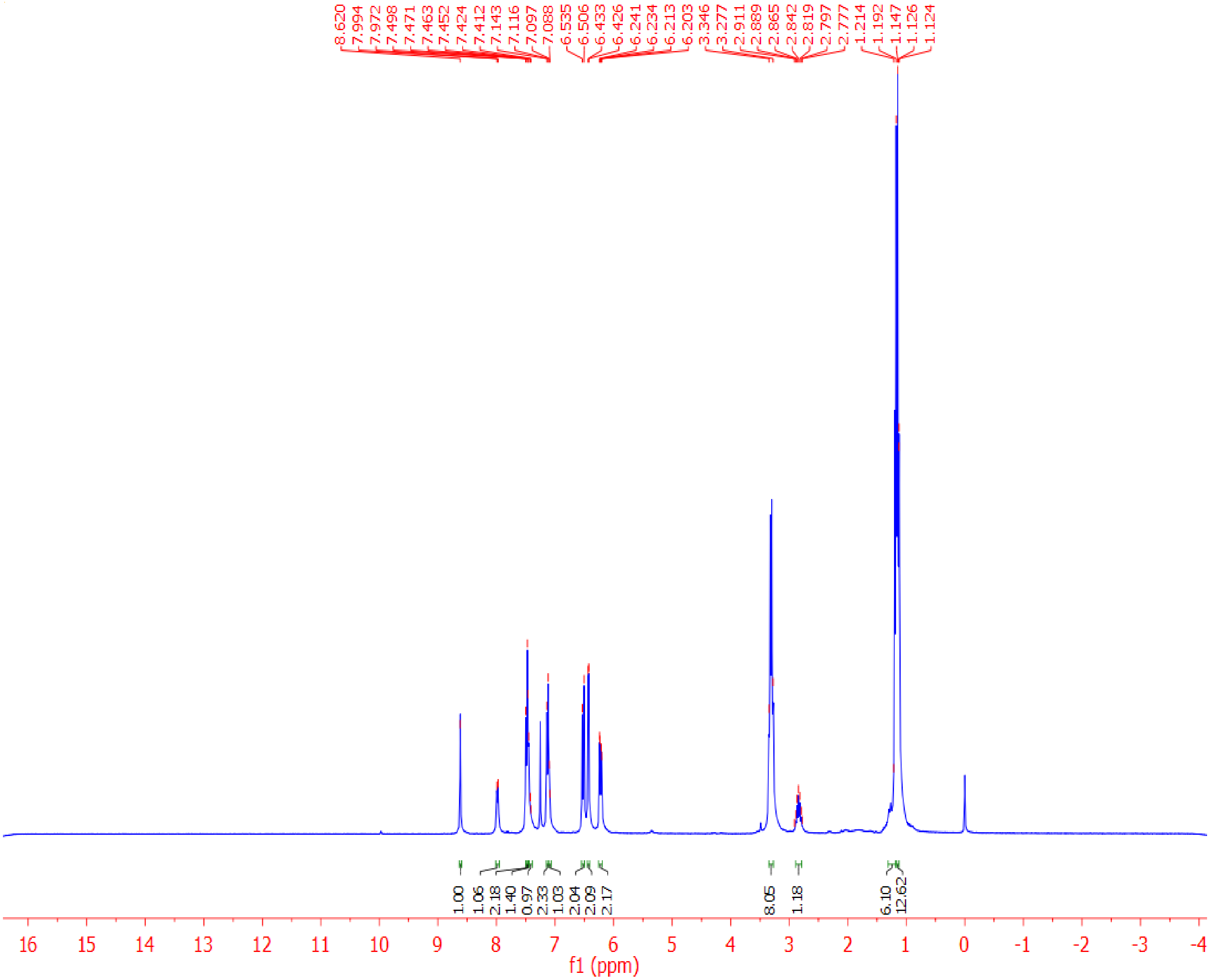


Fig. 1. ^{1}H NMR spectrum of RCD

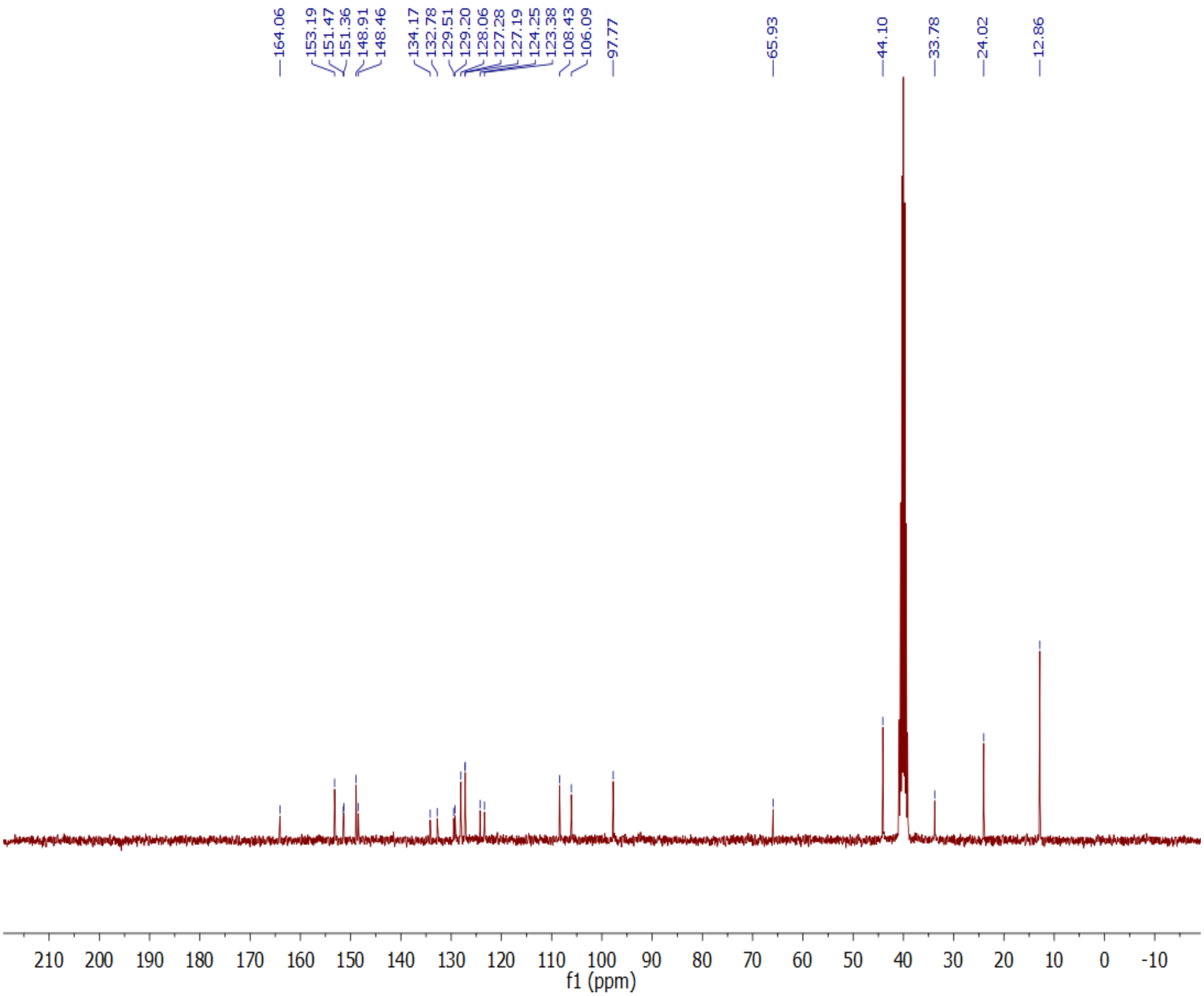


Fig. 2. ^{13}C NMR spectrum of RCD

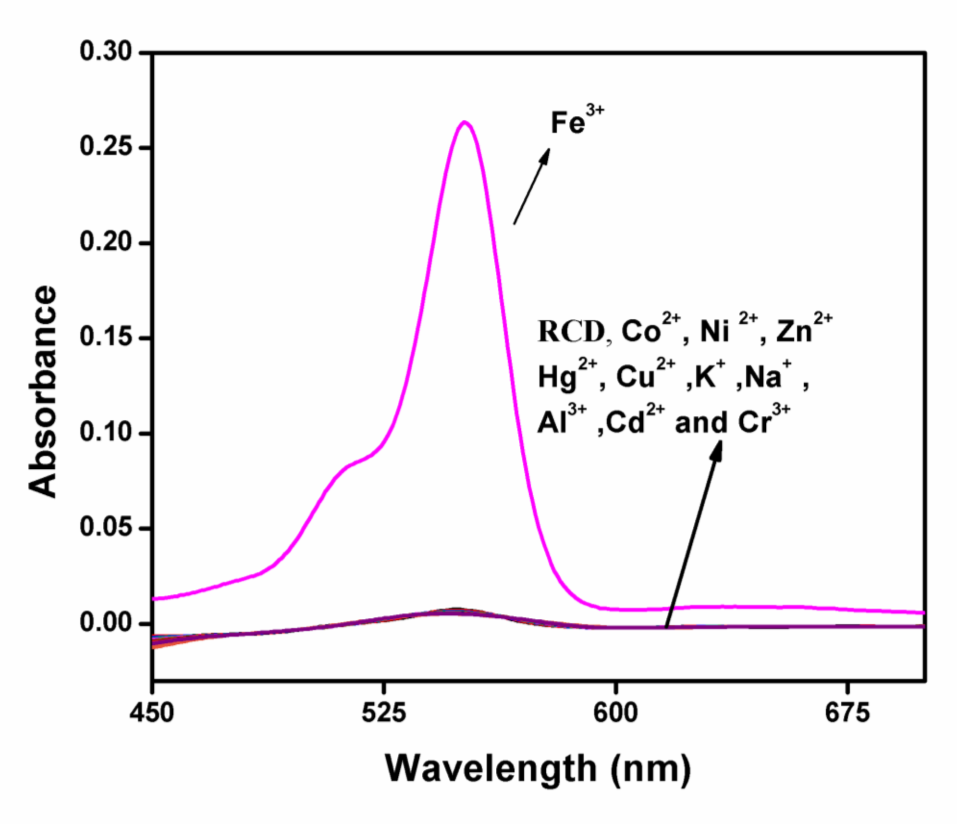


Fig. 3a. UV-visible spectra of RCD (10μM) in the presence of various metal ions in buffered solution. (10^{-5}M)

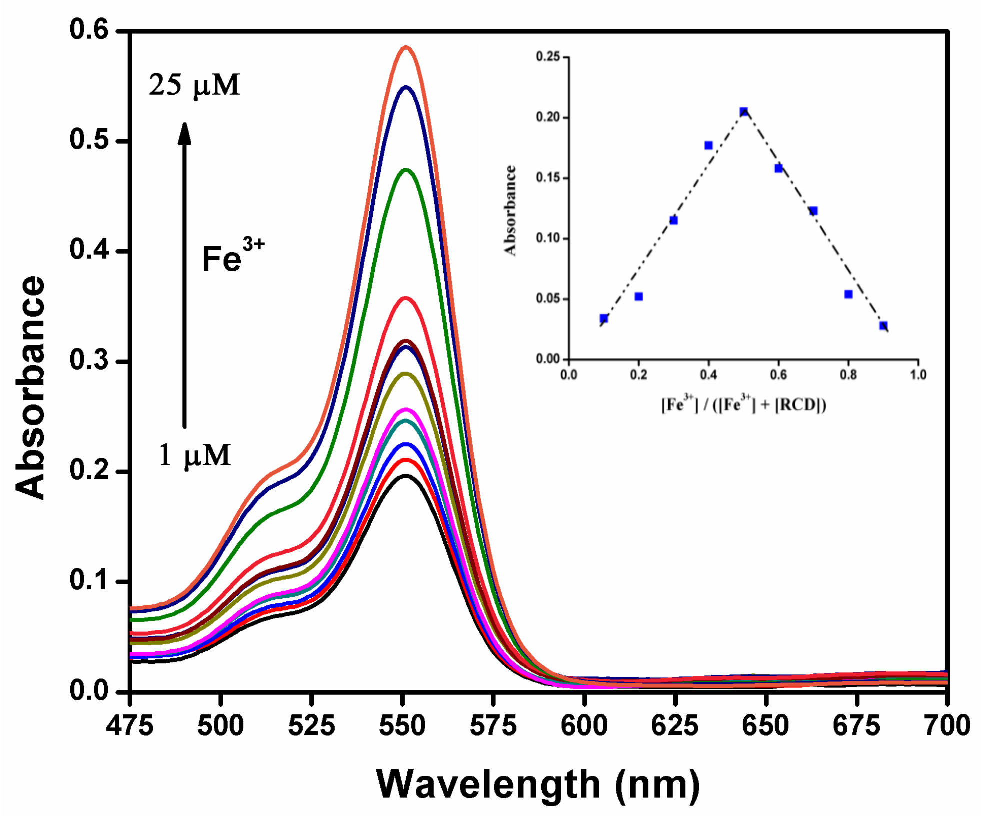


Fig. 3b. Absorption spectra of RCD in buffered solution upon addition of different amounts of Fe^{3+} (1-25μM). Job's plot for Fe^{3+}-RCD system $[Fe^{3+}]$+ [RCD] =1.0×10^{-5}M.

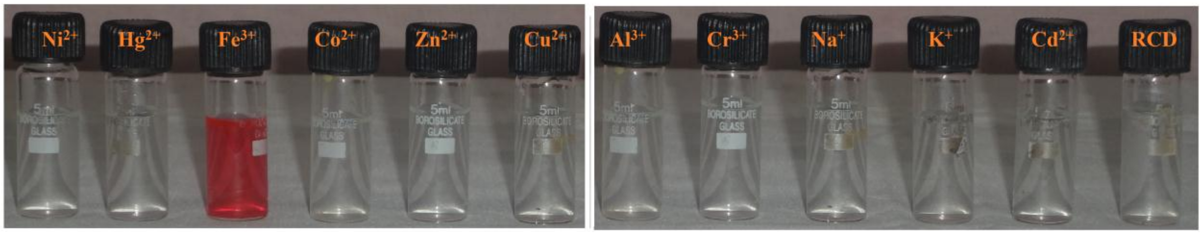


Fig. 4. Color changes of RCD upon addition of various metal ions.

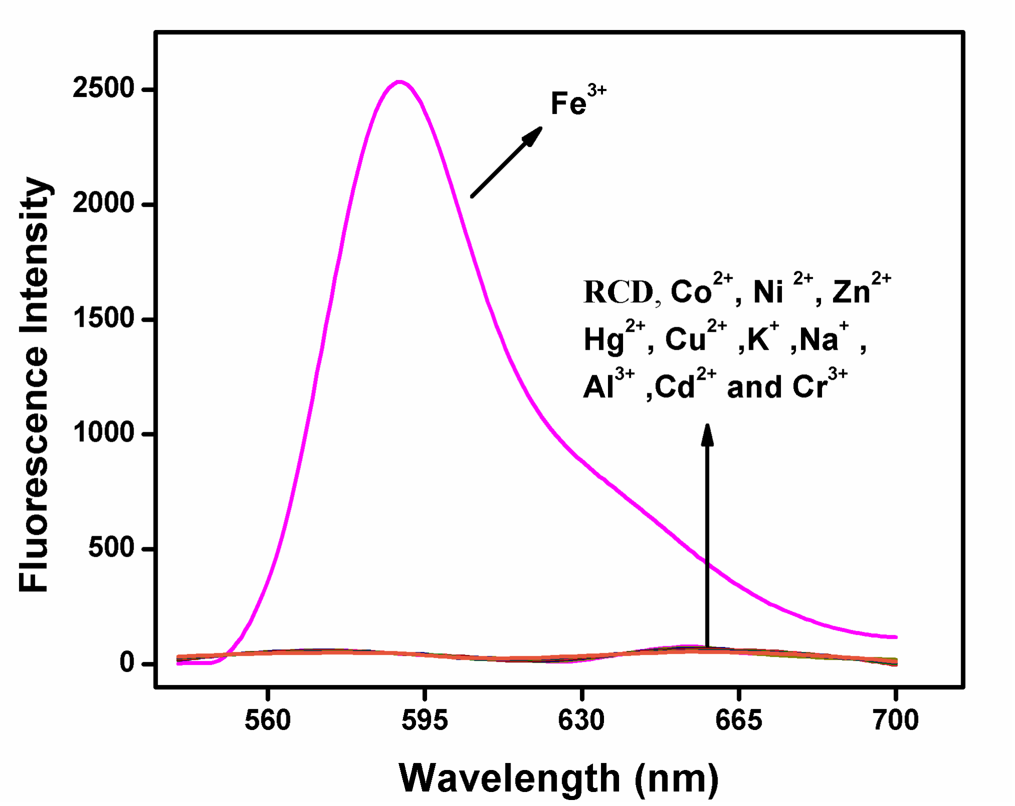


Fig. 5a. Fluorescence spectroscopic response of RCD to different metal ions in CH_3CN- aq. HEPES buffer medium.

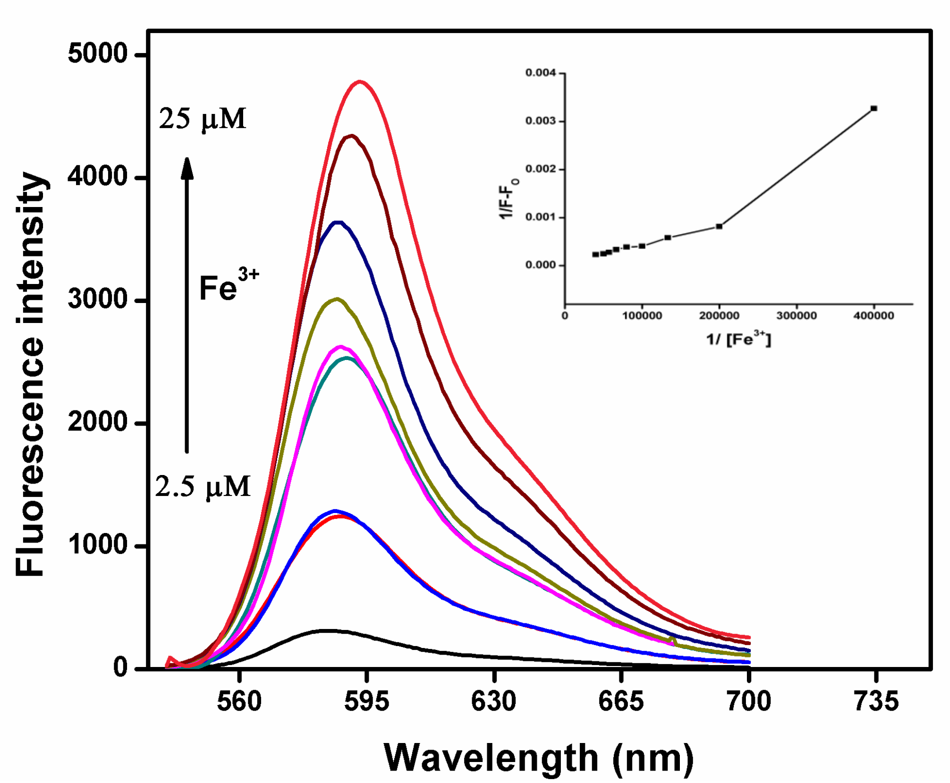


Fig. 5b. Fluorescence spectra of RCD upon addition of increasing concentrations of Fe^{3+} (1-25µM) in CH_3CN- aq. HEPES buffer medium.

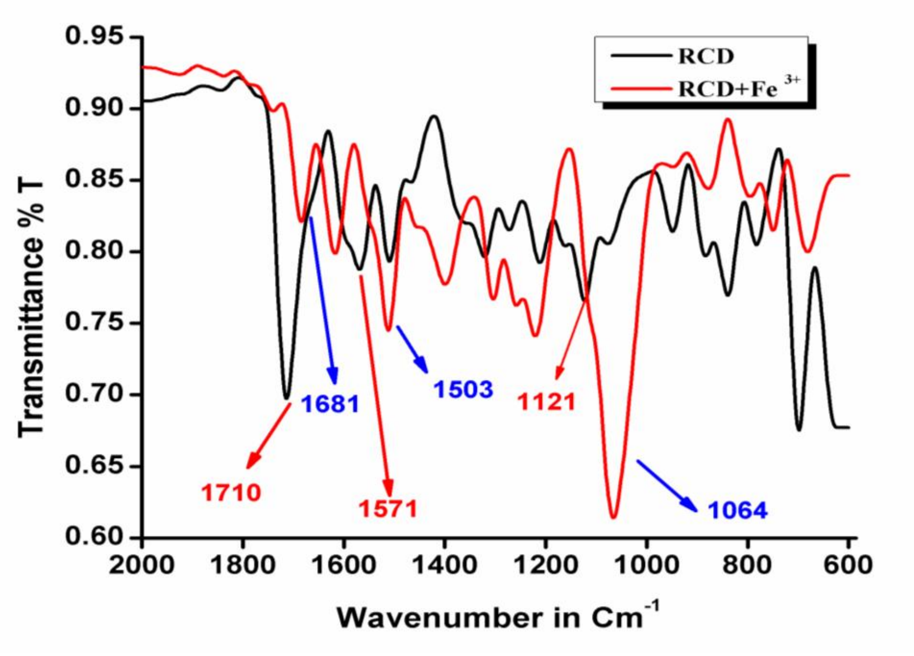


Fig. 6. FTIR spectra of RCD alone and RCD-Fe^{3+} complex.

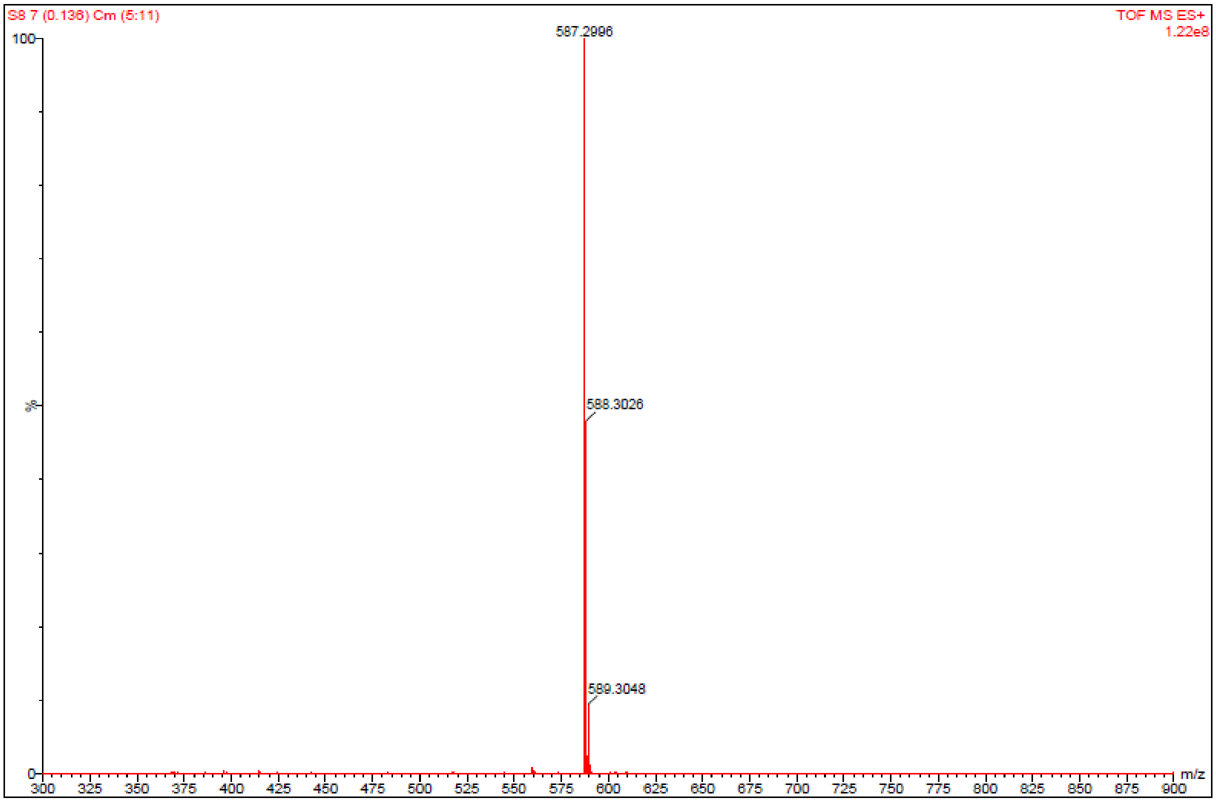


Fig. 7a Mass spectrum of RCD.

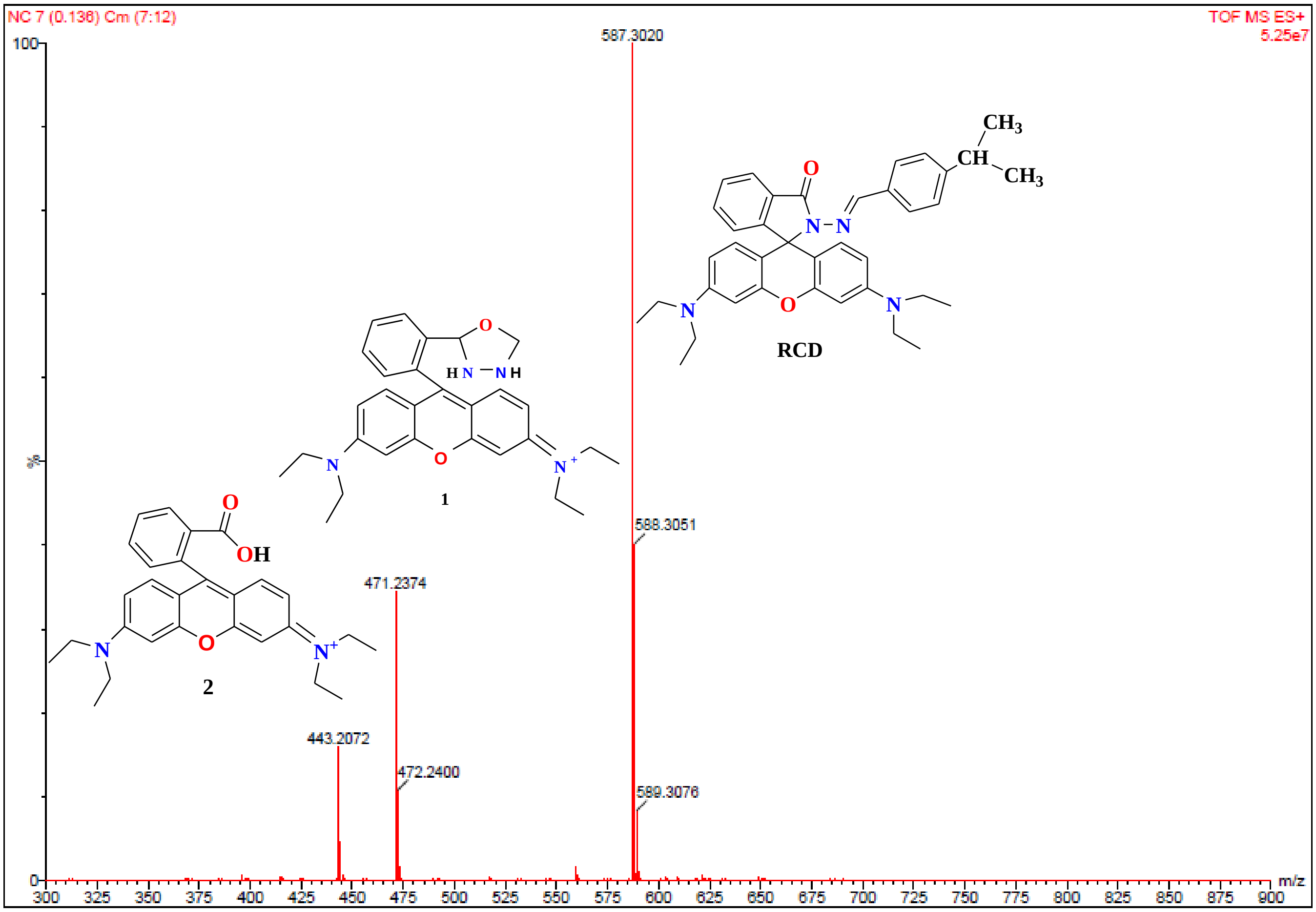


Fig. 7b Mass spectrum of RCD-Fe^{3+} adduct

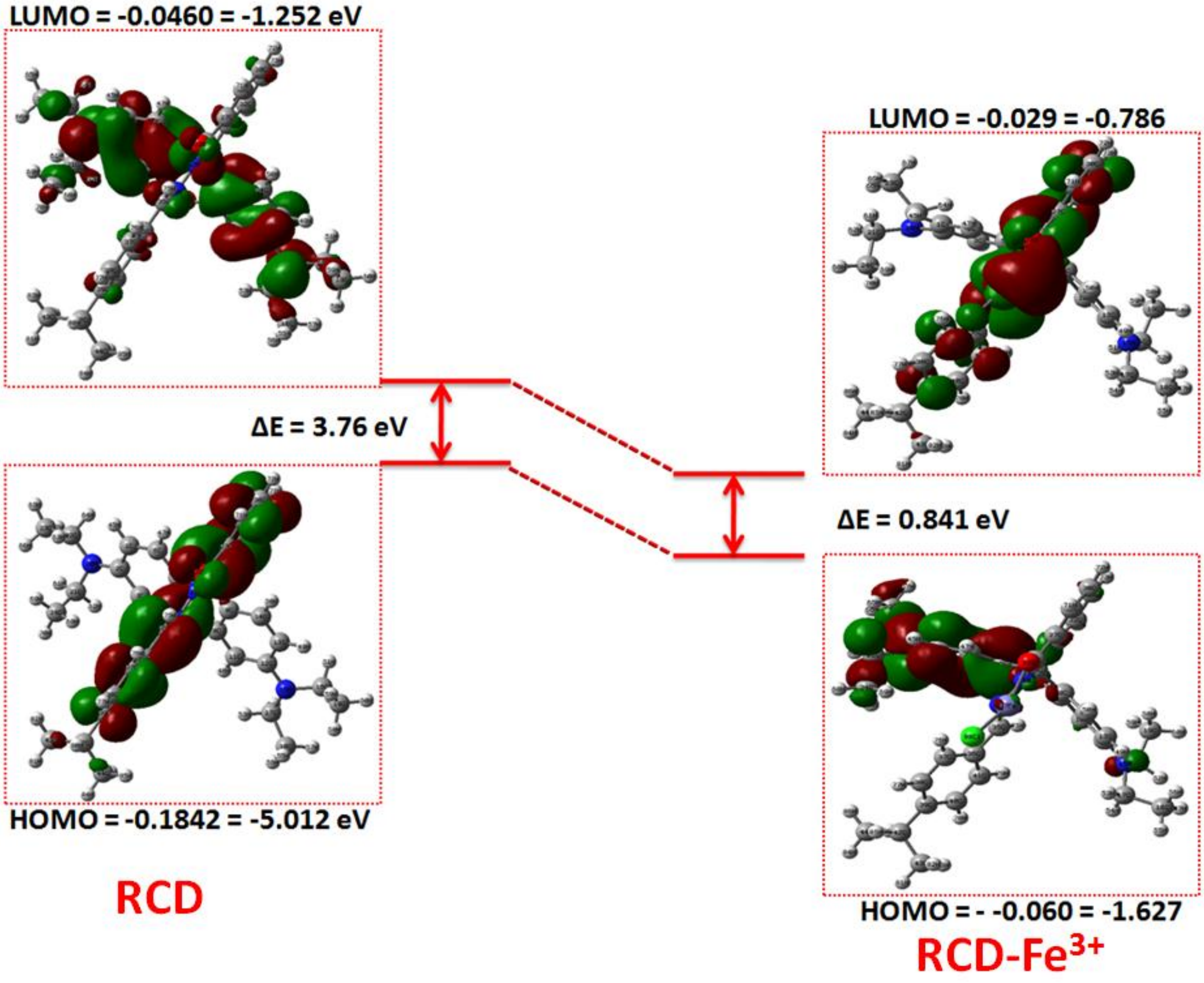


Fig. 8 HOMO and LUMOdistributions of RCD and RCD–Fe^{3+} complex.

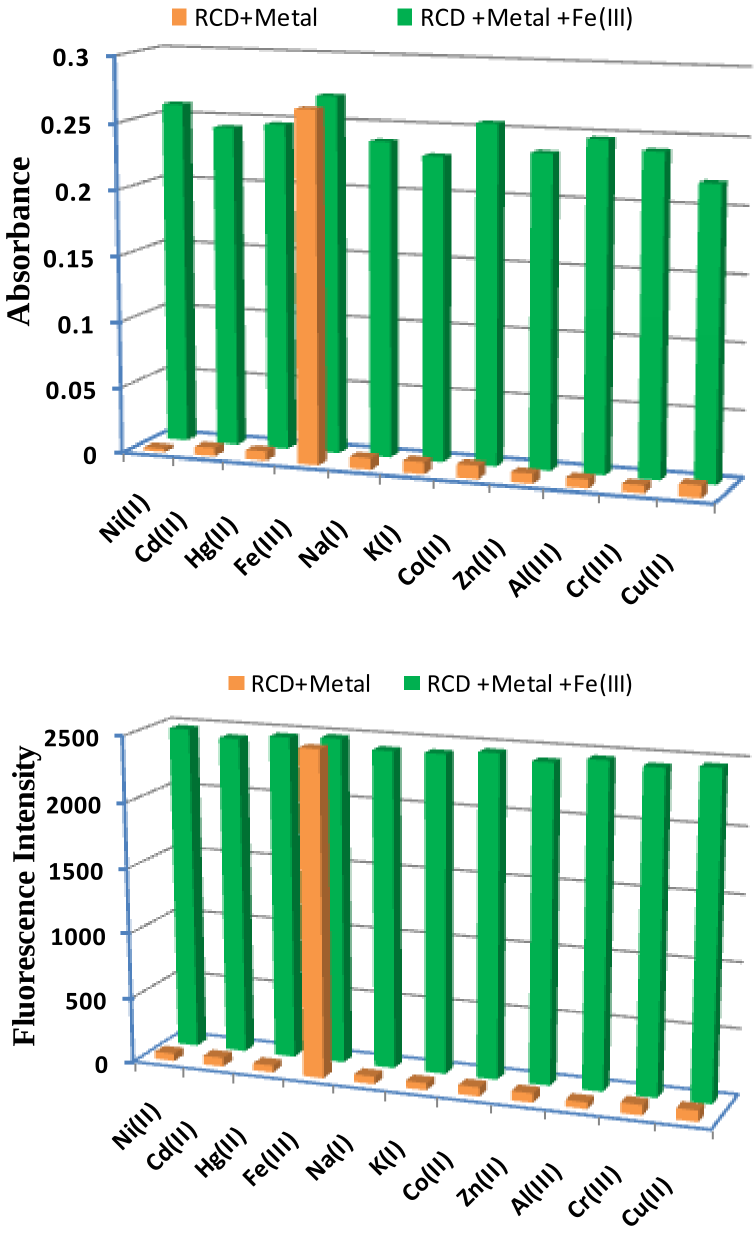
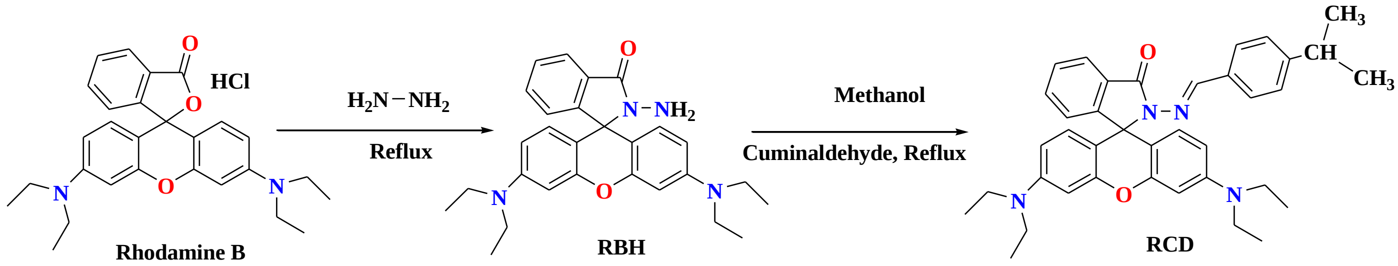
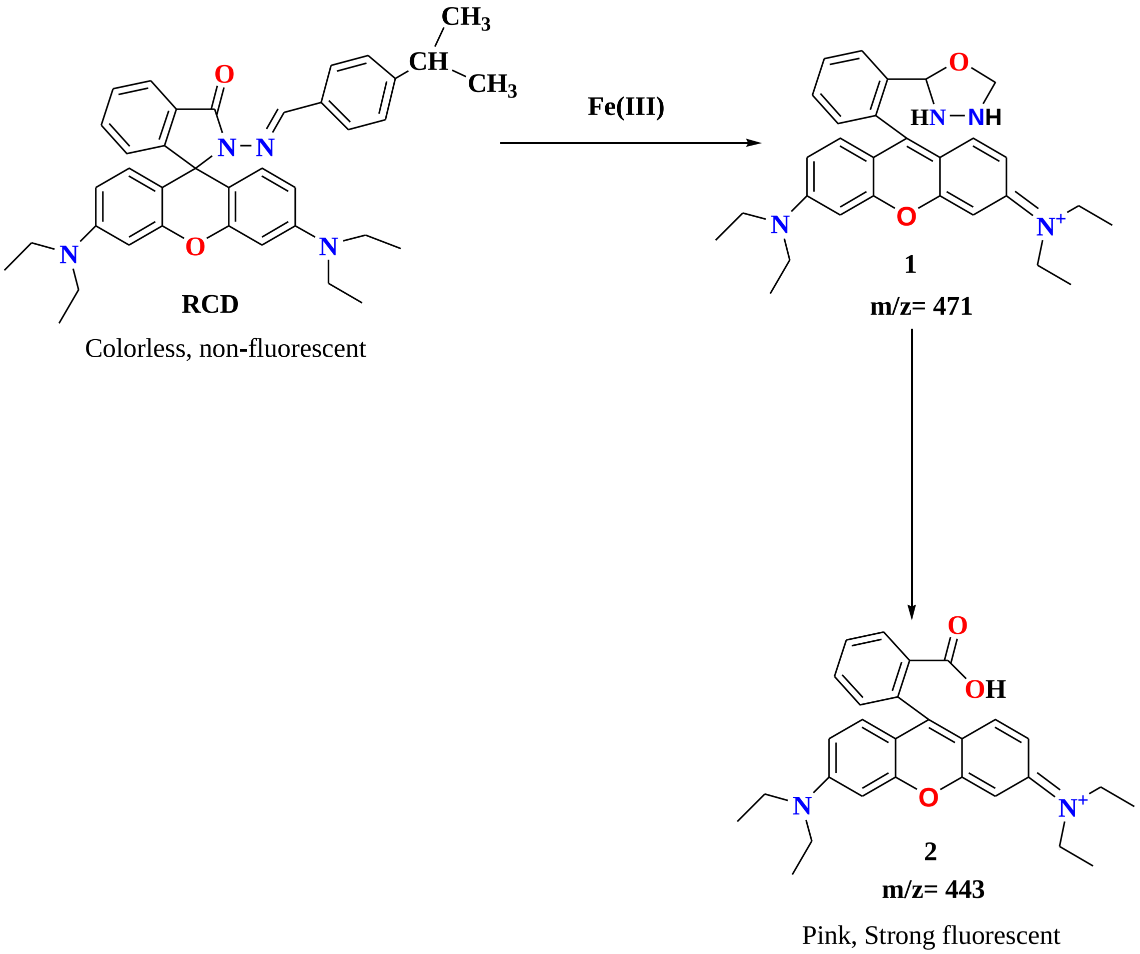


Fig. 9. Histograms representing A) Absorbance B) Fluorescence changes in the presence of different metal ions.



Scheme 1: Synthesis of RBH and sensor, RCD



Scheme 2: Moleculat structures of RCD, 1 and 2

Tables:

Table 1

The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}) and the HOMO-LUMO energy gap of RCD and its Fe^{3+} complex**.**

Entry	**HOMO**	**LUMO**	**$E_{HOMO-LUMO}$**
RCD	-5.012 eV.	-1.252 eV	$\Delta E = E_{HOMO-LUMO} =$ 3.76 eV
RCD+Fe^{3+}	-1.627 eV	-0.786 eV	$\Delta E = E_{HOMO-LUMO} =$ 0.841 eV

Table 2

Comparision of some sensors for Fe^{3+} detection.

Sensor type	**Detection Method**	**LOD**	**Association constant(M^{-1})**	**Ref.**
2-pyridyl thiazole derivative	Ratiometric probe	4.47μM	$1.58x10^5$	[29]
Bis(rhodamine)-based polyether	Turn-on fluorescent sensor	10μM	ND	[30]
Poly(3,4-propylene dioxy thiophene)	Colorimetric sensor	23μM	$0.96x10^4$	[31]
Rhodamine- indole conjugate	Fluoregenic probe	20μM	ND	[32]
Rhodamine based probe	Colorimeteric and fluorescent	6.6μM	$1.13 x10^5$	[15]
Rhodamine - Cuminaldehyde conjugate	Fluoremetric and colorimetric	5.05μM	$3.42x10^4$	This work

Table 3. Analytical results of Fe^{3+} in different water samples.

Sample	**Fe^{3+}**			
	Added (µM)	Found (µM)	Recovery (%)	RSD(n=3)
Tap water	10.0	10.5	105.0	1.90
Drinking water	5.0	5.3	106.6	4.72
Distilled water	7.5	7.6	101.3	1.32

➢