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SHORT COMMUNICATION

Urea Based Dipodal Fluorescence Receptor for Sensing of Fe^{3+} Ion in Semi-Aqueous Medium

Umesh Fegade · Hemant Sharma · Sanjay Attarde · Narinder Singh · Anil Kuwar

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Abstract Urea based fluorescent chemosensor **1** was synthesized. Receptor **1** shows unique selectivity for the Fe^{3+}ion and no such significant response was noticed with other metal ions (Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Bi^{3+}) in DMSO/H_2O (50:50,v/v) semi-aqueous solution. The binding features have been established by absorption and fluorescence spectroscopic methods. The binding constant (K) values obtained from Benesi-Hildebrand, Scatchard and Connor plot for receptor **1** is (8.3±0.3) × 10^3 M^{-1} and has good detection limit 0.7 μM. The stoichiometry of **1**.Fe^{3+} complex was confirmed by mass spectroscopy and Job's plot.

Keywords Dipodal receptors · Semi-aqueous medium · Binding constant

Introduction

The architecture of noncovalent bonding interactions array in the construction of host molecules for selective complexation with guest molecules is on the verge of getting transferred towards non-cyclic analogues of crown ether, cryptands, cyclodextrins and spherends because of their solubility problem. Now a day, noncyclic receptors have been made to develop the field of supramolecular chemistry in which the molecular recognition, transport and catalysis phenomena have been deeply studied with the hope of shedding light on enzymatic and more complicated biological processes [1–3].

Over the past few decades, noncyclic compounds also have been utilized as the essential synthetic targets for further applications in host–guest chemistry [4–6]. Noncyclic compounds containing multiples sites for noncovalent bonding interaction have gained considerable attention because of their ability of complexation towards broad range of analytes like ionic and/or neutral/non-ionic molecules [7]. With the plan of synthesis of metallo-supramolecular complexes which can act as sensors and precursors, we made an attempt to design the ligands having selective and significant binding abilities towards various metal ions.

Among transition metal ions Fe^{3+}, Co^{2+} and Zn^{2+} have considerable biological importance and play significant role in many biochemical processes. The human body contains four grams of iron [8]. Most of the iron present in biological systems is tightly associated with enzymes and specialized transport and storage proteins and found in hemoglobin, the red pigment in the erythrocytes and rest of stored in ferretin. It plays a vital role in oxygen transfer processes in DNA and RNA synthesis. The deficiency of Fe^{3+} causes anaemia, hemochromatosis, liver damage, diabetes, Parkinson's disease and cancer. Accumulation of copper and iron leads to over production of H_2O_2 in tissues; causes oxidative stress and neurodegenerative diseases [9–12].

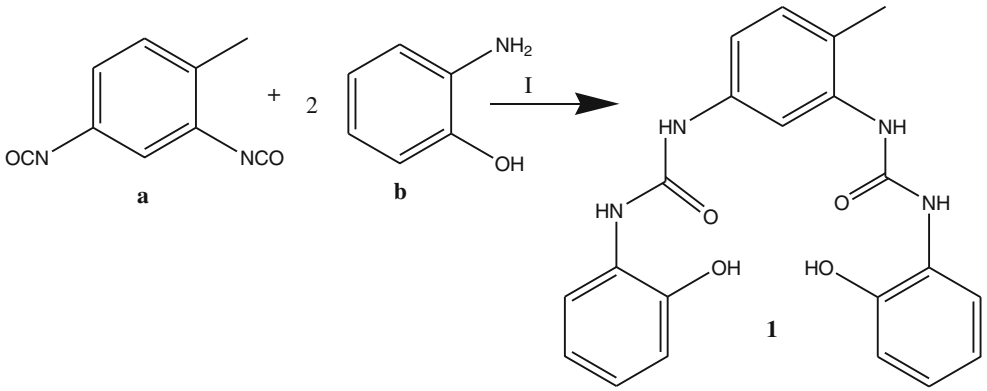
Herein, we have paid attention towards synthesis and designing of fluorescent sensors that utilize photoinduced electron transfer (PET) to translate a cation binding event into a fluorescence signal. Generally these types of molecules were mostly used as an anion sensor due to the presence of amide groups but in the present work, we have reported a fluorescent sensor **1** designed for selective recognition of iron. Coordination sites in the receptors **1** show that there are two amide groups along with hydroxyl groups (Scheme 1). The binding ability of receptors **1** with Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+},Zn^{2+}, Cd^{2+}, Hg^{2+},

U. Fegade · A. Kuwar (✉)
School of Chemical Sciences, North Maharashtra University, Jalgaon 425001, MS, India
e-mail: kuwaras@gmail.com

H. Sharma · N. Singh (✉)
Department of Chemistry, Indian Institute of Technology, Ropar, Rupanagar 140001, Punjab, India
e-mail: nsingh@iitrpr.ac.in

U. Fegade · S. Attarde
School of Earth and Environmental Sciences, North Maharashtra University, Jalgaon 425001, MS, India

Scheme 1 Synthetic route of receptor **1** (**I:** acetone, reflux 1 h)



Pb^{2+} and Bi^{3+} ions in DMSO/H_2O (50:50, v/v) medium was evaluated and binding constant was computed for **1**.Fe^{3+} complex for which fluorescence intensity was distinctly quenched which lead to recognition of Fe^{3+} ion. To date, the synthesized receptor **1** was not reported for any molecular recognition study.

Experimental

Reagents and Apparatus

All commercial grade chemicals and solvents were purchased from Sigma-Aldrich and used as such. ^{1}H and ^{13}C-NMR spectra were recorded on a Varian NMR mercury System 300 spectrometer operating at 300 & 75 MHz in DMSO-d_6 respectively. The fluorescence spectra of the receptor **1** with metal ions (Chloride salts of Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and nitrate salts of Cd^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+} were used) were recorded on Fluoromax-4 spectrofluorometer in DMSO/H_2O (50:50, v/v) solvent system and absorption spectra on Schimadzu UV-24500 UV-visible spectrophotometer at room temperature using 1 cm path length quartz cell.

General Procedure for Synthesis of Receptor 1 and its Complexes

Synthesis of Receptor 1'-(4-methylbenzene-1,3-diyl)bis [3-(2-hydroxyphenyl)urea] (1)

Receptor **1** was synthesized by reaction of one mole of 2,4-diisocyanato-1-methylbenzene (1.74 g, 1 mmol) with two moles of 2-amino phenol (2.18 g, 2 mmol) in acetone (50 ml) and reflux for 1 h. Receptor **1** was obtained with quantitative yield and having appearance of white powder. Yield-82 %, Solubility in DMSO, mp≥250°C. ^{1}H-NMR (300 MHz, DMSO-d_6, ppm) δ=2.47 (s, 3H, Ar-CH_3), 7.37–7.42 (d, J=7.2Hz, 2H, Ar-H), 7.87–8.08 (m, 8H, Ar-H), 8.21 (s, 1H, Ar-H), 9.23 (s, 2H, Ar-OH), 9.86 (s, 4H, NH).^{13}C NMR, (75 MHz, DMSO, ppm) δ=14.4, 113.9, 115.6, 116.0, 121.3,

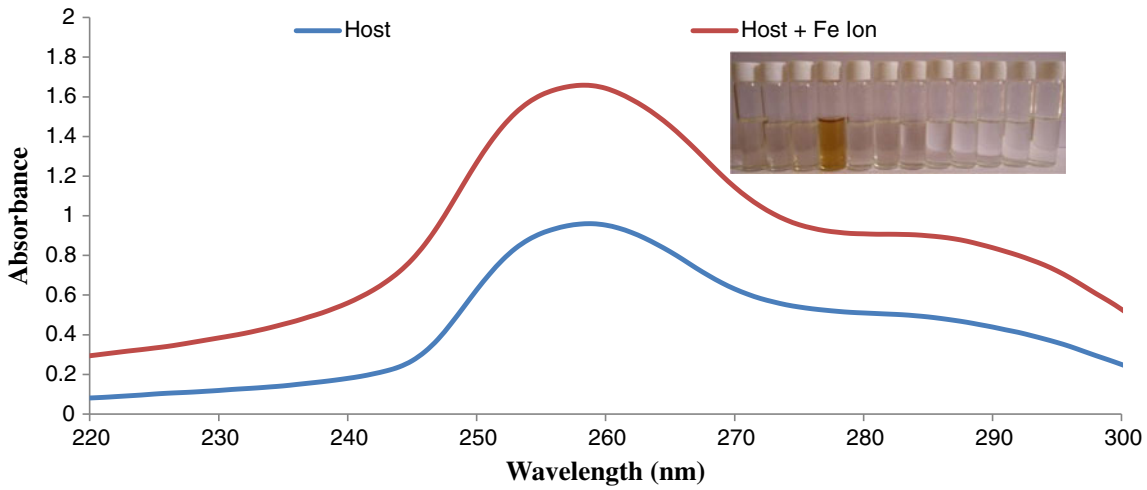


Fig. 1 Changes in absorbance spectrum of receptor **1** (0.07 mM) upon the addition of Fe^{3+} metal ion (0.7 mM) in DMSO/H_2O (50:50, v/v) solvent system (*inset* represent the change in colour upon addition of various cations)

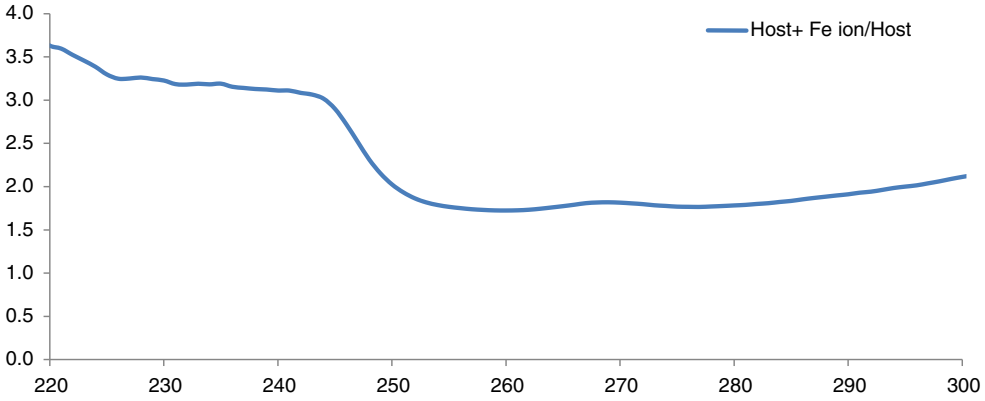


Fig. 2 Graph of $A_{(host+Fe)}/A_{host}$ vs wavelength (nm) from the selectivity Fig. 1

123.7, 126.0, 129.2, 129.9, 132.9, 135.6, 149.2, 154.6. IR (KBr, cm^{-1}) υ =750, 878, 1,036, 1,538, 1,650, 2,924, 3,268. MS (ESI): m/z required $C_{21}H_{20}N_4O_4$:392.43, found 393.00.

Synthesis of Receptor 1.Fe^{3+} Complex. 1 Fe^{3+} complex was synthesized by reaction of one mole of receptor **1** (0.78 g, 0.2 mmol) with one moles of $FeCl_3$(0.32 g, 0.2 mmol) in 50 ml of DMSO:MeOH (10:90, v/v) reflux with stirring for 3 h. The precipitation was collect at room temperature and dried in vacuum. Further, it was washed with water then ethanol followed by petroleum ether. Yield- 72 %, IR (KBr, cm^{-1}) υ=742, 870, 1,030, 1,377, 1,597, 2,853, 2,923. MS (ESI): m/z requires $C_{21}H_{18}FeN_4O_4$: 446.24, found 446.88.

General UV-Visible and Fluorescence Spectral Measurements

For recognition studies, a stock solution of receptor **1** was prepared having a concentration of 0.07 mM. Similarly, stock solutions of metal ions were prepared, concentration of 0.7 mM. The metal binding study was performed using 5 ml volumetric flasks, each contain a stock solution of receptor **1** along with particular amount of different transition metal ion. Each solution was placed for 20 min to get rid from non-homogenous error. The titration was performed in 10 ml volumetric flask with gradual addition of metal ion with constant interval of time. For whole set of experiment DMSO/H_2O (50:50 v/v) choice as solvent system. The selectivity of receptor **1** towards Fe^{3+} in the presence of other metal ions was confirmed through interference study. To perform this, a set of solutions were prepared each contain a 1 eq. of receptor **1** and 1 eq. of Fe^{3+} along with 2 eq. of other competing ions. The stoichiometry of **1**.Fe^{3+} complex was confirmed through the job's plot in which total concentration of host and guest will remain same but molar variations were varied. The plot between [HG] and [H] /[H] + [G] illustrate the stoichiometry of the complexes formed. The concentration of [HG] was calculated by the equation [HG] = ΔA /Ao x [H].

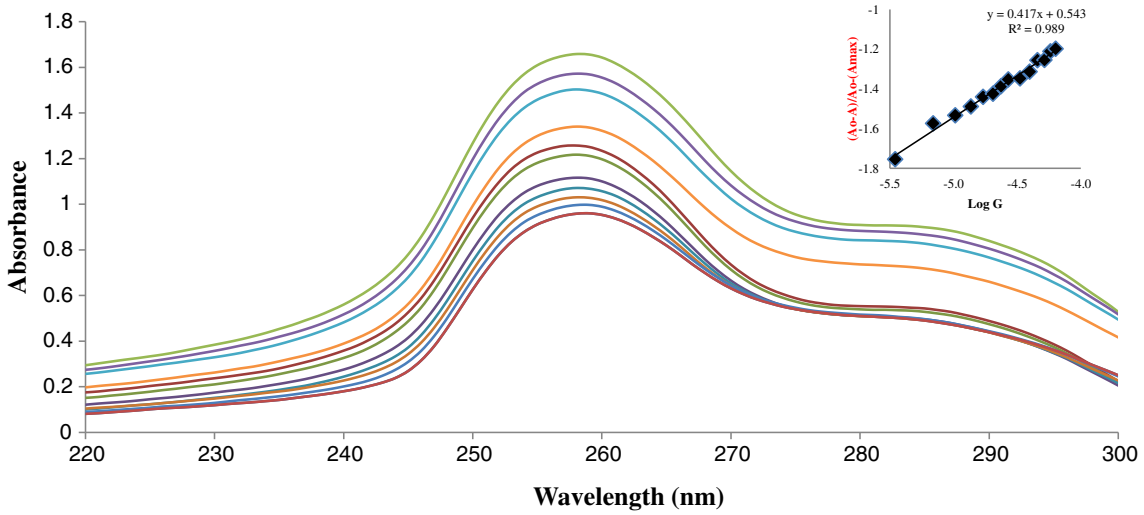


Fig. 3 Changes in absorbance spectrum of receptor **1** (0.07 mM) upon the gradually addition of Fe^{3+} metal ion (0.7 mM) in DMSO/H_2O (50:50, v/v) solvent system (inset depict the plot between (Ao-A)/(Ao-Amax), where A_0 represents the fluorescence intensity in the absence of guest ion, A represents the fluorescence intensity in presence of guest ion)

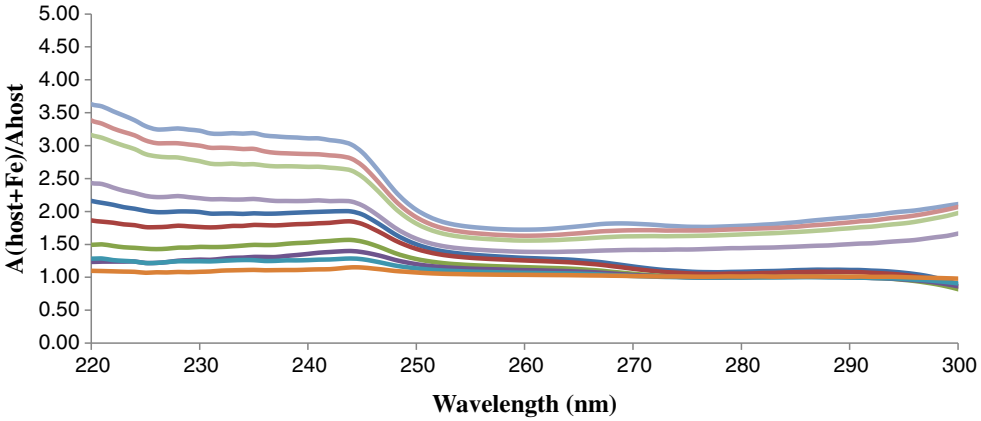


Fig. 4 Graph of $A_{(host+Fe)}/A_{host}$ vs wavelength (nm) from the titration graph Fig. 3

Result and Discussion

Receptor **1** was synthesized by condensation reaction between 2,4-diisocyanato-1-methylbenzene and 2-amino phenol in acetone with stirring and refluxing for 1 h (Scheme 1). A white color product was obtained in good amount. The synthesized receptor **1** was characterized by melting point, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic methods. The spectral investigation gave consistent data with structure of receptor **1**.

In order to check its binding behaviour with different metal ions, metal binding test of receptor **1** was evaluated on absorption and emission spectroscopy. Firstly, the absorption profile of receptor **1** was checked upon addition of metal ions and the appreciable change in absorbance was observed for Fe^{3+} metal ion in DMSO/H_2O (50:50 v/v) solvent system as shown in Fig. 1. The absorbance spectrum of receptor **1** is broad and has two absorption maxima at 260 and 289. Further, a titration was performed between receptor **1** and Fe^{3+} ion shown in Fig. 2 and to understand the relationship between absorbance and concentration of Fe^{3+}; calibration plot was drawn (Fig. 2 inset). The plot represents that with the increase of concentration of Fe^{3+}, absorbance is also increased.

Furthermore, fluorescence response of receptor **1** towards various metal ions (Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Bi^{3+}) was studied in DMSO/H_2O (50:50, v/v) at room temperature, keeping the solvent ratio constant throughout the experiment. For the recognition studies Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, $Pb^{2+}$and Bi^{3+} chloride salts were used (0.7 mM) in DMSO/H_2O (50:50, v/v) solvent system. The fluorescence spectra of **1** were recorded upon addition of different metal ion as shown in Figs. 3 and 4. It is noticed that addition of Fe^{3+} lead to decrease in fluorescence intensity as depict in Fig. 5. In order to unleash the mechanism of sensing a titration was performed between receptor **1** and Fe^{3+} (Fig. 6). Receptor **1** has shown selective quenching behavior towards Fe^{3+} ion. The gradual addition of Fe^{3+} ions to a solution of receptor **1** results in a decrease in the fluorescence intensity at 345 nm upon excite at 289 nm. This decrease in the fluorescence intensity is ascribed to the participation of amide nitrogens and phenolic oxygens towards the coordination of Fe^{3+} ions, which represent the photoinduced electron transfer (PET) phenomenon and hence Turn-Off the fluorescence emission [13, 14].

IR spectra of receptor **1** and **1**.Fe^{+3} complex revealed the importance of hydroxyl groups in Fe^{3+} ion binding. The IR of

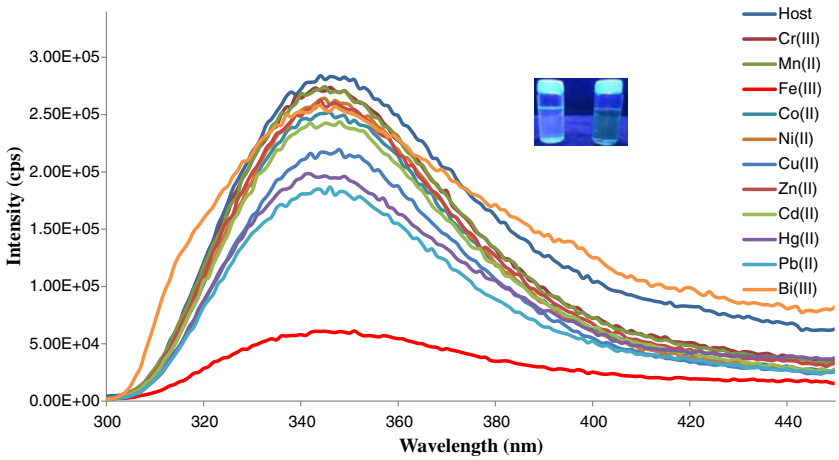


Fig. 5 Fluorescence spectra (λ_{ex}=289 nm) of receptor **1** (0.07 mM) upon addition of a fixed amount of metal salts (0.7 mM) in DMSO /H_2O (50:50, v/v) solvent system; inset shows change in color of receptor **1** upon addition of Fe^{3+} in the presence of UV light

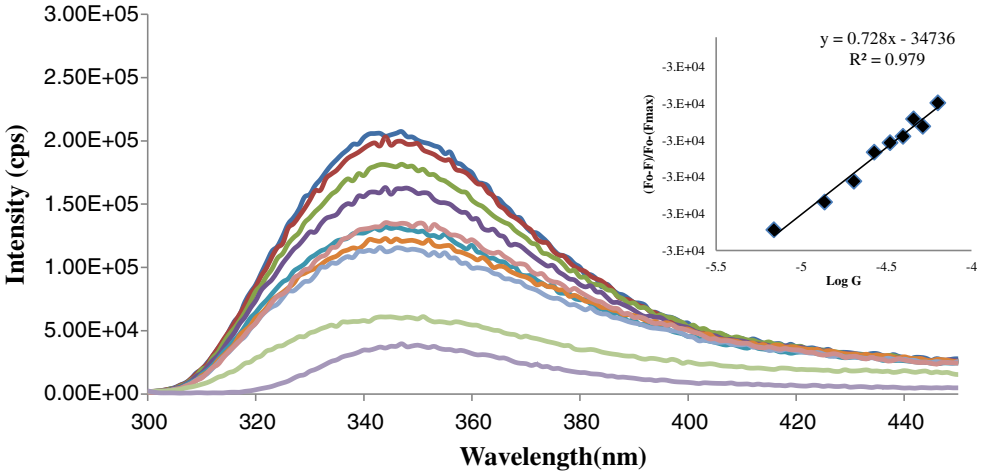


Fig. 6 Fluorescence titration of receptor **1** (0.07 mM) upon the addition of Fe^{3+} salt (0–200 μL) in DMSO/H_2O (50:50, v/v); *inset* represent the plot between (Fo-F)/(Fo-Fmax) and log of concentration of Fe^{3+}

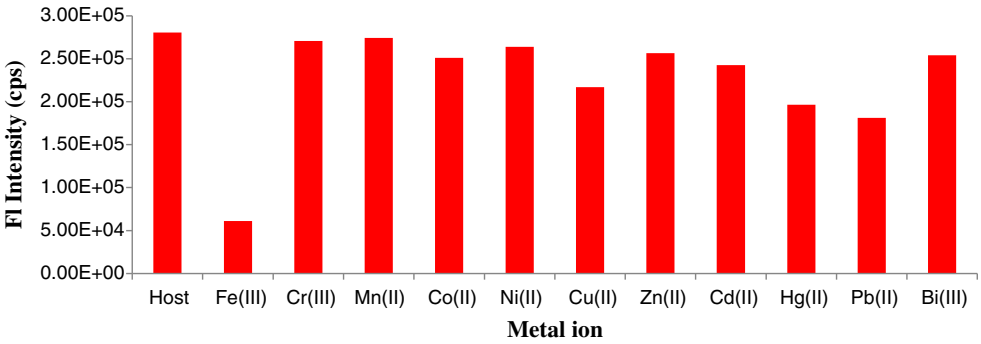


Fig. 7 Fluorescence ratiometric response (I_0-I/I_0) of receptor **1** (0.07 mM) upon the addition of metal salt (0.7 mM) in DMSO/H_2O (50:50, v/v) solvent system

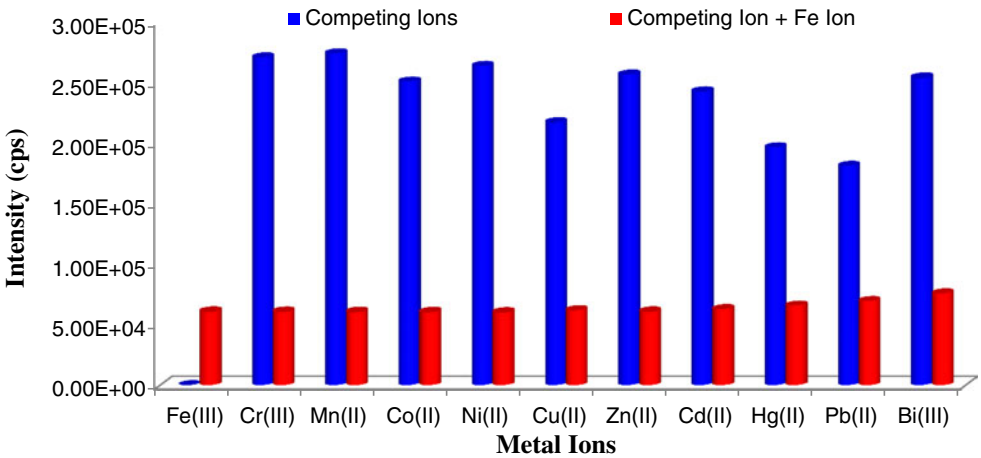


Fig. 8 Recognition of Fe^{3+} ion by receptor **1** in the presence of other metal ion

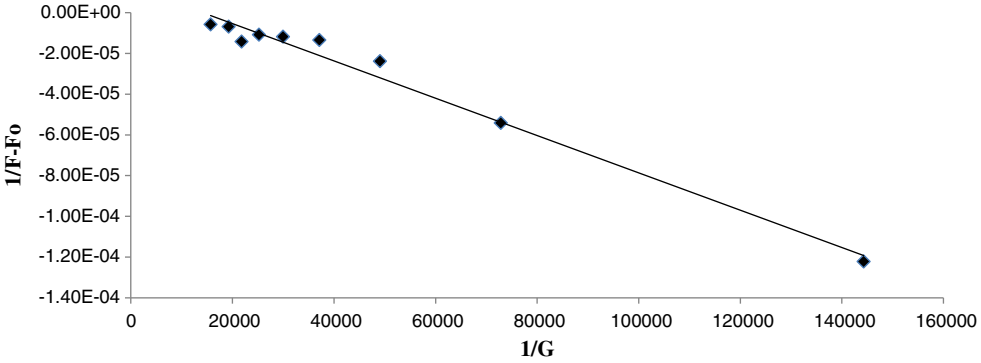


Fig. 9 Benesi-Hildebrand Plot receptor **1** (adjusted equation: $1/F\text{-}F_0 = -6E\text{-}10 + 5E\text{-}06\ 1/[G]$, $R = 0.9811$) at the K value $8333 M^{-1}$

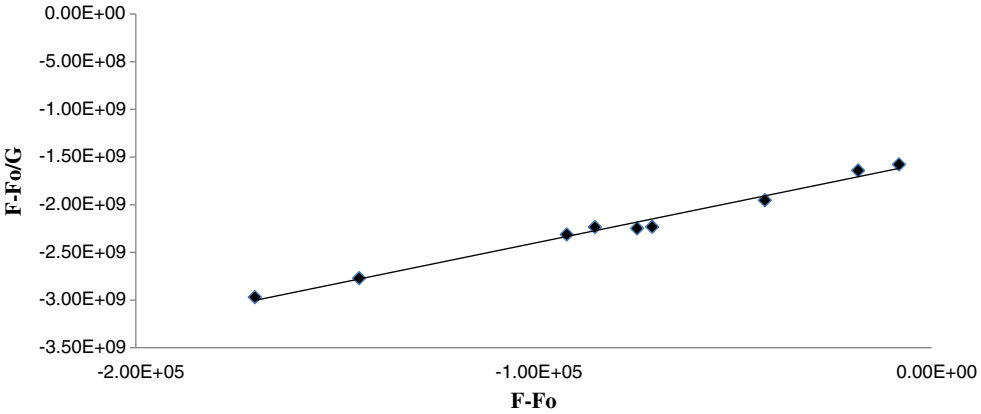


Fig. 10 Scatchard Plot for receptor **1** (adjusted equation: $F\text{-}F_0/[G] = -8556x + 2E+09$, $R = 0.987$) at the K value $8556 M^{-1}$

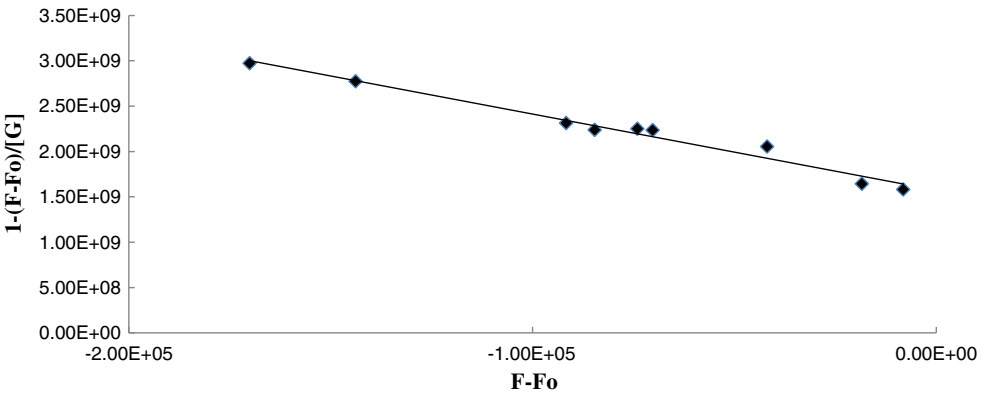


Fig. 11 Connor Plot receptor **1** (adjusted equation: $y = -8556x - 2E+09$, $R = 0.986$) at the K value $8556 M^{-1}$

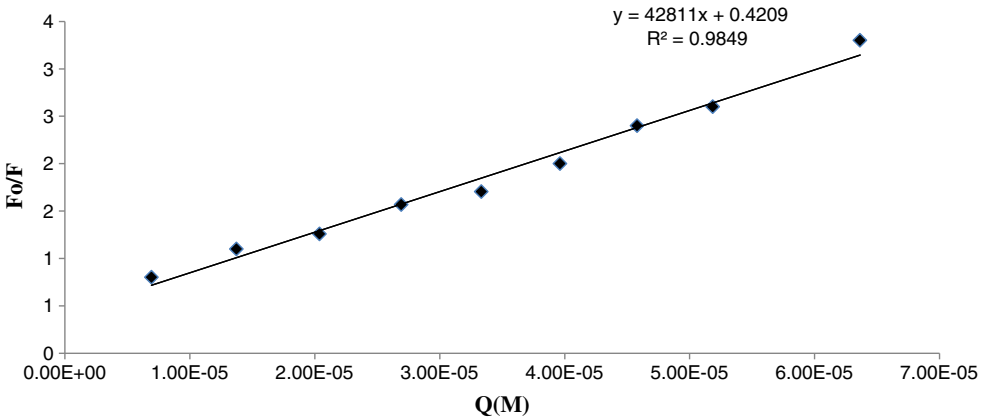


Fig. 12 The Stern–Volmer plot of the titrations of probe **1** with different concentrations of Fe^{3+} metal salt

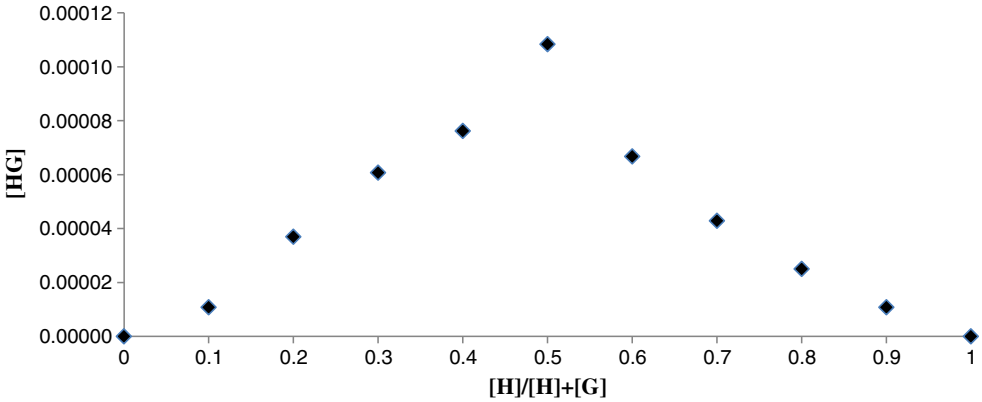


Fig. 13 1:1 Stoichiometry of the host guest relationship realised from the Job's plot for receptor

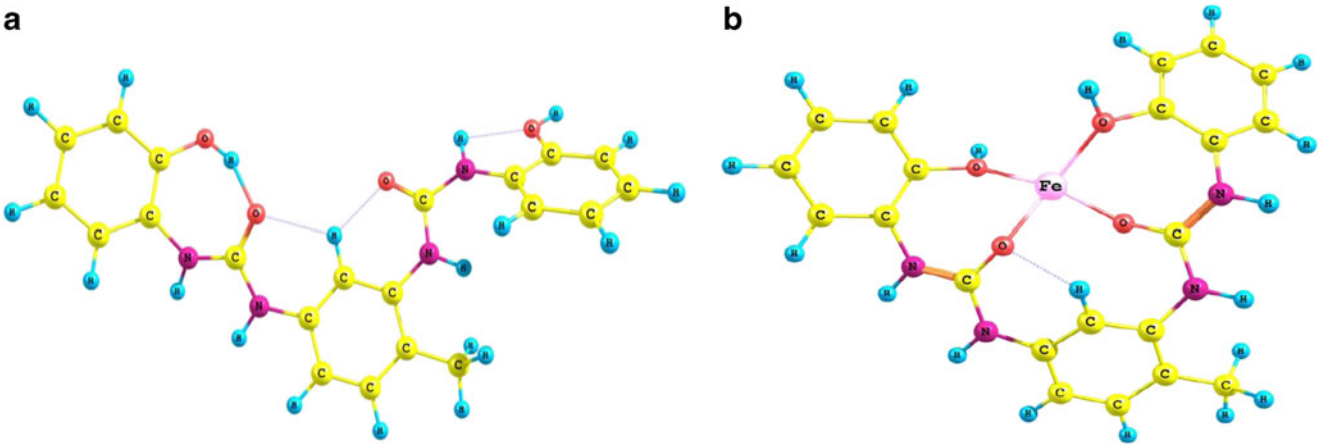


Fig. 14 The optimized structure of: **a** receptor **1**, **b** **1**.Fe^{3+} calculated by using B3LYP/6-31G basis set on Gaussian 09 program; *red*, *pink*, *yellow* and *turquoise spheres* refer to O, N, C and H atoms respectively and *dotted line* represent H-bonds

Table 1 represent the optimized values of energy and HOMO-LUMO gaps calculated by using B3LYP/6-31G basis set

Compound	Energy(eV)	$E_{HOMO-LUMO}$ (eV)
Receptor **1**	36241.48	4.825
Receptor **1**.Fe^{3+}	70599.7	1.006

1.Fe^{+3} complexes (Figs. 15 and 16) shows the absence of hydroxyl group it means that the deprotonation was take place during the complexation [15, 16]. The hydroxyl group acts as a good binding site and plays an effective role in binding of transition metal ions. To explore the possibility of using receptor **1** as a practical ion-selective fluorophore for Fe^{3+} ions, competitive experiment was carried out, in which receptor **1** was firstly mixed with 1 equivalent of Fe^{3+} ion and 2 equivalents of other surveyed metal ions. The Fe^{3+} ion still had shown an excellent turn-off response for the Fe^{3+}ion in the presence of other metal ions. From the interference study, it was confirmed that there was moderately low interference of other metal ions in detection of Fe^{3+} ion (Figs. 7 and 8). The quenching of fluorescence distinctly selective for Fe^{3+} ion from other surveyed metal ions.

Normalized response of fluorescence signal to changing Fe^{3+} ion concentration for receptor **1** was plotted as shown in inset of Fig. 6. The fluorescence intensity decrease for receptor **1** with gradually increased amount of Fe^{3+}guest concentration**.** These results confirmed that the Fe^{3+} ion binding of receptor **1** in semi aqueous solution is chemically reversible. The chemosensor could therefore be used for real time tracking of Fe^{3+} in biological samples. Under optimal conditions, the detection limit for Fe^{3+} ion is as low as 0.7 μM [17]. It suggested that receptor **1** can be use for sensing even in submicromolar range. This high selectivity of receptor **1** increased its application for sensing in biological system. For a normal human being 20 mg iron is required per day for the

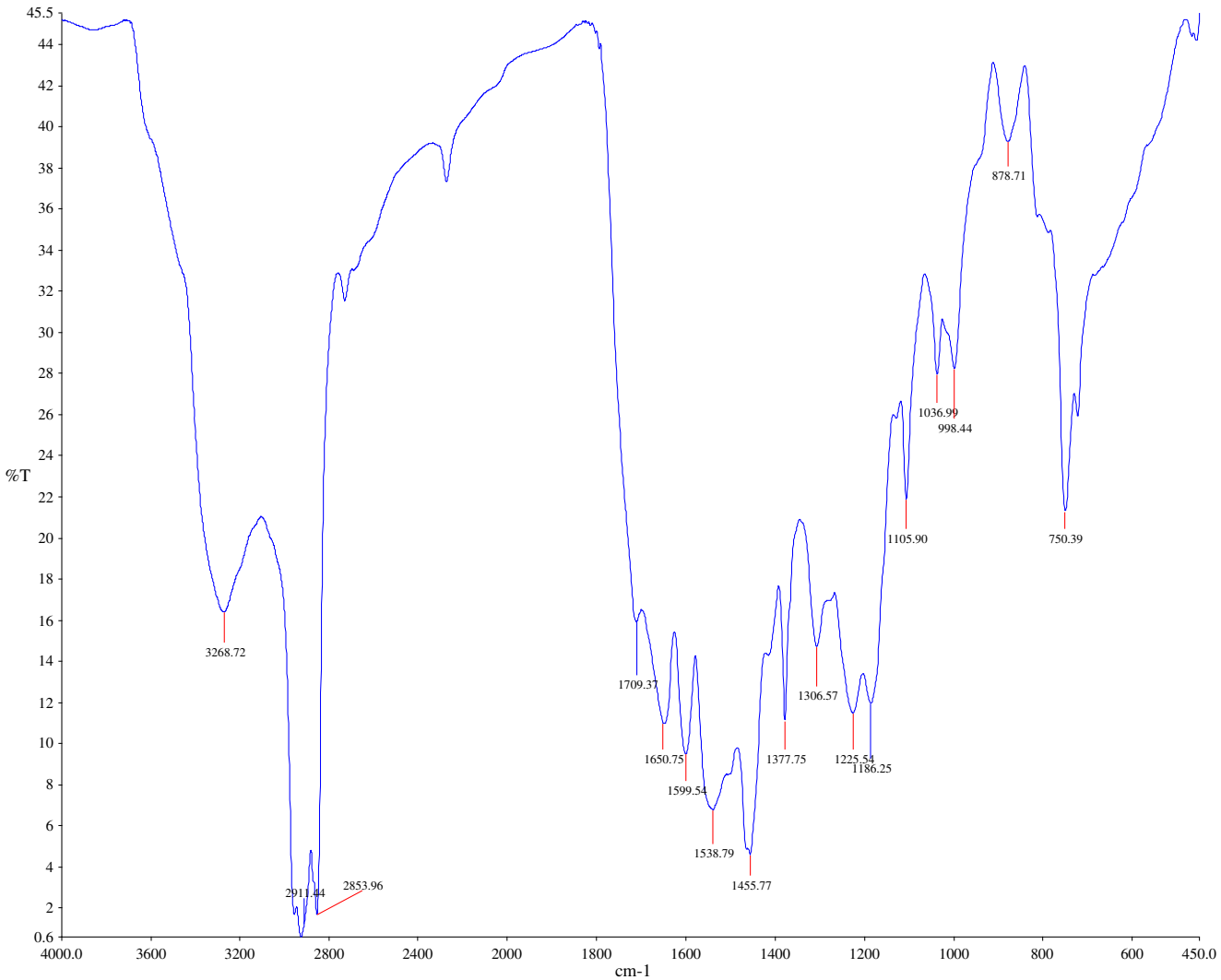


Fig. 15 IR of receptor **1**

production of red blood cells. Till date, only few receptors are available which have very less detection limit [26]. These things enhance the scope of receptor **1** as an efficient sensor of Fe^{3+}.

Using the Benesi-Hildebrand plot [18] (Eq. 1), Scatchard plot (Eq. 2) [19] and Connor plot [20] (Eq. 3) methodologies binding constant (K) was calculated.

$$1/F-F_0 = 1/(F_\infty-F_0)K[G] + 1/(F_\infty-F_0) \quad (1)$$

$$F-F_0/[G] = (F_\infty-F_0)K-(F-F_0)K \quad (2)$$

$$1-F/F_0/[F] = K(F/F_0)-\alpha K \quad (3)$$

Applying the above equations for receptor **1**.Fe^{3+} ion complexation the Benesi-Hildebrand plot, Scatchard plot and Connor's plot obtained were illustrated in Figs. 9, 10 and 11 respectively. Where, F_0 represents the fluorescence intensity in the absence of guest ion, F represents the fluorescence intensity in presence of guest ion, F_∞ represents fluorescence intensity after titration and [G] represents the concentration of guest ion. The binding constant (K) value obtained from Benesi-Hildebrand, Scatchard and Connor plot for receptor **1**.Fe^{3+} ion was in conformance and it was $(8.3\pm0.3) \times 10^3\ M^{-1}$.

The Stern–Volmer Quenching Plot

The quenching can be mathematically expressed by the Stern–Volmer Eq. (4), which allows us to determine the type of quenching. If the Stern Volmer plot is linear then the quenching is of static type rather than the dynamic quenching. For the receptor **1**.Fe^{3+} ion the linear stern volmer plot indicates that static quenching is obtained [21].

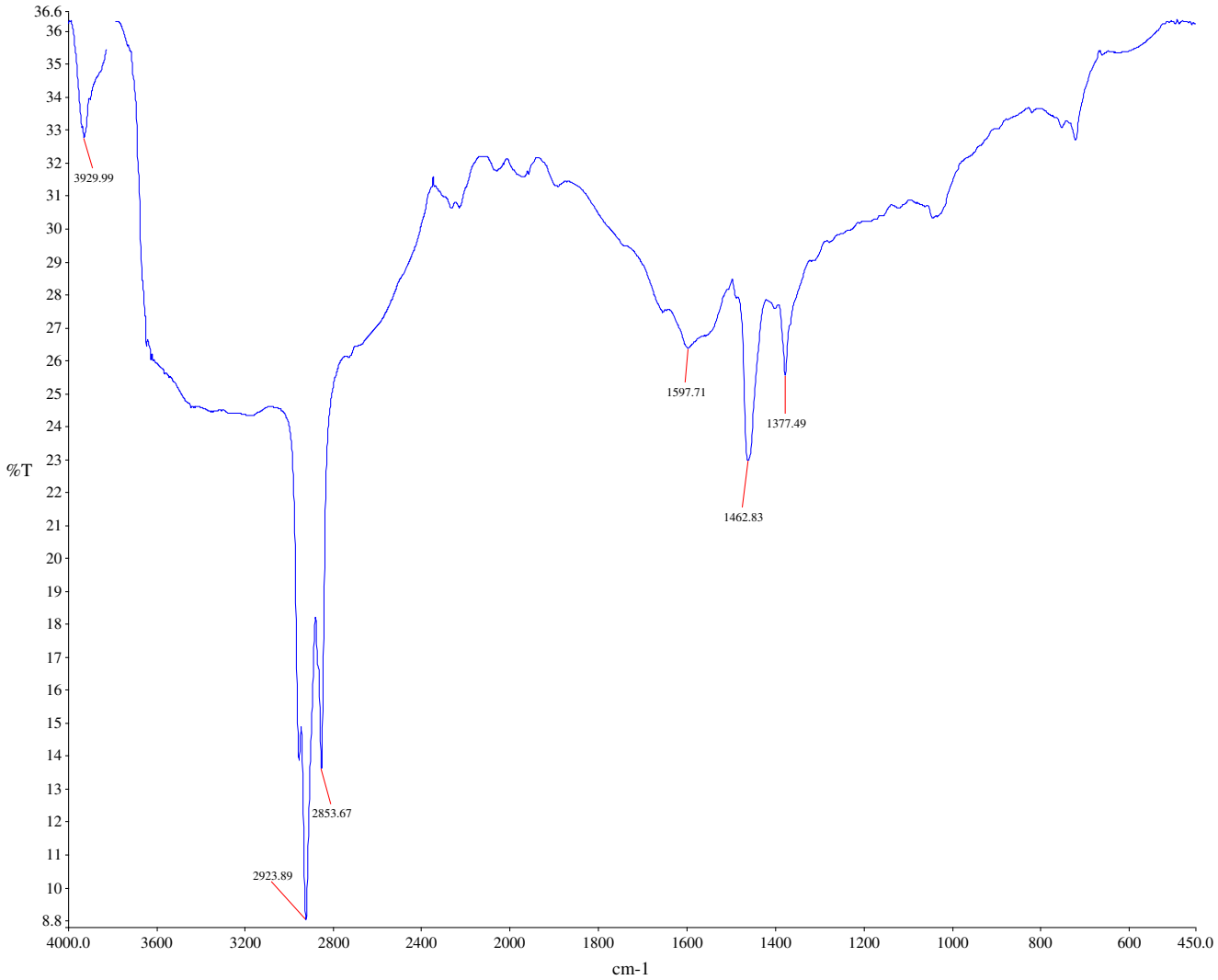


Fig. 16 IR of **1**.Fe^{3+}

This confirmed the formation of one type of complex between receptor **1** and Fe^{3+} ion.

$$F_0/F == 1 + k_q\tau_0[Q] = 1 + K_{sv}[Q] \quad (4)$$

Where F_0 and F are the fluorescence intensities in the absence and presence of the quencher, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorescence in the absence of the quencher [Q] is the concentration of the quencher, and K_{sv} is the Stern–Volmer quenching constant. In the presence of a quencher, the fluorescence intensity is reduced from F_0 to F. The ratio (F_0/F) is directly proportional to the quencher concentration [Q].

Evidently:

$$Ksv = kq\ \tau_0 \quad (5)$$

$$F_0/F = 1 + Ksv[Q] \quad (6)$$

According to Eq. (6), a plot of F_0/F versus [Q] shows a linear graph with an intercept of **1** and a slope of K_{sv}. A typical plot of F_0/F versus Fe^{3+} concentration is shown in Fig. 12.

To determine the binding stoichiometry of complex **1**.Fe^{3+}, Job's continuous variation method was used [22]. Job's plot of the fluorescence intensity of free receptor **1** and the intensity of the system with the molar fraction of the host [H]/([H] + [G]) for a series of solutions, in which the total concentration of host and guest was kept constant, with the molar fraction of host continuously varying. The results showed the formation of a 1:1 (Host: Guest) complex (Fig. 13). Using the equation: $[G]_{tot} = a/2K(1-a)^2[H]_{tot} + a[H]_{tot}/2$, where $[G]_{tot}$ is total concentration of guest, $[H]_{tot}$ is the total concentration of host, $a = (F- F_0)/(F_i- F_0)$ with F being the fluorescent intensity at a particular guest ionconcentration while F_0 and F_i are the intensities at zero and infinite guest concentrations, respectively. IR spectrum of free receptor **1** exhibits a broad band at 3,268 cm^{-1} which can be assigned for OH group on the ring. On complexation deprotonation of OH group take place and OH band was disappeared [23]. Similarly, the ν(C = O) band was 1,650 $cm^{-1}$for free receptor **1**, after complexation the shift of ν(C = O) band up to 1,597 cm^{-1}. Furthermore, we have confirmed these trends by mass spectroscopic data. MALDI/TOF–MS data showed the formation 1:1 complex between two deprotonated ligand (receptor **1**) and a metal ion [(MS (ESI): m/z requires (Calculated) $C_{21}H_{18}FeN_4O_4$: 446.24, found 446.88]. All attempts were failed to grow the single crystal of receptor **1**.Fe^{3+}ion complex. Selective recognition of receptor **1** by Fe^{3+} gave a remarkable colorimetric and fluorescent color change which can be visualized by the naked eye and under UV irradiation. Visual detection studies of receptor **1** (0.07 mM) were conducted with cations of all metals.

The receptor **1** in DMSO/H_2O (50:50 v/v) medium was appeared to be colorless at room temperature. The results showed that color of the solution changes from colorless to brown upon addition of Fe^{3+} ion. In contrast, no obvious changes in color were observed upon addition of other cations as shown in the inset of Fig. 1. Fluorescent color change was showed in Fig. 5 inset.

From the fluorescence spectra, proposed binding model of receptor **1.**Fe^{3+} ion complexation was depicted using DFT calculations, which were performed to explain the photo physical properties of these receptors by using Becke's three parameterized Lee-Yang-Parr (B3LYP) exchange functional with 6-31G basis sets, on Gaussian-09 programs [24–26]. The optimized structure of receptor **1** showed that it has non-planar arrangement of atoms and has three H-bonds between O and H atoms (Fig. 14). The formation of complex between **1** and Fe^{3+}, lead to stabilize the system as confirmed from comparing the value of energies of **1** and **1**.Fe^{3+} (Table 1). It was observed that **1**.Fe^{3+} has more symmetry instead of receptor **1** (Figs. 15 and 16).

Conclusion

In summary, we have designed and developed a selective and sensitive fluorescent receptor **1** for the detection of Fe^{3+} in semi aqueous medium. The addition of Fe^{3+} ion gave rise to major fluorescent color change, which can be easily detected by the naked eye and under UV irradiation. Furthermore, receptor selectivity and sensitivity were not affected in the presence of other competing metal ions. We have successfully detected Fe^{3+} ion even in semi aqueous media. The 1:1 stoichiometry of the host guest relationship was realized from the titration curves. The association constant (K) obtained from Benesi-Hildebrand, Scatchard and Connor plot for receptor **1.**Fe^{3+} ion complexation was $(8.3\pm0.3)\times10^3\ M^{-1}$.

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