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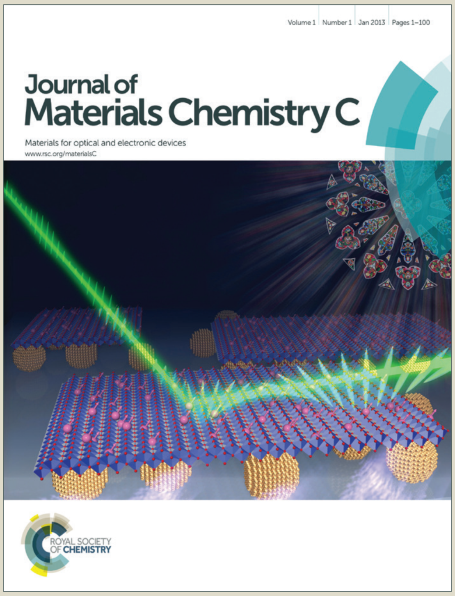

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A two-in-one dual channel chemosensor for Fe^{3+} and Cu^{2+} with nanomolar detection mimicking IMPLICATION logic gate

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Abstract

A novel and easy-to-synthesize colorimetric and fluorescent chemosensor **1** was developed for the highly selective and sensitive recognition of Fe^{3+} and Cu^{2+}. Receptor **1** showed a detectable color change from yellow to colorless with a blue-shift in the absorption spectra with Cu^{2+}, while Fe^{3+} induced a color change from yellow to orange and a red-shift in the absorption spectra. In emission study of **1**, Fe^{3+} showed a significant fluorescent enhancement with a slight red-shift while a selective fluorescent quenching was observed with Cu^{2+} over a wide range of tested metal ions. With Cu^{2+}/Fe^{3+} as the chemical inputs, the 'on-off' emission profile of receptor **1** was developed as an IMPLICATION type logic gate at molecular level.

Keywords: Chemosensor, Colorimetric, fluorescence, Fe^{3+}, Cu^{2+}, molecular logic gate.

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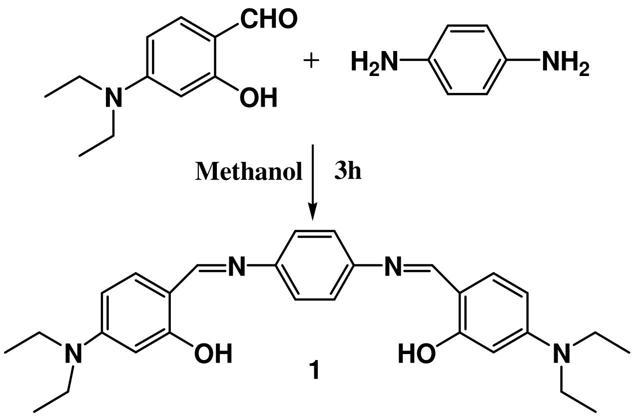
1. Introduction

The synthesis and development of colorimetric and fluorescent receptors for the selective detection of biologically and environmentally important metal ions have gained a significant interest in the field of supramolecular chemistry and chemosensors. Fluorescent receptors normally consist of an ion recognition unit (ionophore) linked through the suitable spacer to a light-emitting group (fluorophore). The design of synthetic chemosensors for qualitative and quantitative detection of different metal ions have received massive attentions because of their advantages of high sensitivity, selectivity and detection limit up to a very low concentration. In addition, significant importance has also been given to develop colorimetric chemosensors for the naked-eye detection of cations without the need of any spectroscopic instrumentation. Therefore, many proficient colorimetric and fluorescent sensors for transition metal ions have been developed during the last two decades [1-6]. However, dual-mode (chromogenic and fluorogenic) sensor for the selective detection of multiple analytes are still under search. In addition, chemosensors based on colorimetric and fluorescent responses are extensively used for constructing molecular devices such as molecular logic gates, switches, diodes, wires, molecular keypads etc. after the first AND molecular logic gate reported by de Silva et al. [7]. With molecular systems and cations as chemical inputs, numerous logic gates of types such as AND, OR, NOT, INHIBIT etc. were reported based on fluorescent signals as output and their capability to execute some special arithmetic operations were investigated [8]. However, the research on molecular IMPLICATION logic gates which are equivalent to the IF-THEN operation and the NOT operation has rarely been reported [9].

Among the transition metal ions of interest, divalent copper (Cu^{2+}) is particularly attractive, because it is not only an ecological pollutant at high concentrations, but also an essential trace element for many biological processes and systems. Therefore, many excellent works on Cu^{2+} sensing by colorimetric and fluorescent sensors have been reported and investigated [10-14]. Similarly, Fe^{3+} is also of much significance, as it plays a vital role in the growth and development of living systems. Numerous enzymes use iron as a catalyst for oxygen metabolism, electron transfer as well DNA and RNA synthesis [15]. However, both its lack and excess in the body can cause serious detrimental effects to the metabolic processes and diseases. According to U. S Environmental Protection Agency standard concentration of Fe^{3+} and Cu^{2+} in drinking water is limited to 0.3 mg/L and 1.0 mg/L respectively. Therefore, design of fluorescent chemosensors for simultaneous detection of Fe^{3+} and Cu^{2+} is also of great importance [16]. However, the reported fluorescent chemosensors for Fe^{3+} are mostly signaled by fluorescence quenching due to the paramagnetic nature of Fe^{3+} [17-22]. Thus, there is bourgeoning need to develop selective fluorescent chemosensors for Fe^{3+} with fluorescence enhancement, which is more sensitive than the sensors with fluorescence quenching due to high signal-to-noise ratio [23].

Herein, as a part of our ongoing research on analytes recognition, we have investigated the cations sensing ability of a novel receptor **1** (**Scheme 1**), which displays not only selective colorimetric changes but also gave distinct fluorescence responses for the selective detection of Cu^{2+} and Fe^{3+}. Beside selective determination of Cu^{2+} and Fe^{3+}, receptor **1** is also the first IMPLICATION logic gate ‘two-in-one’ type chemosensor, which exhibits dual channel fluorescence signals (‘turn-on’ and ‘turn-off’) for the selective and nanomolar detection of Fe^{3+} and Cu^{2+} respectively.



Scheme1. Synthesis of receptor **1**

2. Experimental details

All commercial grade chemicals and solvents were used without further purification. The fluorescence and UV-Visible spectra were recorded respectively on a HORIBA JOBIN YVON Fluoromax-4 Spectrofluorometer and Shimadzu UV-24500 spectrophotometer at room temperature using a 1 cm cell. Ultrapure water with a Millipore Purification System (Milli-Q water) was used throughout the analytical experiments. ^1H spectra were recorded with a Jeol instrument operating at 400MHz in $CDCl_3$.

Spectral analysis

All stock and working solutions were prepared in ultrapure water and spectroscopic grade acetonitrile. The stock solutions of receptor **1** ($c = 1 \times 10^{-4}$ M and 1×10^{-6} M) were prepared in acetonitrile and cations ($c = 1 \times 10^{-3}$ M and 1×10^{-5} M) were prepared in water. Then, the UV-visible absorption and fluorescence experiments were carried out at room temperatures (298 K) with the aim of determining the selectivity of the receptor **1** towards different metal ions such as Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cs^{2+}, Sr^{2+} and Al^{3+}. The absorption and fluorescence titrations with the selective metal ions (Cu^{2+} and Fe^{3+}) showed satisfactory linear relationship between the added concentrations and the absorbance intensity. These titrations were accomplished through a stepwise addition of metal salt solutions (0.02 ml, 1× 10^{-5} M) in water to a solution of receptor **1** (2 ml, 1 × 10^{-6} M) in acetonitrile. The collected data were processed using the Hyperquad program to calculate the association constant (K_a) of the appropriate cation complexes. The fluorescence spectra were recorded at an excitation wavelength of 420 nm. The excitation and emission slits were both set to 5.0 nm.

Synthesis of receptor 1

Receptor **1** was synthesized by stirring 1,4-diaminebenzene (0.108 gm, 1 mM) and 4-(diethylamino)-2-hydroxybenzaldehyde (0.386 gm, 2 mM) in methanol (50 mL) at room temperature for 3hr. Receptor **1** was obtained with good yield and having orange powder. The orange powder at room temperature was filtered and recrystallized from methanol (yield = 0.40 gm, 89 %). Crystals suitable for X-ray diffraction determination were obtained by slowly evaporating a methanol solution of receptor **1** at room temperature (**Figure 1a**). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ:1.21 (t, 12H, $4CH_3$), 3.41 (d, 8H, $4CH_2$), 6.26(d, 2H, Ar-H), 6.39(s, 2H, Ar-H), 7.17(d, 2H, Ar-H), 7.25 (d, 4H, Ar-H), 8.36(s, 2H, CH=N); ^{13}C-NMR (100MHz, $CDCl_3$, ppm): 12.82, 45.05, 97.99, 99.92, 105.09, 112.16, 114.92, 134.81, 137.56, 164.54; IR (KBr, cm^{-1}) υ = 598, 750, 778, 894, 893, 1101, 1307, 1610, 1652, 3049, 3205; MS (ESI, M+1): m/z required for $C_{28}H_{34}N_4O_2$: 459.6, found 459.2.

Development of Organic Nanoparticles (ONP) of receptor 1 (R1):

The organic nanoparticles were prepared by re-precipitation method. A solution of receptor 1 (1 mM) in acetonitrile was prepared. 1 mL of above solution was slowly injected into 100 mL of water with a micro-syringe under vigorous stirring. The solution was than sonicated for 20 minutes. The size of ONP was analyzed by DLS (differential light scattering), which was found to be 35 nm (**Fig S8**), also TEM (transmission electron microscopy) image was taken to check the uniformity of ONP (Fig S9). It was revealed from TEM image that those particles are uniformly distributed.

Results and Discussion

Receptor **1** was synthesized by Schiff base condensation of one mole of 1,4-diaminebenzene with two moles of 4-(diethylamino)-2-hydroxybenzaldehyde in methanol (**Scheme1**). The molecular structure of the receptor **1** was characterized by various spectral (IR, ^{1}H- NMR and mass) data (**S1-3**, Supporting information) and finally confirmed by single crystal X-ray crystallography (**Figure 1**). The crystallographic data are listed in **Table S1**. The CIF file for receptor **1** was deposited in the Cambridge Structure Database with CCDC No 996876. Then, the chemosensing behaviour of receptor **1** was investigated using UV–Vis and fluorescence measurements.

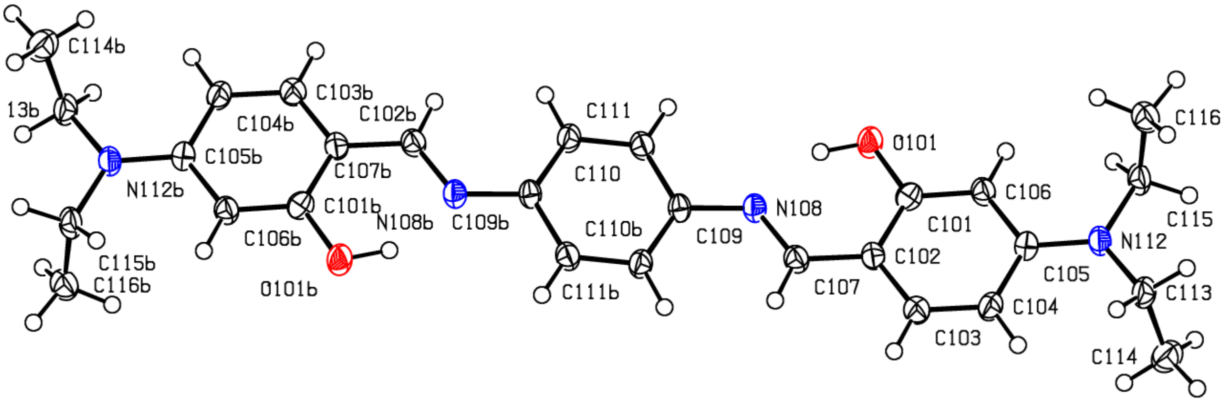


Figure 1. Molecular structure of receptor **1** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

The metal recognition properties of receptor **1** were initially evaluated by naked-eye and UV-Vis analysis. The effect of various cations on receptor **1** was shown in **Figure 2**. Addition of 10 equivalents of metal ions (Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+} Cs^{2+}, Sr^{2+} and Al^{3+}) was prepared in water to a solution of receptor **1** (1× 10^{-6}

M) in acetonitrile caused a dramatic color change from yellow to colorless for Cu^{2+} where as yellow to orange for Fe^{3+} (**Figure 2**). No significant color change of **1** was observed with other metal ions. The drastic color changes toward Fe^{3+} and Cu^{2+} were next detected by UV–Vis absorption spectroscopy (**Figure 2**), which indicates the selective chelation occurred between these metal ions and receptor **1**. In presence of Fe^{3+}, the receptor **1** showed a red shift from 420 nm to 475 nm while a blue shift from 420 nm to 395 nm was observed with Cu^{2+}.

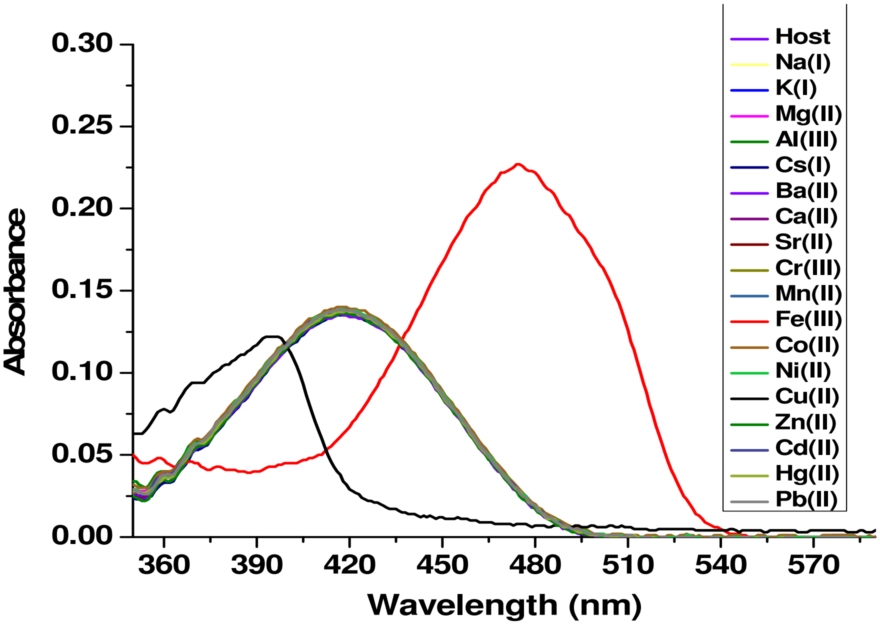


Figure 2: UV–Vis spectral changes of receptor **1** ($c = 1\times 10^{-6}$ M) in acetonitrile upon addition of 10.0 equivalents of various metal ions ($c = 1\times 10^{-5}$ M) in water.

The absorption titrations of receptor **1** (1×10^{-6} M) with the increasing amounts of Fe^{3+} (**Figure 3**) and Cu^{2+} (**Figure 4**) were performed. The linear relationship between the concentrations of added cations (Fe^{3+}/Cu^{2+}) vs normalized absorbance at 475/395 nm was plotted (**Figure 3** and **4**). A satisfactory linear relationship was observed with acceptable correlation coefficient, which clearly delineated that the receptor **1** can be applied for the quantitative estimation of Fe^{3+} and Cu^{2+} by absorption spectroscopy.

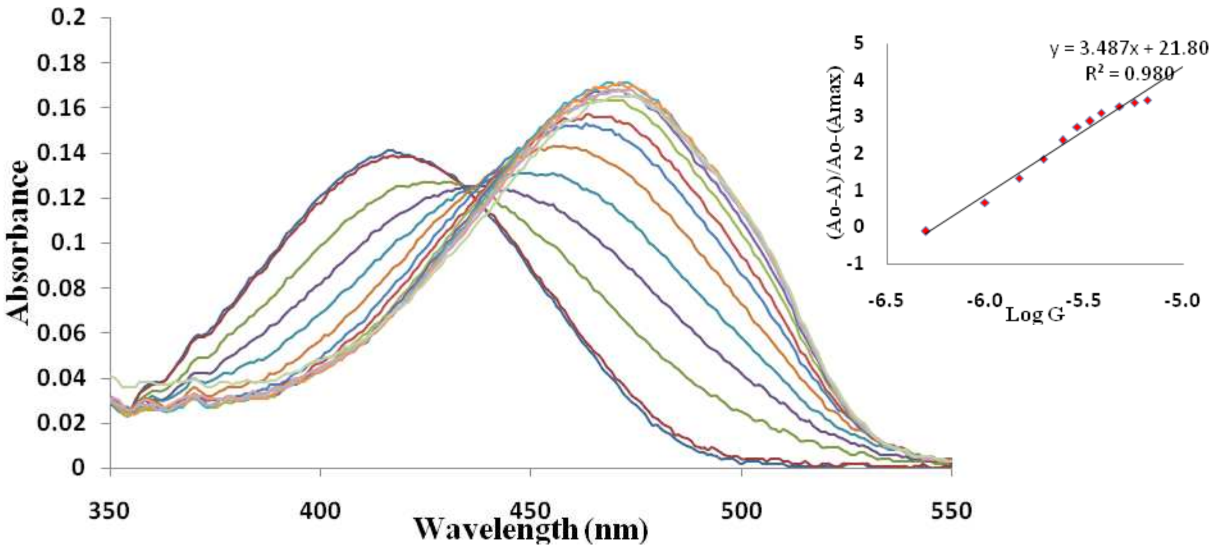


Figure 3: Absorption spectra of receptor **1** (c =1× 10^{-6} M) in acetonitrile after the addition of increasing concentration of Fe^{3+} (c = 1× 10^{-5} M) in water. Inset showing the normalized response of absorbance signal with regression 0.980.

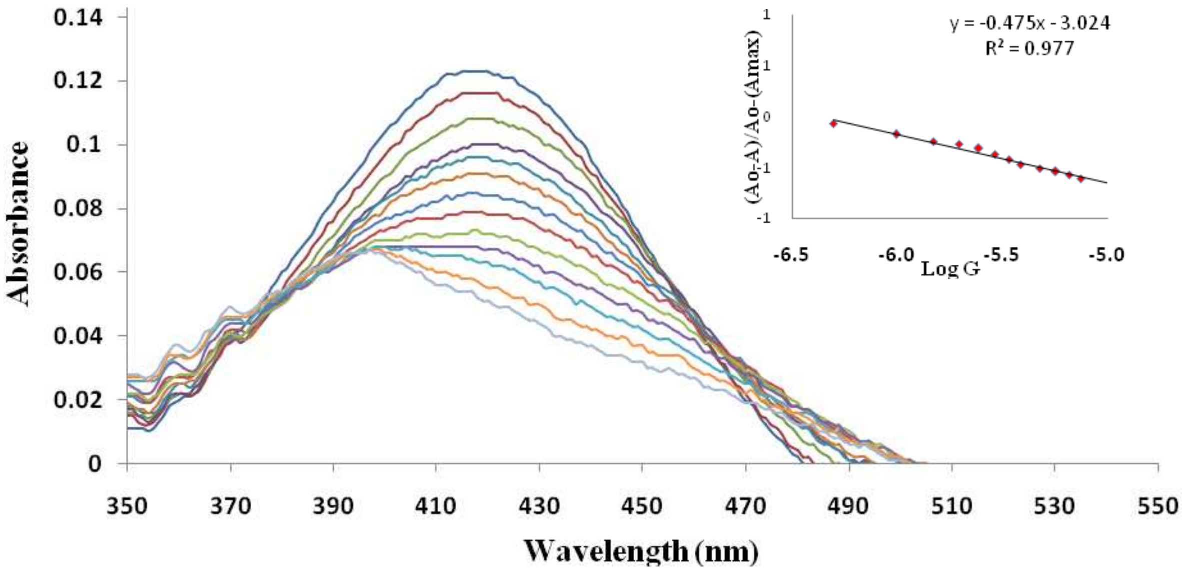


Figure 4: Absorption spectra of receptor **1** (c =1 × 10^{-6} M) in acetonitrile afer the addition of increasing concentration of Cu^{2+} salt of (c = 1 × 10^{-5} M) in water. Inset showing the normalized response of absorbance signal with regression 0.977.

The fluorimetric responses of receptor **1** toward metal ions were also studied in the same conditions. The receptor **1** showed an emission band at 504 nm on excitation at 417 nm. Theoretical calculations at the density functional theory (DFT) method at B3LYP/6-31G(d,p) level were performed to examine the structure and electronic properties of the receptor by using the computational code Gaussian 09W [24]. As summarized in **Table 1**, the enolimine form of **1** was more stable than the ketoamine both in the ground and excited state. Also, the spectroscopic properties of enolimine form of **1** were more close to the experimental results. Based on the DFT results, the enolimine form of **1** was experimentally giving emission at 504 nm. On addition of Fe^{3+}, the receptor **1** induced a selective fluorescence enhancement with a 22 nm red-shift from 504 nm to 526 nm, making it easy to distinguish from the other tested metal ions (**Figure 5**). The fluorescence enhancement was observed presumably due to deprotonation of the phenolic-OH protons on coordination with hard Fe^{3+}, which inhibited the -C=N isomerization and/or the ESIPT process at the excited state. Also, the red-shift indicates the possible intramolecular charge transfer (ICT) occurred in receptor **1** on interaction with Fe^{3+}. In contrast, the fluorescence of receptor **1** was quenched upon addition of Cu^{2+}. The quenching by Cu^{2+} was most likely due to an energy transfer process occurred between the receptor **1** and paramagnetic Cu^{2+} which caused a faster and more efficient non-radiative decay of the excited states of receptor **1**.

Table 1: Some important calculated physicochemical parameters of **1** by B3LYP or TDB3LYP/6-31G(d,p) level in the gas phase.

Receptor 1; E_T	**E_{LUMO}; E_{HOMO}**	**ΔE^a**	**OH….N; O….HN (Å)**	**N…..O(Å)**	**(λ_{max}, nm)**	
					Calc.	**Expt.**
Enolimine; -1456.98223535	-0.05385; -0.17450	0.12065	1.710; 1.001	2.620	421 (2.0309)^b	420
Ketoamine; -1456.96893847	-0.06642; -0.17610	0.10968	1.056; 1.625	2.556	459 (1.5703) 426 (0.5880)	
*Enolimine**; -1456.97609591	-0.06584; -0.16525	0.09941	1.666; 1.010	2.594	490 (2.3806)	504
*Ketoamine**; -1456.95554903	-0.07546; -0.16755	0.09209	1.049; 1.706	2.617	586 (0.0596) 478 (1.7180)	

*TDDFT optimized parameters at the excited state.

$^a\Delta E = E_{LUMO} - E_{HOMO}$.

^{b}Data in parenthesis are the oscillator strength *f*.

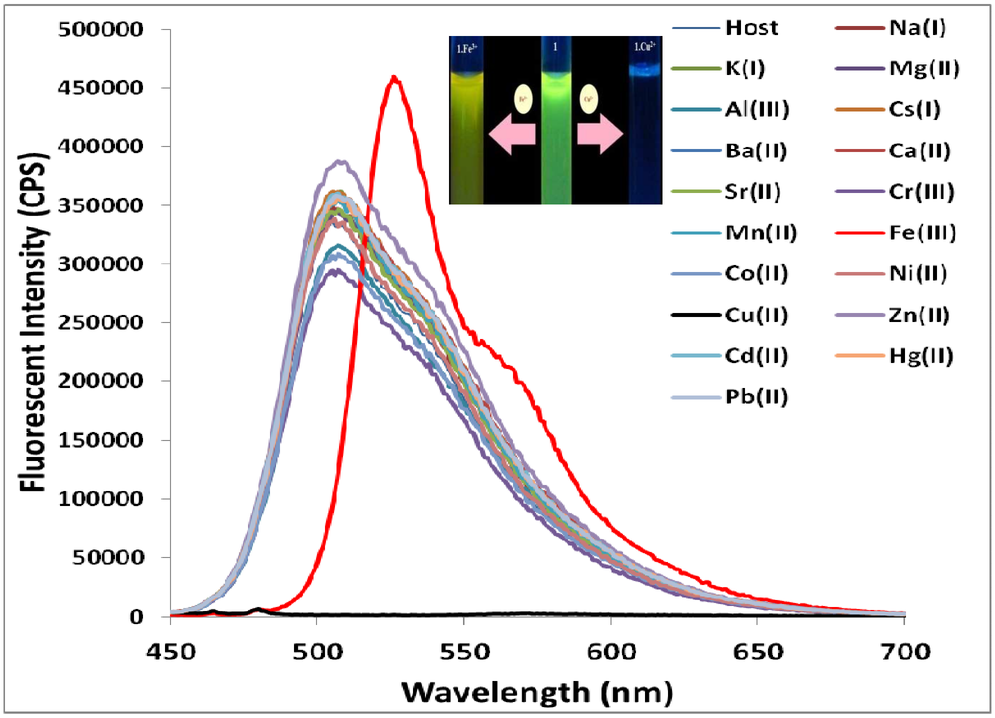


Figure 5: Fluorescent emission spectra of receptor **1** (λ_{ex} = 417 nm) in acetonitrile upon the addition of 0.5 equiv of different metal ions.

The fluorescence titrations with Fe^{3+} and Cu^{2+} were carried out to examine the quantitative binding affinity of receptor **1** (**Figure 6a** and **6b**). The association constants (K_a)

were determined by nonlinear curve fitting of the fluorescence titrations data of **1** at 530 nm for Fe^{3+} and at 510 nm for Cu^{2+}, and were found to be 700000 and 857143 M^{-1} for Fe^{3+} and Cu^{2+}, respectively (**Figure S4** and **S5, SI**) [25]. The association constants inferred that the receptor exhibits similar binding strength towards the metal ions, Fe^{3+} and Cu^{2+}. From the titration results, the detection limits for the sensing of Fe^{3+} and Cu^{2+} ions were respectively estimated to be 10 nM and 15 nM which is lower than the reported sensors so far. Further, the Job's plot [26] of receptor **1** with Fe^{3+} and Cu^{2+} were drawn to explore the binding stoichiometry (**Figure S6** and **S7**). A maximum emission was observed when the molar fraction was reached 0.5, which indicates a 1:1 binding stoichiometry between the receptor**1** and Fe^{3+}/Cu^{2+}.

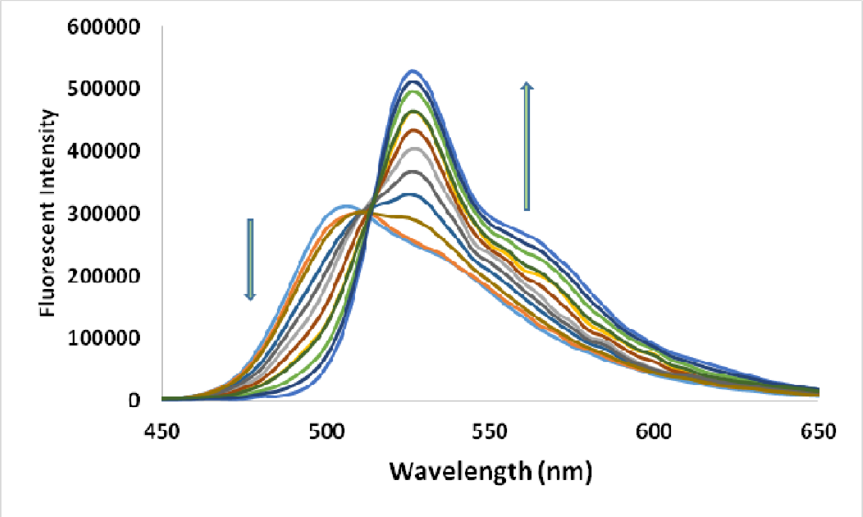


Figure 6a: Fluorescence spectra of receptor **1** ($c = 1 \times 10^{-6}$ M) in acetonitrile after the successive addition of Fe^{3+} ($c = 1 \times 10^{-5}$ M) in water.

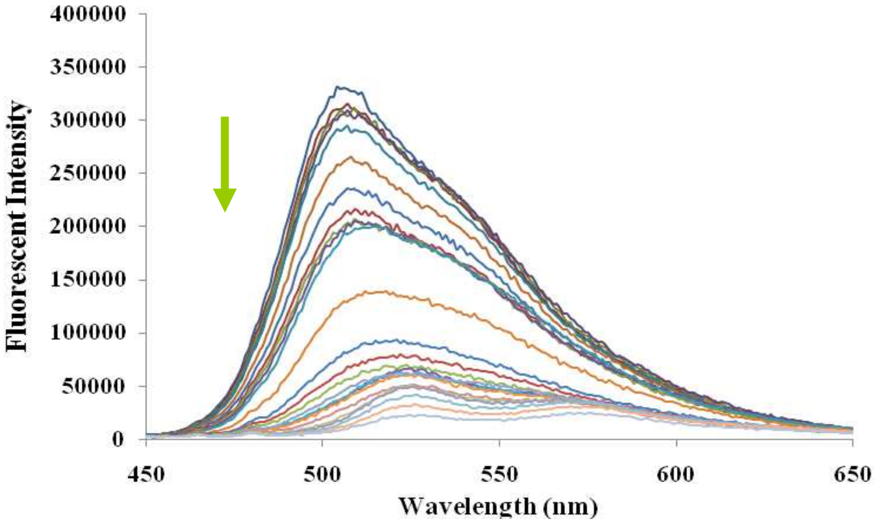
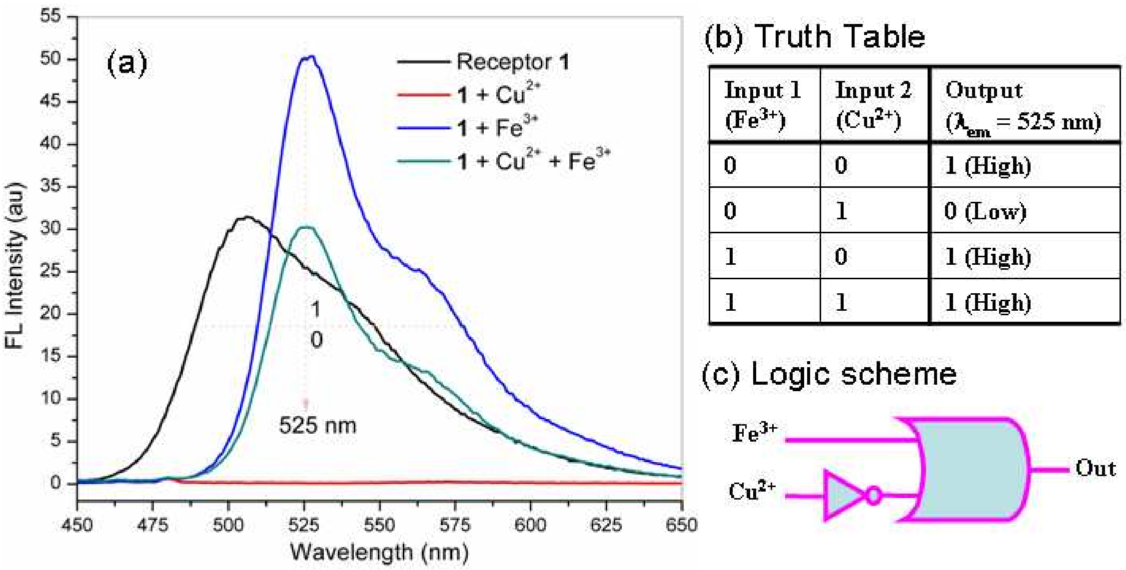


Figure 6b: Fluorescence spectra of receptor **1** ($c = 1 \times 10^{-6}$ M) in acetonitrile after the successive addition of Cu^{2+} ($c = 1 \times 10^{-5}$ M) in water.

The fascinating 'on-off' emission properties of receptor **1** in the presence of Cu^{2+} and Fe^{3+} encouraged us to construct a molecular logic gate. The development of molecular logic gate has gained considerable interest for the designing molecular-scale computers for their applications in the field of biochemical systems, biosensing, functional materials, diagnostic etc [27]. In our system, the presence and absence of the two chemical inputs Fe^{3+} and Cu^{2+} was defined as '1' and '0' states, and the fluorescence intensity of **1** at 525 nm as output for the logic gate. As summarized in **Figure 7**, the fluorescence of the receptor **1** was quenched only in the presence of Cu^{2+} (0, 1) due to the energy transfer process. However, the enhanced fluorescence of the receptor **1** above the threshold level was observed in the absence (0,0) and presence of both the inputs (1,1) and also Fe^{3+} alone (1,0). Therefore, monitoring the fluorescence at 525 nm of receptor **1** and with the two-inputs (Fe^{3+} and Cu^{2+}), an IMP (IMPLICATION) type logic gate can be constructed at the molecular level. To the best of our knowledge, this is the first example of an IMP logic gate with the two-inputs as Fe^{3+} and Cu^{2+}.



(b) Truth Table

Input 1 (Fe^{3+})	Input 2 (Cu^{2+})	Output (λ_{em} = 525 nm)
0	0	1 (High)
0	1	0 (Low)
1	0	1 (High)
1	1	1 (High)

Figure 7: The changes in the fluorescence intensity of the receptor **1** at 525 nm in the absence and presence of Cu^{2+} and Fe^{3+} for the fabrication of IMP logic gate.

Effect of pH on emission profile of ONP

The emission spectra responses of the ONP of receptor 1 in aqueous medium at different pH values were monitored. The fluorescence intensity was observed to be stable in a wide pH range. No change in the emission spectra of the nanoaggregates was observed in a pH range from 5.5–9 (Figure. S10) So these nanoaggregates can be applied in the pH range 5.5–9.

Effect of water content on photo-physical properties

Fluorescence spectra of receptor **1** was recorded with 10 µM concentrations in acetonitrile and showed peak in region 500-510 nm. As the solvent system changes from acetonitrile to water peak become sharper. Also fluorescence spectrum of ONP of receptor **1** was recorded in presence of 20 µM of Fe^{3+} and Cu^{2+} in water (**Figure 8**). Calibration curve was plotted between change in fluorescence intensity upon change in concentration of Fe^{3+} and Cu^{2+} respectively in aqueous system.

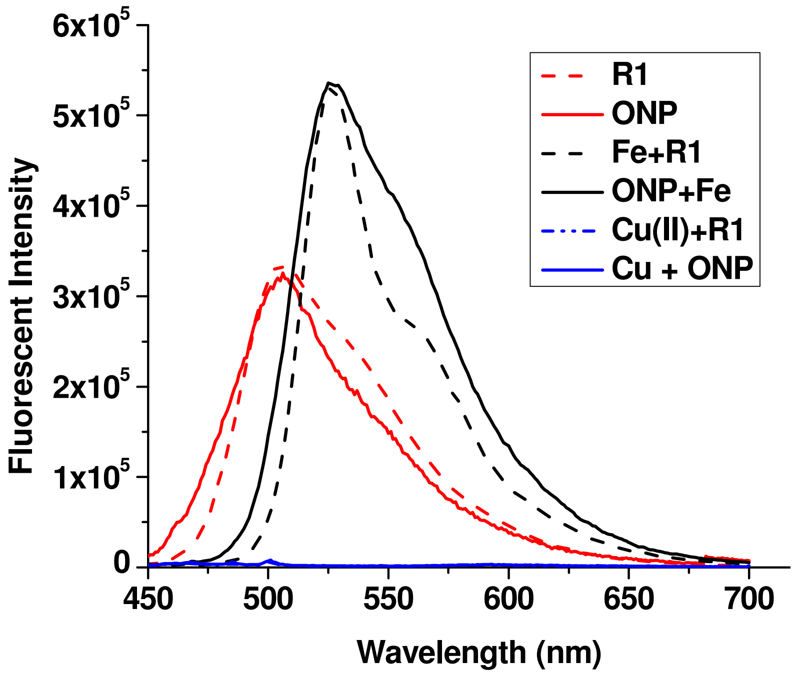


Figure 8: Change in fluorescent emission spectra of receptor **1** (10 μM, λ_{ex} = 417 nm) in acetonitrile and **ONP of receptor 1** (10 μM) in aqueous medium upon addition of 50 μM of Fe^{3+} and Cu^{2+}.

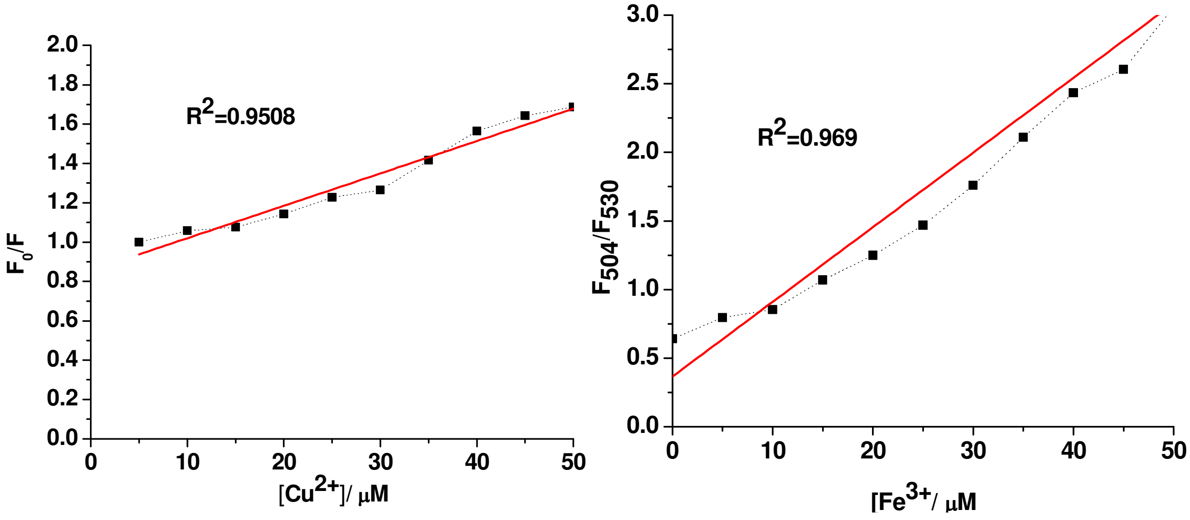


Figure 9: Fluorescence intensity ratio (F_o/F) of organic nanoparticles **ONP of receptor 1** as a function of concentration of Cu^{2+} and Fe^{3+}. Calibration curve in this concentration range is linear.

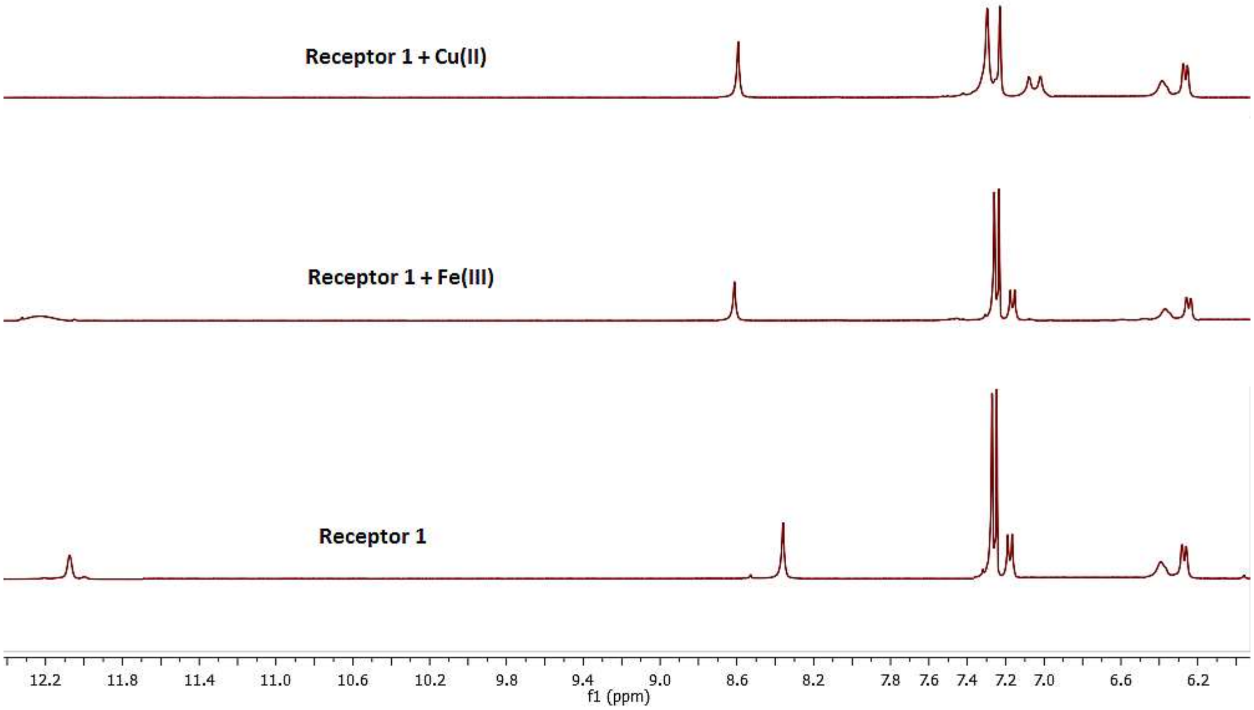


Figure 10. NMR spectra of receptor 1 on addition of ntirate salt of Fe(III) and Cu(II) respectively.

To authenticate and understand the binding behaviour of the Cu(II) and Fe(III) ions with 1, ^{1} H -NMR of receptor 1 has been taken in presence of 1 equivalent nitrate salt of Cu(II) and Fe(III) ions in $CDCl_3$-DMSO-d^6, addition of Fe(III) induces a shift of $\Delta\delta = 0.32$ ppm in the signal of shiff base CH=N- (8.38 ppm). Also in case Cu (II), the signal of shiff base shifted to 8.59 and become broad. The signal of OH (12.1 ppm) also become broad on addition of Fe(III) and Cu(II). This indicates, shift of nitrogen lone pain towards metal ion.

Detection of Fe^{3+} and Cu^{2+} in different iron and copper sample respectively

To assess the practical application of ONP of receptor **1**, the concentration of Fe^{3+} and Cu^{2+} was analyzed in different iron (FEFOL Iron, Rarical) and copper supplements (Bicadexamin) that are available in the market. To evaluate the concentration of metal ions in given supplements, first tablet was dissolved in 25 mL of water and then 5 mL of nitric acid added to the solution. The mixture was refluxed for 30 minutes. Then, 1 mL of hydrogen peroxide was added to the solution. After digestion, the pH of solution was adjusted to 4.0 with NaOH and buffer solution. Fluorescence spectrum was recorded by the addition of 100 µL of solution of iron to the fixed concentration (10 µM, 5 ml) of nano-aggregates **R1.** Amount of Fe^{3+} and Cu^{2+} was determined by comparing the intensity ratio of drug-*R1* sample with the calibrated data (**Figure 9**). It was found that the concentrations measured with fluorescence spectroscopy using nano-aggregates of **R1** were in good agreement with the data given by the corresponding company (Table 2).

Table 2: Comparison of calculated concentration of iron using nano-aggregates **R1** by fluorescence spectroscopy in iron tablets and their reported concentration by the manufacturers.

Entry No.	**Name of supplement**	**Concentration of Fe^{3+} in drugs**	
		Given conc.	**Calculated (Mean[a])**
1.	FEFOL Iron	87.4mg	84 ± 1.6mg
2.	Raricap	25mg	22.1 ±1.1mg
		Concentration of Cu^{2+} in drugs	
1.	Bicadexamin	100 µg	89.2 ± 5 µg

[a] Mean of three determinations.

Conclusions

In summary, we have developed a novel easy-to-prepare chemosensor **1** for the selective and sensitive detection of Cu^{2+} and Fe^{3+} by dual chromogenic and fluoregenic responses with the detection limit down to nanomolar level. Both the analytes interact with receptor **1** in 1:1 binding stoichiometry. The fluorescence of **1** was selective quenched and enhanced in the presence of Cu^{2+} and Fe^{3+}, respectively. This dual signal is of significance because there are few models in the novel of optical receptors showing an accent of the selectivity by the choice of the output signal. Also, the fluorescence turn-on response in the presence of both Fe^{3+} and Cu^{2+} can be helpful in the selective detection of Fe^{3+} in the presence of Cu^{2+}. Its practical application was explored to detect iron and copper in different drug supplements available in the market and found the prepared sensor in total agreement with the data provided by the manufacturer. Further, with the two inputs Cu^{2+} and Fe^{3+}, the emission properties of **1** was successfully explained as IMPLICATION type logic gate at molecular level.

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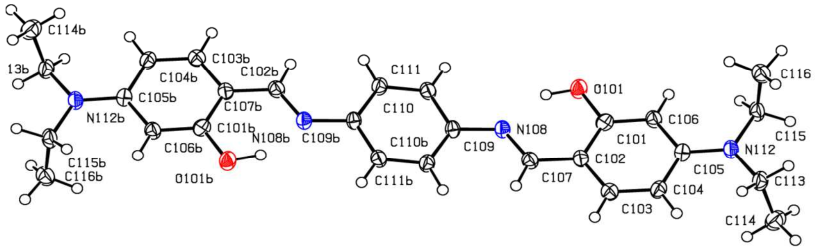

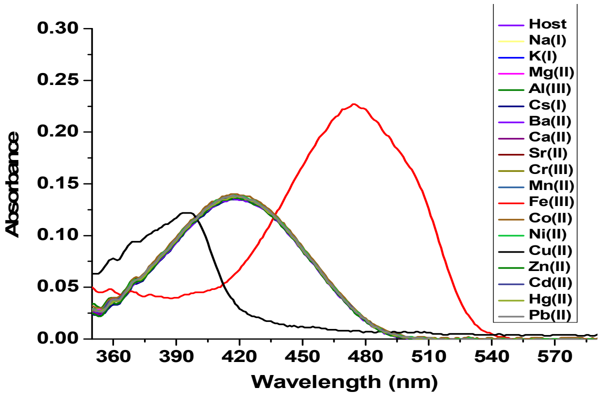

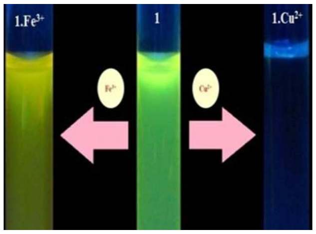

Highly Selective colorimetric as well as fluorescence sensor for Fe (III) and Cu (III) in 99% aqueous medium