**M.Sc. Thesis**

**On**

# Diphenyl ether based receptors for chemical sensing of Iron(III) using Spectrofluorimetry

**For the Degree of**
**Master of Science**

**Gagandeep Kaur**
**(Roll No. 301202005)**

**Under the Supervision**
**Of**

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**SCHOOL OF CHEMISTRY & BIOCHEMISTRY**
**THAPAR UNIVERSITY,**
**Patiala-147004**
**July, 2014**

# Dedicated To

## My mother

For being my first teacher. A strong and gentle soul who taught me to trust in Allah, believe in hardwork and that so much could be done with little.

## My father

For earning an honest living for us and for supporting and encouraging me to believe in myself

# Acknowledgement

It’s said that life is a carnival of experiences and a journey with various goals. So in my journey where I experienced this project I want to thank the supreme almighty for his presence in my soul and in my mind.

I take this opportunity to thank my guide Dr. Susheel Mittal, Senior Professor, School of Chemistry and Biochemistry and Dr. Manmohan Chhibber, Associate Professor, School of Chemistry and Biochemistry without whose presence the whole project just would have been a dream. I am extremely indebted to them for the scientific attitude and patience they had installed in me which will definitely stand in all future endeavor and it was because of them that I was able to learn so much in this short period.

My sincere thanks to Dr. Bonamali Pal, Head, School of Chemistry and Biochemistry for his guidance and suggestions. I express my regards to all faculty members of the School of Chemistry and Biochemistry for their help and moral support during my stay.

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Last but not least I owe my thesis to God, my parents and my siblings who are the building pillars of my life.

Gagandeep Kaur

## Candidate's declaration

I, hereby declare that the work being presented in the dissertation entitled **"Diphenyl ether based receptors for chemical sensing of Iron(III) using Spectrofluorimetry"** in partial fulfillment of the requirements for the award of the degree of Masters of Science (Chemistry), School of Chemistry and Biochemistry (SCBC), Thapar University, Patiala, is my own my work during the period of January 2014 to July 2014, under the supervision of Dr. Susheel Mittal, Senior Professor, School of Chemistry and Biochemistry and Dr. Manmohan Chhibber, Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala.

Patiala

Date: 17 July, 2014

Gagandeep Kaur

Gagandeep Kaur

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

| | | |
|---|---|---|
| Susheel Mittal<br>17.7.14 | 18/7/2014 | 18/7/14 |
| Dr. Susheel Mittal | Dr. Manmohan Chhibber | Dr. Bonamali Pal |
| Supervisor, | Supervisor, | Professor & Head, |
| Senior Professor , | Associate Professor | (SCBC) |
| (SCBC) | (SCBC) | |

# Certificate

This is to certify that the project entitled **"Diphenyl ether based receptors for chemical sensing of Iron(III) using Spectrofluorimetry"** being submitted by Gagandeep Kaur in partial fulfillment of the requirement for the award of degree of Master of Science (Chemistry), Thapar University, Patiala, is a bonafide work carried out under the joint supervision of Dr. Susheel Mittal and Dr. Manmohan Chhibber and that no part of this work has been submitted for the award of any other degree.

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## List of contents

**1.** Introduction 1-5

**2.** Literature review 6-11

**3.** Materials and methods 12-14

**4.** Results and discussion 15-20

**5.** Conclusions 21

**6.** References 22-24

## 1. Introduction

A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information, mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated[1]. A chemical sensor is an essential component of an analyzer. In addition to the sensor, the analyzer may contain devices that perform the following functions: sampling, sample transport, signal processing, data processing. An analyzer may be an essential part of an automated system. The analyzer working according to a sampling plan as a function of time acts as a monitor. A physical sensor is a device that provides information about a physical property of the system.

Chemical sensors contain two basic functional units[2], a transducer part and a receptor part. Some sensors may include a separator which is, for example, a membrane. The transducer part is a device capable of transforming the energy carrying the chemical information about the sample into a useful analytical signal. The transducer as such does not show selectivity. In the receptor part of a sensor the chemical information is transformed into a form of energy which may be measured by the transducer[3].

The receptor part of chemical sensors may be based upon various principles:

**Physical**: These are the sensors where no chemical reaction takes place. Typical examples are those based upon measurement of absorbance, refractive index, conductivity, temperature or mass change.

**Chemical:** Sensors in which a chemical reaction with participation of the analyte gives rise to the analytical signal.

**Biochemical:** Sensors in which a biochemical process is the source of the analytical signal. Typical examples are microbial potentiometric sensors or immune sensors. They may be regarded as a subgroup of the chemical ones. Such sensors are called biosensors. In some cases it is not possible to decide unequivocally whether a sensor operates on a chemical or on a physical principle[4]. This is, for example, the case when the signal is due to an adsorption process.

Sensors are normally designed to operate under well defined conditions for specified analytes in certain sample types. Therefore, it is not always necessary that a sensor responds specifically to a certain analyte. Under carefully controlled operating conditions, the analyte signal may be independent of other sample components, thus allowing the determination of the analyte without any major preliminary treatment of the sample[5]. Otherwise unspecific but satisfactory reproducible sensors can be used in series for multi component analysis using a multivariate calibration software and signal processing. Such systems for multi component analysis are called sensor arrays[6].

## CLASSIFICATION OF SENSORS

The development of instrumentation, microelectronics and computers makes it possible to design sensors utilizing most of the known chemical, physical and biological principles that have been used in chemistry. Chemical sensors may be classified according to the operating principle of the transducer[8].

1. **Optical devices** transform changes of optical phenomena, which are the result of an interaction of the analyte with the receptor part. This group may be further subdivided according to the type of optical properties which have been applied in chemical sensors:

a) Absorbance, measured in a transparent medium, caused by the absorptivity of the analyte itself or by a reaction with some suitable indicator[9].

b) Reflectance is measured in non-transparent media, usually using an immobilized indicator.

c) Luminescence, based on the measurement of the intensity of light emitted by a chemical reaction in the receptor system.

d) Fluorescence, measured as the positive emission effect caused by irradiation. Also, selective quenching of fluorescence may be the basis of such devices.

e) Refractive index, measured as the result of a change in solution composition. This may include also a surface plasmon resonance effect.

f) Optothermal effect, based on a measurement of the thermal effect caused by light absorption.

g) Light scattering, based on effects caused by particles of definite size present in the sample.

The application of many of these phenomena in sensors became possible because of the use of optical fibres in various configurations. Such devices have also been called optodes. It should be emphasized that fibre optics now commonly used are only technical devices applicable in a large group of optical sensors which can be based on various principles.

2. **Electrochemical devices** transform the effect of the electrochemical interaction analyte – electrode into a useful signal. Such effects may be stimulated electrically or may result in a spontaneous interaction at the zero-current condition. The following subgroups may be distinguished:

a) Voltammetric sensors, including amperometric devices, in which current is measured in the d.c. or a.c. mode. This subgroup may include sensors based on chemically inert electrodes, chemically active electrodes and modified electrodes. In this group are included sensors with and without (galvanic sensors) external current source.

b) Potentiometric sensors, in which the potential of the indicator electrode (ion-selective electrode, redox electrode, meta1 oxide electrode) is measured against a reference electrode.

c) Chemically sensitized field effect transistor[10] (CHEMFET) in which the effect of the interaction between the analyte and the active coating is transformed into a change of the source-drain current. The interactions between the analyte and the coating are, from the chemical point of view, similar to those found in potentiometric ion-selective sensors.

d) Potentiometric solid electrolyte gas sensors, differing from class 2b) because they work in high temperature solid electrolytes and are usually applied for gas sensing measurements.

3. **Electrical devices** based on measurements, where no electrochemical processes take place, but the signal arises from the change of electrical properties caused by the interaction of the analyte.

a) Metal oxide semiconductor sensors used principally as gas phase detectors, based on reversible redox processes of analyte gas components.

b) Organic semiconductor sensors, based on the formation of charge transfer complexes, which modify the charge carrier density.

c) Electrolytic conductivity sensors.

d) Electric permittivity sensors.

4. **Mass sensitive devices** transform the mass change at a specially modified surface into a change of a property of the support material[11]. The mass change is caused by accumulation of the analyte.

a) Piezoelectric devices used mainly in gaseous phase, but also in solutions, are based on the measurement of the frequency change of the quartz oscillator plate caused by adsorption of a mass of the analyte at the oscillator.

b) Surface acoustic wave devices depend on the modification of the propagation velocity of a generated acoustical wave affected by the deposition of a definite mass of the analyte.

5. **Magnetic devices** based on the change of paramagnetic properties of a gas being analysed. These are represented by certain types of oxygen monitors.

6. **Thermometric devices** based on the measurement of the heat effects of a specific chemical reaction or adsorption which involve the analyte. In this group the heat effects may be measured in various ways, for example in the so called catalytic sensors the heat of a combustion reaction or an enzymatic reaction is measured by use of a thermistor. The

devices based on measuring optothermal effects (If) can alternatively be included in this group.

In theory, the principle of sensing materials is based upon the fact that a host or a sensor molecule can recognize guest molecules in a very selective way using weak and generally reversible non covalent bonds[12]. In practice, host is either an organic building block or a bio -molecule that can hold a guest which is a cation, anion or a neutral molecule. One or more building blocks orient themselves in such a way that that a subsequent covalent bond forming reaction can be used to generate a new mechanical bond between the ligands.

Among the guest molecules, cations such as sodium, potassium, magnesium and calcium are ubiquitous in biological systems. Some transition metal ions such as Cu(I or II), Co(II), Zn(I) and Mn(II) plays important roles in metallo enzymes and other proteins[13] . Further, other metals such as Hg, Cd, and most radioactive species are very toxic. Thus, the facile detection and, in some cases, extraction of these cations are very important. A number of motifs, including crown ethers, cryptands, aza-crowns, polyamines and carboxylic acid derivatives, have been studied as cation complexants and their selectivity is highly dependent on structure.[14-16]

Organic chemistry provides an excellent tool to design and synthesize receptors that can accommodate charged or neutral species selectively. Present proposal relates to the synthesis, characterization and exploring receptor properties of some new organic molecules for ions.

## 2. Literature review

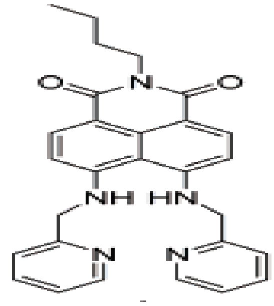
A lot of chemosensors have been synthesized and used for detection of various ions. Few such examples from the literature are reported below in which spectroscopic techniques have been used for the study of complexation with the ions.

Stephanie *et al. (2004),*[17] developed chromophores based on a donor-acceptor-donor structure possessing a large two-photon absorption cross section and one or two mono-aza-15-crown-5 ether moieties, which can bind metal cations. The influence of $Mg^{2+}$ binding on their one- and two-photon spectroscopic properties has been investigated. Upon binding, the two-photon action cross sections at 810 nm decrease by a factor of up to 50 at high $Mg^{2+}$ concentrations and this results in a large contrast in the two-photon excited fluorescence signal between the bound and unbound forms, for excitation in the range of 730 to 860 nm. Experimental and computational results indicate that there is a significant reduction of the electron donating strength of the aza-crown nitrogen atom(s) upon metal ion binding and that this leads to a blue shift in the position as well as a reduction in the strength of the lowest-energy two-photon absorption band. The molecules reported here can serve as models for the design of improved two-photon excitable metal-ion sensing fluorophores.

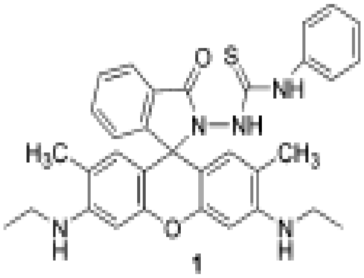
Xu *et al. (2009),*[18] designed a $Cu^{2+}$-sensing, ratiometric, and selective fluorescent sensor N-butyl-4,5-di[(pyridin-2-ylmethyl)amino]-1,8-naphthalimide (a) and synthesized it on the basis of the mechanism of ICT( Internal charge transfer). In aqueous ethanol solutions of (a), the presence of $Cu^{2+}$ induces the formation of a 1:1 metal-ligand complex, which exhibits a strong, increasing fluorescent emission centered at 475 nm at the expense of the fluorescent emission of (a) centered at 525 nm.

Yang *et al. (2005),*[19] described the development of a highly selective and sensitive chemodosimeter for $Hg^{2+}$ ion in aqueous solution. Rhodamine derivative (b) is monitored by colorimetric and fluorescence intensity changes that respond instantaneously at room temperature in a 1:1 stoichiometric manner to the amount of $Hg^{2+}$. The selectivity of this system for $Hg^{2+}$ over other metal ions is remarkably high. The fluorescence intensities of derivatives of rhodium exhibit at 556 nm.

Kwon *et al. (2005),*[20] synthesized a new fluorescent sensor based on rhodamineB (c) for $Pb^{2+}$. Examined in acetonitrile, the new fluorescent sensor showed an extreme selectivity for $Pb^{2+}$ over other metal ions. Upon the addition of $Pb^{2+}$, an overall emission change of 100-fold was observed, and the selectivity was calculated to be 200 times that of $Zn^{2+}$. The signal transduction occurs reversible of CHEF (chelation-enhanced fluorescence) with this inherent quenching metal ion.



**(a)**



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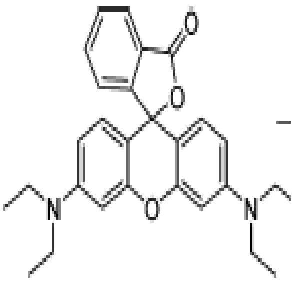


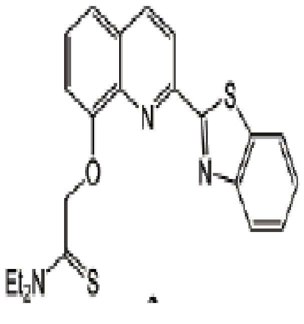
**(c)**

Song *et al. (2006),*[21] developed a new ionophore based on the 8-hydroxyquinoline molecular framework was prepared, and its fluorogenic chemodosimetric behavior was investigated. The thioamide derivative showed highly $Hg^{2+}$-selective fluorescence enhancing properties (167-fold) in 30% aqueous acetonitrile solution. The selective and sensitive signaling behaviors were found to originate from the $Hg^{2+}$ ion induced transformation of the very weak fluorescent thioamide (d) derivative into a highly fluorescent (e) amide analogue.

Gong *et al. (2006),*[22] synthesized Methylazacalix [4]pyridine (MACP-4) (f) which shows an extraordinary selectivity toward $Zn^{2+}$. In MACP-4 excitation was provided at 345 nm, and the emission was integrated between 370 and 600 nm. Theoretical calculation of HOMOs and LUMOs of MACP-4 1 were also done. MACP-4 complex showed partial contribution to the LUMO, which led to the quench of the fluorescence of MACP-4 by $Cu^{2+}$ through the electron- and/or energy-transfer processes.

Aragoni *et al. (2007),*[23] synthesized and characterized two new fluorescent chemosensors for metal ions, they are the macrocycles i.e. 5-(2-quinolinylmethyl)-2,8-dithia-5-aza-2,6-pyridinophane (L5) and 5-(5-chloro-8-hydroxyquinolinylmethyl)-2,8-dithia-5-aza-2,6-pyridinophane(L6). Both systems have pyridyl thioether- containing 12-membered macrocycle as a binding site. The coordination properties of these two ligands toward $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$, and $Pb^{2+}$ have been studied in MeCN/ $H_2O$ (1:1 v/v) and MeCN solutions and in the solid state. The stoichiometry of the species formed at 25 °C has been determined from absorption, fluorescence, and potentiometric titrations. The complexes $[CuL^5](ClO_4)^2$.1/2MeCN, $[ZnL^5(H_2O)](ClO_4)^2$, $[HgL^5(MeCN)](ClO_4)^2$, $[PbL^5\text{-}(ClO_4)^2]$, $[Cu_3(5\text{-Cl-8-HDQH-1})(L^6H_{-1})_2](ClO_4)^3.7.5H_2O$ (HDQ = hydroxyquinoline), and $[Cu(L^6)_2](BF_4)_2.2MeNO_2$ have also been characterized by X-ray crystallography

Zhu *et al. (2007),[24]* developed a novel NIR probe (MCy-1) towards $Hg^{2+}$ ions. A large red-shift (122 nm) of the absorption maximum of MCy-1 was observed upon titration with $Hg^{2+}$ ions followed by a solution color change from blue to colorless, making the “naked-eye” detection of $Hg^{2+}$ ions possible. In Fluorescence responses of MCy-1 to various metal ions like $Fe^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Li^+$, $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$ excitation was provided at 695 nm, and the emission was integrated over 705-900 nm. The selectivity of this system for $Hg^{2+}$ over other metal ions is extremely high.



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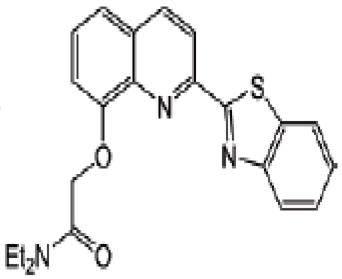

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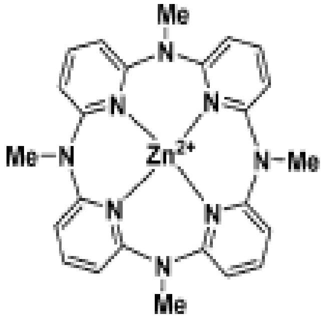
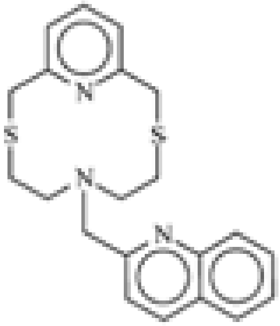


**(f)**

Aragoni *et al (2007),*[25] synthesized and characterized two chemosensors for metal ions, i.e. 5-(2-quinolinylmethyl)-2,8-dithia-5-aza-2,6-pyridinophane (g) and 5-(5-chloro-8-hydroxyquinolinylmethyl)-2,8-dithia-5-aza-2,6-pyridinophane (h). The binding properties of these two chemosensors toward $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$, and $Pb^{2+}$ have been studied in $MeCN/H_2O$ (1:1 v/v). The stoichiometry of complexes has been determined from absorption, fluorescence, and potentiometric studies.

Kumar *et al (2008),*[26] developed a chromofluorescent probe for selective and ratiometric estimation of $F^-$ ($CH_3CN$) ions. These new N-aryl imidazolium based probes 2 and 3, enabled naked eye and dual channel (absorption and fluorescence) detection of $F^-$ and $AcO^-$ ions, The presence of a lipophilic dodecyl appendage at imidazolium nitrogen successfully allowed the selective determination of $AcO^-$ ions in protic ($CHCl_3$-MeOH, 1:1) solvent.

Carofiglio *et al (2009),*[27] developed a dimeric metalloporphyrin hosts by reacting the cyanuric chloride scaffold, with 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (i). Receptor was found selective for $Zn^{2+}$. The supramolecular properties of these porphyrin receptors have been investigated by spectroscopic and theoretical studies including multidimensional NMR, UV-Vis, molecular modelling, and computational NMR methods. Binding constants are in the range $4.2 \times 10^6$ to $3.4 \times 10^7 M^{-1}$ .



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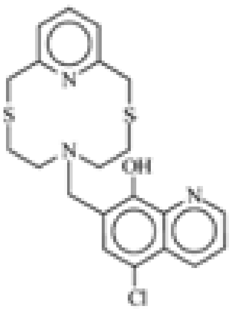

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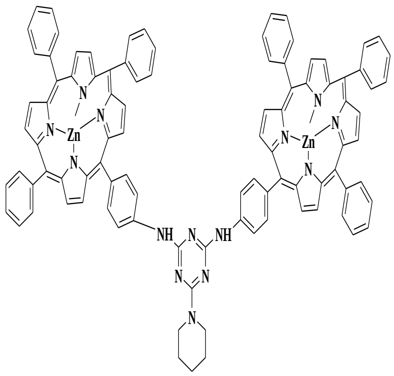
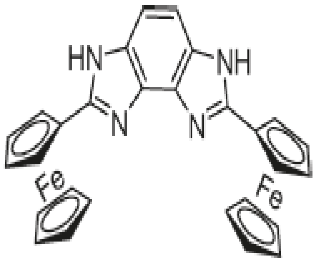


**(i)**

Alfonso *et al (2010),*[28] developed the synthesis and electrochemical, optical, and ion-sensing properties of ferrocene -imidazophenazine dyad (j). In the presence of $Pb^{2+}$ cations, a new low-energy band appeared at 502 nm, in its UV/Vis spectrum, and the oxidation redox peak is anodically shifted ($\Delta E_{1/2}$=230 mV). The presence of $Hg^{2+}$ cations also induced a perturbation of the redox potential although in less extension than those found with $Pb^{2+}$ cations.

Issaddi *et al (2012),*[29] developed 4,4’-bis(salicyleneimino) diphenyl ether (k) which acts as a tetradentate ligand and its complexes with $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ were characterised using spectroscopic determinations. In these compounds, the coordination occurs through the non-ionised phenolic hydroxyl of the ligand and the nitrogen atom of the azomethine moiety.

Sharma *et al (2013),*[30] synthesized a benzimidazole-based $Co^{3+}$ complex (l) and evaluated as a sensor for $I^-$ and $HSO_4^-$in semi-aqueous media. The complex showed electrochemical changes with $I^-$ over other anions, whereas it had a ratiometric response to $HSO_4^-$ with UV–visible spectroscopy even in the presence of other anions.



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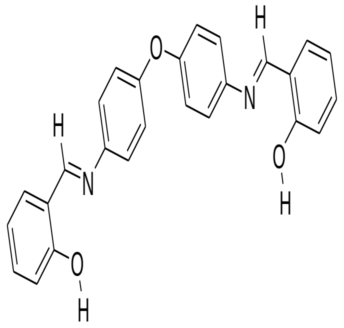

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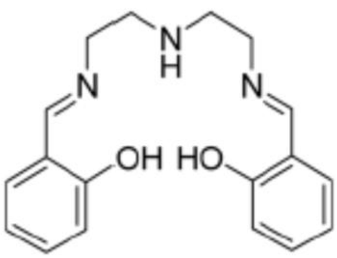

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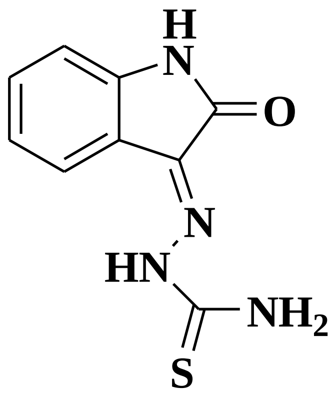
Tian *et al. (2013),*[31] developed a highly efficient fluorosensor based on ultrathin graphitic carbon nitride (g-C3N4) nanosheets for $Cu^{2+}$. In the absence of metal ions, the nanosheets exhibit high fluorescence; the strong coordination of the Lewis basic sites on them to metal ions, however, causes fluorescence quenching via photo induced electron transfer leading to the qualitative and semi quantitative detection of metal ions. This fluorosensor exhibits high selectivity toward $Cu^{2+}$. The detection limit found was as low as 0.5 nM.

Sivaraman *et al (2014),*[32] developed two rhodamine-based sensors RDI-1, RDI-2 by incorporation of the rhodamine 6G fluorophore and 2-formyl imidazole as the recognizing unit via the imine linkages. RDI-1, RDI-2 exhibits very high selectivity and an excellent sensitivity towards $Fe^{3+}$ ions in aqueous buffer solution on compared with other probes. The color change from colorless to pink and turn-on fluorescence after binding with $Fe^{3+}$ was observed. Based on jobs plot, the 1:1 binding mode was proposed.

Sariguney *et al (2014),*[33] synthesized 2,3-Indoledione 3-thiosemicarbazone (m) and a novel compound 3-(2-(4-(4-phenoxyphenyl)thiazol-2-yl)hydrazono)indolin-2-one (n) with high yield and characterized by analytical and spectroscopic techniques. The complexation behaviours of receptor (m) and (n) for various anionic species were investigated in $CH_3CN$ and compared by UV–Vis spectroscopy. Receptor (n) showed high degree of selectivity for fluoride over other anions.



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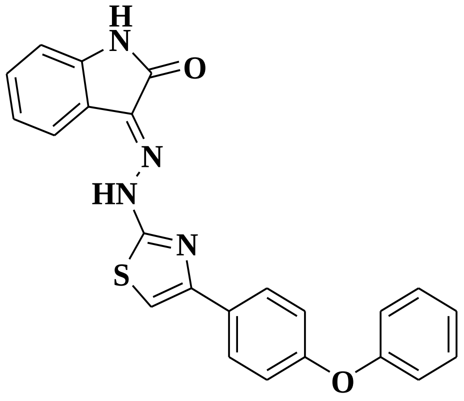


**(n)**

## 3. Materials and methods

Reagent grade 2,4-dinitrofluorobenzene, vanillin, potassium carbonate and 18-crown-6 were purchased from S.D. Fine Chemicals, Mumbai. Solvents dimethylformamide (DMF), ethyl acetate, petroleum ether and methanol were also purchased from S.D. Fine Chemicals, Mumbai and Merck and used as such. TLC analysis was done on silica coated aluminum plates (Aluchrosep Silica Gel/ $UV_{254}$ for TLC) and column chromatography was carried out over silica gel (mesh 100–200), all procured from S.D. Fine Chemicals Limited, Mumbai.

### 3.1 Synthesis

Synthesis of compound was done by a known procedure[34]. Brief details are given below:

### (I) 4-(2, 4-Dinitrophenoxy)-3-methoxybenzaldehyde (DPE-I)

2, 4- Dinitrofluorobenzene (0.34mL, 20.9mmol) and vanillin (0.51g, 26.3mmol) were taken in round bottom flask and DMF (15 mL) added. To the solution were added $K_2CO_3$ (1.40g, 83.9mmol) and added catalytic amount of 18-Crown-6 and stirred at room temperature overnight. Progress of the reaction was monitored by TLC. After completion of reaction, mixture was diluted with $CH_2Cl_2$ (100 mL), washed with water (50 mL), 1 N NaOH (3x10 mL) and again with water (50 mL) until neutral to litmus paper to finally dry over $Na_2SO_4$. Evaporation of organic solvent gave yellow colored solid (0.8g) as crude product. It was purified by chromatography using $SiO_2$, petroleum ether and ethyl acetate (75:25, v/v) as solvent. Evaporation of solvent gave yellow solid as product (0.5gm). Product obtained was characterized by $^1H$ and $^{13}C$ NMR and was consistent with the proposed structure. Melting point is 132$^oC$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$3.8 (s, 3H), 6.9(d, J = 6.9 Hz, 2H), 7.4 (m, 1H), 7.6 (m, 2H), 8.3 (dd)J = 2.8 Hz, 1H), 8.9 (d, J = 2.4 Hz, 1H), 10.0 (s, 1H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 56.3, 111.9, 117.9, 122.1, 122.6,125.2, 128.6, 135.8, 139.0, 141.9, 146.6, 151.7, 155.3.

### (II) 4-(2, 4-Dinitrophenoxy)-3-methoxybenzylalcohol (DPE-II)

**DPE-I** (0.5g, 18.2mmol) obtained above was suspended in MeOH (100ml). To an ice cold suspension of **DPE-I** and MeOH, $NaBH_4$ (0.8g, 21.8mmol) was added in small portions over a period of 15 min. TLC monitoring was done to check the progress of reaction. After completion of reactions methanol was evaporated and product extracted with ethyl acetate (3x 30 mL) and the combined organic layers were washed with water, brine and dried over $Na_2SO_4$. Evaporation of solvent gave a crude product that was purified by using $SiO_2$, petroleum ether and ethyl acetate (70:30, v/v) as solvents in the chromatography. Yellow colored pure product (**DPE-II**; 0.6g) was obtained. Product synthesized was analyzed and confirmed by $^1H$ and $^{13}C$ NMR. Melting point is 110$^oC$. $^1H$ NMR (400 MHz,$CDCl_3$): $\delta$3.8 (s, 3H), 4.7 (s, 2H), 6.9 (d, J = 9.3 Hz,1H), 7.0–7.3 (m, 3H), 8.3 (m, 1H), 8.9 (m, 1H), 10.9(br s, 1H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 56.0, 64.7, 111.7,117.3, 119.7, 122.1, 122.4, 128.7, 138.5, 140.5, 141.0,146.0, 151.0, 156.

### 3.2 Spectroscopic studies

Ion recognition studies were carried out by using different metal ion salts purchased from Sigma Aldrich and used as such. Double distilled deionised water was used throughout the experiments. Solvent used for the studies was acetonitrile ($CH_3CN$) and purchased from Merck( India). UV-Vis spectroscopy experiments were carried out on Specord PC 205 spectrophotometer by using glass/quartz cells of width 1.0 nm. Fluorescence experiments were carried out on a Perkin ELMER LF55 spectrophotometer. All absorption and emission readings were saved as ACS II files and further processed in Excel to produce all the graphs. Origin software was also used to produce the graphs.

For titrations of metal ion the solutions were also prepared in acetonitrile: water/medium (9:1) containing 10 mM HEPES buffer. The solutions of metal ions were prepared in distilled water. The solutions of metal ions were added directly into the cuvette containing the receptor solution.

## I. Preparation of stock solutions

Stock solution of **DPE-I** was prepared in $CH_3CN$. Stock solution of **DPE-I** was prepared using acetonitrile: water system in the ratio of 9:1 v/v. Receptor **DPE-I** was weighed 7.95 mg accurately and transferred to 25 mL volumetric flask. It was dissolved in above mentioned solvent system and volume made up to 25 mL.

## II. Selectivity co-efficient studies

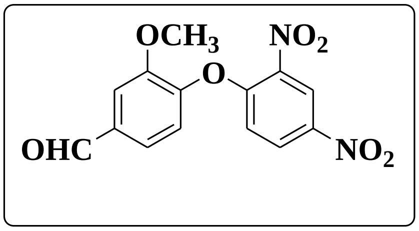
Receptor, **DPE-I** was serially diluted to get best response at 20μM in UV-Vis spectrophotometric using same solvent system in which stock was prepared giving $\lambda_{max}$ value at 245 nm . Solution of metal ions ($10^{-1}$M) containing $Na^+$, $K^+$, $Mg^{2+}$, $Cu^{2+}$, $Ba^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$,$Cd^{2+}$, and $Pb^{2+}$ were added in excess to **DPE 1**. In case of $Fe^{3+}$ an additional peak appeared at 385nm as shown in **Figure 5(a).**

## III. Fluorescence studies

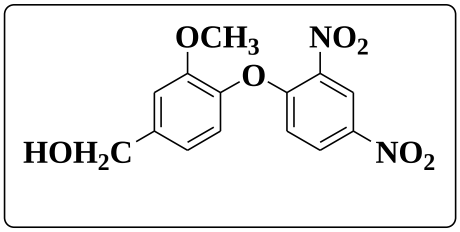
Receptor, **DPE-I** was serially diluted to get best response at 20μM in fluorescence spectrometer using same solvent system. Solution of metal ions ($10^{-1}$M) containing $Na^+$, $K^+$, $Mg^{2+}$, $Cu^{2+}$, $Ba^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$,$Cd^{2+}$, and $Pb^{2+}$ were added in excess to **DPE 1**. In case of $Fe^{3+}$ fluorescence quenching took place as shown in **Figure 7(a).**

## 4. Results & Discussion

In the present work, diphenylethers (**DPE-I** & **DPE-II**) have been synthesized. One of the compounds **DPE-I** has been used for complexation with metal ions. The studies were carried out by spectroscopic methods (UV-Vis. and Fluorescence) and supported by Gaussian 03W software.



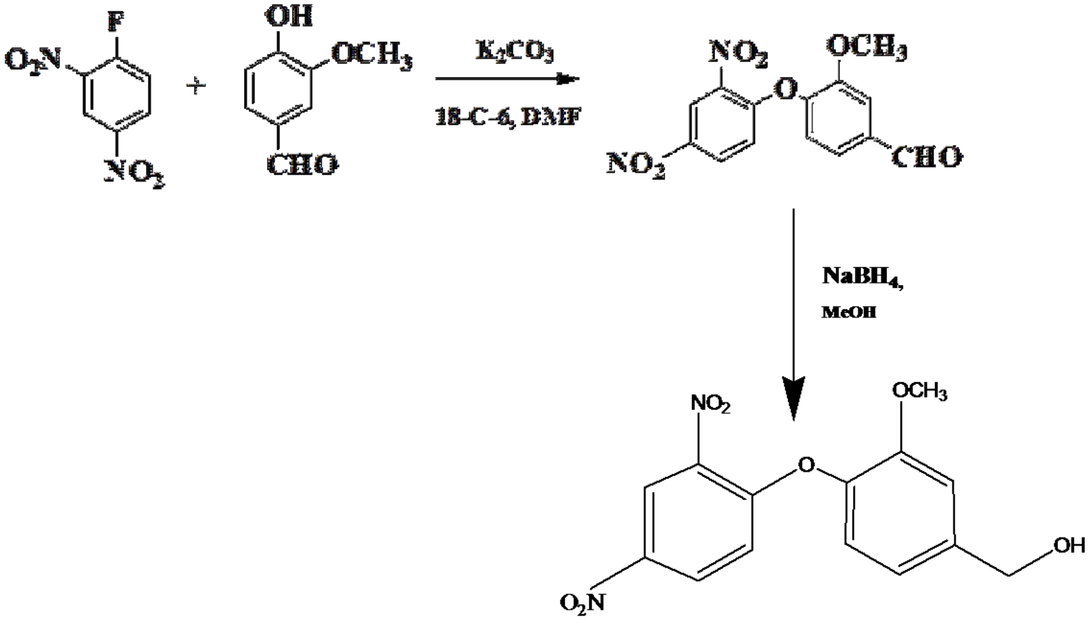
**DPE-I**



**DPE-II**

### 4.1 Synthesis

Receptor (**DPE-I**) was synthesized by nucleophilic aromatic substitution of fluoro in 2, 4- dinitrofluorobenzene with phenoxide of vanillin in the presence of a mild base $K_2CO_3$



**Scheme-I**

and catalytic amount of 18-Crown-6 in aprotic solvent, DMF. The product obtained was purified by column chromatography and analysed by $^1$H NMR that matched previously synthesized product[32]. The aldehyde group of **DPE-I** was reduced to corresponding alcohol using sodium borohydride and methanol as shown in Scheme-I. This was also analyzed by $^1$H NMR and matched the reported values.

### 4.2 Spectroscopic Studies (DPE-I)

The ion-recognition studies of receptor **(DPE-I)** has been studied through UV-Vis and Fluorescence spectroscopies. Complexation of the receptor with metal ions was confirmed by theoretical studies using GAUSSION 03W software.

#### 4.2.1 UV-Vis studies of DPE-1 receptor

UV-Vis spectroscopic studies of receptor **DPE-I** (20 µM) were investigated in $CH_3CN:H_2O$ (9:1; v/v). **DPE-I** displayed an absorption band centered at 245 nm. On addition of different metal ions, viz. $Na^+$, $K^+$, $Mg^{2+}$, $Cu^{2+}$, $Ba^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$,$Cd^{2+}$, and $Pb^{2+}$ to the solution of **DPE-I,** there was no significant changes in its UV-Vis spectrum except in case of $Fe^{3+}$ ions as in **Figure 4.**

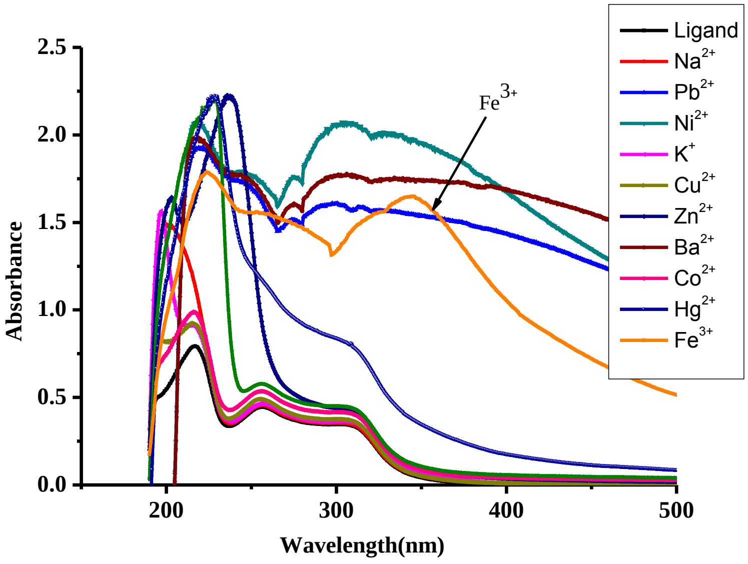


**Figure 4:** UV spectra of **DPE-I** in $CH_3CN$: $H_2O$ (9:1; v/v) in presence of different metal ions

In order to evaluate the complete structural behavior of **DPE-I** towards $Fe^{3+}$, the UV titrations of **DPE-I** was performed at different concentrations of metal ions. On successive additions of $Fe^{3+}$ to the solution of **DPE I (Figure 5a),** the absorption band at 240 nm gets flattened at 17 equivalents, and there is formation of new band at 385 nm appeared at 18 equivalents Further addition of iron solution resulted in corresponding increase in the absorption intensity at 385 nm and attained a saturation point on 46 equivalents **DPE-1** could be used to determine $Fe^{3+}$ ions ratio metrically between concentrations of $0.2 \times 10^{-4}$ -$10 \times 10^{-4}$ M as shown in **Figure 5b.** The lower detection limit for $Fe^{3+}$ was calculated to be $4.23 \times 10^{-4}$ M with coefficient of regression value 0.999.

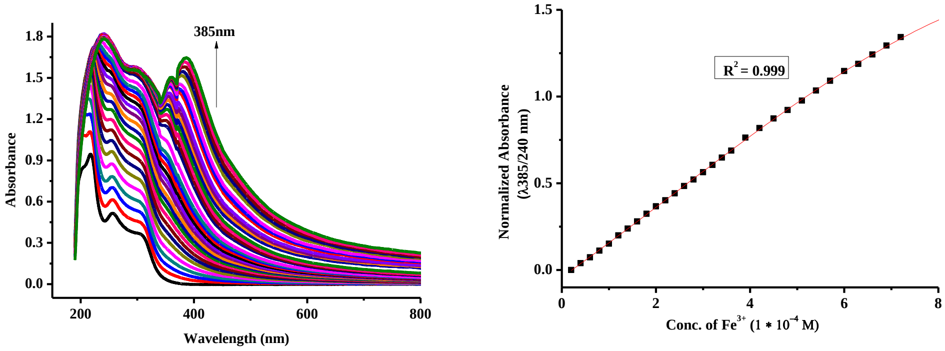


**Figure 5:** (a) Absorption spectra of **DPE- I** (20 µM) in $CH_3CN:H_2O$ (9:1; v/v) upon complexation with increasing concentration of $Fe^{3+}$ ions. **(b)** Ratio metric response of different concentrations of $Fe^{3+}$ ions on **DPE-I** (20 µM, $CH_3CN:H_2O$ (9:1; v/v).)

## Interference studies

UV- Vis studies of **DPE-I** were performed in the presence of other metal ions viz. $Na^+$, $K^+$, $Cu^{2+}$, $Ba^{2+}$, $Cr^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$,$Cd^{2+}$, and $Pb^{2+}$, under same conditions as those used for the $Fe^{3+}$ ions titration. However, no significant change in the absorbance spectrum was observed in the presence of other metal ions. To determine the practical applicability of **DPE-I**, competitive experiments were carried out in the presence of 50 equiv. of each of the various metal ions and then 25 equiv. of $Fe^{3+}$ ions was mixed. No significant variation in the absorbance was found when comparing the results with or without the other metal ions as shown in **Figure 6.**

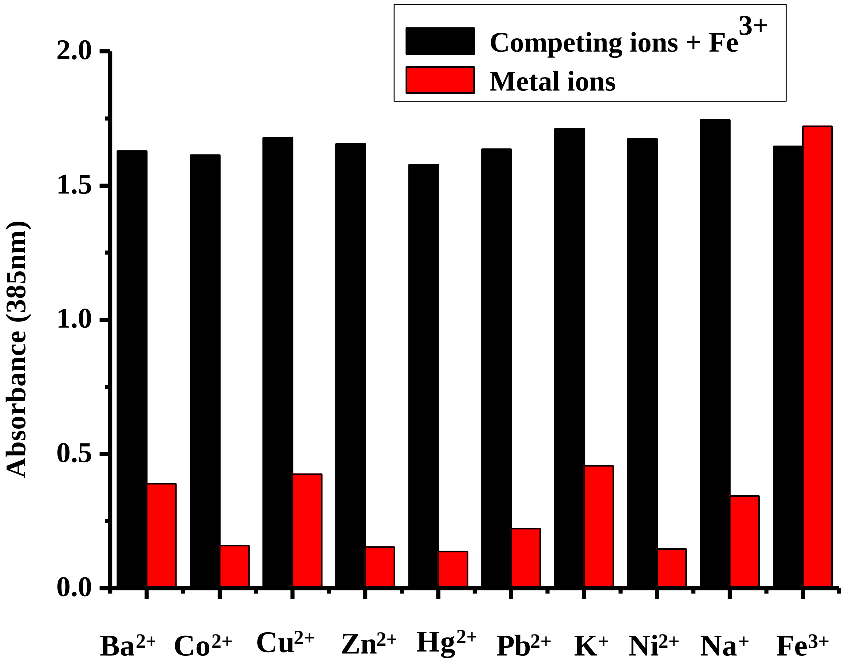


**Figure 6:** Red bars represent selectivity of **DPE-I** upon addition of different metal ions in $CH_3CN$: $H_2O$ (9:1; v/v) and black bars show the competitive selectivity of **DPE-I** in the presence of interfering metal ions

### 4.2.2 Emission properties of DPE I on complexation with different metal ions

To obtain an insight into the fluorescent properties of **DPE-I,** ligand was excited at 240 nm, displayed emission band at 350 nm and further complexation with different metal ions such as $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Cr^{3+}$,$Fe^{3+}$,$Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Ag^+$ and $Pb^{2+}$ in $CH_3CN$: $H_2O$ (9:1, v/v) were studied , which underwent fluorescence quenching selectively on addition of $Fe^{3+}$, whereas other metal ions did not show any significant change**.** In order to evaluate the complete structural behavior of **DPE-I** towards $Fe^{3+}$, the fluorescence titrations of **DPE-I** were performed at different concentrations of metal ions as shown in **Figures 7a and 7b.**

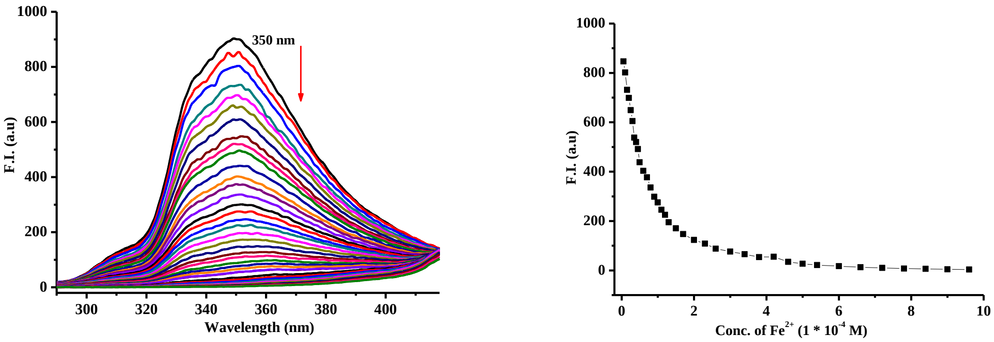


**Figure 7:** **(a)** Emission spectra of **DPE- I** {20 µM, $CH_3CN$: $H_2O$ (9:1; v/v)} upon complexation with increasing concentration of $Fe^{3+}$ ions. **(b)** Ratiometric response of different concentrations of $Fe^{3+}$ ions on **DPE-I** (20 µM, $CH_3CN$: $H_2O$ (9:1; v/v).

## Job's plot

The job`s plot analysis and binding stoichiometry showed the 1: 1 complexation **(DPE I: $Fe^{3+}$)**

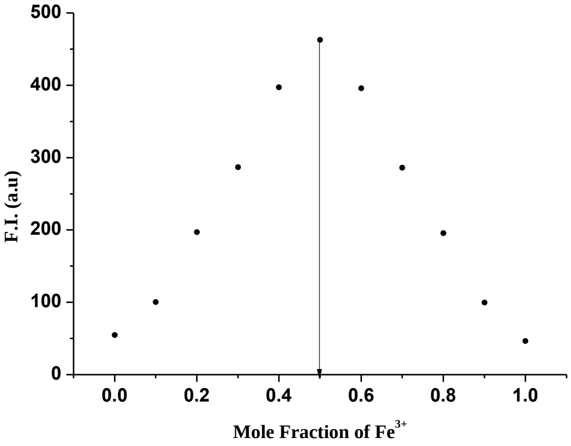


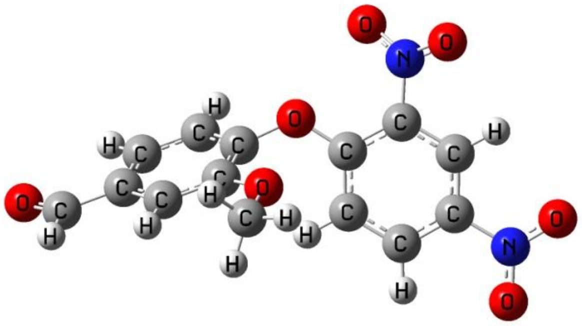
**Figure 8:** Job's plot at of **DPE-I- $Fe^{3+}$** complex showing (1:1) stoichiometry

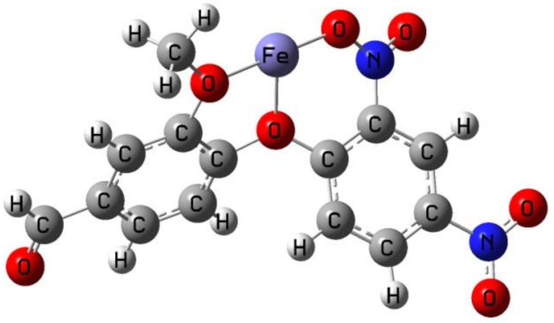
### Quenching mechanism of fluorescence of DPE I by $Fe^{3+}$

Fluorescence titration of **DPE I** with $Fe^{3+}$ ions were performed and the plot of $I_o$/ I ($I_0$ and I, fluorescence intensity of **DPE I** without and with $Fe^{3+}$ ions) vs. Fe(III) concentration was not a straight line. This indicated that the fluorescence quenching of **DPE I** by $Fe^{3+}$ ions did not obey the Stern–Volmer quenching equation ($I_0/I = 1 + K\ [Fe]$)[35]. Therefore, the fluorescence quenching is a static quenching. The formation of the **DPE I - $Fe^{3+}$** complex and the intramolecular charge transfer (ICT) from iron to the **DPE I** unit should be the main reasons why $Fe^{3+}$ ions quench the emission. Moreover, from theoretical studies it was disclosed that the **DPE I** is a good electron donor, which can display an ability to coordinate positive $Fe^{3+}$ ions, hence it was possible for charge transfer to occur between **DPE I** and $Fe^{3+}$ ion.

### 4.3.) Theoretical studies:

To explore the origin of induced absorption band, theoretical computation was employed by using Gaussian 03W to optimize the structure and calculate the electronic transitions through DFT and TD-SCF calculation with B3LYP method by setting 6-31G (d, p) as its basis sets and for $Fe^{3+}$ ions LAN2DZ method was adopted. B3LYP, 6-31G are Basis sets.





## 6. Conclusions

1. New diphenyl ether based receptors have been synthesized and developed as a chemical sensor for Iron(III).

2. Jobs plots were drawn to know stoichiometry of complexation with Iron(III) ions which was observed as 1:1.

3. The proposed sensor has been studied for interference from metal ions. No interference was observed from metal ions like $Na^+$, $K^+$, $Mg^{2+}$, $Cu^{2+}$, $Ba^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Hg^{2+}$, $Cd^{2+}$, and $Pb^{2+}$. The chemical sensor shows linear response in concentration range $10^{-4}$ to $10^{-3}$M of Iron (III) ions.

4. Theoretical studies using GAUSSION 03W was done to know complexation of receptor with iron (III) in their energy minimization state. The results supported the experimental observation.

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