Synthesis and Photophysical Properties of Naphthalimide Schiff Bases

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IN
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PATIALA, PUNJAB
July, 2019

CANDIDATE'S DECLARATION

I, hereby declare that the work which being presented in the thesis entitled, **''Synthesis and Photophysical Properties of Naphthalimide Schiff Bases"** in the partial fulfillment of the requirement for the award of degree of Master's of Science in Chemistry, Thapar Institute of Engineering & Technology, Patiala, is an original record of m0y own research work carried out under the guidance and supervision of Dr. Vijay Luxami, Associate Professor, School of Chemistry and Biochemistry, Thapar Institute of Engineering & Technology, Patiala, India. The content in the dissertation has not been submitted to any other university or institute for award of any other degree.

Date: 15 July, 2019

Place: T.I.E.T Patiala

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CERTIFICATE

This is to certify that the dissertation entitled **"Synthesis and Photophysical Properties of Naphthalimide Schiff Bases"**, submitted to School of Chemistry and Biochemistry, T.I.E.T, Patiala in partial fulfillment for the award of Master's of Science in Chemistry, is a record of bonafide work carried out by **Ms. Anchal Sharma** (Regd. No. 301702004) under the supervision and guidance of **Dr. Vijay Luxami**, Associate Professor, School of Chemistry and Biochemistry, Thapar Institute of Engineering, Patiala.

All help received by her from various sources have been duly acknowledged.

No part of this dissertation has been submitted elsewhere for award of any other degree.

Date: 15 July, 2019

(Anchal Sharma)

Candidate

It is certified that the above statement made by the candidate is correct to the best of my knowledge.

Date: 15 July, 2019

(Dr. Vijay Luxami)

Supervisor

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ABBREVIATION

NMR	Nuclear magnetic resonance
TLC	Thin Layer Chromatography
PET	Photoinduced Electron Transfer
ICT	Intramolecular Charge Transfer
ESIPT	Excited state intramolecular proton transfer
AIE	Aggregation induced emission
ACQ	Aggregation caused quenching
CN^-	Cyanide
SCN^-	Thiocyanate
OAc^-	Acetate
HSO_4^-	Sulfate
$H_2PO_4^-$	Dihydrogen Phosphate
NO_3^-	Nitrate
F^-	Fluoride
Br^-	Bromide
Cl^-	Chloride
PPi	Pyrophosphate
Na^+	Sodium
Mg^{2+}	Magnesium
K^+	Potassium
Al^{3+}	Aluminium
Cr^{3+}	Chromium
Fe^{3+}	Ferric
Co^{2+}	Cobalt

Ni^{2+}	Nickel
Cu^{2+}	Cupric
Zn^{2+}	Zinc
Pd^{2+}	Palladium
Hg^{2+}	Mercuric
Ag^{+}	Silver
µM	micro meter
DMSO-d_6	Dimethyl sulfoxide
$CHCl_3$	Chloroform
CH_3OH	Methanol
EtOH	Ethanol
HCl	Hydrochloric acid
IPA	Isopropanol
DMF	Dimethylformamide
THF	Tetrahydrofuran
H_2O	Water
DBS	Dodecyl Benzene Sulphonic acid
DCM	Dichloromethane

ABSTRACT

A designed novel napthalimide based derivatives (abbreviated as probe **1** and probe **2**) were synthesized and used as chromo-fluorescent sensor potentially. Probe **1** showed absorption peak at 420 nm and emission peak at 500 nm. Upon addition of CN^- ions, probe **1** displayed instant colour change from yellow to brown with a red shift of 40 nm. However, in case of emission spectra, formation of two emission bands was observed at 500 nm and 560 nm. The binding constant for probe **1**.CN^- was determined to be 2.9×10^{8} M^{-1} and limit of detection was found to be 7.5×10^{-7} M. Probe **1** also showed its high selectivity towards Cr^{3+} ions through "*turn-on*" emission response at 500 nm. The determined binding constant for probe **1**.Cr^{3+} was determined to be 6.0×10^{4} M^{-1}, while limit of detection was calculated to be 7.6×10^{-9} M. On the other hand, probe **2** showed absorption peak at 430 nm and emission peak at 500 nm. In the presence of CN^- anion, red shift of 72 nm and formation of new band at 502 nm has been observed whereas no such change was detected in fluorescence spectra. Binding constant and limit of detection for CN^-, was found to be 6.5×10^{5} M^{-1} and 6.0×10^{-8} M respectively.

Chapter 1

Introduction and review of literature

1.1 Introduction

Supramolecular chemistry has been defined as **"**chemistry of molecular assemblies and of the intermolecular bonds". The primary goal of supramolecular chemistry is to design and synthesize novel compounds formed by joining small molecular units through non-covalent interactions.[1, 2] Now-a-days, supramolecular chemistry is well-known in most of research field like molecular devices, sensor, drug development, catalysis, nanoscience etc.[3, 4] A supramolecule is formed by interrelation between two different molecules in which one molecule act as receptor, having donor atom and form hydrogen bonding and another molecule act as an analyte, having hydrogen bond acceptor atom. Chemosensor are used as detection of active ionic species present in our environment. It is a low cost sensing process for anions as well as metal ions. A variety of chemosensors have been synthesized on the basis of host-guest interactions (like vander Waals interaction, hydrogen bonding, metal ligand coordination and electrostatic force) used as qualitative analysis by targeting different molecules.[5-9] These are used to detect analyte/mixture of species in solution. The change that occurs by measuring a variety of physical properties such as the photophysical properties are observed in the absorption / emission in which different range of wavelength of EM spectrum are used. The aim of supramolecular chemistry is to design the ligands for selective recognition of metal ions and anions. Chemosensors could be classified as electronic or/and optical sensors. Herein, we are interested in optical sensors, which are categorized as chromogenic and fluorogenic, depending upon their responses towards analytes. In first type, signal observed by change in colour of the analyte whereas in fluorogenic chemosensor, signal observed by changes in fluorescence behavior.

The presence of metal ions and anions are important to abiotic and biotic community. However, the excess of such ions have adverse effects to environment and living organism. For instance, the industries waste polluted the water, which further directly affects the human health and environment.[10] Most of the abundant elements present in our earth crust are involved in many life processes. CN^- is a hypertoxic anion having harmful effects to environment and living organisms. CN^- compound consists of hydrogen cyanide, potassium cyanide and sodium cyanide gas. Sources of CN^- poisoning include smoke inhalation,

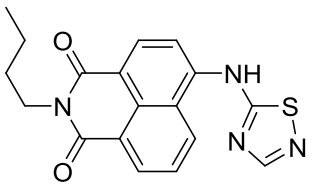
industries in form of synthetic plastics and electroplating, cigarette smoke. The large dose of CN^- ions limits the oxygen content in the cell by binding with cytochrome–c oxidase which inhibits the mitochondrial electron transport chain causes death.[11] On the other Cr^{3+} well known for its carcinogen effects. The effect of Chromium on human body includes respiratory tract irritation and lung cancer.[12, 13] Therefore, development of new chemosensor for the identification of various harmful ions present in our environment is very important. Chemosensor must have biological and environmental applications.

Naphthalimide is one of the simplest heterocyclic systems, which contained a flat ring and has π-deficient aromatic behaviour. This was used as core unit in different molecular architectures, which were further utilized as fluorescent probes for medical and biological purposes.[14-17] The introduction of different functional groups to naphthalimide core, these substances show various mechanism like photoinduced electron transfer (PET) an important photochemical process in which movement of electron take place from an electron-rich species to an electron deficient species, leads to quenching in fluorescence spectra. Excited state intramolecular proton transfer (ESIPT) is an important principle of naphthalimide derivatives in which formation of tautomer take place with different electronic structures from original to excited state. Fluorophore show two emission bands due to intramolecular H-bonding interaction between a H-bond donor (-OH and NH_2) and H-bond acceptor (=N- and C=O). A large stoke shift is an important feature of ESIPT molecule. Naphthalimides derivatives act as environmentally responsive fluorophore due to strong intramolecular charge transfer (ICT). Naphthalimide derivatives shows aggregation due to aggregation caused quenching (ACQ) and aggregation induced emission (AIE) phenomenon. It is the process in which aggregated state shows high emission after absorption of photon than solution state which is achieved by resisting intramolecular rotations.

1.2 Review of literature

Krasteva *et.al.* synthesized and analyzed photophysical properties of 1,8-naphthalimide fluorophore containing 2-amino-1,3,4-thiadiazole fragment at C-4 position.[18] Compound **1** is a receptor showed pH dependence fluorescent property and show practical application for detection of metal cations in buffer solution. The photophysical properties were analyzed in H_2O/EtOH (1:1/ v,v) solution by varying pH values. Compound **1** was selective towards Hg^{2+} ions with a pH independent response and this result was based on aggregation caused quenching (ACQ) process. In the presence of Hg^{2+}, it didn't show any significant change

from pH: 3-10, but as the pH increases above 10, fluorescence quenching effect take place along with red shift of absorption maxima from 402 nm to 518 nm due to deprotonation of the aromatic amine at C-4 position which enhanced the push-pull character in ICT transitions. Moreover, it did not show any major change in the fluorescence as a function of pH. Hence, Compound **1** is highly selective for Hg^{2+} in H_2O/EtOH (1:1/ v,v) solution in a wide pH ratio.



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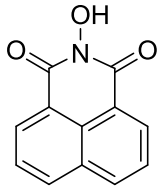

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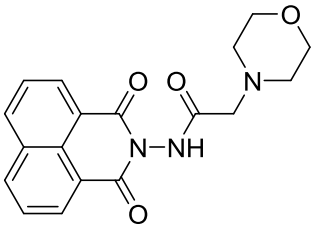
Ramasamy *et.al.* synthesized a novel dual emission N-hydroxy1,8-naphthalimide compound **2**, which showed high selectivity towards Bi^{3+} ions and sufficient stability as pH sensor in range of pH 5.0 to 12.0.[19] Absorption and emission maxima was observed at 342 and 383 nm respectively. Its photophysical studies were observed in aqueous media. In absorption spectra, compound **2** showed red shift in presence of Bi^{3+} whereas in fluorescence showed enhancement with Bi^{3+}. Binding stoichiometry determined the formation of complex (1:1) between Bi^{3+} and compound.

Georgiev *et.al.* synthesized two 1,8 naphthalimide derivatives, highly water-soluble and their fluorescence sensing properties based on ICT and PET.[20] Compound **3** and **4** had a great affinity towards Cu^{2+} and Hg^{2+} based on the function of pH. These two compounds were designed on the basis of fluorophore-$receptor_1$ and space-$receptor_2$ composed of N-$imide_1$ and N-$phenylpiperazine_2$ respectively. Compound **3** showed absorption and emission spectra at 290 nm and 350 nm respectively and compound **4** showed absorption and emission spectra at 375 nm and 475 nm. In an acidic medium, PET quenching process could not be possible in $receptor_2$ while compound **3** and **4** showed strong blue fluorescence due to protonation of the tertiary ammine. In neutral medium, PET quench the fluorescence intensity of compound **3** and **4** and in an alkaline medium, due to $receptor_1$ the push-pull character of the ICT transition was reduced and compound **3** and **4** showed a blue shift in absorption maxima due to deprotonation of the imide unit.



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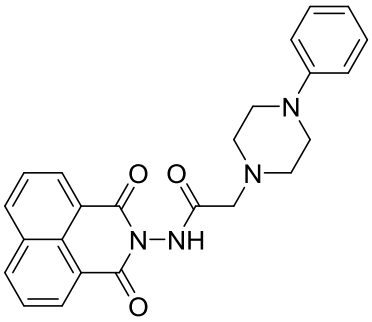

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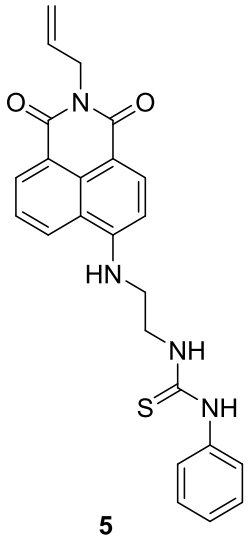
Alaei *et.al.* synthesized a novel 1,8-naphthalimide derivative, containing thiourea as a functional group for selective detection of F^- ion. The absorption maxima was at 423-443 nm and emission maxima was at 509-541 nm. Photophysical properties were investigated in DMF solution.[21] From results, it was indicated that in the presence of F^- ion, the fluorescence emission of dyes were switched off. On addition of F^- ion instant colour change observed from green-yellow to purple. Hence, compound **5** was highly selective for F^- anion in the presence of DMF solution.



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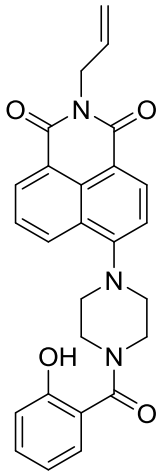

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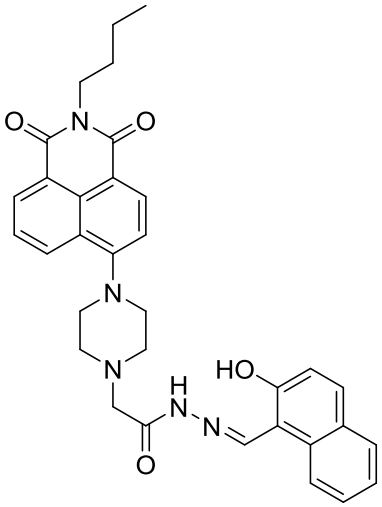

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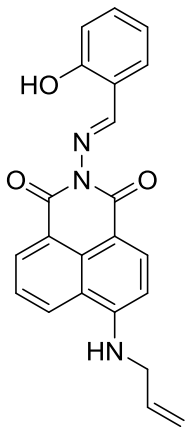
Xu *et.al.* synthesized a naphthalimide derivative which was highly selective for Fe^{3+} ions sensing glass slides.[22] Compound **6** having terminal bonds which was copolymerized in the presence of HEMA occurred on the activated area of the glass slides by UV radiation. On addition of Fe^{3+} in 0.05 mol/L Tris/HCl, the fluorescence emission intensity was decreased at 408 nm and 521 nm respectively. The binding stoichiometry determined the formation of complex (1:1) in between Fe^{3+} and compound **6** and also showed undeviating response

towards Fe^{3+} binding constant found in the range from 1.0×10^{-4} to 1.0×10^{-2} M and detection limit of 4.6×10^{-5} M. Hence, compound **6** was highly selective for Fe^{3+}.

Kang *et.al.* synthesized a schiff base receptor on naphthalimide derivative.[23] Compound **7** was highly selective for Al^{3+} and visible colour change was observed from pale yellow to bright green. All the photophysical properties were analyzed in CH_3OH solution. Absorption and emission maxima was observed at 401 nm and 524 nm. In the presence of Al^{3+}, compound **7** showed 39-fold fluorescence enhancement and emission peak shift from 524 nm to 508 nm. This compound also showed a little fluorescent enhancement with Hg^{2+}. Therefore, compound **7** showed good selectivity for Al^{3+} metal ion in chemical, environmental and biological systems.

Aderinto *et.al.* synthesized a fluorescent sensor, based on 1,8-naphthalimide derivatives used for the detection of Cu^{2+} ion.[24] Compound **8** act as a good fluorophore and its schiff base group act as receptor which shows high sensitivity and selectivity towards Cu^{2+}. Absorption and emission maxima was observed at 430 and 444 nm respectively. All the photophysical properties of compound **8** were characterized in organic solvent. Binding stoichiometry determined the formation of 1:1 complex between compound **8** and Cu^{2+}. Hence, compound 8 was highly selective towards Cu^{2+} in organic solvent.



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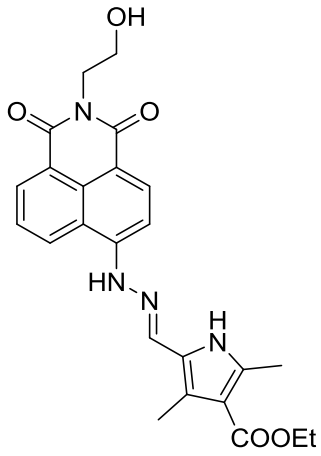
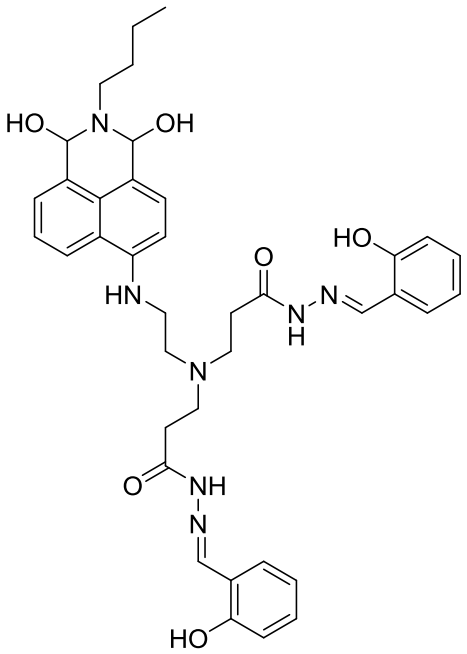


9

Wang *et.al.* synthesized a 1,8-naphthalimide hydrazone derivative contain pyrrole unit.[25] This compound was highly sensitive towards Cu^{2+} metal ion, used to monitor Cu^{2+} ions present within Hela cells. The photophysical study was observed in CH_3CN/H_2O (9:1, v/v) solution. Absorption maxima showed four bands at 480 nm, 264 nm, 335 nm and 288 nm were due to n-π^*, n-σ^* and π-π^* transitions of imine bond and pyrrole units, respectively. After

addition of Cu^{2+} in the buffered solution of compound **9**, the absorption maxima decreased to 335 nm and instant colour changed was observed from orange to colourless. This is due to decomposition of compound **9** in the presence of Cu^{2+}. In fluorescence spectroscopy, emission band was observed at 620 nm. Hence, compound **9** was highly selective towards Cu^{2+} and also showed some biological applications.

Xu *et.al.* synthesized a 1,8-naphthalimide derivative compound.[26] Compound **10** was highly selective towards Al^{3+} ions. Compound **10** act as turn on sensor. Photophysical studies were observed in different organic solvents. The absorption maxima at 288-442 nm and fluorescence maxima was at 505-534 nm corresponding to π-π* transitions and S_0-S_1 transition respectively. In presence of Al^{3+} ions, compound displayed a fluorescence enhancement due to formation of complex (1:1) between Al^{3+} and compound inhibiting PET process.



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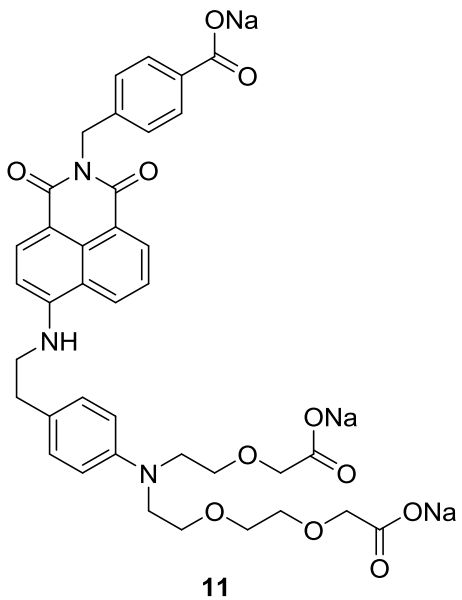
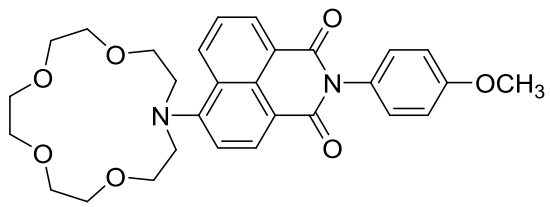


11

Liu *et.al.* synthesized a novel 4-amino-1,8-naphthalimide based sensor.[27] Compound **11** showed selectivity and sensitivity for Cd^{2+} and also detected Cd^{2+} ions concentration in the presence of excess amount of Zn^{2+}. All the photophysical properties of compound **11** were analyzed in aqueous solution (HEPES buffer, pH:7.4). Absorption and emission maxima was observed at 470 nm and 550 nm. On addition of Cd^{2+}, enhancement was observed in the emission band at 550 nm. It showed a significant sensor property towards the Cd^{2+} metal

ions with 24 fold fluorescent enhancement in aqueous solution. From binding stoichiometry, determined the formation of complex (1:1) in between Cd^{2+} and compound.

Hou *et.al.* synthesized a naphthalimide derivative having an aza-15-crown-5-macrocycle group which was highly selective fluorescent probes for Hg^{2+} ions.[28] All the photophysical properties were analyzed in aqueous buffer (containing 20% CH_3OH) solution. Absorption maxima were displayed at 432 nm and on addition of Hg^{2+}, formation of new peak at 346 nm was analyzed and peak at 432 nm was decreased. Fluorescence emission was at 537 nm and on addition of Hg^{2+} showed a blue shift of 22 nm. There was intramolecular charge transfer in between nitrogen atom on the aza-15-crown-5-macrocycle. Hence, compound **12** was highly selective towards Hg^{+} over other metal cation in aqueous solution.



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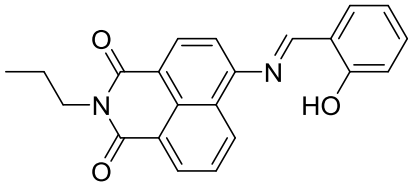
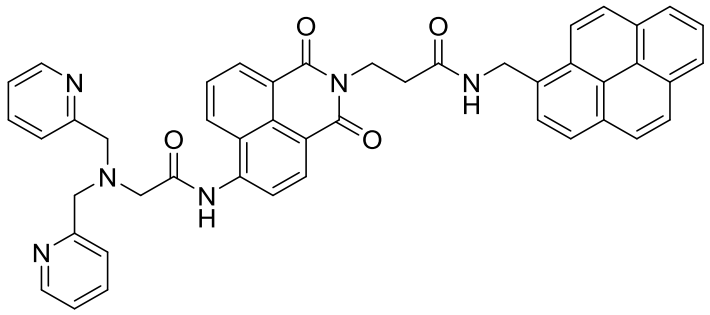


13

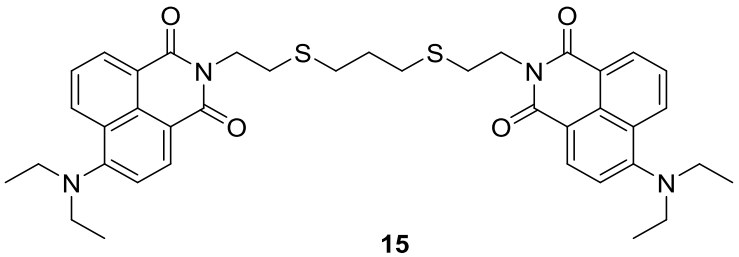
Goel *et.al.* synthesized a novel naphthalimide Schiff base for the detection of Hg^{2+} and HSO_4^-.[29] All the photophysical studies were observed in CH_3OH. Absorption maxima was at 380 nm and emission maxima was at 530 nm. On gradual addition of Hg^{2+}, formation of isobestic point at 415 nm with new absorption band at 430 nm. Whereas on addition of HSO_4^-, absorption maxima at 380 nm was decreased with formation of new band at 430 nm and isobestic point at 420 nm. Compound **13** showed strong intramolecular charge transfer because H-bonding interactions and also showed DNA intercalation properties.

Yoon *et.al.* synthesized a novel pyrene-appended napthalimide-dipicolylamine compound, which was used as sensor for the detection of Zn^{2+} ions.[30] Its photophysical studies were observed in HEPES buffer (containing 10% DMSO,v/v). Compound **14** showed absorption band at 347 nm and 390 nm for pyrene and naphthalimide respectively. Fluorescence showed a strong range from 370 nm to 425 nm for pyrene and napthalimide respectively. In presence of Zn^{2+}, compound **14** gave colour change from blue to green which increased the fluorescence intensity of naphthalimide at 530 nm while no change was observed for the pyrene moiety. Binding stoichiometry determined the formation of complex (1:1) in between Zn^{2+} and compound **14**.



14

Thavornpradit *et.al.* synthesized a novel naphthalimide-based fluorescent compound containing disulfide bond.[31] Showed absorption maxima at 419 nm and emission maxima at 524 nm. Compound **15** was highly selective and sensitive toward Cu^{2+} ion. In presence of Cu^{2+}, compound **15** showed strong fluorescence enhancement with high quantum yield. Formation of binding stoichiometry ratio 1:2 in between Cu^{2+} and compound **15** took place. The LOD of compound **15**.Cu^{2+} was found to be 0.83 ppm, which was sufficient for the detection of maximum copper level in environmental and dietary sources.



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1.3 Research gap in studies

Naphthalimide is a structural fragment that can be modified using complex compound and organic functional material. Derivatives of naphthalimide have been used as supramolecular units to analyze photoinduced electron transfer as fluorescence, laser dyes and sensors. From literature survey, it has been observed that nitrogen atom in naphthalimide core attached by other group with the help of linker or alkyl group and if we fused this nitrogen atom with aryl group it will enhance the properties of naphthalimide derivatives. However, there is scope of novel and simple design of naphthalimide derivatives and learning its photophysical behavior towards different ions. In this respect, compound **13** (in literature survey) was designed and synthesized in our group, where propyl chain was incorporated on naphthalimide core and evaluated for the sensing properties. In this study, the effect of incorporation of aromatic unit has been studied. Therefore, the designed probe **1** and probe **2**

were synthesized. Further, the photophysical behavior of probe **1** and **2** were evaluated for sensing of ions.

1.4 Objective

The aim of this study is to design and synthesize naphthalimide derivatives which are used as chromo-fluorogenic sensor for anions and metal ions. In order to fulfill our purpose we have to:

- Synthesize of Schiff bases based on naphthalimide core unit with increased aromaticity.
- Analyzing their photophysical properties towards abiotic ions.

Chapter 2

Materials and Methods

2.1 Materials and Methods

All the chemicals used in the synthesis of probe **1** and probe **2,** have been obtained from Sigma Aldrich Chemical Ltd. and Loba Chemie on the basis of their accessibility. All the solvents used in the synthesis were of spectroscopic grade, purchased from Spectrochem Limited. The progress of reactions were observed with the help of thin-layer chromatography. The stock solutions of individual anions were prepared in CH_3CN solution of concentration 1×10^{-1} $molL^{-1}$ from their corresponding salt and stock solution of ligand were prepared at 10^{-3} M (25ml) in CH_3CN/DMSO solution. Formation of complex was determined by Job plot stoichiometry ratio, formed between metal ion and ligand. Binding stability constant was calculated with the help of Benesi-Hildebrand equation

2.2 Instrumentations

^1H NMR spectra were recorded on BRUKER ECS-400 MHz spectrometer at ambient temperature. NMR samples were prepared in DMSO (d_6) and TMS used as an internal reference. Absorption spectra of probe **1** and probe **2** were measured with UV-2600, Shimadzu spectrophotometer and fluorescent spectra were measured with carry eclipse spectrophotometer.

2.3 Binding constant and limit of detection

Binding constant was detected with the help of Benesi- Hildebrand equation.

$$\frac{1}{I - Io} = \frac{1}{K_a (I_{max} - I_o) [C]^n} + \frac{1}{I_{max} - I_o}$$

Where, I_o, I and I_{max} are the intensities of Probe in the absence of analyte; at an intermediate analyte concentration and at a concentration of complete interaction, respectively. C: Concentration of analyte and K_a : Binding constant.

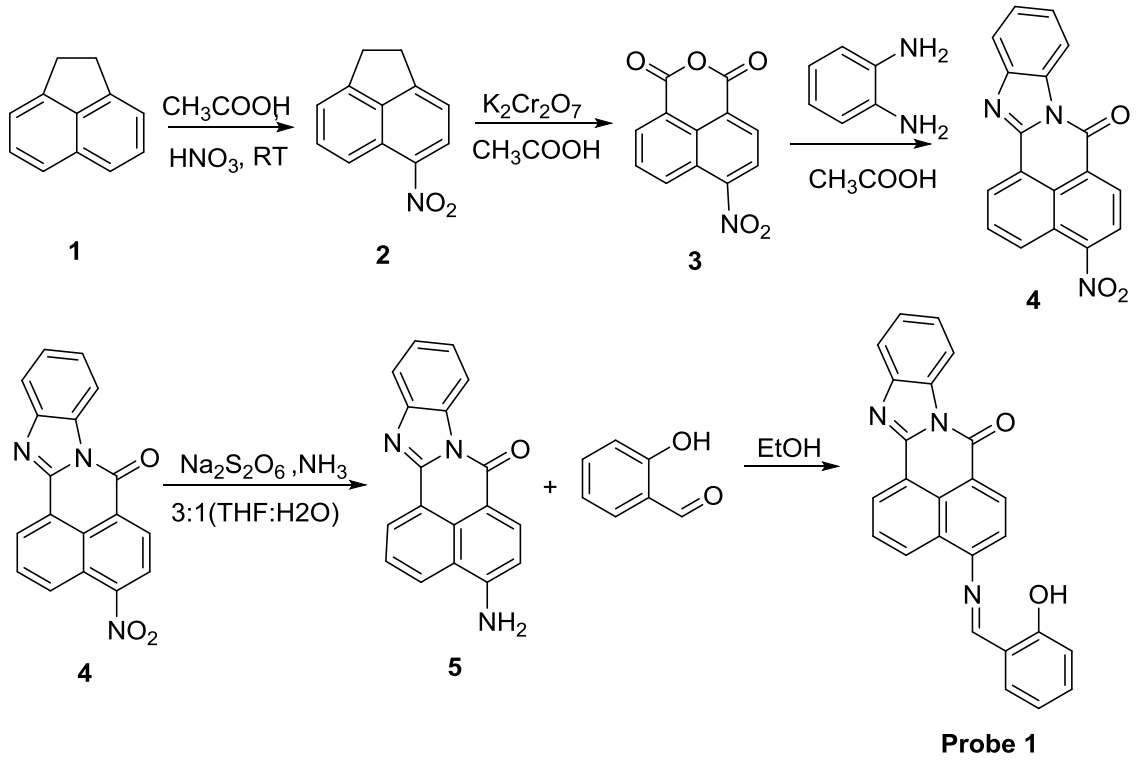
The detection limit (DL) was calculated as follow :

$$DL = \frac{K \times \text{Standard deviation of the blank solution}}{\text{slope of calibration curve}}$$

2.4 Experimental section

2.4.1 Synthesis of probe 1

Acenaphthene (524 mg, 1mmol) was dissolved in acetic acid (30-40ml) and HNO_3 (1.5 eq.). The reaction mixture was stirred at room temperature for 3 hrs. After the completion of reaction 250 ml water was poured to it and solid separated **(2)** was filtered out. Further, the obtained solid **(2)** was oxidized in acetic acid using potassium dichromate at refluxing condition. On adding 250 ml of water, solid was separated out and filtered it out. The formed product **(3)** was dissolved in acetic acid and o-phenylene diamine (108mg, 1mmol) was added to it and the reaction mixture was refluxed overnight. The reduction of compound **4** was carried out by using sodium thionate (5 eq.), THF: H_2O (3:1), and ammonia solution (3-4ml) and it was stirred for 1 hr. The reaction mixture was extracted using ethyl acetate and water and the ethyl acetate layer was washed thrice with water and the formed product **(5)** was obtained by evaporating ethyl acetate using rotary evaporator. Finally compound **5** was reacted with salicylaldehyde in ethanol at refluxing condition for 24 hrs. Washed it with ethanol and then filtered it out. Brown coloured solid was obtained. Further, the compound was analyzed by spectroscopic technique. Yield : 72%; Colour : Brown; Melting point : 176-178 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 9.01 (s, 1H, CH), 8.79 (d, *J* = 6.36 Hz, 2H, ArH), 8.72 (d, *J* = 6.68 Hz, 1H, ArH), 8.47-8.44 (m, 1H, ArH), 8.03 (t, *J* = 6.52 Hz, 1H, ArH), 7.88-7.86 (m, 1H, ArH), 7.75 (d, *J* = 6.32 Hz, 1H, ArH), 7.68 (d, *J* = 6.84 Hz, 1H, ArH), 7.54-7.48 (m, 3H, ArH), 7.75 (d, *J* = 6.32 Hz, 1H, ArH), 6.42 (d, *J* = 1.76 Hz, 1H, ArH).



Scheme 2.1. Synthesis of probe **1**

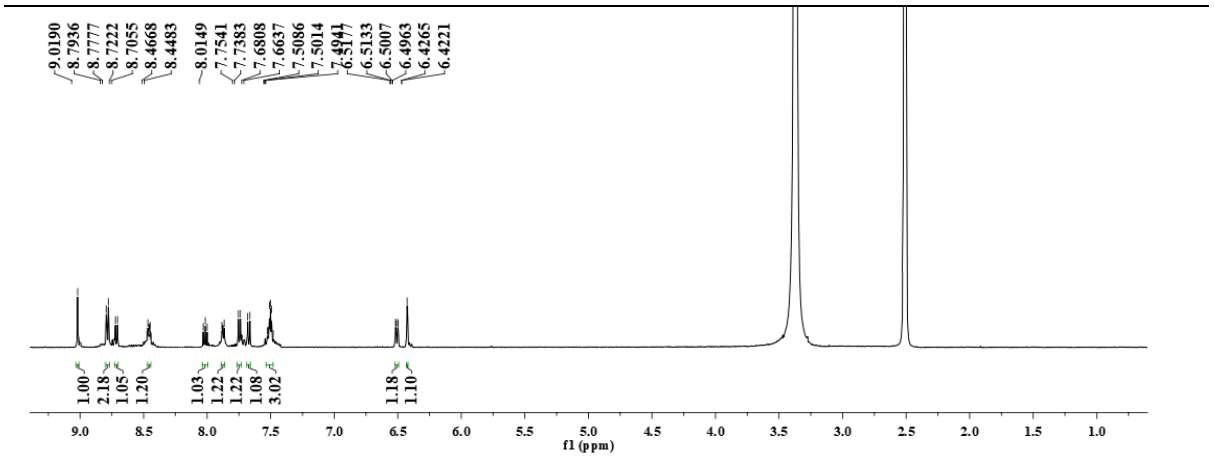
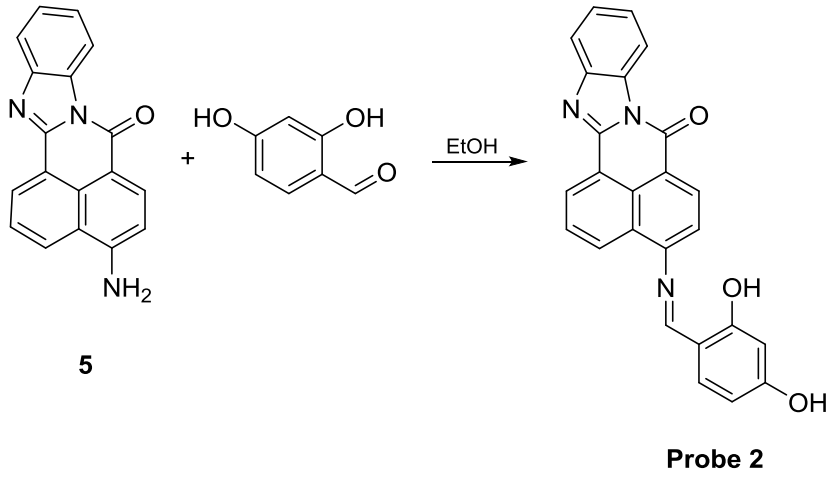


Figure 2.1. ^{1}H NMR of probe **1**.

2.4.2 Synthesis of probe 2

Probe **2** was synthesized by following the same procedure as followed for Probe **1**. Product **(5)** was reacted with 2,4-dihydroxy benzaldehyde (138 mg,1mmol) in ethanol at refluxing condition for 24 hrs. Wash it with ethanol and then filter it out. Brown coloured solid was obtained which was analyzed by spectroscopic technique. Yield : 75%; Colour : Brown; Melting point :178^{o}-179^{o}C ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 9.15 (d, J = 12.84 Hz,

1H, CH), 8.83-8.71 (m, 3H, ArH), 8.46 (s, 1H, ArH), 7.98-7.86 (m, 2H, ArH), 7.77-7.71 (m, 1H, ArH), 7.55-7.50 (m, 3H, ArH), 7.08 (d, *J* = 6.12 Hz, 2H, ArH).



Scheme 2.2. Synthesis of probe **2**

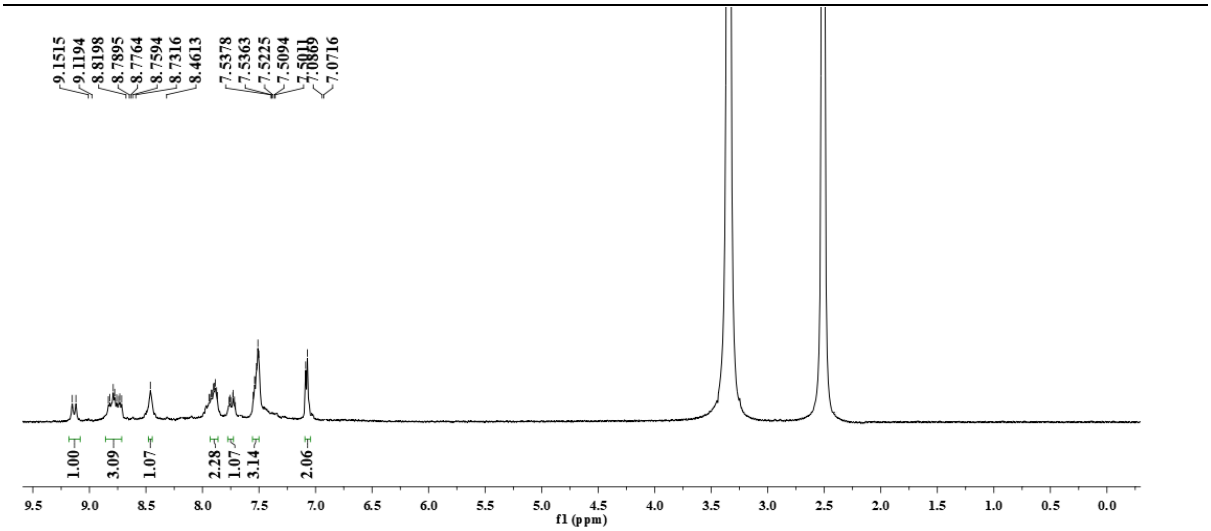


Figure 2.2. ^{1}H NMR of probe **2**

Chapter 3

Results and discussion

3.1 Photophysical properties of probe 1

Photophysical properties of probe **1** were measured by steady state absorption and emission spectroscopy. The probe **1** (10 µM, CH_3CN) displayed the absorption and emission peak at 420 nm and 500 nm, respectively. Further, the absorption and emission spectra were measured in different polarity systems. It was noted that the probe **1** displayed an absorption red shift of ~80 nm on varying the polarity from hexane (non-polar) to DMSO (polar). Likewise, the emission spectra also displayed the red shift of ~35 nm on changing the polarity from hexane to DMSO (Figure 3.1). This signified that the probe **1** was more stabilized in polar solvents in excited state. The significant red shifts in spectra displayed the presence of charge transfer phenomenon.

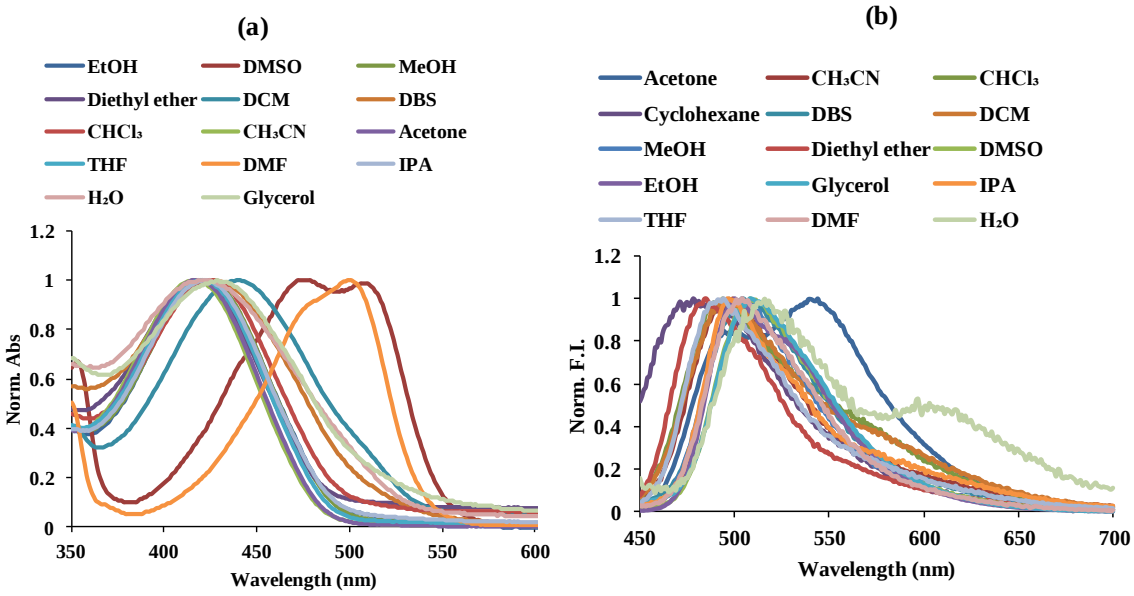


Figure 3.1 (a) Absorption and **(b)** Emission spectra in different solvent ranging from non-polar to polar on probe **1** (10µM).

It could be noted that the probe **1** contained molecular flexibility through single bonds and thus, could have the molecular motion. In order to study the effect of ceasing molecular motion, the absorption and emission spectra were measured in binary solvent system (H_2O/CH_3CN). It was noted that the absorption peak were decreased in intensity with slight

blue shift. Likewise, the emission spectra of probe **1** also displayed decreased emission intensity on increasing the H_2O content (Figure 3.2). Thus, the absorption and emission alteration signified the formation of H-aggregates.

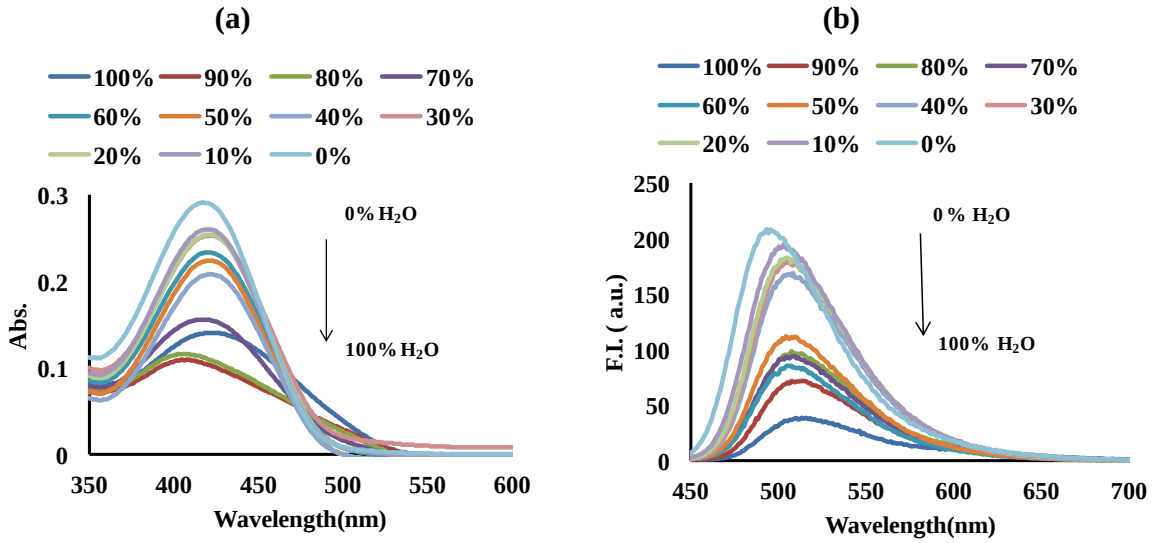


Figure 3.2 Effect of increasing volume of H_2O on **(a)** absorption spectra **(b)** emission spectra of probe **1** in CH_3CN.

3.1.1 Sensing properties of probe 1

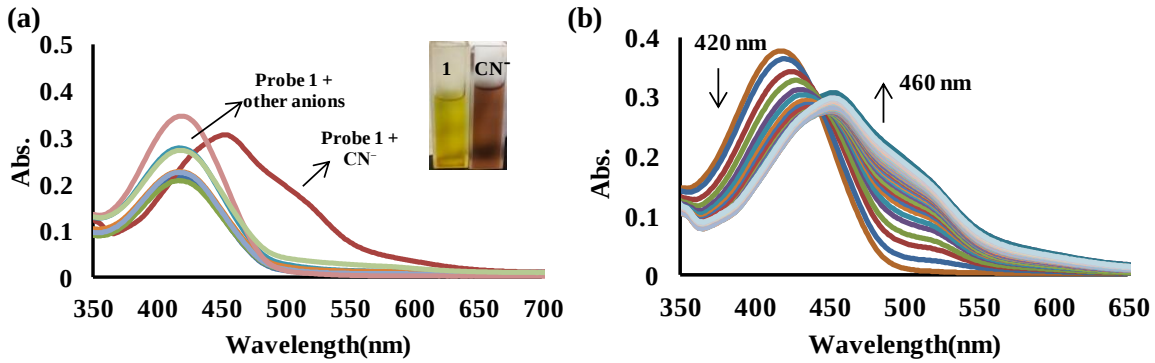


Figure 3.3 (a) Absorption spectra of probe **1**(10µM, CH_3CN) upon addition of different anions **(b)** The effect of incremental addition of CN^- to probe **1** (10µM, CH_3CN) on absorption spectra.

3.1.1.1 Spectral response towards anions

The recognition behaviour of probe **1** was examined in CH_3CN towards different anions like Cl^-, F^-, I^-, Br^-, OAc^-, $H_2PO_4^-$, CN^-, HSO_4^- and PPi. The presence of anions displayed insignificant change at absorption spectra of probe **1**, except for CN^- ions. On addition of

CN^- ions, the absorption spectra showed red shift of 40 nm to 460 nm (Figure 3.3). During the experiments, an instant and detectable visible colour change was observed from yellow to brown. Further, the quantitative estimation of CN^- ions was performed through titration experiment. The incremental addition of CN^- ions (0-400µM) into probe **1** showed a gradual decrease in absorbance at 420 nm corresponding with an increase in absorbance at 460 nm with an isobestic point at 440 nm.

The emission behaviour of probe **1** (10 µM) was examined in CH_3CN against different anions like HSO_4^-, OAc^-, I^-, Br^-, Cl^-, CN^-, F^-, $H_2PO_4^-$, SCN^- and PPi. Upon excitation at 420 nm, the probe **1** displayed emission at 500 nm. The presence of ions displayed insignificant change at emission spectra of probe **1**, except for CN^- ions. On addition of CN^- ions, there was formation of two emission bands at 500 nm and 560 nm (Figure 3.4). Further, the quantitative estimation of CN^- ions was performed through titration experiment. The incremental addition of CN^- ions (0-190 µM) into probe **1** showed rise of emission intensity at 500 nm with formation of new band at 560 nm. The new band formation could be due to presence of deprotonated form of probe **1**, which was also endorsed with presence of red shifted absorption peak at 460 nm.

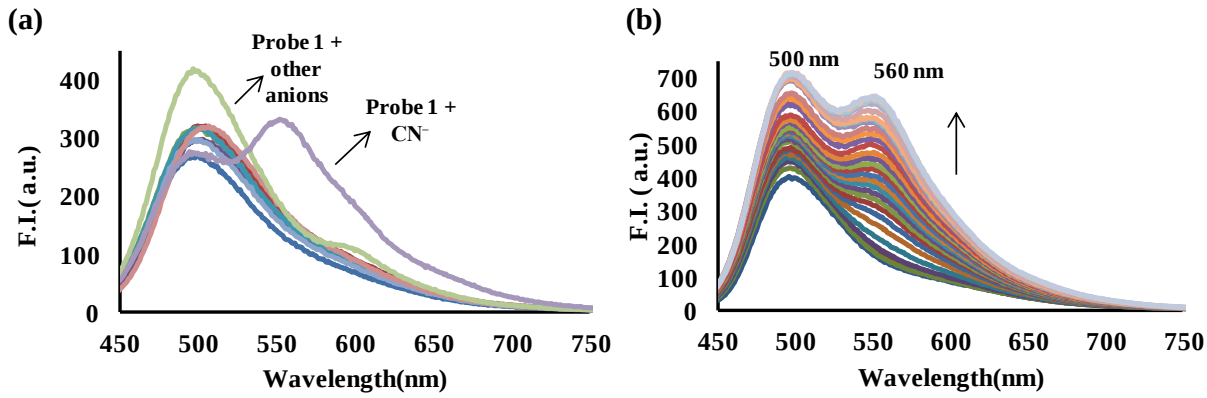


Figure 3.4 (a) Emission spectra of probe **1** (10µM, CH_3CN) upon addition of different anions **(b)** The effect of incremental addition of CN^- anion to probe **1**(10µM, CH_3CN) on emission spectra.

3.1.1.2 Interference Study

In order to check the sensitivity of probe **1** towards CN^- ions, the interference experiment was performed in the presence of other examined ions. The performed competitive experiment in the presence of Cl^-, I^-, F^-, Br^-, $H_2PO_4^-$, HSO_4^-, CN^-, OAc^-, SCN^- and PPi did not alter the spectral response of probe **1** towards CN^- ions (Figure 3.5). Thus it could be concluded that the probe **1** could selectively responds towards CN^- ions.

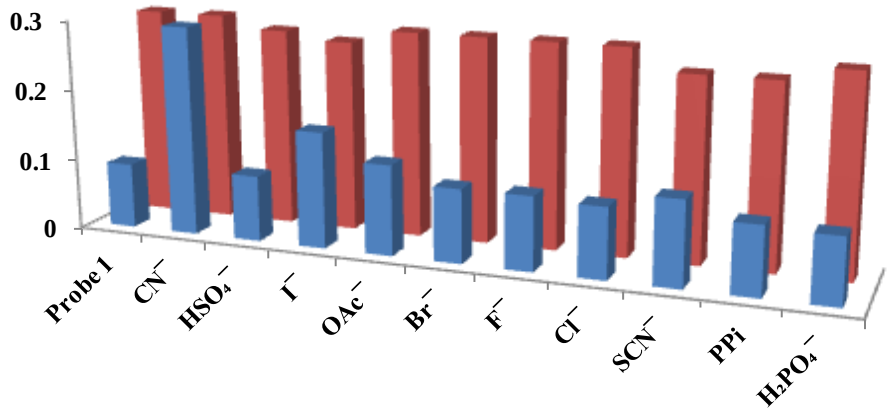


Figure 3.5 Blue bars represent the selectivity of probe **1** towards different ions. Red bars represent the competitive selectivity of probe**1**.CN^- in presence of other ions.

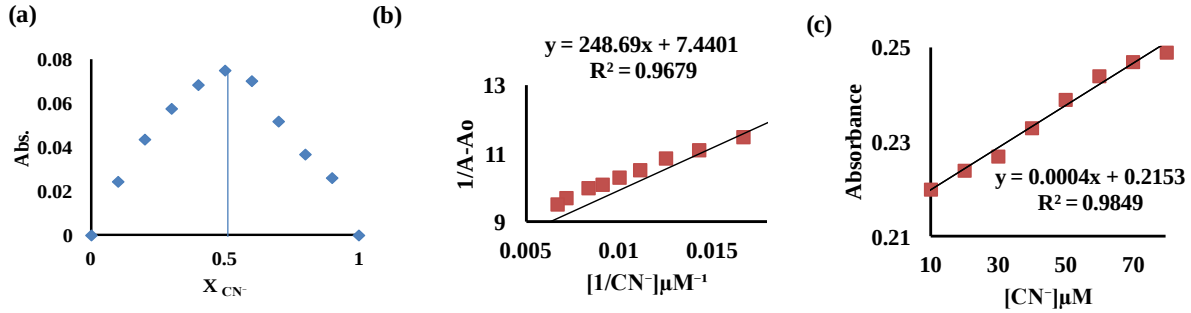


Figure 3.6 (a) Jobs plot of probe **1**.CN^- in CH_3CN solvent **(b)** Binding constant and **(c)** Limit of detection of probe **1**.CN^-

3.1.1.3 Stoichiometry, binding constant and limit of detection

In order to examine the binding ratio between probe **1** and CN^-, Jobs plot was performed. Identical formal concentrations (2.0×10^{-5} mol L^{-1}) of probe **1** and CN^- were used, volume were kept constant by varying in their volume in ratio. It was noted that the intensity maxima was observed for 0.5 mole fraction CN^- ions, and thus displaying the 1:1 (probe **1**: CN^-) stiochiometry (Figure 3.6). The binding constant for probe **1**.CN^- was determined to be 2.9×10^{8} M^{-1} showed almost linearly response with increasing CN^- concentration upto 400µM and limit of detection was found to be 7.5×10^{-7} M.

3.1.1.4 Spectra response towards common metal ions

The recognition behaviour of probe **1** (10µM) was examined in CH_3CN/H_2O (7:3,v/v) towards various metal ions such as Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+},

Pb^{2+}, Hg^{2+}. The presence of metal ions displayed insignificant change at absorption spectra of probe **1**. However, it was Cr^{3+} ions, which significantly increased the emission intensity of probe **1**. The presence of other metal ions did not alter the emission behaviour of probe **1**, whereas no such was observed in absorption spectra. Further, the quantitative estimation of Cr^{3+} ions was performed through titration experiment (Figure 3.7). On incremental addition of Cr^{3+} ions (0-100 µM) to probe **1**, the emission intensity of probe **1** was gradually increased at 500 nm. This hyperchromic effect could be due to coordination of Cr^{3+} ions to the phenolic oxygen and imine nitrogen and thus restricting the molecular motion. Also, the coordination of Cr^{3+} ions could be characterized due to intramolecular charge transfer (ICT).

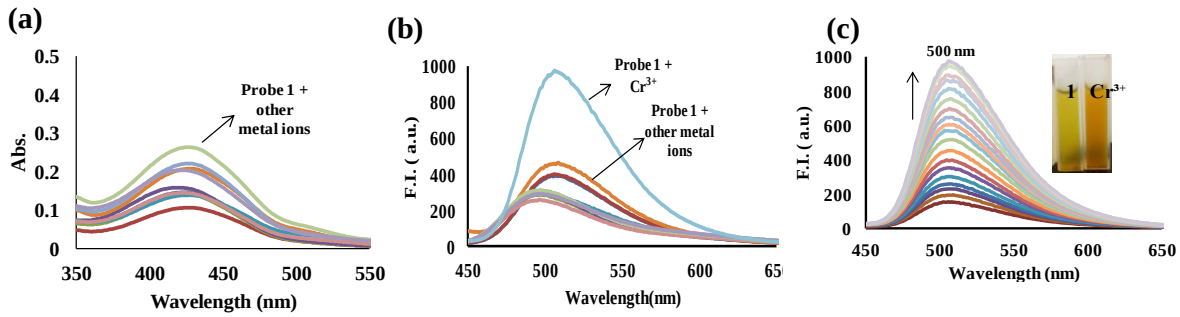


Figure 3.7 (a) Absorption spectra **(b)** Emission spectra of probe **1** (10µM, CH_3CN/H_2O:7:3) upon addition of different metals **(c)** The effect of incremental addition of Cr^{3+} to probe **1**(10µM , CH_3CN/H_2O, (7:3, v/v)) on emission spectrum.

3.1.1.5 Interference Study

In order to check the sensitivity of probe **1** towards Cr^{3+} ions, the interference experiment was performed in the presence of other examined ions. The performed competitive experiment in the presence of Na^{+}, Mg^{2+}, Al^{3+}, K^{+}, Ca^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+} ions did not alter the emission response of probe **1** towards Cr^{3+} ions (Figure 3.8). Thus it could be concluded that the probe **1** could selectively responds towards Cr^{3+} ions.

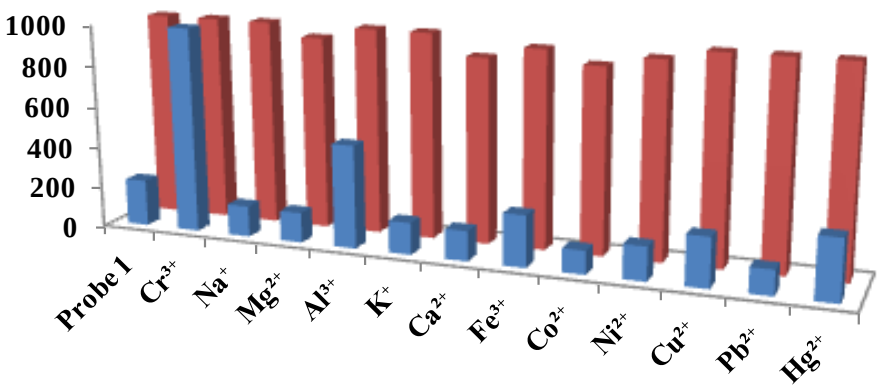


Figure 3.8 Blue bars represent the selectivity of probe **1** towards different ions and red bars represent the competitive selectivity of probe **1**.Cr^{3+} in presence of other ions.

3.1.1.6 Stoichiometry, binding constant and limit of detection

In order to examine the binding ratio between probe **1** and Cr^{3+}, Jobs plot was performed. Identical formal concentrations (2.0×10^{-5} mol L^{-1}) of probe **1** and Cr^{3+} were used, volume were kept constant by varying in their volume in ratio. From graph it was indicated that probe **1** bound to Cr^{3+} with binding stoichiometry of 1:1. The binding constant for probe **1**.Cr^{3+} was determined to be 6.0×10^{4} M^{-1} and also observed that intensity of fluorescence spectra rise with increasing the concentration of Cr^{3+} upto 101µM while limit of detection was detemined to be 7.6×10^{-9} M with fine linear relationship (Figure 3.9).

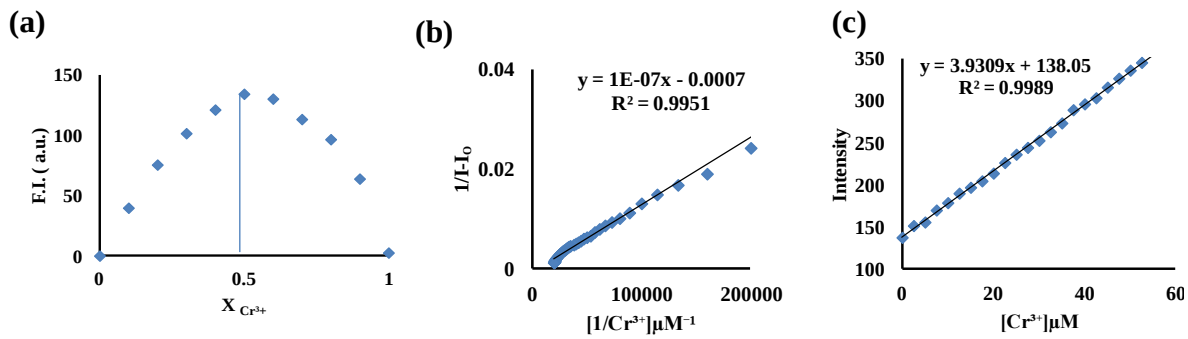


Figure 3.9 (a) Jobs plot of probe **1**.Cr^{3+} in (CH_3CN/H_2O (7:3,v/v)) solvent **(b)** Binding constant and **(c)** Limit of detection probe **1**.Cr^{3+}.

3.1.1.7 The Effect of pH

Consistency of probe **1** and its complex were detected with the help of pH studies. The pH alteration affects the charge dispersal on molecule due to protonation/deprotonation equilibrium of the –OH group of the ligand. Emission response of probe **1** and its Cr^{3+}

complex has been investigated in CH_3CN/H_2O (7:3, v/v). The results indicated that probe **1** is stable in range of 3.2-13.0 whereas probe **1.**Cr^{3+} complex are stable in range of 3.1-12.8.(Figure 3.10).

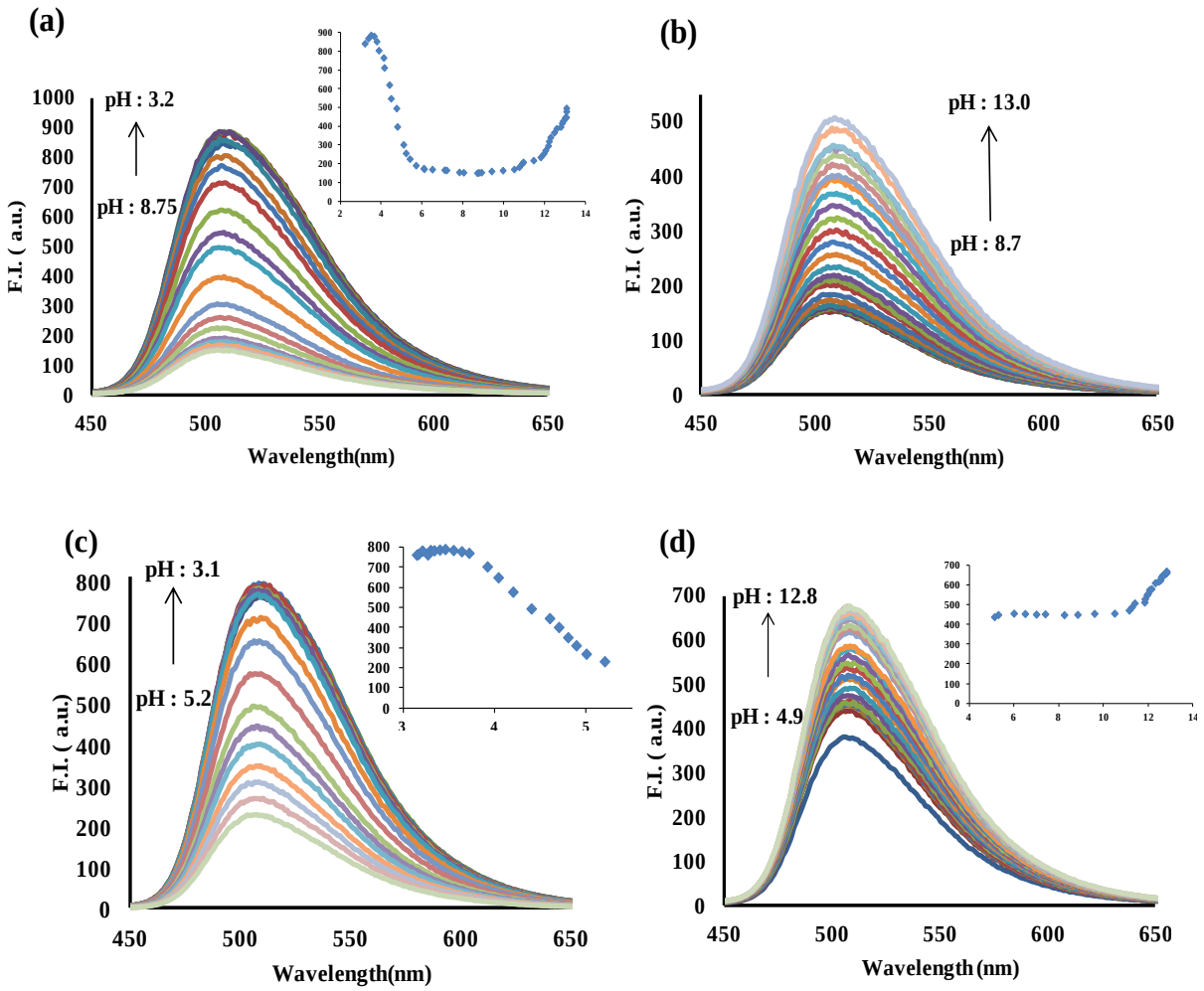


Figure 3.10 (a) Emission spectra of probe **1** by varying pH 8.75-3.2 **(b)** Emission spectra of probe **1** by varying pH 8.7-13.0 **(c)** Emission spectra of probe **1**.Cr^{3+} by varying pH 5.2-3.1 **(d)** Emission spectra of probe **1**.Cr^{3+} by varying pH 4.9-12.8.

3.2 Photophysical properties of probe 2

Photophysical properties of probe **2** were examined through steady state absorption and emission spectroscopy. The probe **2** (10 µM, CH_3CN) displayed the absorption and emission peak at 430 nm and 500 nm, respectively. Further, the absorption and emission spectra were measured in different polarity systems (Figure 3.11). It was noted that the probe **2** displayed a hyperchromic shift in absorption spectra on varying the polarity from hexane (non-polar) to DMSO (polar). Likewise, the emission spectra also displayed the red shift of ~45 nm on

changing the polarity from hexane to DMSO. This signified that the probe **2** was more stabilized in polar solvents in excited state. The significant red shifts in spectra displayed the presence of charge transfer phenomenon.

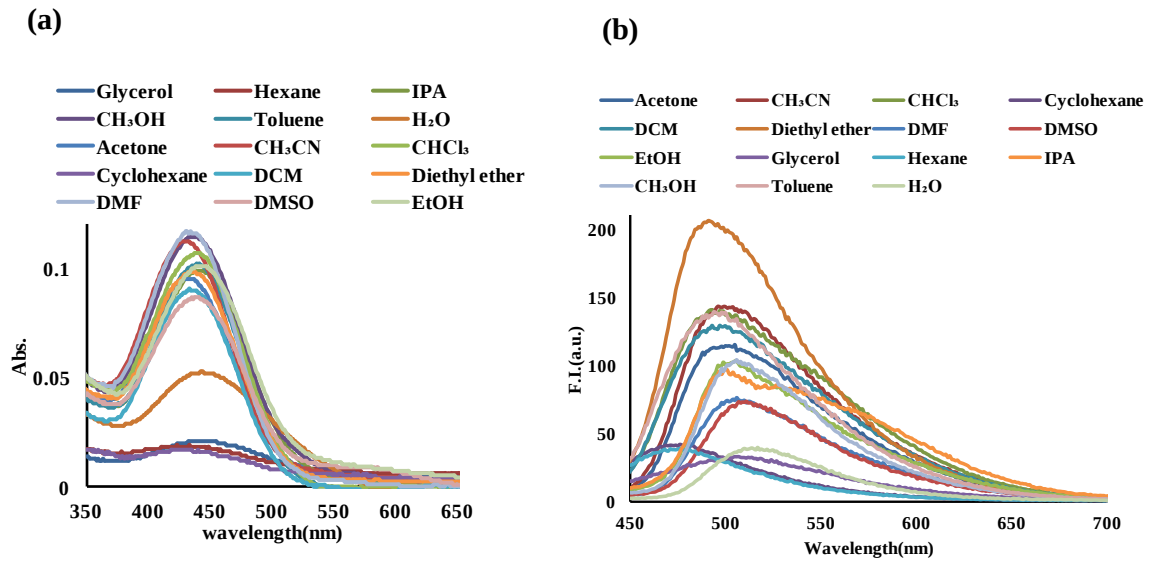


Figure 3.11 (a) Absorption and **(b)** Emission spectra in different solvent ranging from non-polar to polar on probe **2** (10µM).

3.2.1 Sensing properties of probe 2

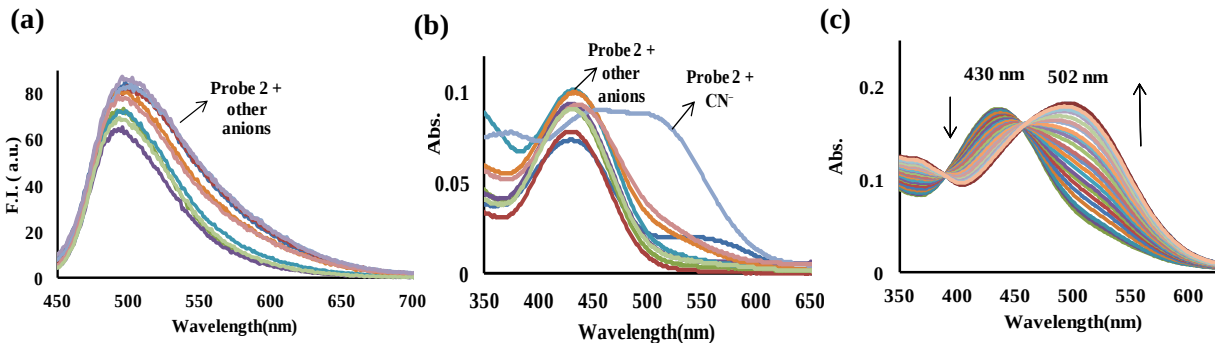


Figure 3.12 (a) Emission spectra and **(b)** Absorption spectra of probe **2** (10µM in CH_3CN/H_2O (9:1/v,v)) with absence and presence of different anions **(c)** The effect of incremental addition of CN^- to probe **2** (10µM in CH_3CN/H_2O (9:1/v,v)) on the absorption spectrum.

3.2.1.1 Spectral response towards anions

The recognition behaviour of probe **2** was examined in CH_3CN/H_2O (9:1/v,v) towards various anions like Cl^-, I^-, F^-, Br^-, HSO_4^-, CN^-, OAc^-, $H_2PO_4^-$, SCN^- and PPi. The presence of anions displayed insignificant change at absorption spectra of probe **2**, except for CN^- ions. On addition of CN^- anion, new band was observed at 502 nm, whereas no such was

observed in emission spectra. During the experiments, an instant and detectable visible colour change was observed from yellow to brown. Further, the quantitative estimation of CN^- ions was performed through titration experiment (Figure 3.12). The incremental addition of CN^- anion (0-2 x 10^{-2} µM) induced an isobestic point at 460 nm which clearly indicate a formation of new species without any intermediate.

3.2.1.2 Interference Study

In order to check the sensitivity of probe **2** towards CN^- ions, the interference experiment was performed in the presence of other examined ions. The performed competitive experiment in the presence of Cl^-, I^-, F^-, Br^-, $H_2PO_4^-$, HSO_4^-, CN^-, OAc^-, SCN^- and PPi did not alter the spectral response of probe **2** towards CN^- ions. However, HSO_4^- moderately reduced the fluorescence intensity of probe **2**.CN^- complex, but clearly recognized (Figure 3.13). Thus it could be concluded that the probe **2** could selectively responds towards CN^- ions.

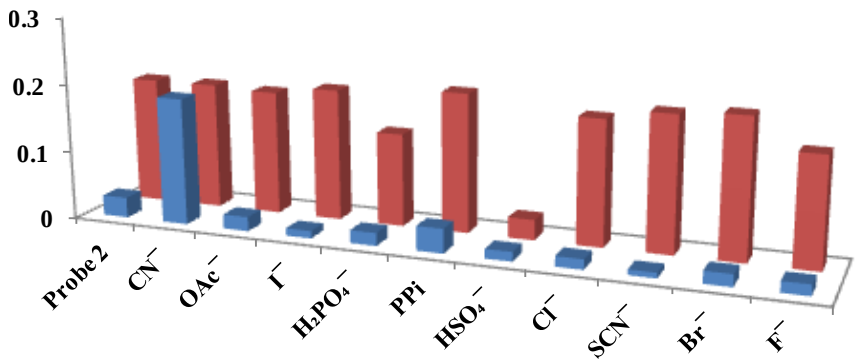


Figure 3.13 Blue bars represent the selectivity of probe **2** towards different ions. Red bars represent the competitive selectivity of probe **2**.CN^- in presence of other ions.

3.2.1.3 Stoichiometry, binding constant and limit of detection

In order to examine the binding ratio between probe **2** and CN^-, Jobs plot was performed. Identical formal concentrations (2.0×10^{-5} mol L^{-1}) of probe **2** and CN^- were used, volume were kept constant by varying in their volume in ratio. It was noted that the intensity maxima was observed for 0.5 mole fraction CN^- ions, and thus displaying the 1:1 (probe **2**: CN^-) stiochiometry. The binding constant for probe **2.**CN^- was determined to be 6.5×10^5 M^{-1} and limit of determined was calculated to be 6.0×10^{-8} M with fine linear relationship (Figure 3.14).

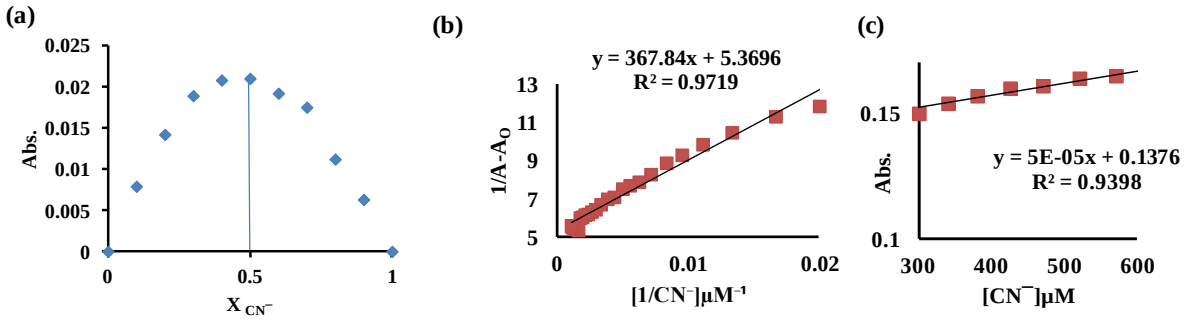


Figure 3.14 (a) Jobs plot of probe **2**.CN^- in CH_3CN/H_2O (9:1,v/v) solvent **(b)** Binding constant **(c)** Limit of detection of probe **2**.CN^-.

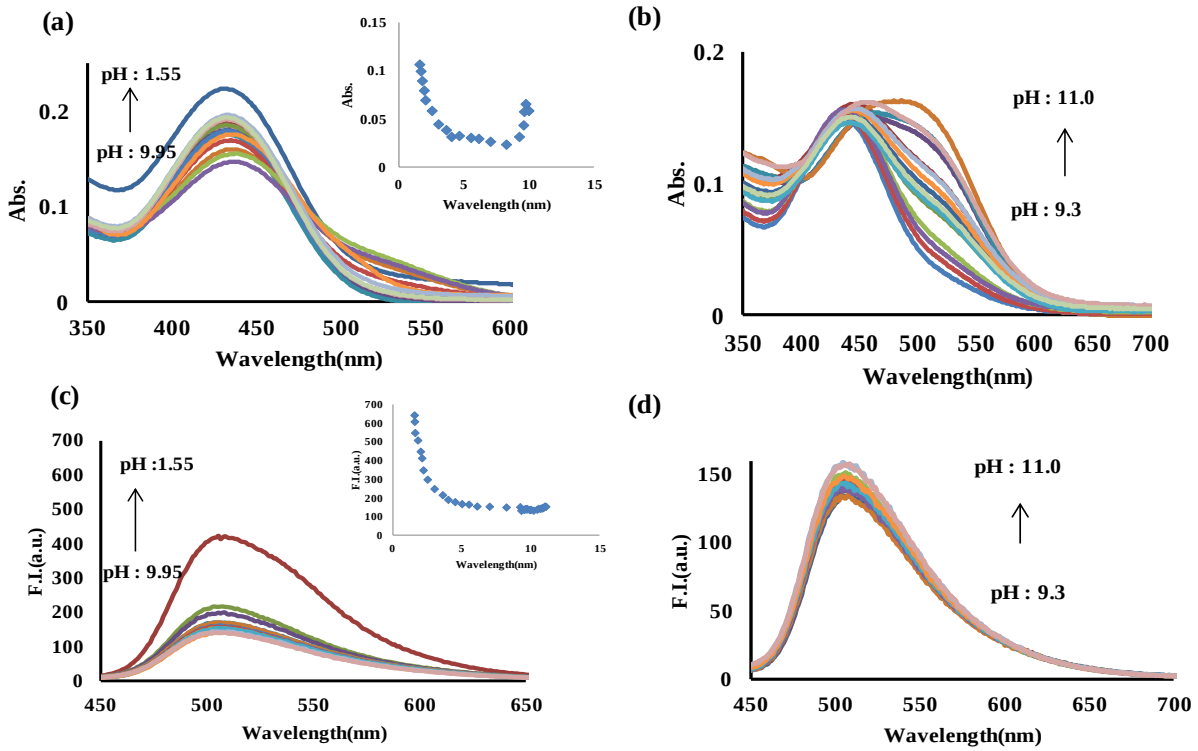


Figure 3.15 (a) Absorption spectra of probe **2** by varying pH 9.95-1.55 **(b)** Absorption spectra of probe **2** by varying pH 9.3-11.0 **(c)** Emission spectra of probe **2** by varying pH 9.95-1.55 **(d)** Emission spectra of probe **2** by varying pH 9.3-11.0.

3.2.1.4 Effect of pH

Consistency of probe **2** was detected with the help of pH studies. pH alteration effects the charge dispersal on molecule due to deprotonation / protonation equilibrium of the –OH group of the ligand. Emission and absorption response of probe **2** has been investigated in CH_3CN/H_2O (9:1, v/v). From absorption spectra, it was indicated that probe **2** is stable in range of 1.55-11.0 and in fluorescence spectra probe **2** was stable in pH range of 2.5-11.0. (Figure 3.15).

3.3 Mechanism

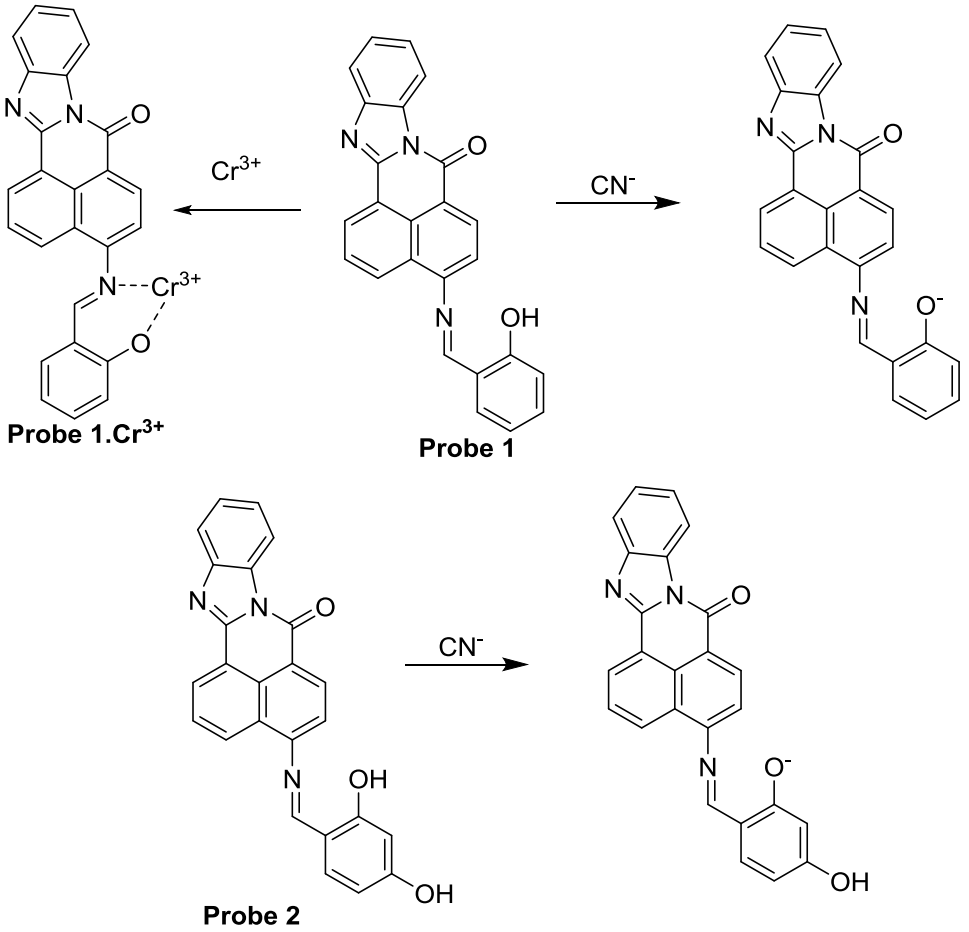


Figure 3.16 Possible mechanisms of interaction.

Probe **1** (10 µM, CH_3CN) displayed absorption and emission peak at 420 nm and 500 nm, respectively. While, the probe **2** (10 µM, CH_3CN) displayed absorption peak and emission peak at 430 nm and 500 nm, respectively. On increasing the polarity of medium, the probe **1** and probe **2** displayed a red shift of 35 nm and 45 nm, respectively. The increased red shift

for probe **2** was due to presence of –OH unit, which influence the intramolecular charge transfer. The probe **1** displayed the interaction of CN^- ions and Cr^{3+} ions through absorption and emission spectroscopy. The addition of CN^- ions abstract the proton transfer form probe **1** and thus lead to anionic form of probe **1**. The generated phenoxide ion push the electron density towards the naphthalimide core. The electron density shift lead the intramolecular charge transfer and the phenomenon was endorsed by observed absorption red shift of 40 nm. On the other hand, Cr^{3+} ions coordinate to phenolic oxygen and imine nitrogen. Thus, the complex formation restrict the molecular motion and thus, enhance the emission intensity at 500 nm. Next, the interaction of probe **2** towards CN^- ions could be elaborated based on the deprotonation of probe **2**. The phenomenon was endorsed by the absorption red shift of 72 nm (Figure 3.16).

3.4 Conclusion

In this work, naphthalimide based derivatives was easily synthesized used as chromo-fluorogenic sensor. Probe **1** showed absorption peak at 420 nm and emission peak at 500 nm, detects selectively CN^- ions through absorption and emission spectroscopy. On addition of CN^-, instant colour change was observed along with red shift of 40 nm. Probe **1** exhibits linear response towards CN^- in the concentration of 2.9×10^{8} M^{-1} and detection limit of 7.5×10^{-7} M. On the other hand, probe **1** also detects Cr^{3+} ions through emission spectroscopy. On addition of Cr^{3+}, colour change was observed along with formation of two emission bands at 500 and 560 nm. Probe **1** exhibits linear response towards Cr^{3+} in the concentration of 6.0×10^{4} M^{-1}, detection limit of 7.6×10^{-9} M. Probe **2** showed absorption peak at 430 nm and emission peak at 500 nm. Thus, probe **1** act as chromo-fluorogenic sensor. On addition of CN^-, formation of new band at 502 nm along with red shift of 72 nm. Probe **2** exhibits linear response towards CN^- in the concentration of 6.5×10^{5} M^{-1} and detection limit of 6.0×10^{-8} M. Thus, probe **2** act as chromogenic sensor.

References

1. J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons, 2013.
2. J. L. Atwood, *Comprehensive Supramolecular Chemistry II*, Elsevier, 2017.
3. H.-J. Schneider and A. K. Yatsimirsky, *Principles and Methods in Supramolecular Chemistry*, Wiley Chichester, 2000.

4. K. Ariga and T. Kunitake, *Supramolecular Chemistry-Fundamentals and Applications: Advanced textbook*, Springer Science & Business Media, 2006.
5. G. R. Desiraju, *Angew. Chemie International Edition in English*, 1995, **34**, 2311-2327.
6. J. P. Desvergne and A. W. Czarnik, *Chemosensors of Ion and Molecule Recognition*, Springer Science & Business Media, 2012.
7. M. E. Moragues, R. Martínez-Manez and F. Sancenon, *Chem. Soc. Rev.*, 2011, **40**, 2593-2643.
8. P. S. Sharma, Z. Iskierko, A. Pietrzyk-Le, F. D'Souza and W. Kutner, *Electrochem. Commun.*, 2015, **50**, 81-87.
9. T. W. Bell and N. M. Hext, *Chem. Soc. Rev.*, 2004, **33**, 589-598.
10. F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407-418.
11. J. L. Way, *Annu. Rev. Pharmacool. Toxicol.*, 1984, **24**, 451-481.
12. J. B. Vincent, *The J. Nutr.*, 2000, **130**, 715-718.
13. R. Shrivastava, R. Upreti, P. Seth and U. Chaturvedi, *FEMS Immunol Med Microbiol*, 2002, **34**, 1-7.
14. J. F. Zhang, S. Kim, J. H. Han, S.-J. Lee, T. Pradhan, Q. Y. Cao, S. J. Lee, C. Kang and J. S. Kim, *Org. Lett.*, 2011, **13**, 5294-5297.
15. J. Shi, Y. Wang, X. Tang, W. Liu, H. Jiang, W. Dou and W. Liu, *Dyes Pigm.*, 2014, **100**, 255-260.
16. J. Fan, P. Zhan, M. Hu, W. Sun, J. Tang, J. Wang, S. Sun, F. Song and X. Peng, *Org. Lett.*, 2013, **15**, 492-495.
17. R. Tandon, V. Luxami, H. Kaur, N. Tandon and K. Paul, *Chem. Rec.*, 2017, **17**, 956-993.
18. P. V. Krasteva, M. D. Dimitrova, N. I. Georgiev and V. B. Bojinov, *JCTM*, 2018, **53**.
19. K. Ramasamy and S. Thambusamy, *Sens. Actuators, B*, 2017, **247**, 632-640.
20. N. I. Georgiev, M. D. Dimitrova, Y. D. Todorova and V. B. Bojinov, *Dyes Pigm.*, 2016, **131**, 9-17.
21. P. Alaei, S. Rouhani, K. Gharanjig and J. Ghasemi, *Spectrochim. Acta, Part A*, 2012, **90**, 85-92.
22. J.-H. Xu, Y.-M. Hou, Q.-J. Ma, X.-F. Wu and X.-J. Wei, *Spectrochim. Acta, Part A*, 2013, **112**, 116-124.
23. L. Kang, Y.-T. Liu, N.-N. Li, Q.-X. Dang, Z.-Y. Xing, J.-L. Li and Y. Zhang, *J. Lumin.*, 2017, **186**, 48-52.

24. S. O. Aderinto, Y. Xu, H. Peng, F. Wang, H. Wu and X. Fan, *J. Fluoresc.*, 2017, **27**, 79-87.
25. Y. Wang, P.-D. Mao, W.-N. Wu, X.-J. Mao, X.-L. Zhao, Z.-Q. Xu, Y.-C. Fan and Z.-H. Xu, *Sens. Actuators, B*, 2017, **251**, 813-820.
26. Y. Xu, S. Mao, H. Peng, F. Wang, H. Zhang, S. O. Aderinto and H. Wu, *J. Lumin.*, 2017, **192**, 56-63.
27. D. Liu, J. Qi, X. Liu, Z. Cui, H. Chang, J. Chen and G. Yang, *Sens. Actuators, B*, 2014, **204**, 655-658.
28. C. Hou, A. M. Urbanec and H. Cao, *Tetrahedron Lett.*, 2011, **52**, 4903-4905.
29. R. Goel, S. Sharma, K. Paul and V. Luxami, *Sens. Actuators, B*, 2017, **246**, 776-782.
30. S. A. Yoon, J. Lee and M. H. Lee, *Sens. Actuators, B*, 2018, **258**, 50-55.
31. S. Thavornpradit, J. Sirirak and N. Wanichacheva, *J Photoch Photobio A*, 2016, **330**, 55-63.

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