Synthesis and Photophysical Properties of Symmetrical Phenolphthalein Derivatives

A

Thesis submitted

In the partial fulfilment of the requirement for the degree of

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IN

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Submitted By

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UNDER THE SUPERVISION OF

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ENGINEERING AND TECHNOLOGY,

PATIALA-147004

2018

CERTIFICATE

I hereby declare that the thesis entitled **"Synthesis and Photophysical Properties of Symmetrical Phenolphthalein Derivatives"** is an authentic record of my work carried out as requirements for the award of degree of **Masters of Science** in **Chemistry** at **Thapar Institute of Engineering and Technology, Patiala** under the supervision of **Dr. Vijay Luxami**, Associate Professor, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala during January, 2018 to June, 2018. No part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

Manveer Kaur

Date: 29 / 6 /2018

MANVEER KAUR

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

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After an intensive period of six months, today is the day writing this note of thanks is the finishing touch on my dissertation. It has been a period of intense learning for me, not only in the scientific arena but also on a personal level. I would like to reflect on the people who have supported and helped me so much throughout this period.

I would first like to thank my supervisor, **Dr. Vijay Luxami,** who expertly guided me through my research project. Her unwavering enthusiasm for chemistry kept me constantly engaged with my research, and providing me with an excellent atmosphere for doing research.

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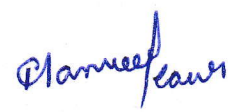
In the end, I want to thank my family especially my parents for being pillars of strength and always being so supportive of me and encouraging me with their love and best wishes.



Manveer Kaur

ABSTRACT

Novel phenolphthalein based compounds was synthesized and potentially used for detection of Hg^{2+} ions in CH_3CN as solvent calorimetrically. Compound **3** exhibited absorption maxima at 290 nm, which showed a red shift to 480 nm in CH_3CN. **3** displayed fast colour change from colorless to reddish brown in the presence of Hg^{2+} ions. The binding constant for **3**.Hg^{2+} was found to be 3.2×10^4 M^{-1}. The lowest detection limit of **3** for Hg^{2+} ions was determined to be 7.2×10^{-8} M. Compound **5** showed three absorption peaks at 480 nm, 350 nm and 240 nm. Compound **5** also showed strong emission at 550 nm.

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1. INTRODUCTION

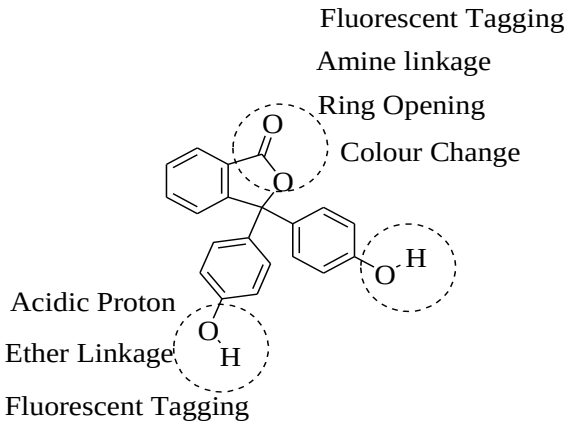
Supramolecular chemistry is the domain of chemistry that's created from a specific range of assembled molecular small units. There are several forces that are accountable for the spatial organization which change from weak (intermolecular forces or H-bonding) to strong (covalent bonding) provided that the degree of electronic coupling remains small between the molecular element and with relation to energy parameters of the component.[1] "In distinction to molecular chemistry that is widely based mostly upon the covalent bonding of the atoms, it relies upon intermolecular interactions, i.e. of the association of two or numerous building blocks that are occupied together by the intermolecular bonds"."Supramolecular chemistry is characterized as chemistry "beyond the molecule". In these molecules, information is reserved in the form of structural peculiarities.

The simplest example of supramolecular structure is a host-guest complex. The host (receptor) is consistently a large organic molecule alongside a cavity possessing distinctive binding sites in centre and a guest is neutral or charged species that fits precisely in the host. This type of interaction leads to the formation of Supramolecule.[2] The host, respectively, is known as chemosensor and guest is recognized as analyte. Chemosensor is a molecule of abiotic region, which by any mode of energy endure change in its own state and characteristics such as the intensity and wavelength, along with the appearance of the new absorption peaks. It binds with various analytes by covalent or non-covalent bonding to generate colour change and optical properties. This transformation is used to detect and investigate the chemical stimuli.[3] Chemosensors are that which converts chemical signal into an action potential. Therefore it is also called as Chemoreceptor. It binds to a metal such as chromophore or fluorophore. During interactions, metal ions generate a signal with binding units which results in modification of absorption wavelength or emission intensity. Fluorescent chemosensors have high sensitivity that has been developed to be a useful tool to sense biological important species.

Phenolphthalein is a powerful pH indicator, and it has two binding types' sites as phenolic group and spirolactam ring. It enhances the color from colorless to pink depending on the pH conditions.In past few years, phenolphthalein has been used chemosensor for metal ions, thiols detection (discussed in literature section). The derivatives facilitated the naked-eye detection by changing the colour from colourless to pink. There are other fluorescent moieties were tagged with the phenolphthalein showed an emission and absorption response. Also, the nitrobenzofurazan is known to be electron rich, fluorescent moiety. Due to high sensitivity of

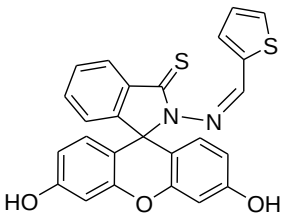
NBD to the environmental changes and high fuorescence quantum yields, it is extensively used as a fuorophore for sensing and imaging in life sciences.

In the recent times thiolysis of NBD (nitrobenzofurazan) ether has been utilized for H_2S detection.[4-9] Also, thiolysis of NBD based ether is more suitable in aqueous medium, and advanced the thiolysis of (dinitrophenyl) DNP for H_2S probes.[10-14] In recent times, a FRET-based H_2S detector was invented based on thiolysis of NBD amine, that showed extraordinary selectivity towards H_2S over the cysteine molecules.[4] Some new fluorescent probes based on the thiolysis of NBD ether was discovered that could be used to detect H_2S with more reaction rate, but these NBD ether probes exhibit lower selectivity between Cysteine and H_2S.[15]



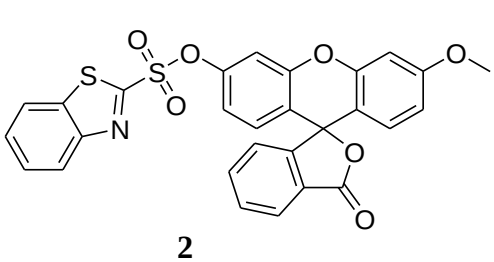
2. LITERATURE REVIEW

Feng *et al*. designed a completely unique water-soluble fluorescent detector **1** based on thio oxofluorescein derivative.[16] Probe **1** showed high selectivity and sensitivity towards Hg^{2+} according to the absorption and fluorescence spectra studies. Additionally, the probe **1** has been used as a naked-eye indicator for Hg^{2+}.Within the presence of only 2.0 equivalents of Hg^{2+} probe **1** showed almost 37-fold fluorescent enhancement at 529 nm and the detection limit was determined at around 39 M. The absorption spectra of probe **1** enhanced gradually upon addition of Hg^{2+} to it**.** It displayed a well-defined spectrum at 509 nm upon addition of Hg^{2+} ions with colour modification from colourless to red-brown.



1

Zhang *et al.* developed two sulfonyl benzothiazole-based fluorescent probes **2** and **3** for the detection of biothiols (homocysteine, cysteine and glutathione).[17] UV-Visible and fluorescence spectra studies showed that probe **2** and **3** exhibited excellent selectivity and sensitivity towards biothiols over different analytes. These probes showed fluorescence enhancements at 480 and 490 nm within the presence of biothiols. The fluorescence intensity (at 518 nm) enhanced adequately when **2** and **3** were present in the solution.



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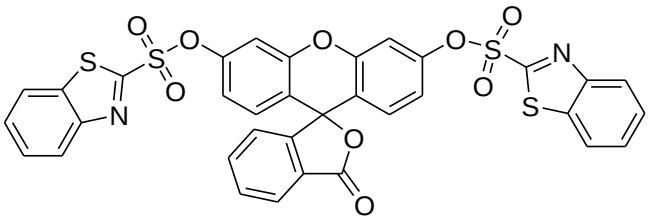
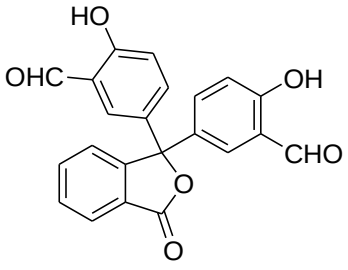


3

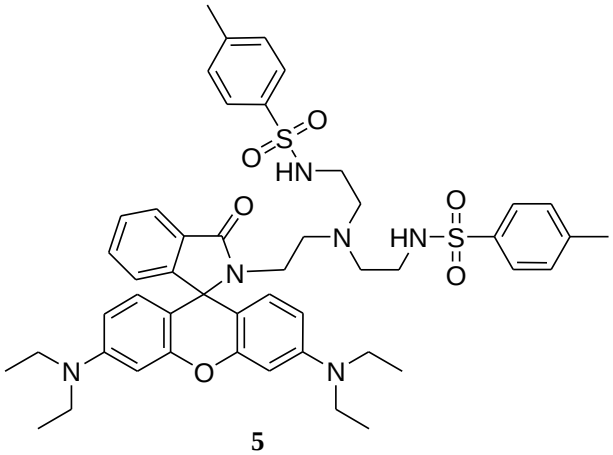
Guo *et al.* incorporated the phenolphthalein based probe **4** that is used to turn on fluorescent for the detection of Ho^{3+} (holmium ion).[18] Probe **4** showed high selectivity and sensitivity towards the Ho^{3+} ions over different metal ions. With an incremental addition of Ho^{3+} solution to probe **4**, fluorescence intensity was found to be increased at 480 nm. On addition of 260 μM Ho^{3+} to the solution containing probe **4,** more than 25-fold increase in the fluorescence intensity at 526 nm was ascertained.



4

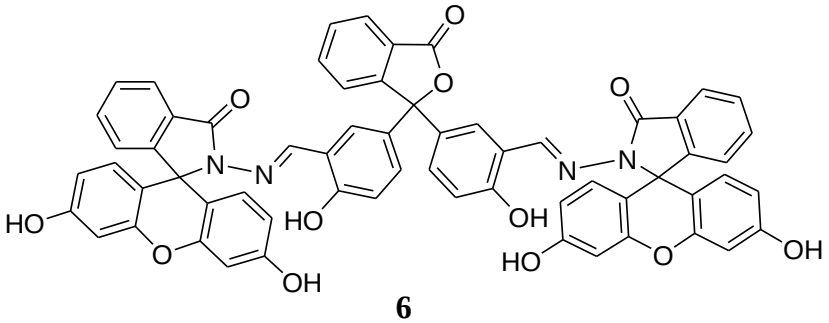
Lee *et al.* designed a completely unique tren-based tripodal probe **5** having a rhodamine and two tosyl groups.[19] Detector**5** displayed high selectivity and sensitivity towards Hg^{2+} according to absorption and fluorescence spectra studies. Addition of a Hg^{2+} ions to a solution of **5** gave a visual colour amendment as well as considerably enhanced fluorescence whereas alternative ions including Zn^{2+}, Cu^{2+}, Ca^{2+},Co^{2+}, Mg^{2+}, Cs^{+} and Na^{+} induced no or much smaller color/spectral changes. Upon addition of 10 equivalents of Hg^{2+} to the solution of Probe **5**, a new absorption band focused at 556 nm was noticed. When 10 equivalents of

Hg^{2+} ions were added to the solution containing probe, fluorescence enhancement at 575 nm (OFF-ON) was noted but other metal ions(Ba^{2+}, $Ca^{2+}$and Cu^{2+}) did not induce any change .



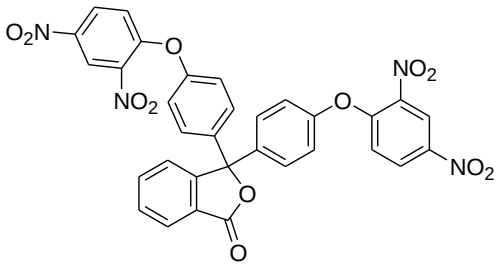
5

Erdemir *et al.* designed a completely unique phenolphthalein- fluorescein based chemosensor **6**.[20] Probe **6** exhibited a high selectivity and sensitivity towards Zn^{2+} and Hg^{2+} as a dual channel probe in EtOH-H_2O over the different cations and the significant fluorescene enhancement was noticed in the presence of Zn^{2+} and Hg^{2+} centred at 500 and 520 nm. The absorption spectra of probe **6** focused peaks at 278 and 342 nm indicating π-π* and n-π* transitions.



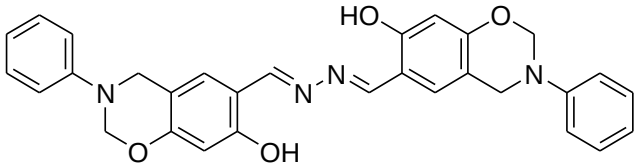
6

Kim *et al*. incorporated a phenolphthalein-based colorimetric detector **7** having a dinitrobenzene group as a thiophenol (PhSH)-selective chemodosimeter.[21] The addition of PhSH to the solution of **7,** undergo a colour modification from colourless to pink colour. According to its absorption spectra, only thiophenol persuade a new absorption peak which is focused at 547 nm and also red shift of 305 nm to 344 nm was noticed.



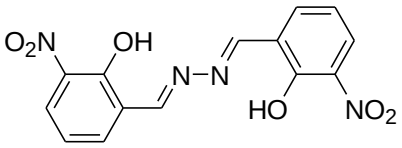
7

Mohamed *et al*. undergo Mannich condensation reaction in 1,4-dioxane to synthesized compound **8** by using aniline and paraformaldehyde with 1,2-bis(2,4-dihydroxybenzylidene)hydrazine.[22] The benzoxazine/zinc ions complexes that is made by mixing **8** with zinc salt [$Zn(ClO_4)_2$] not solely influenced the thermal properties due to physical cross linkage via metal–ligand interactions however also promote the ring-opening chemical process and therefore lowering the curing temperature from 213 to 184 ^oC. From fluorescence results, in THF, compound **8** and azine-BZ/ $Zn(ClO_4)_2$ were non-emissive. On addition of water, their fluorescence enhanced gradually. Monomer **8** displayed a well-defined spectrum at 370 nm in THF (1×10^{-4} M) upon addition of zinc ions.

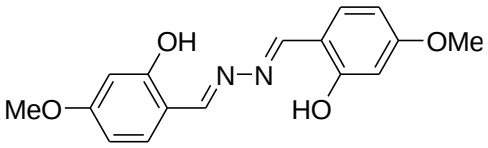


8

Ma *et al*. synthesized a series of luminescent azines **9 (a) and 9 (b)** that exhibit strong green, blue and red fluorescence with large Stokes shifts in both solid and water medium.[22] UV-Vis spectrum of **9 (a)** in water and in solid medium is 364 nm and 504 nm and its emission band focused at 565 nm and 566 nm whereas **9 (b)** shows absorption peak focused at 362 nm and 340 nm and emission spectra at 507 nm and 508 nm.

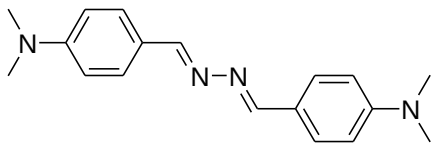


9 (a)

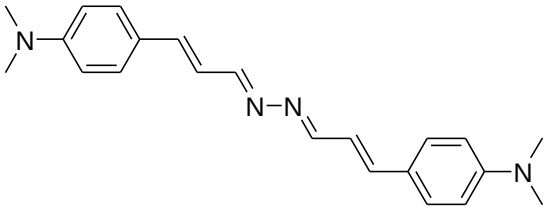


9 (b)

Ray *et al*. synthesized azine molecules **10**and **11** via Schiff base condensation that showed an absorption band due to intra-ligand charge transfer (ILCT).[23] The presence of Ag^+ ions to compound **10** and **11** in tetrahydrofuran, metal gets cross-linked with azine moiety which results in high intensity emission (~400 fold) whereas Cu^{2+} shows a small transformation of emission. Compound **10** in THF shows absorption peak focused on 428 nm. For **11**, the ILCT band seems at 384 nm.

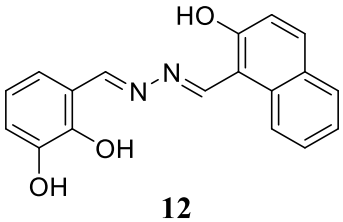


10

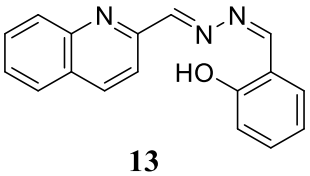


11

Saini *et al*. reported a combination of two characteristic properties of an azine **12**: in a solid-state crystalline material, it exists as extremely versatile and elastic behaviour.[24] Moreover, within the solution state, it serves as an extremely sensitive and selective Al^{3+} detector having a detection limit of about 42 nM. The UV spectra of probe **12** in an ACN was governed by the two absorption peaks focused at 325 and 382 nm, indicating π–π* and n–π* transitions. Severally, the increment of Al^{3+}as $Al(NO_3)_3.9H2O$ leads to a continuous decrease of absorption maxima at 325 nm. This provides strong proof for enhanced binding of **12** towards Al^{3+} ions. The emission spectra of **12** showed a weak fluorescence peak at 500 nm.

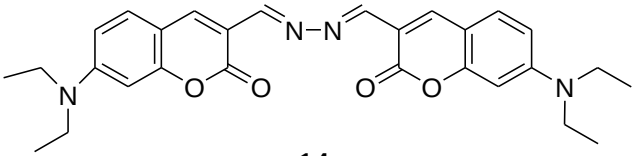


12



13

Pie *et al*. designed a completely unique chemosensor **13** that exhibited both colourimetric and "turn-on" light responses for CN^- (cyanide ion) in DMSO/H_2O.[25] The detector **13** was successfully utilised to observe cyanide ion in bitter almond. The light sensing capability of **13** was examined with numerous anions (F^-, Cl^-, I^-, CO_3^{2-}, PO_4^{3-}, NO_2^-, $H_2PO_4^-$, ClO_4^-, SCN^- and CN^-). Upon 50 equivalents numerous anions were severally added into a solution of **13**, solely CN^- induce a dramatic colour modification from colourless to yellow, that can be simply seen by the naked eyes. A noticeable red shift was noticed from 350 nm to 435 nm in its absorption spectra. Compound **13** exhibited a weak fluorescence peak at 440 nm with a detection limit of 4.5×10^{-7} M. Further increment of 50 equivalents of CN^- into it, a significant fluorescence response was noted and band shifted to 516 nm with a colour modification from colourless to green under an ultraviolet lamp.

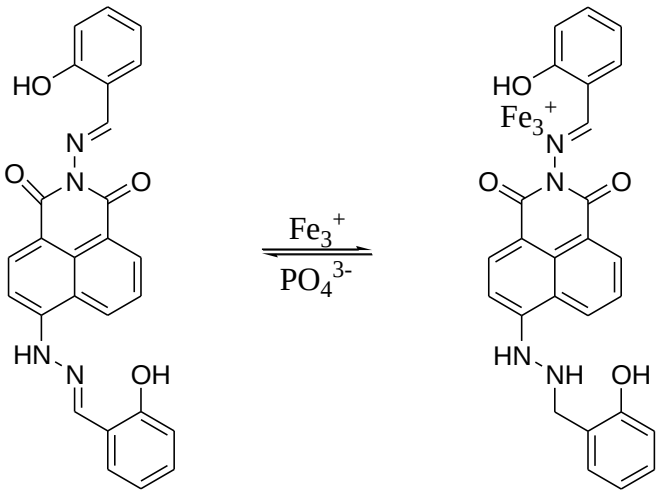


14

Sheng *et al*. designed azine derivatives as probe **14** that has been used as a colourimetric sensor for Hg^{2+}.[26] The absorption maximum of probe **14** presents a large red shift from 490 nm to 565 nm within the presence of Hg^{2+}. The amendment in colour is simply observed by naked eye, whereas alkali metals and other alternative metal cations like Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+},Cu^{2+}, Fe^{3+}, Pb^{2+} and alkaline earth metal cations don't induce such a modification. From the spectrum of probe **14** in a solvent CH_3CN:H_2O, it had been noticed that an intensive

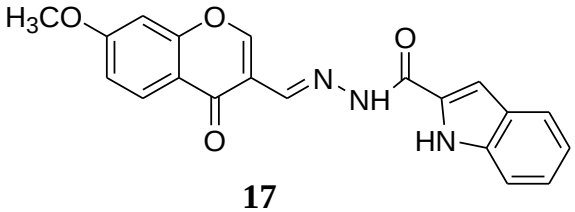
absorption band appeared in visible region pointed at 490 nm, that may be allotted to the change transfer absorbance.

Jiang *et al.* reported Fe(III) complex as Schiff base **15** and **16** which showed turn-on light sensors for PO_4^{3-}.[27] In each solution and solid-state film, phosphate anions like HPO_4^{2-}, $H_2PO_4^-$ displayed high selectivity and sensitivity.

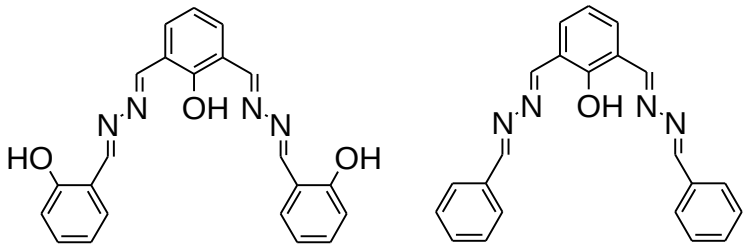


15 **16**

Long *et al.* incorporated a Schiff-base **17** that exhibited fluorescence enhancement and fluorescence turn "OFF–ON" for Al^{3+} ion in an alcohol solution.[28] The probe showed visible light excitation (423 nm) and emission (507 nm) colour modified from colourless to yellow-green upon binding of Al^{3+}. No such result on the visible light was investigated by different metal ions. The detection limit of the sensor **17** towards Al^{3+} was low as $5x10^{-8}$ M that was satisfactory for observation Al^{3+} levels in physiological and environmental systems.



17

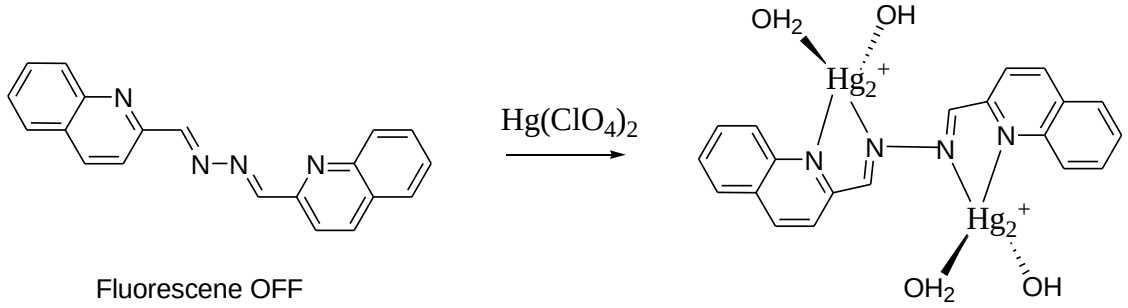


18a **18b**

Nandi *et al.* developed an azine primarily based sensible probe **18a** and **18b** for the naked eye

and fluorescence identification of iodide ions.[29] It shows acute red change within the presence of I^- in THF. Upon excitation at 390 nm, it shows the emission spectra at 636 nm in DMSO and THF and CH_3OH.

Suresh *et al*. designed azine-based probe **19** which is found to indicate outstanding peculiarity to the Hg^{2+} ion in the aqueous media over another metal ions.[30] Coordination of **19** towards Hg^{2+} prompt a detectable modification in colour and a turn-on light response. The UV spectra of **19** in THF/H_2O displayed two main absorption bands at λ_{max} 265 nm and 330nm. Further addition of Hg^{2+} to the solution containing probe **19**, new absorption spectra was noted and band shifted to 370 nm.

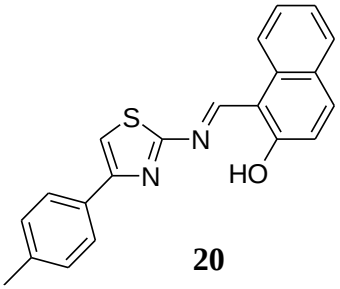


Fluorescene OFF

19

Fluorescene ON

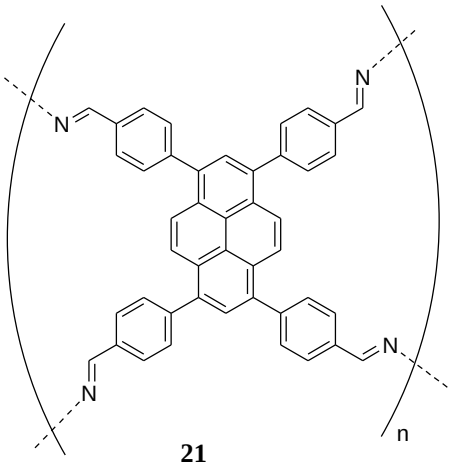
Kim *et al.* developed a brand new colourimetric detector **20** that showed particularly colourimetric responses to CN^- and S^{2-} in the aqueous solution.[31] Transparent colour modification of **20** from yellow to colourless was determined with CN^- via a nucleophilic addition process, whereas S^{2-} was sensed via a deprotonation mechanism with a definite colour modification from yellow to the orange. UV spectrum of **20** implied abroad band within the range of 375 to 500 nm. Further increment of CN^- to a solution containing **20** will lead to gradual decrease in its absorption band at 423 nm and reached a minimum upon 45 equivalents of CN^-.



20

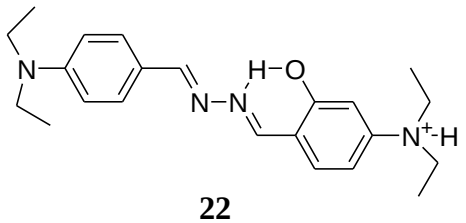
Dalapati *et al*. developed a brand new probe **21** underneath solvothermal atmosphere yields extremely crystalline 2-D covalent organic frameworks.[32] Pyrene units fill at the vertices and

therefore the diazabutadiene linker locates at the edges of rhombic-shaped polygonal shape sheets. These azine-joined frameworks have the characteristic feature of everlasting porosity with the high surface area and possess superior chemical stability. These frameworks are very luminescent, while azine units act as open docking sites for H-bonding interactions. The absorption spectrum of **21** distributed in ACN displayed a broad absorption peak focused at 470 nm, that can be assigned to $S_0 \rightarrow S_1$ transitions. However, **21** displayed the absorption peak at 415 nm. Upon excitation at 415 nm, probe **21** in ACN gives out a blue-green colour focused at 462 nm. Upon excitation at 470 nm, compound gives a yellow luminescence with a shifted band focused at 522 nm.



21

Jana *et al*. developed a Schiff bases moieties **22** and **23** and their photophysical characteristics like ICT (intramolecular charge transfer) and ESIPT (excited state proton transfer) processes were described.[33] **22** shows the wide absorption band at ~395 nm in non-polarsolvents. However, the same absorption band seems at ~410 nm in polar aprotic and protic solvents. **23** showed the same however slightly red-shifted absorption band at ~407 nm in non polar solvents like CCl_4. **23** shows a similar absorption band focused at 415 nm.



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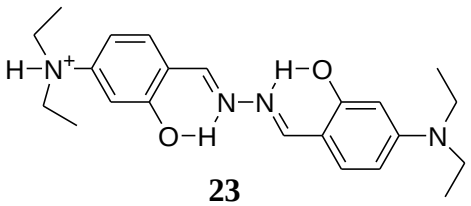
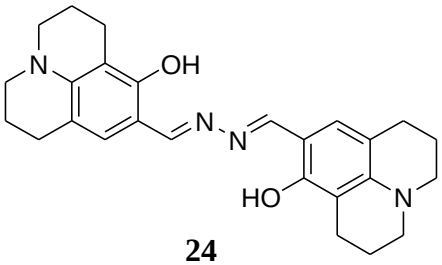


23

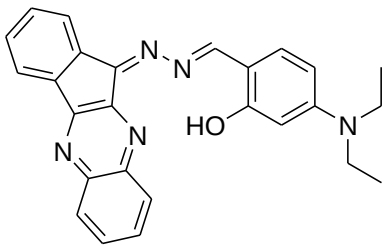
Narayanaswamy *et al*. have designed new aldazine-based detector **24** that showed high selectivity and sensitivity towards Cu^{2+}.[34] This was synthesized by the condensation of N-

Ndiethylamino-salicylaldehyde and 8-hydroxyjulolidinal with hydrazine. The spectrum of **24** shows the absorption band at 445 nm in the presence of Fe^{3+}. Further addition of Fe^{3+} to the solution containing Probe **24**, new absorption spectra was noted and band shifted to 575 nm with a colour modification from yellow to violet.



24

Balamurugan *et al*. developed azine derivatives **25** and **26** from ninhydrin and light sensing studies of these derivatives were performed with numerous anions and cations.[35] **25** and **26** displayed extremely selective colour modification from orange/yellow to violet/ blue for Cu^{2+} ions. The probe showed sensible binding constants. According to UV–Visible spectra, upon addition of Cu^{2+} to **25**, the band at 500 nm attributed to n-π* transition of the detector was altered to 570 nm. Correspondingly, the band at 430 nm (due to n-π* band of the probe) was altered and a new band fashioned at 560 nm equivalent to d-d transition within the **26**.



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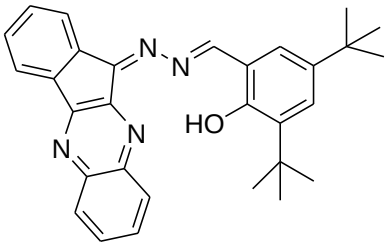


26

3. RESEACH GAP IN STUDIES

During the literature survey, we have found reports on phenolphthalein derivatives, Schiff bases which were used as cationic and anionic sensors. Also, we have observed gap in research for where symmetrical phenolphthalein derivatives were not explored as chemosensors. On the other hand, NBD moiety known to be electron rich and thus, has tendency to transfer energy to acceptor. There is no report, where NBD was incorporated to phenolphthalein. Based on the research gap, following objectives were designed.

4. OBJECTIVE

To address the research gap, we approached the synthesis of symmetrical phenolphthalein based Schiff bases, and incorporation of NBD on phenolphthalein. Therefore, following objectives were proposed:

1. Synthesis of symmetrical phenolphthalein based Schiff bases.
2. Incorporation of NBD moiety on phenolphthalein.
3. Photophysical studies of synthesized compounds and their sensing ability for common metal ions and anions.

5. EXPERIMENTAL

5.1 Materials and Instruments

All the chemicals and reagents used for were of spectroscopic grade purchased from Sigma-Aldrich Chemical Ltd., Loba Chemie and Spectrochem Ltd. and were used without any supplementary purification. The improvement of the reaction was monitored by thin-layer chromatography (TLC) technique. At ambient temperature, ^{1}H NMR and ^{13}C NMR spectra were reported on JEOL ECS-400 MHz spectrometer in $CDCl_3$ or/and DMSO (d_6) with TMS as an internal reference. All chemical shifts were noticed in ppm analogous to the reference.

The stock solutions of Hg^{2+} of concentration 1×10^{-1} $molL^{-1}$ were prepared in ACN from its complementary salts. Stock solution of ligands was prepared at 10^{-3} M (25mL). For the photophysical studies, the solutions were further dilutes in the corresponding solvents. SHIMADZU-2600 spectrophotometer was used to record the absorption spectra of the ligand using quartz cuvettes of path length1 cm. Varian Cary Eclipse fluorescence spectrophotometer was used to record fluorescene spectra using a slit width (excitation = 20 nm, emission = 20 nm) at stated excitation. The Jobs Plot was used to determine the stoichiometry of the complexes. Using Benesi-Hildebrand equation, stability constants were resolved.

5.2 Absorption and emission titrations

For performing the absorption and emission titrations, stock solution of the anionic i.e. Hg^{2+} of concentration 1×10^{-1} $molL^{-1}$ was prepared from its corresponding salts in ACN. Stock solution of compound **3** of concentration 10^{-3} M (25mL) was prepared in ACN.

Further, incremental addition of Hg^{2+} was done and the spectra were recorded in absorption spectrophotometer and emission spectrophotometer. On completion of titration and achievement of the desired spectra, the data was compiled in M. S. Excel and graphs were plotted.

5.3 Calculation of Binding Constant and Detection Limit

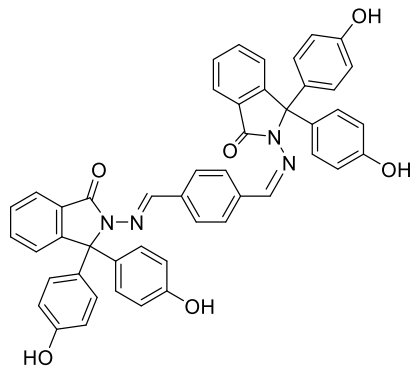
Binding constant of ligands for various analyte were determined using the Benesi-Hildebrand equation,

$$\frac{1}{I - Io} = \frac{1}{K_a (I_{max} - I_o) [C]^2} + \frac{1}{I_{max} - I_o}$$

Where, I, I_o and I_{max} are the absorption/emission intensities of ligand in the absence of analyte, at an intermediate analyte concentration, and at a concentration of complete interaction with analyte respectively. C is the concentration of analyte, K_a is the binding constant and n is number of analytes bound per ligand molecule.

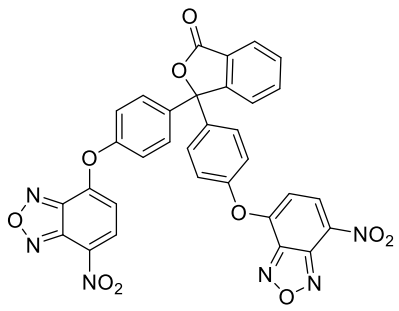
The detection limit (DL) is determined from the following equation:

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



Compound 3

^{1}HNMR (400 MHz, DMSO-d_6 (δppm)): 9.43 (s, 2H, OH), 9.16 (s, 1H, HC=N), 7.81 (d, *J =7.6,*1H, ArH), 7.45-7.36 (m, 3H, ArH), 6.86 (dd, 4H, J=7.6,ArH), 6.66-6.14 (m, 6H, ArH), 6.22 (s, 1H, ArH);^{13}C NMR (100 MHz):δ(ppm)164.2, 156.5, 146.7, 133.5, 131.3, 129.9, 128.2, 127.3, 126.9, 114.1



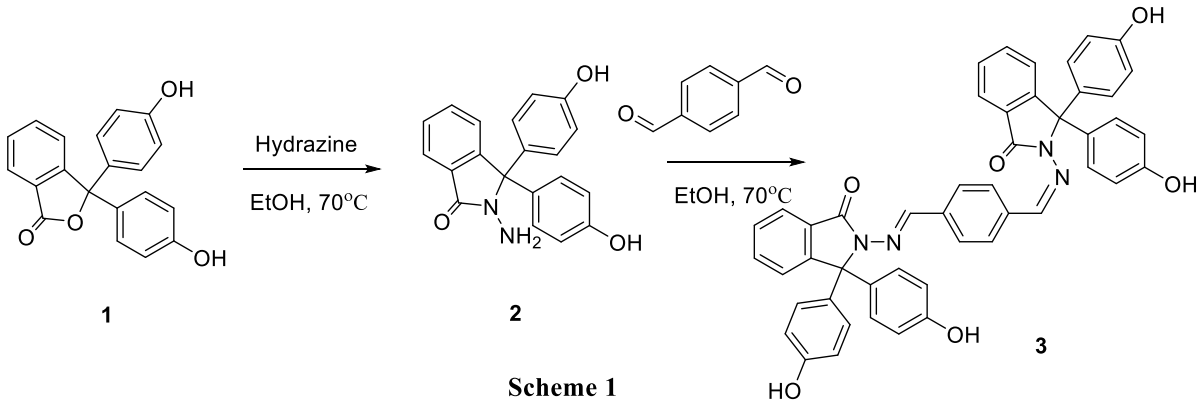
Compound 5

^{1}HNMR (400 MHz, $CDCl_3$ (δppm)):8.47 (d, *J* =9.2,2H, ArH), 8.02 (s, 1H, ArH), 7.94 (d,*J* =7.6,1H, ArH), 7.70 (t, J_{12} = 6, 1H, ArH), 7.56 (m, 2H, ArH), 7.19 (d, *J* =8.4, 3H, ArH), 6.79 (d, *J* = 8.4, 4H, ArH), 6.15 (d, *J* = 9.2, 2H, ArH)

6. RESULTS AND DISCUSSIONS

6.1 Synthesis of Compound 3:

Phenolphthalein (636 mg, 2 mmol) was dissolved in ethanol followed by addition of hydrazine (2 mmol). The reaction mixture was refluxed for 10 h. The reaction was monitored by TLC. After complete consumption of reactant materials, the terethaldehyde (135 mg, 1 mmol) was added *insitu* reaction mixture. The reaction mixture was further refluxed for 24 h **(Scheme 1)**. Fine white coloured solid was obtained and filtered. The solid was washed with cold ethanol. Further, the compound was characterized by NMR analysis.^{1}HNMR (DMSO-d_6, 400 MHz): showed 2H singlet at δ (ppm) 9.43 for OH, showed 1Hsinglet at δ9.16 for Schiff base units (HC=N), showed 1H doublet at δ7.81for Ar-H, showed 3H multiplet at δ 7.45-7.36 for ArH, showed 4H doublet of doublet at δ 6.86 for ArH, showed 6H multiplet at δ6.66-6.14 for ArH, showed 1H singlet at δ6.22 for ArH **(Figure 1).**^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) 164.2, 156.5, 146.7, 133.5, 131.3, 129.9, 128.2, 127.3, 126.9, 114.1 **(Figure 2)** and hence confirming the structure for compound **3.**



Scheme 1

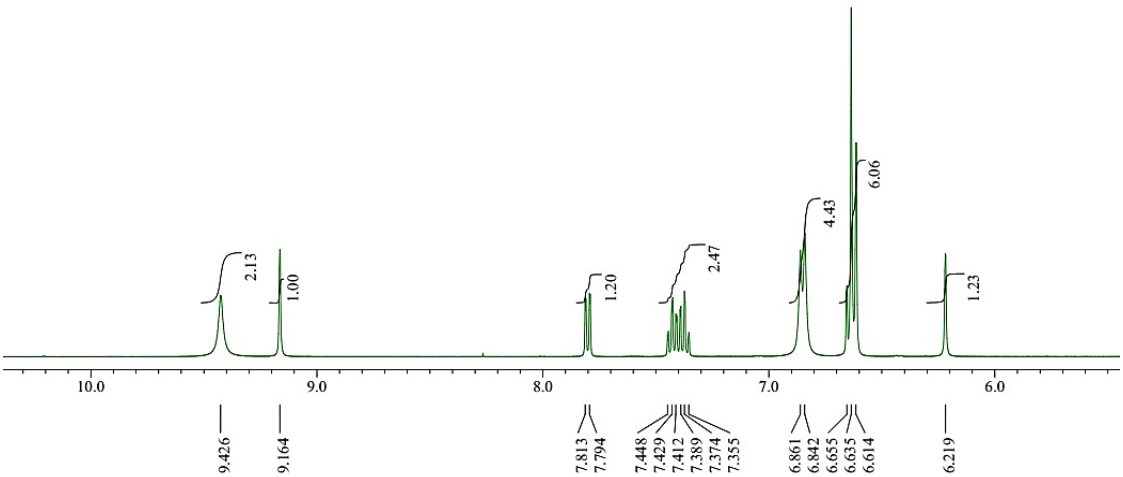


Figure 1. 1H NMR spectrum of compound **3**

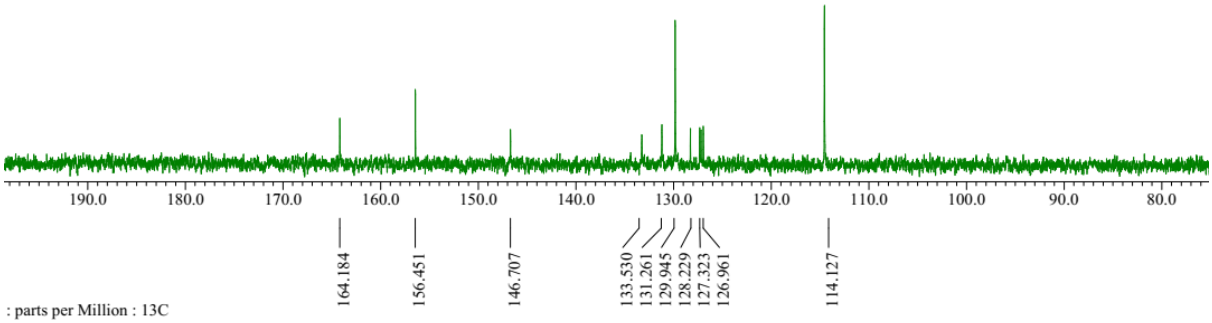
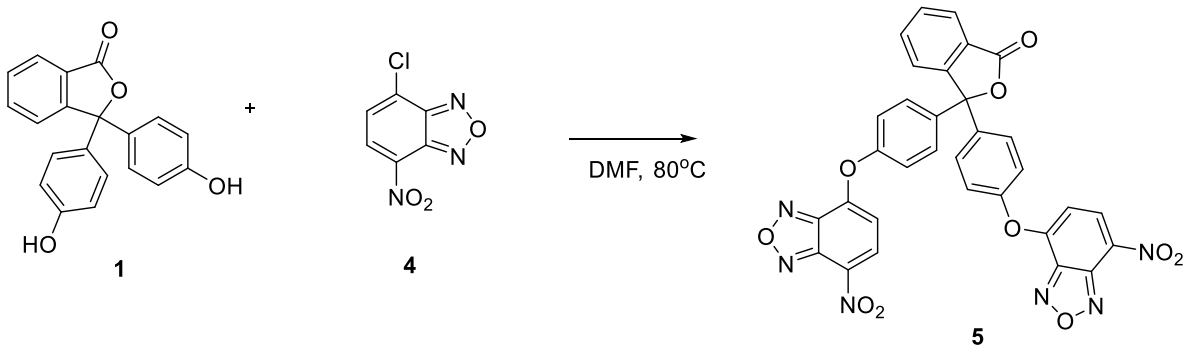


Figure 2.^{13}C NMR spectrum of Compound **3**

Synthesis of Compound 5:

Phenolphthalein (318 mg,1 mmol) was dissolved in dimethylformamide followed by catalytic addition of triethylamine. NBD (200 mg, 1 mmol) was added to the above solution. The reaction mixture was heated at 80 ^{0}C for 12 h **(Scheme 2)**. After completion of reaction (monitored by TLC), ice cold water was added to it. The product was extracted using chloroform as organic solvent. The collected organic layer was dried using Na_2SO_4 and concentrated. The obtained crude was then purified using column chromatography using chloroform/hexane (80/20; v/v) as a eluting solvent. The obtained compound was characterized by Spectroscopic technique.

^{1}HNMR ($CDCl_3$, 400 MHz): showed 2H doublet at δ (ppm) 8.47 for ArH, showed 1H singlet at δ 8.02 for ArH, showed 1H doublet at δ 7.94 for ArH, showed 1H triplet at δ7.70 for ArH, showed 2H multiplet at δ7.56 for ArH, showed 3H doublet at δ7.19 for ArH, showed 4H doublet at δ 6.79 for ArH, showed 2H doublet at δ 6.15 for ArH **(Figure 3)** and hence confirming the structure of compound **5.**



Scheme 2

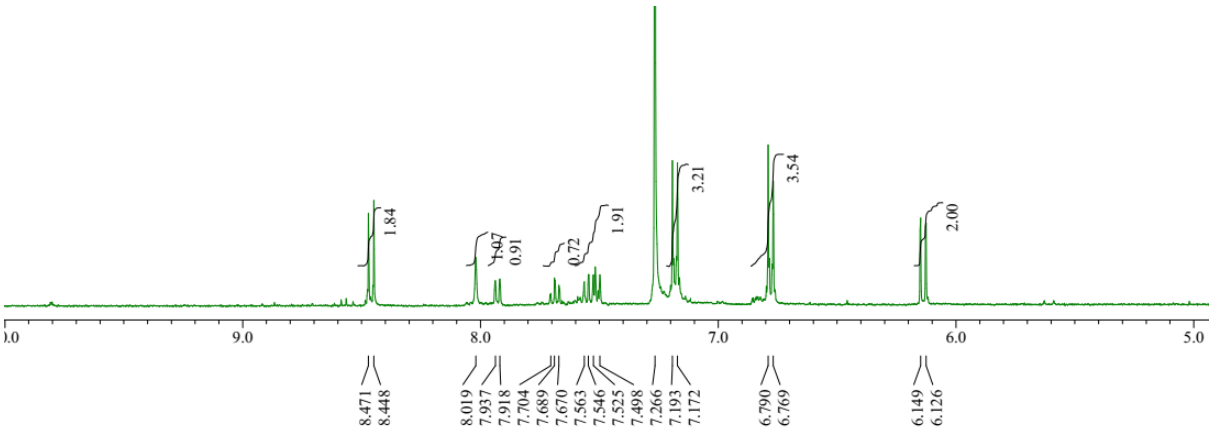


Figure 3. ^{1}H NMR spectrum of compound **5.**

6.2 Photophysical Properties of 3 and 5

Photophysical properties of synthesized compounds were measured through absorption and emission spectroscopy. Compound **3** exhibited the absorption maxima at 280 nm and showed no emission **(Figure 4)**. On the other hand, the compound **5** exhibited absorption maxima at 490 nm, 360 nm and 240 nm. Compound **5** exhibited strong emission at 560 nm **(Figure 5)** upon excitation at 490 nm. Further, the interaction of common metal ions and anions for compound **3** and **5** were also studied through absorption and emission spectra. The obtained results were discussed in following sections.

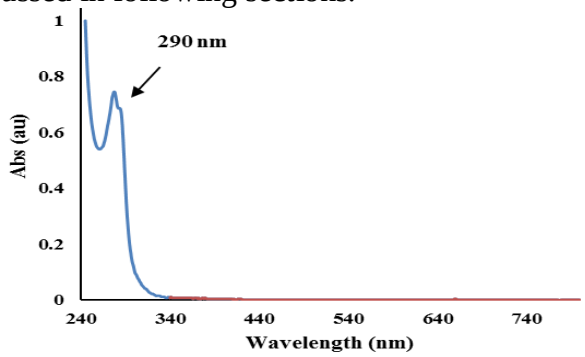


Figure 4: Normalized absorption spectra of compound **3** (20 µM, CH_3CN)

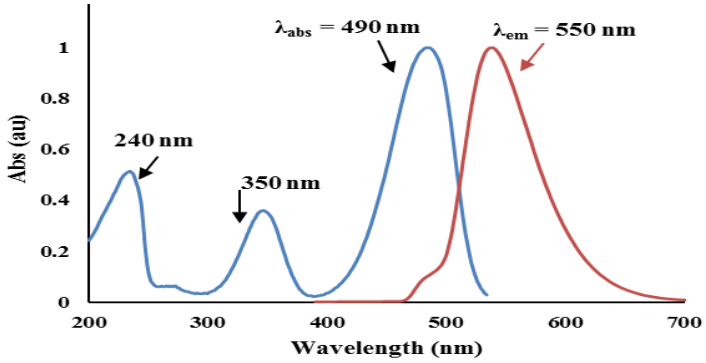


Figure 5: Normalized absorption and fluorescence spectra of compound **5** (20 µM, CH_3CN)

6.2.1 Ion recognition behaviour of compound 3

The recognition behaviour of compound **3** for different common metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Pb^{2+}, Fe^{3+},Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Ag^+ and anions *viz*., SCN^- ,CH_3COO^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, F^-, Cl^-, Br^-, and I^- were studied through the absorption and emission spectroscopy in CH_3CN as solvent. The absorption spectra of **3** showed a red shift of 190 nm on the introduction of Hg^{2+} ions. However, no other ions showed any significant change to absorption spectra of **3**. On gradual addition of Hg^{2+} ions to solution of **3**, absorption peak rises at 480 nm **(Figure 6)**. These spectral changes are accompanied with the quick colour change from colourless to reddish brown. The binding constant for 3.Hg^{2+} complex was calculated through Benesi-Hildebrand equation and found to be 3.2×10^4 M^{-1}. The compound **3** showed a linear response for absorption on increasing the Hg^{2+} ions concentration from 2-400 µM, and thus, used to calculate the lowest detection limit, which was found to be 7.2×10^{-8} M.

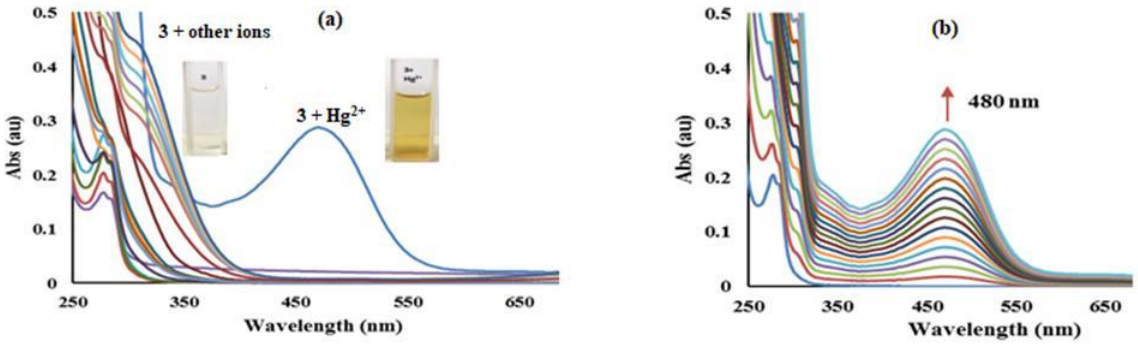


Figure 6: **(a)** UV-Vis absorption spectra of compound **3** (20 µM) in the absence and presence of different metal ions (1000 µM) and colour change of compound **3** on addition of Hg^{2+} ions. **(b)** Effect of incremental addition of Hg^{2+} (0-400 µM) to compound **3** (20 µM, CH_3CN) on absorption spectrum.

6.2.2 Interference Study

In order to check the interference of other cations for Hg^{2+} competitive examination were performed in the presence of other cations (50equiv. each) such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Ag^+ in CH_3CN **(Figure 7)**. No significant alteration was observed for absorption of compound 3 for Hg^{2+} ions. Therefore, chromogenic signal of compound **3** is a good indication for the prime presence of Hg^{2+} ions.

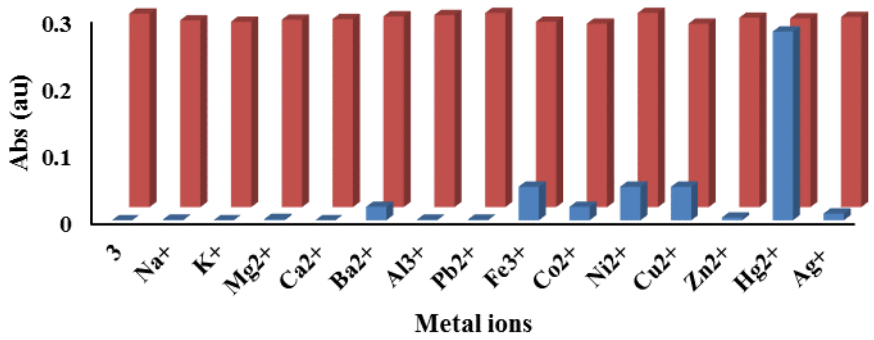


Figure 7. Relative absorption intensity of compound **3** (20 µM) in CH_3CN with different competing metal ions (1000 µM) in the absence and presence of Hg^{2+} (500 µM), at λ_{abs} = 480 nm, where blue bars represent the absorption intensity change of compound **3** with different metal ions and red bars represent compound **3** + Hg^{2+} in the presence of different relevant competing metal ions.

6.2.3 Job's plot analysis of Compound 3 towards Hg^{2+}

To determine complexation behaviour of compound **3** towards Hg^{2+}ion**,** Job's Plot was drawn**.** A stock solution of the same concentration of compound **3** and Hg^{2+} was prepared of the order of 2.0×10^{-5} M in CH_3CN solvent system. The absorption of each case with different compound analyte ratio but equal volume was recorded. Job plots were drawn by plotting absorption intensity *vs* $X_{analyte}$ (ΔI = change of intensity of the absorption spectrum during titration and $X_{analyte}$ is the mole fraction of the analyte in each case, respectively) and found that there exists a 1:2 stoichiometry. **(Figure 8)**

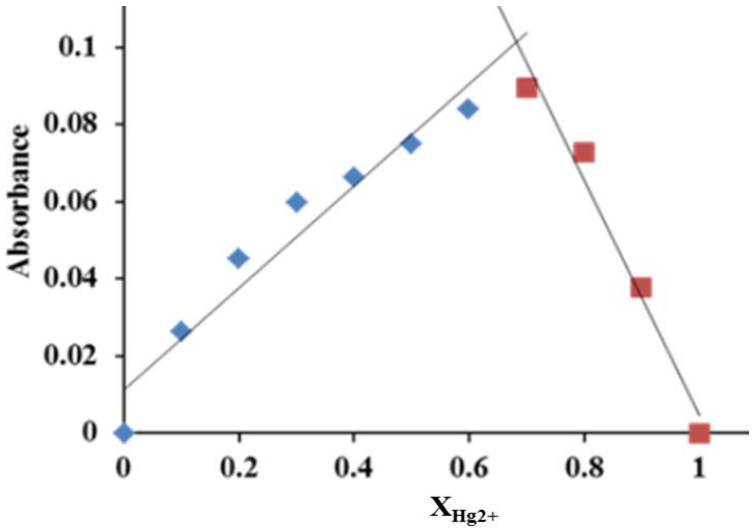


Figure 8: Job plot diagram of compound **3** with mercury ions in CH_3CN

6.3 Possible mechanism for Hg^{2+}

The possible coordination of Hg^{2+} ions for compound **3** could be the nitrogen atom of hydrazine linker and the oxygen atom of phenolphthalein moiety. To obtain preliminary insight for the coordinated structure of compound **3** with Hg^{2+}, semiempirical calculation were performed for compound **3** and its complex with Hg^{2+} ions. Also, the Job plot analysis revealed the 1:2 stoichiometry of compound **3** toward Hg^{2+} ions. Therefore, the 1:2 stoichiometry was used for structure optimization of compound **3**. Hg^{2+} complex (**Figure 9**).

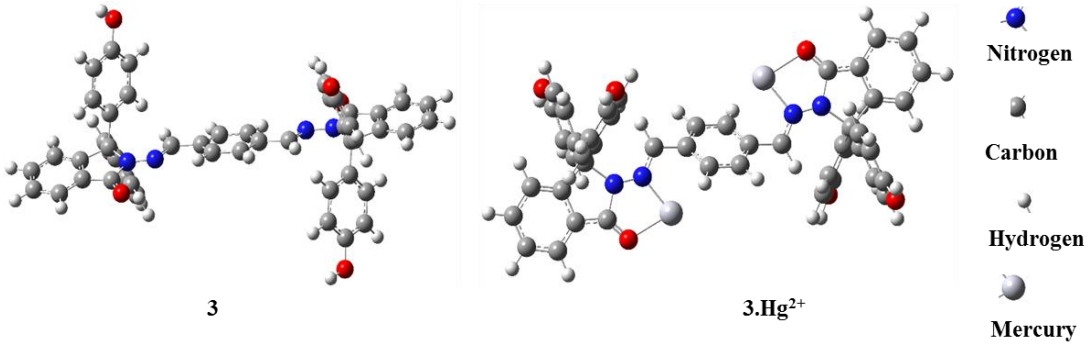


Figure 9. Optimized structure of compound **3** and its complex with Hg^{2+} ions (**3**.Hg^{2+})

It was observed that the compound **3** was optimized in symmetrical way, where the phenolphthalein moiety was at trans-geometry with respect to each other through Schiff base linkage. Further, the optimization of **3** with Hg^{2+} ions resulted in coordination through oxygen of phenolphthalein moiety and nitrogen atom of hydrazine linker. Thus, the coordination could result in charge transfer form phenolphthalein to mercury and resulted in reddish brown colour change. Also, the ring opening for phenolphthalein was not observed during structure optimization, which could be possible reason of colour absence of pink colour in presence Hg^{2+} ions.

7. Conclusion

1. We have synthesized phenolphthalein based Schiff base to study photophysical behavior towards different metals and anions.
2. The Schiff bases have been successfully used for the detection of Hg^{2+} ions colorimetrically.
3. The presence of Hg^{2+} ions showed a red shift of 190 nm in its absorption spectra. Further increment of Hg^{2+} ions results in a shift of absorption peak at 480 nm along with an instant change modification from colorless to reddish brown.

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