SYNTHESIS AND PHOTOPHYSICAL STUDIES OF DANSYL DYADS CONTAINING ANTHRAQUINONE AND COUMARIN MOIETY

A
dissertation report submitted
in partial fulfillment of the requirement of the degree of

MASTER OF SCIENCE
IN
CHEMISTRY
By
Princedeep Kaur
Roll No. 301702021

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Under the Supervision of
Dr. Vijay Luxami
(AssociateProfessor)

SCHOOL OF CHEMISTRY AND BIOCHEMISTY
THAPAR INSTITUTE OF ENGINEERING AND TECHNOLOGY, PATIALA, PUNJAB
July, 2019

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and photophysical studies of dansyl dyads containing anthraquinone and coumarin moiety**" being submitted by **Ms. Princedeep Kaur (Roll No. 301702021)** in partial fulfillment of the requirements for the award of degree of **Masters of Science in Chemistry**, Thapar Institute of Engineering and Technology, Patiala, Punjab is a bonafide work carried out under the supervision and conception of Dr. Vijay Luxami and that no part-of this thesis has been submitted for the award of any other degree.

- Princedeep Kaur

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

Vijay Luxami

Dr. Vijay Luxami
Associate Professor/Supervisor
School of Chemistry and Biochemistry (SCBC)
Thapar Institute of Engineering and Technology
Patiala, Punjab

CANDIDATE DECLARATION

I hereby declare that the work being presented in thesis entitled **"Synthesis and photophysical studies of dansyl dyads containing anthraquinone and coumarin moiety"** is submitted in partial fulfillment of requirements for the award of degree of **Master in Chemistry**, School of Chemistry and Biochemistry, **Thapar Institute of Engineering and Technology, Patiala** is my own laboratory work during the period of January 2019 to June 2019, under the conception and supervision of **Dr. Vijay Luxami**, Associate Professor, School of Chemistry and Biochemistry (SCBC), **Thapar Institute of Engineering and Technology**, Patiala. I have not submitted the matter embodied in this thesis for award of any other degree.

Place: Patiala

Princedeep Kaur

Date: 15 July, 2019

Vijay Luxami

Dr. Vijay Luxami
Associate Professor/Supervisor
School of Chemistry and Biochemistry (SCBC)
Thapar Institute of Engineering and Technology
Patiala, Punjab

ACKNOWLEDGEMENT

It is not the right way of expressing by writing few words on a piece of paper for all those who have helped me in the completion of this project, because there is no mode of communication for all those words coming in my heart.

I avail the great opportunity to express deep sense of gratitude to my honorable project guide, **Dr.Vijay Luxami**, Associate Professor, School of Chemistry and Biochemistry, T.I.E.T, Patiala, Punjab for their worthy guidance, valuable suggestions, constructive criticism, magnanimous behavior and for congenial help during the course of investigation and preparation of this manuscript. Without her help and concrete suggestions, the execution of this research work, would not have been completed on time.

I would like to place my heartfelt gratitude to **Dr. Amjad Ali, Head, School of Chemistry and Biochemistry, T.I.E.T, Patiala (Punjab)** for providing me an opportunity to do this project work. My gratitude is due to all faculty members for their help, inspiration and moral support, during the course of my study.

I respectfully thank **Mr. Gulshan Kumar,** whose diligent guidance, unending zeal, constant encouragement and a great support during my dissertation and always being the source of inspiration and motivation during my project. I would also thank other research scholars **Mrs. Ruhi Mehta**, Ms. **Richa Bansal**, **Mr. Iqubal Singh**, **Ms. Sudesh Rani**, **Ms. Aastha Palta**, **Mr. Dinesh Singla** for helping me and guiding me in their best possible way.

My whole hearted thanks to **Mr. Hemant Kumar, Mr. Chander Thakur** and all other lab attendants for their valuable help and immense support.

I thank the almighty whose blessings have enabled me to accomplish my dissertation work successfully. Last but not the least; I want to thank my family members for their prayers and goodwill. My friends **Mr. Saurabh Gupta**, Ms. **Rohini Gupta**, Ms. **Anchal Sharma** and **Ms. Diksha Bansal** who helped me in the research work. I want to thank them for all their help, support, interest and valuable hints. I feel privilege to express my true cardiac feelings and gratitude for all those who had been instrumental directly or indirectly in the successful completion of my dissertation.

Princedeep Kaur

Place: Patiala

Date: 15 July, 2019

Content

ABBREVIATIONS

μM	Micromolar
Ag^+ -	Silver cations
Al^{3+}	Alminium cation
Br^-	Bromide ions
$CDCl_3$	Deuterochloroform
Cl^-	Chloride ions
CN^-	Cyanide ions
Co^{2+}	Cobalt (II) cation
Cr^{3+}	Chromium cation
Cu^{2+}	Cupric cation
D	Doublet
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
ESIPT	Excited State Intramolecular Proton Transfer
EtOH	Ethanol
F^-	Fluoride ions
Fe^{3+}	Ferric cation
FRET	Froster Resonance Energy Transfer
G	Gram
$H_2PO_4^-$	Dihydrogen Phosphate Anion
Hg^{2+}	Mercuric cation
HOMO	Highest Occupied Molecular Orbital
HSO_4^-	Hydrogen Sulfate anion
Hz	Hertz
ICT	Intramolecular Charge Transfer

J	Coupling constant
K^+	Potassium cation
LUMO	Lowest Unoccupied Molecular Orbital
M	Multiplet
MeCN	Acetonitrile
MeOH	Methanol
Mg	Milligram
Mg^{2+}	Magnesium cation
Na^+	Sodium cation
Ni^{2+}	Nickel cation
nM	Nanomolar
Nm	Nanometer
NMR	Nuclear magnetic resonance
NO_3^-	Nitrate anion
OAc^-	Acetate anion
OCl^-	Hypochlorite ion
PET	Photoinduced Electron Transfer
$PhNO_2$	Nitrobenzene
PhSH	Thiophenol
PPi	Pyrophosphate
r.t	Room temperature
S	Singlet
SCN^-	Thiocyanate
T	Triplet
TBET	Through Bond Energy Transfer
THF	Tetrahydrofuran

ABSTRACT

Anthraquinone and coumarin based dyads with dansyl chloride were synthesized for the detection of CN^- ions. Probe **1** showed absorption and emission band at 390 nm and 510 nm in CH_3CN : H_20 (95 : 5 , v/v) respectively. The addition of CN^- ions led to red shift of 63 nm in absorption spectra hence, shifted the band from 387 nm to 486 nm. Similarly, there was a red shift of 100 nm in emission which led to appearance of band at 610 nm from 510 nm accompanied by a visible color change from colorless to dark yellow and fluorescence changed from green to red. The mechanism responsible for the change was cleavage of S-O bond on encounter of CN^- ions. The detection limit estimated was 3.5 nM. Probe **2** showed the emission band at 520 nm in CH_3CN : H_2O (90 : 10, v/v). The addition of CN^- ions resulted in an enhancement and a blue shift of 70 nm, thus shifted the band from 520 nm to 450 nm. The fluorescence changed from green to blue.The reason being cleaveage of S-O bond. The detection limit was calculated as 17 nM. Probe **3** showed absorption band at 330 nm and emission was at 466 nm. Probe **3** did not show change with any anion in CH_3CN : H_2O (90 : 10, v/v).

Chapter 1

Introduction and literature review

Supramolecular chemistry is defined as a branch of chemistry that deals with molecular assemblies which correspond to a large molecule. This huge molecule has a number of atoms such as oxygen, sulphur and nitrogen in the form of functional groups or present in the ring, which can act as sensing entities for anions, metals and neutral species.[1-3] The sensing can occur due to binding at one place or two etc. depending upon the architecture of the supramolecule and nature of the ion to be sensed. A chemosensor is actually an entity to which ion binds, and thus it sends optical signals and convert it to analytical signals which are studied, recorded and interpreted using instruments such as UV-Visible and spectro-fluorometer in the form of absorbance and intensity variation with respect to wavelength. The molecule can form different kinds of non-covalent interactions, such as hydrogen bonding, complexation, self-assembly, Π-Π stacking etc.[3-5] On basis of these interactions the chemosensor exhibit different phenomenon as ICT, ESIPT, CHEF, PET, C=N isomerization, FRET, TBET or scission in the bond thus leads to release energy in the form of fluorescence these are referred as "*off-on*" sensors. Sometimes, the above phenomenon is already present in the molecule, but the encounter of some anion can quench fluorescence, unlike other ions which do not affect its fluorescence such type of chemosensors are called as "*on-off* "sensors. Chemosensors is thus an abiotic molecule that binds with an analyte through coordination that is; the reaction is reversible.[6-9] Chemodosimeters, on the other hand, are abiotic molecules that combine with the analyte and cause particular breaking and making of bonds thus responsible for the irreversible reaction. eg. Ring-opening in rhodamine B, S-O bond scission in nosylate based sensors etc. Chemosensors and Chemodosimeters both act as sensors for the detection of the ions.[10-13]

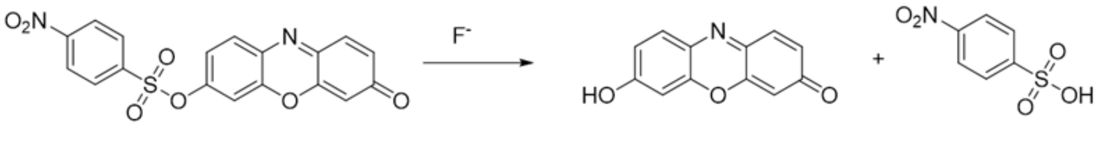


Figure 1.1. Chemodositmeter based on resorufin nosylate[20]

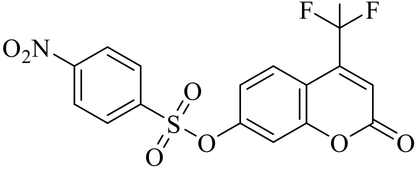
There are other techniques which help in the detection of anions, metals and neutral species such as atomic absorption spectroscopy, electrochemical sensing, inductively plasma atomic emission spectrometry but these methods are expensive and tedious hence designing of fluorescent probes as sensors are encouraged as they are highly sensitive and responds immediately to the analytes in the form of ratiometric and colourimetric changes. Sensors with ratiometric and calorimetric changes are more preferred as ratiometric changes do not get affected by the external environment or reduce chances of instrumental errors, whereas colour changes can be seen quickly by naked eyes.

There are number ions in nature which are required for the normal functioning of the human body. If they are present in an adequate amount, they help the functioning of the human body in an appropriate manner. However, their excess can cause number disease, which leads to abnormalities in the human body such as Hg^{2+}causes Minamata disease, CN^- can bind with haemoglobin, Pb^{2+} affects the nervous system. Hence, the detection of these metals and anions has become an essential area of research.

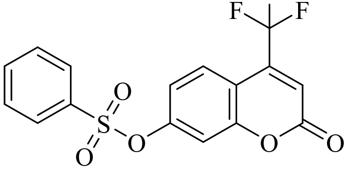
Cyanide is a highly toxic anion which affects human and animal health as a result of which it has become essential to detect its presence in the environment. It has a high nucleophilic character which makes it more prone to undergo various types of reactions with compounds that exist in nature thus, make them either poisonous or create problems in normal functioning like when cyanide combines with the iron of cytochrome c oxidase it leads to electron transport malfunctioning which ultimately reduces oxidative metabolism of humans. It can combine with the blood very quickly hence causes low oxygen content in the body along with symptoms like vomiting, nausea and dizziness. Its inorganic salts such as KCN and NaCN are poisonous which are regarded as one the sources of cyanide along with other industrial water discharges and naturally occurring substances (bitter almonds, peaches etc.). These salts are ionic in nature, thus dissolve in water bodies easily as compared to organic cyanide compounds. All these detrimental effects have encouraged the researchers to develop highly sensitive, ratiometric and colourimetric sensors for the detection of cyanide.

A number of the sensor has been discovered for its detection, some have either ratiometric or colourimetric changes, but sensors with ratiometric as well as colorimetric changes along with high selectivity and sensitivity are very rarely reported in the literature. Herein, we have designed and synthesized a highly sensitive, colourimetric, ratiometric chemosensors based on coumarin and anthraquinone moieties. No doubt, in the fact that a number of chemosensors based on these two moieties has been reported earlier in the literature which show different phenomenon such C=N isomerization, ICT, PET, ESIPT, CHEF but the sensors with dansyl group having amine, undergoing scission at C-O bond are scarce for detection of cyanide . However, coumarin and anthraquinone based sensors, along with nosylate groups, are well known.

Pandey *et al.* synthesized and studied compound **1**, which can be used as a chemodosimeters for F^- ions based on the fact that compound **1** is non - fluorescent initially, due to the presence of nitro group in 4-Nitro benzene sulfonate, but it undergoes cleavage in S-O bond in the presence of fluoride ion which is responsible for the release of green fluorescence.[14] Nitro group stimulated the cleavage of S-O bond which was supported by the fact when they synthesized compound **2** that did not have nitro group as a result, it remained non- fluorescent in presence of fluoride ions. It was the electron-withdrawing nature of the nitro group that facilitated enhanced ICT in compound **1**. The absorption band of compound **1** was observed at 313 nm for in acetonitrile, but the addition of fluoride leads to the appearance of strong absorption band at 419 nm whereas other metals and anions did not show any significant change. Moreover, in fluorescence studies, it was revealed that fluoride was responsible for the appearance of emission band at 503 nm when excited over 432 nm and in addition to that it increased the fluorescence to 40-folds suggesting scission in S-O bond, but other metals and anions do not cause any noticeable or mere changes in fluorescence as well. Thus, all these changes and appearance of green colour which can be seen through naked eye make compound **1** highly selective for fluoride with a detection limit of 9.70×10^{-8} M and 8.78×10^{-9} M in absorption and emission respectively. The compound **1** showed application as a detector for fluoride ions in toothpaste.

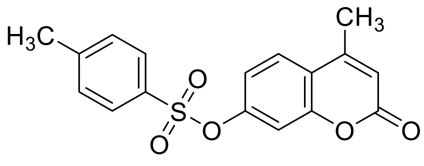


1

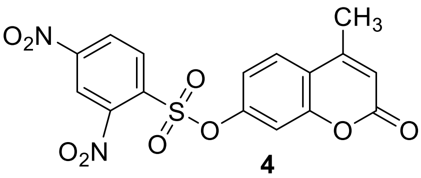


2

Wang *et al.* designed compound **3** that detected captopril in solvents ethanol : water (80: 20) at pH 9.5 NH_3 – NH_4Cl buffer.[15] It was observed that compound **3** showed an absorption band at 261 nm and 308 nm and emission band was at 446 nm in the absence of captopril. However, the addition of captopril corresponded to absorption band at 364 nm and an emission band at 446 nm with an increase in fluorescence. These changes were observed due to scission in S-O bond by thiolate in captopril, which in turn was initiated by electron-withdrawing groups present in the compound **4**. Hence, the fact was proved when the compound **4** having an electron donating group did not show any expected change, which provided evidence about the significant role of withdrawing group in S-O bond scission. The detection limit estimated was 2.2 ng mL^{-1}.

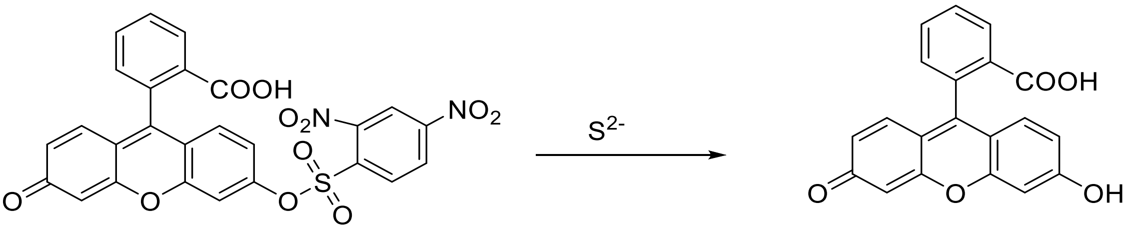


3



4

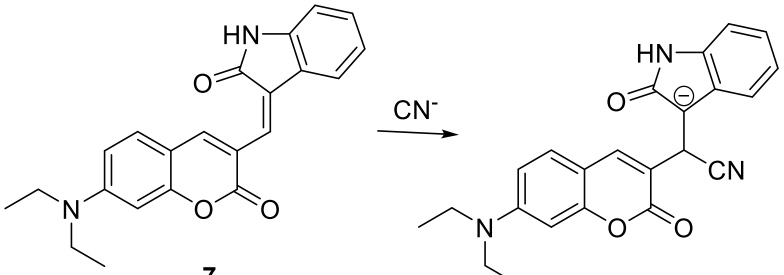
Yang *et al.* synthesized compound **5,** which was based on its nucleophilicity, and it was weakly fluorescent.[16] However, it undergoes S-O bond cleavage and thus leads to strong fluorescence (yellow colour can be seen with the naked eye) as it releases compound **6** when it comes in contact with S^{2-} anion. The absorption band was at 453 nm; however, when incubation with sulphide was done absorption band appeared at 490 nm, and the emission band was at 513 nm with huge enhancement in acetone : water ratio. On the other hand, no interference from other ions was detected; hence, it was selective towards sulphide only. The detection limit was 4.3 nmol L^{-1}. The compound **5** was used to detect sulphide in wastewater.



5

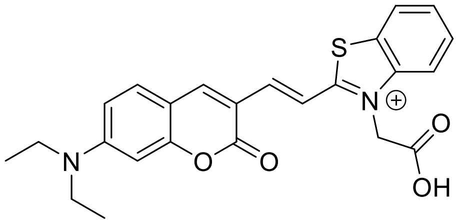
6

Yang *et al.* prepared compound 7, which can sense highly toxic ion cyanide on the basis of its Π-conjugated system, which can induce ICT between coumarin and indole moiety to form compound **8**.[17] This ICT is blocked between two moieties on incubation of cyanide ion as a result of which enhancement in fluorescence is being observed along with a red shift in absorption. Initially, the absorption band was observed in DMSO : H_2O (95:5) at 550 nm but the addition of CN^- was responsible for the new band at 444 nm and disappearance of the former band while in fluorescence studies the emission band appeared at 465 nm and fluorescence enhanced by 20-folds on cyanide addition. Other ions did not show any considerable change in absorption and fluorescence. The compound **7** was used to detect cyanide in natural and tap water.



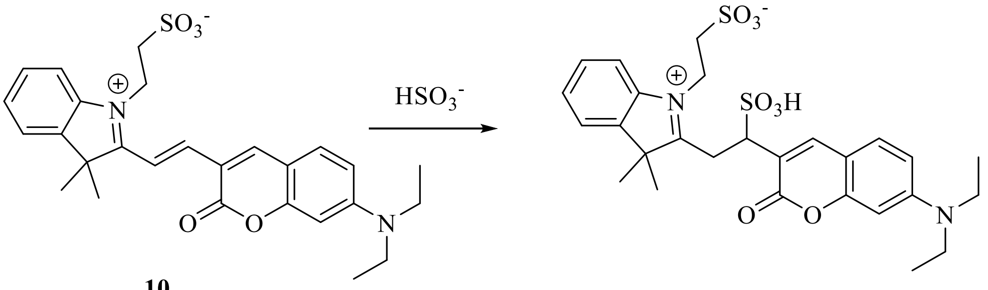
7 **8**

Yang *et al.* designed and prepared compound **9,** which had coumarin and benzethonium connected through a conjugated system and exhibits high ICT in it.[18] It can be used as a detector for cyanide ions in MeCN : water (9:1), which leads to an absorption band at 455 nm instead of appearing at 553 nm in absence of cyanide ion while emission band appeared at 624 nm but addition of cyanide was responsible for appearance of band at 488 nm hence change in color occur from pink to bluish-green in presence of cyanide which had affected ICT and extended conjugation severely. Hence compound **9** is a ratiometric and colourimetric sensor for detection of CN^- as other ions did not show any significant changes. The detection limit was 0.64 µM.



9

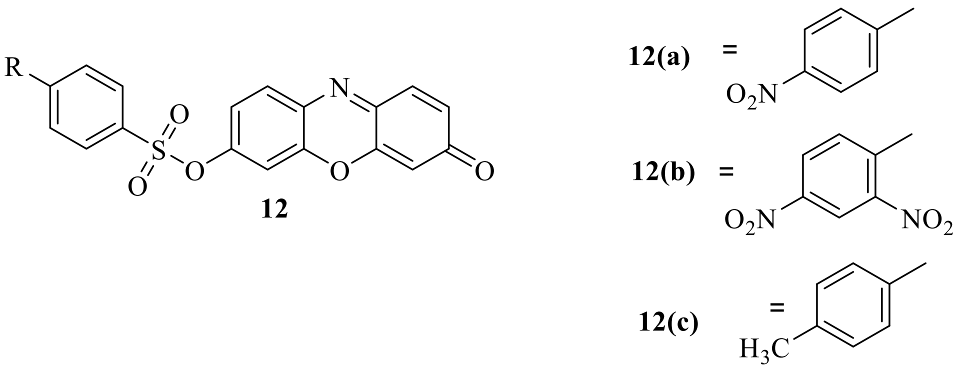
Zang *et al.* designed compound **10** which can be used as a sensor for bisulphite anion based on its ability to attract bisulphite at itself at the conjugated bond that connects the two moieties, hence inhibits ICT but coumarin itself can give fluorescence.[19] The absorption and emission band appeared at 585 nm and 667 nm respectively, while addition HSO_4^- led to band appearance at 430 nm and 460 nm in succession with colour changes from blue to colourless in absorption when studied in MeOH : PBS buffer solution (pH 7.2) . The kinetics was also studied for this reaction. The detection limit was calculated as 27 nM. The moiety is stable between pH 2-8. Hence bisulphite was detected in wine, sugar and ina biological system.



10

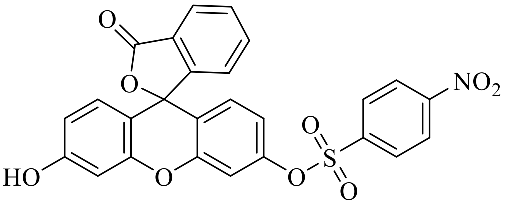
11

Gyu *et al* synthesized compound **12** which can be used as a sensor against F^- and S^{2-} on basis of colorimetric and ratiometric changes induced when compound **12**, encounters with these ions and the changes are attributed due to S-O bond cleavage in the compound.[20] Initially, the absorption band appeared at 335 nm and 433 nm in acetonitrile but on addition of sulphide and fluoride these bands disappeared and lead to formation of new intense bands at 550 nm, 569 nm and 587 nm owing to formation of resorufin fluorochrome which leads to change in color from yellow to pink. The fluorescence studies depicted appearance of band at 550nm before the addition of anions but on addition of 10 equivalents fluoride and sulphide, the band appeared at 591 nm. However, other ions did not show any such change in absorption as well as fluorescence. The selectivity between sulphide and fluoride can be achieved by using Cu (II) along with TPEN (N, N, N’, N’- tetrakis (2- pyridinylmethyl) -1, 2- ethanediamine) as it interact which suppress the signals hence, help to attain selectivity for fluoride ion alone. **12(a)** as it is more selective rather than **R(b)** and **R(c)** which have interferences from other anions as well. The detection limit was estimated to be 1.9×10^{-5} M for fluoride ions.



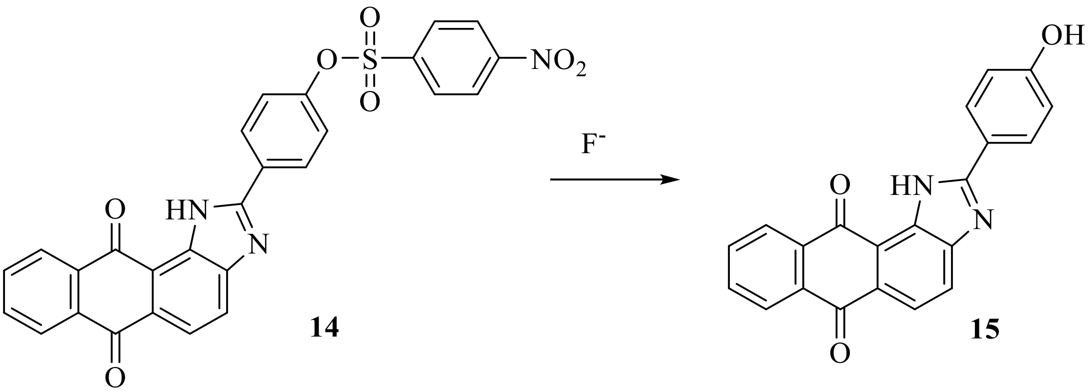
12

Asthana *et al.* synthesized compound **13** on the basis of nucleophilic and basic character of fluorescein nosylate.[21] The moiety undergoes deprotection from nosylate under the presence of fluoride thus it acts as detector against it as gives yellow color instantaneously. The absorption band appeared at 457 nm and 490 nm while emission band was at 590 nm with poor intensity in absence of fluoride. However, on addition of fluoride the absorption band appeared at 517 nm instead of 457 nm and 490 nm while emission band was noticed at 590 nm with enhancement of 60 folds upon excitation was at 490 nm. The process occurred in two steps, the first step involved cleavage in S-O bond followed by deprotection of OH group by fluoride owing to basic character. The studies of other ions did not show any significant change, hence it was selective for fluoride with a detection limit of 4.6×10^{-7} M in UV-visible and 2.6×10^{-8} M in fluorescence as evaluated.



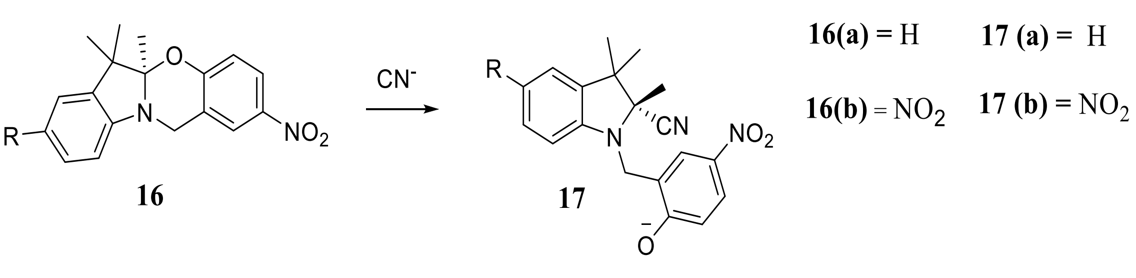
13

Shweta *et.al* designed compound **14** based on anthraquinone nosylate moiety which could sense fluoride ion by giving ratiometric and colorimetric changes due to scission in S-O bond.[22] The absorption band of free compound **14** in MeCN appeared at 395 nm while on incremental addition of fluoride lead to formation of band 470 nm with a red shift of 75 nm and accompanied by color change from yellow to orange. In case of fluorescence, the compound **14** showed an emission band at 510 nm but addition of fluoride to it corresponds to emission band at 592 nm with shift of 82 nm and change in color from yellow to orange. It was observed that other anions did not cause any change in spectra as result it is highly selective for fluoride. Later, it was analysed sulphide can interfere in detection but the color change for sulphide remains only for sometime while in case fluoride it is for longer time explained on basis of HSAB concept. The detection limit calculated using fluorescence titration was 3.45×10^{-10} M. The dry strips were used to ensure the practical applicability.



14 **15**

Ren *et.al* designed compound **16** with R that could undergo C-O bond cleavage when it encounters cyanide and give color change which can be observed with naked eye along with ratiometric changes such as absorption band at 411 nm in presence of cyanide in MeOH : water (19:1) in a buffer sodium phosphate (pH 7.2) while free ligand displayed band at 343 nm when R is ‘nitro’ group.[23] However, when R is ‘H’ then absorption band was observed at 307 nm in absence of cyanide but in presence of cyanide, the band appeared at 410 nm. Furthermore, NMR titrations were done to confirm the observations and cleavage of C-O bond along with oazine ring opening. The substituent present at R position influenced the sensing property of the compound **16**.The detection limit was calculated 1×10^{-6} M.

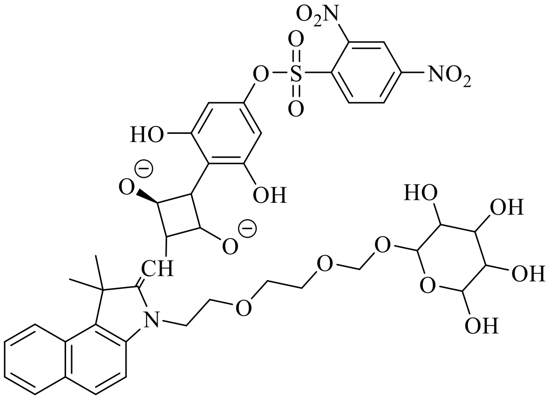


16 **17**

16(a) = H **17 (a)** = H

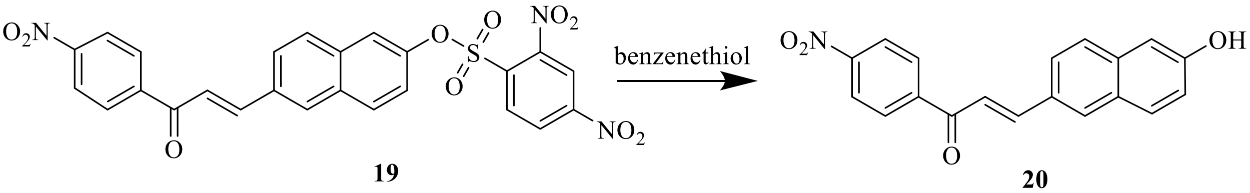
16(b) = NO_2 **17 (b)** = NO_2

Xiong *et. al* synthesized a novel compound **18** for the detection of thiophenols which was chromoflourogenic, water soluble squaraine based sensor which led to oxygen carbon bond scission when thiophenol encounter the compound **18**.[24] The absorption and fluorescence studies were done in aqueous PBS buffer and absorption band was seen at 556 nm however, addition of thiophenol led to red shift and appearance of band at 626 nm along with color change from blue to pink but it showed poor emission band in PBS (pH 7.4) but addition of thiophenol was responsible for a strong band at 635 nm with 30 fold enhanced fluorescence. Compound **18** did not show interference from other species such thiols hence, it is highly selective for thiophenols. The kinetics and equilibrium for the reaction was also studied revealing it was a stable moiety. The water sample from river was collected in order to check the applicability hence it was successfully determined.



18

Wang *et al.* synthesized compound **19** which can be used to detect benzenethiols in food sample, cosmetics, pharmaceutical and chemical industries.[25] The sensing properties were studied between pH 3.0-10.0. It was formulated from that studies no change in emission was observed between pH 5.0-7.4 but enhancement from 3-5 and 7.4–10.0. Hence, led to support the fact benzenethiols are stable from 5.0-7.4 pH range.



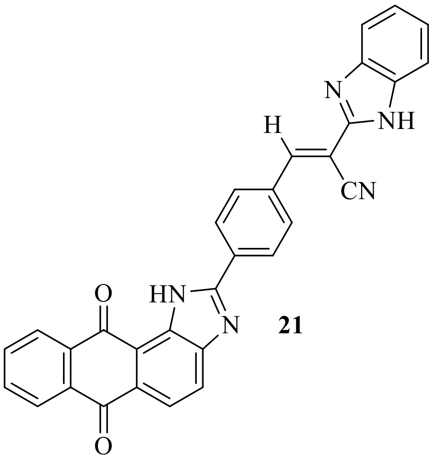
19 **20**

1.1 Research gap

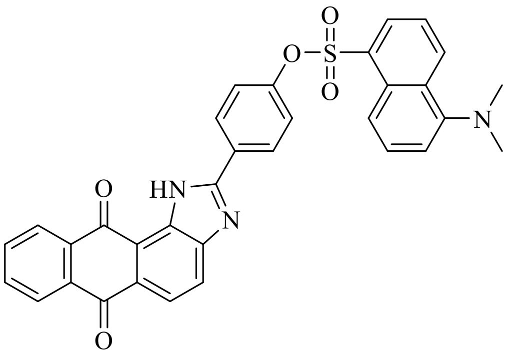
Based on the review of the literature we have found be anthraquinone and coumarin based chemosensor had been synthesized in the past and had been used as sensor for reactive species and nucleophilic ions. However, chemosensor based on S-O bond scission are not much explored particularly having dansyl group in them. Hence, on basis this we have designed, the new molecules containing dansyl moiety which react with reactive species and nucleophilic ions and cause cleavage in the reactions.

1.2 *Motivation*

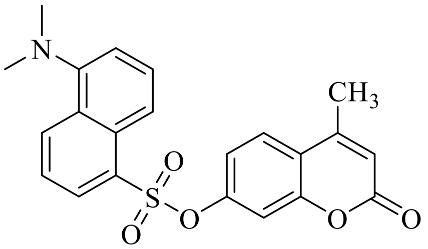
The compound **21** was synthesized in the lab and had both electron acceptor units. This compound **21** served as excellent detector against cyanide ions and had good absorption and emission[13]. Therefore, we appended dansyl, which is an electron donor unit with anthraquinone. Similarly, coumarin was appended with dansyl as coumarin also serves as good electron acceptor unit. Thus, the molecules having donor and acceptor unit was synthesized to check the photophysical properties.



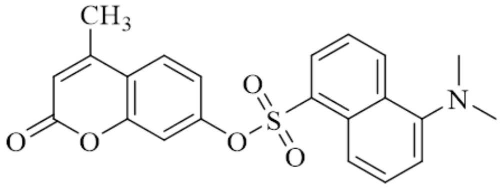
21



Probe **1**



probe **2**



Probe **2**

1.3 *Objective*

On the basis of studied research gaps following objectives were designed :

- Synthesis of highly chromofluoresent compounds containing anthraquinone and coumarin compounds appended with dansyl moiety.
- To study the photophysical properties of synthesized compounds towards reactive species and nucleophilic ions.

Chapter 2

Experimental Section

2.1 *Material and Methods*

The chemicals were purchased from Sigma Aldrich, Loba chemicals and Spectrochem. All these chemicals used were not purified further and used as such. The analytical grade solvents from Spectrochem were used for the studies. The reaction was monitered by using TLC. The characterization of the structure was done by ^{1}H NMR and recorded on JEOL ECS-400 MHz. The samples were soluble in $CDCl_3$ and hence structure analysis was done in it. The chemical shifts were reported in ppm with reference to TMS. The absorption spectra was recorded at SHIMAZDU-2600 and fluorescence spectra at Varian Cary Eclipse spectrophotomter with excitation and emission slit be 10 – 10. The metal and anion solutions were prepared of 1×10^{-1} $MolL^{-1}$in MeCN depending upon solubility which were further diluted using different solvents during photophysical studies depending upon the requirement. The various metallic salts were used to prepare the solution of metals while Tetrabutylammonium salts were used for anion preparation. The stock solutions of the compounds were prepared in DMSO and MeCN of 10^{-3} M concentration. The stoichiometry was calculated by using Job's plot.

2.2 *Calulation of binding constant and detection limit*

Benesi-Hildebrand equation was used to calculate the binding constant of the ligand with the different analyte. The equation is :

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

where,

C = concentration of analyte

K_a = binding constant to be determined

n = number of analyte bound to a single molecule of ligand

I = the absorption and emission intensities in absence of analyte

I_o = the absorption and emission intensity at an intermediate concentration

I_{max} = refers to the concentration at which the analyte interact with the ligand completely

The equation mentioned below was used to evaluate the detection limit (DL) :

$$\mathrm{DL} = \frac{3 \times \text{Standard deviation of the blank solution}}{\text{slope of calibration curve}}$$

2.3 Job’s Plot

The solutions containing probe**,** cyanide were prepared with different concentration such that the total volume of both anion and probe remained constant during each titration but the concentration of either anion or probe was varied. The observed intensity was plotted with mole fraction of cyanide ions at particular wavelength.

2.4 Experimental section

2.4.1 Synthesis of Anthraquinone based moieties

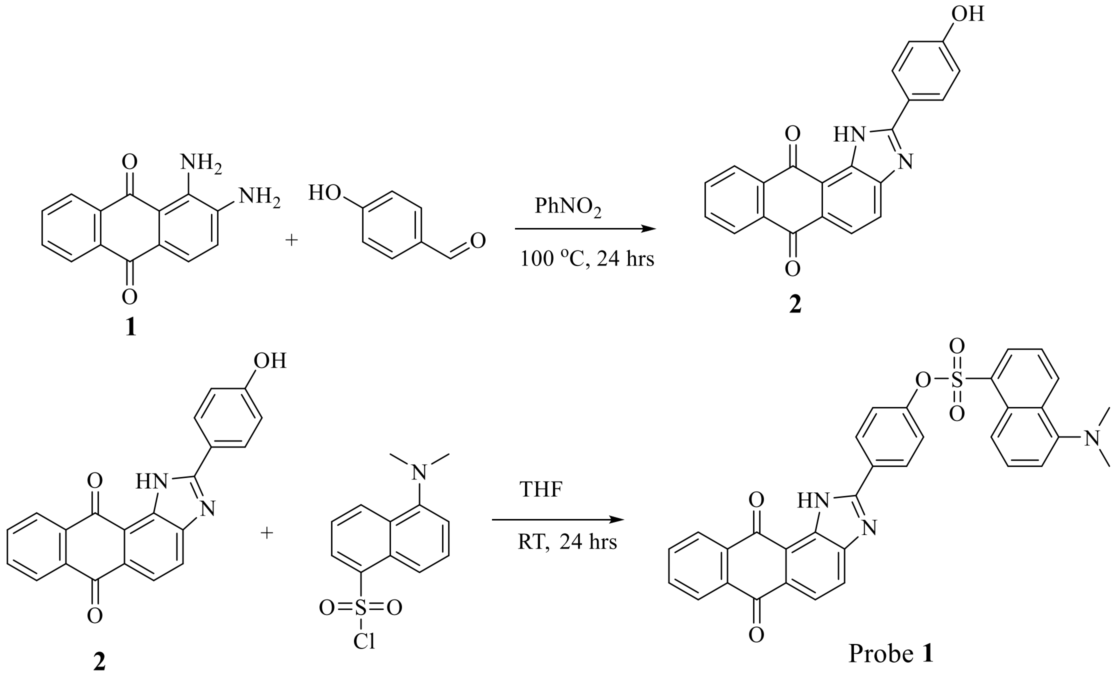
2.4.1.1 *Synthesis of 2-(4-hydroxyphenyl)-1H-anthra[1,2-d]imidazole-6,11-dione :*

1,2 diaminoanthraquinone (1 mol, 0.238 g) and 4- Hydroxybenzaldehyde (1 mol, 0.122 g) was mixed in nitrobenzene and refluxed for about 24 hour (Scheme 2.1). The progress of the reaction was monitored by checking the TLC in ethyl acetate and hexane (1:1, v/v). The product obtained was brown colored solid which was filtered and washed with diethyl ether followed by drying to get pure compound **1**. Yield = 0.293 g

2.4.1.2 *Synthesis of 4-(6,11-dioxo-6,11-dihydro-1H-anthra[1,2-d]imidazol-2-yl) phenyl (dimethylamino)naphthalene-1-sulfonate (probe 1) :*

The synthesized compound ***1*** (0.2 mol, 0.36 g) was refluxed further with dansyl chloride (0.5 mol, 0.135 g) in THF as a solvent for 24 hours (Scheme 2.1) to get desired probe **1**. The reaction was monitored by using TLC with solvent system, ethyl acetate : hexane (1:1, v/v). The structure of the product was confirmed by NMR spectroscopy.

0.430 g, % yield = 86%, red color, m.pt = 230 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm : 8.63 (1H, d, *J* = 8.4 Hz, NH), 8.51 (1H, d, *J* = 8.8 Hz), 8.35-8.33 (1H, m, ArH), 8.28-8.22 (2H, m, ArH), 8.10-8.08 (2H, m, ArH), 8.01-7.99 (2H, m, ArH), 7.84-7.81 (2H, m, ArH), 7.75-7.71 (1H, m, ArH), 7.47-7.44 (1H, m, ArH), 7.13 (2H, d, *J* = 8.8 Hz, ArH), 2.34 (6H, s) (Figure 2.1).



Scheme 2.1. Synthesis of Probe **1**

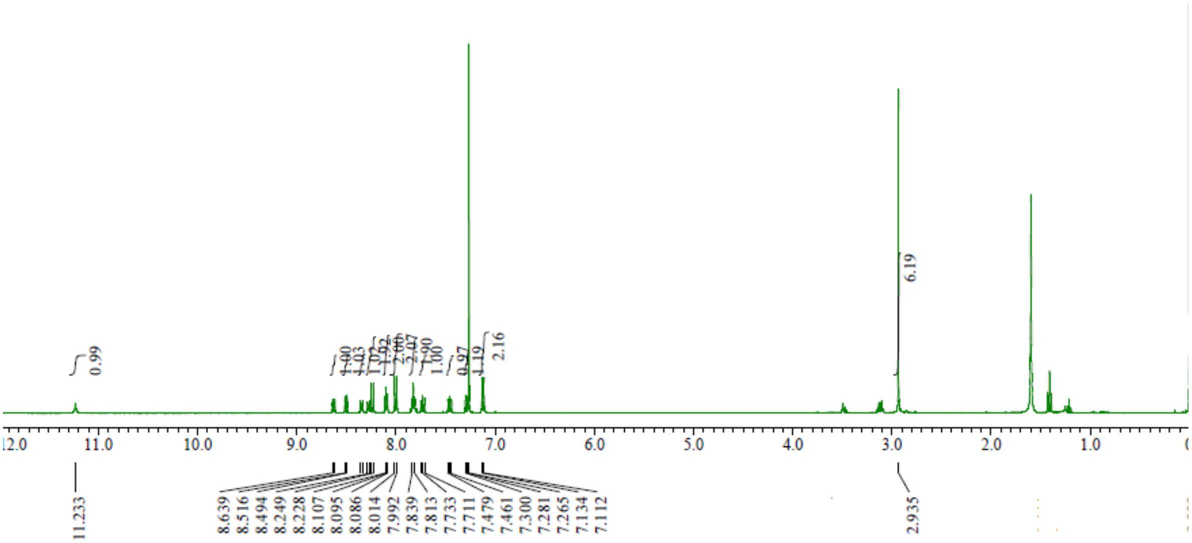
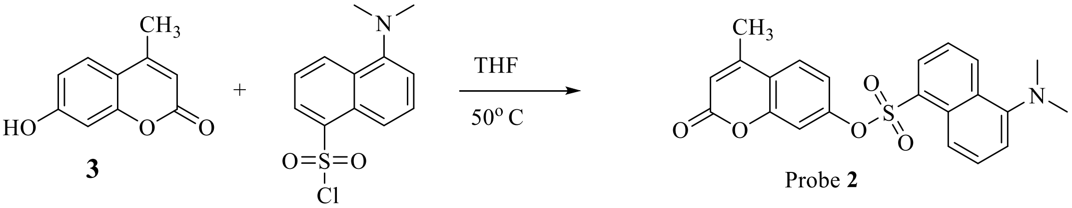


Figure 2.1. ^{1}H NMR of Probe **1**

2.4.2 *Synthesis of Coumarin based moieties*

2.4.2.1 *Synthesis of 4-methyl-2-oxo-2H-chromen-7-yl 5-(dimethylamino)naphthalene-1-sulfonate(probe 2):*

4–methyl lumbelliferone (0.1 mol, 0.176 g) and and dansyl chloride (0.1 mol, 0.270 g) were mixed in THF and refluxed for 24 hours (Scheme 2.2) followed by reaction monitoring using TLC in ethyl acetate:hexane (3:7, v/v) as solvents. A yellow colored solid was obtained. The product was filtered and washed with water. NMR was used to confirm the formation of probe **2** (Figure 2.2). 0.346 g, % yield = 77 % yellow, m.pt = 111.5 ^{o}C, ^{1}H NMR (400 MHz, CDCl$_3$), δ, ppm : 8.62-8.60 (1H, d, *J* = 8.8 Hz), 8.43 (1H, d, J = 8.8 Hz), 8.08 (1H, d, *J* = 8.4 Hz), 7.70 (1H, d, *J* = 16.4 Hz), 7.48 (2H, d, *J* = 8.8 Hz) , 7.24 (1H, s), 7.05 (1H, d, J=7.8), 6.72 (1H, s), 6.21 (1H, s), 2.34 (6H, s, CH$_3$), 1.26 (3H, s).



Scheme 2.2. Synthesis of probe **2**

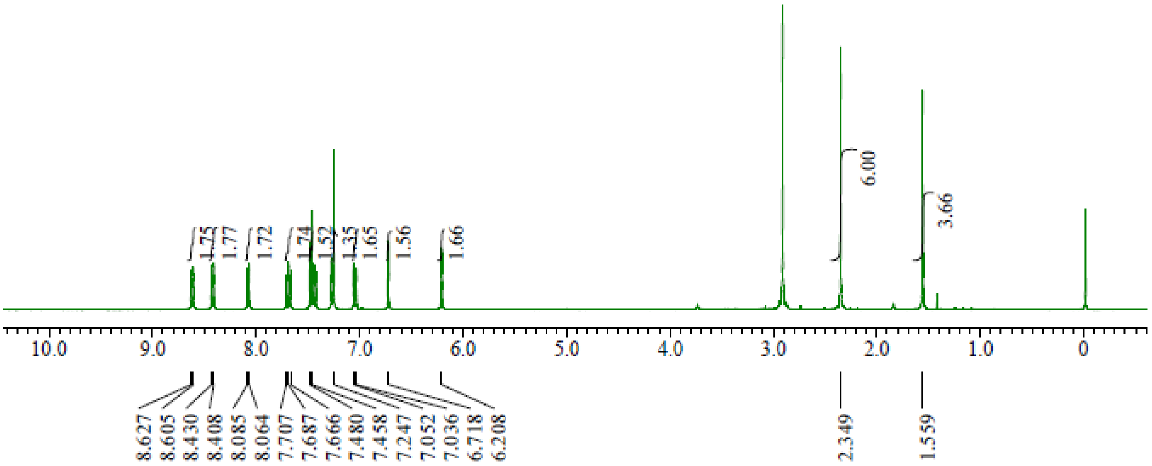


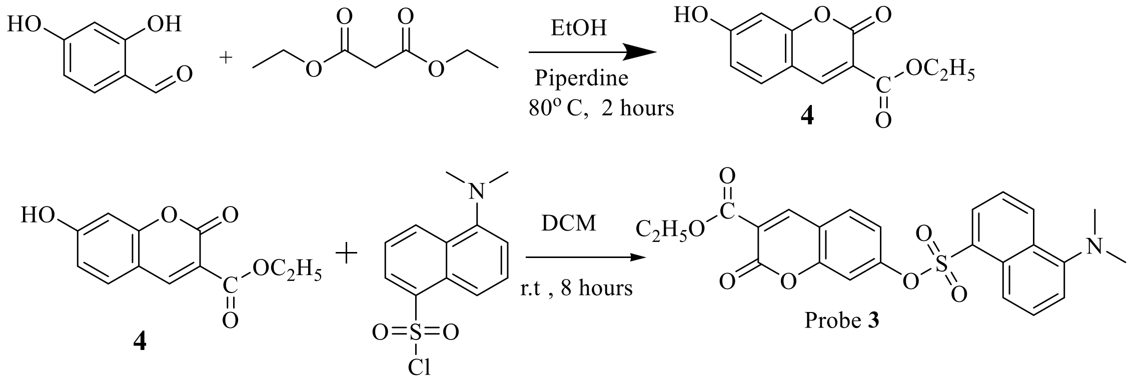
Figure 2.2. ^{1}*H NMR of Probe* **2**

2.4.2.2 Synthesis of ethyl 7-hydroxy-2-oxo-2H-chromene-3-carboxylate

2, 4 dihydroxybenzaldehyde (0.2 mol, 0.414 g) and diethyl malonate (0.3, 0.160 g) were refluxed for 2 hours in ethanol with the addition of piperidine in catalytic amount (Scheme 2.3). The progress of the reaction was done using TLC in pure chloroform as a solvent. A yellow colored solid for compound **4** was obtained which was filter, washed with water and dried.

2.4.2.3 *Synthesis of ethyl 2-oxo-2H-chromene-3-carboxylate compound with methyl 5-(dimethylamino)naphthalene-1-sulfonate (3)*

The compound 4 (0.1 mol, 0.235 g) and dansyl chloride (0.15 mol, 0.300 g) were stirred together at room temperature for 8 hours in DCM solvent (Scheme 2.3). The reaction was monitored using TLC in chloroform. A yellow colorless solid was obtained which was filtered, washed and dried. NMR spectroscopy was done in order to confirm the structure of the compound synthesized (Figure 2.3). 0.500 g, yellow, 105^0 C, ^{1}H NMR (400 MHz, CDCl$_3$), (δ ppm) : 8.65 (1H, d, J = 6.80 Hz, ArH), 8.42 (2H, t, J = 4.05 Hz, ArH), 8.11 (1H, d, J = 5.84 Hz, ArH), 7.71 (1H, t, J = 6.32 Hz, ArH), 7.50-7.45 (2H, m, ArH), 7.29 (1H, d, J = 6.08 Hz, ArH), 7.09-7.07 (1H, m, ArH), 6.78 (1 H, d, J = 1.56 Hz), 4.40 (2H, m), 2.92 (6H, s), 1.39 (3H, t, J = 5.72 Hz, CH$_3$-ethyl).



Scheme 2.3. Synthesis of probe **3**

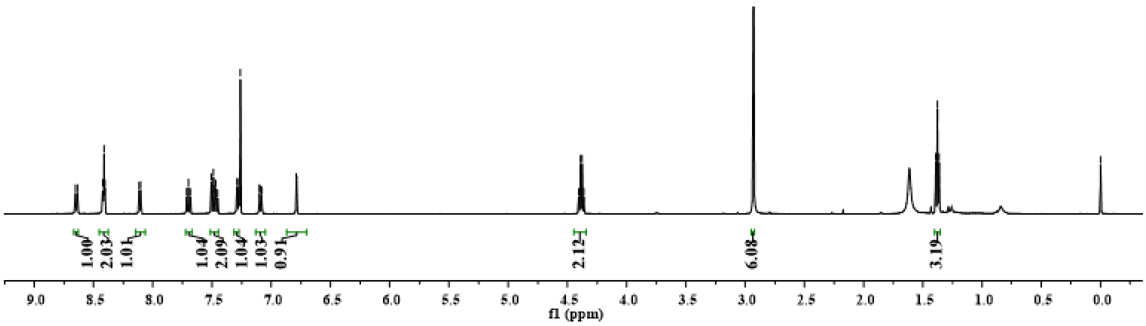


Figure 2.3 *^{1}H NMR of Probe 3*

Chapter 3

RESULTS AND DISCUSSION

3.1 Photophysical studies of probe 1

The photophysical properties of probe **1** were measured using absorption and emission spectroscopy. The probe **1** (10 µM, MeCN) displayed an absorption peak at 380 nm. Upon excitation at 390 nm, the emission peak was observed at 510 nm, with stokes shift of 120 nm. The designed probe **1** contained the -$N(CH_3)_2$ and anthraquinone moiety as electron donor and electron accepter units, which could raise electron density shift. Therefore, spectral measurements were extended to different polarity systems (varying polarity from non-polar cyclohexane (CYCH) to polar DMSO) (Figure 3.1). It was noted that the absorption and emission spectral shape and peaks did not change significantly. It described that no significant electron density shift occurred and probe **1** has neutral nature in different environment.

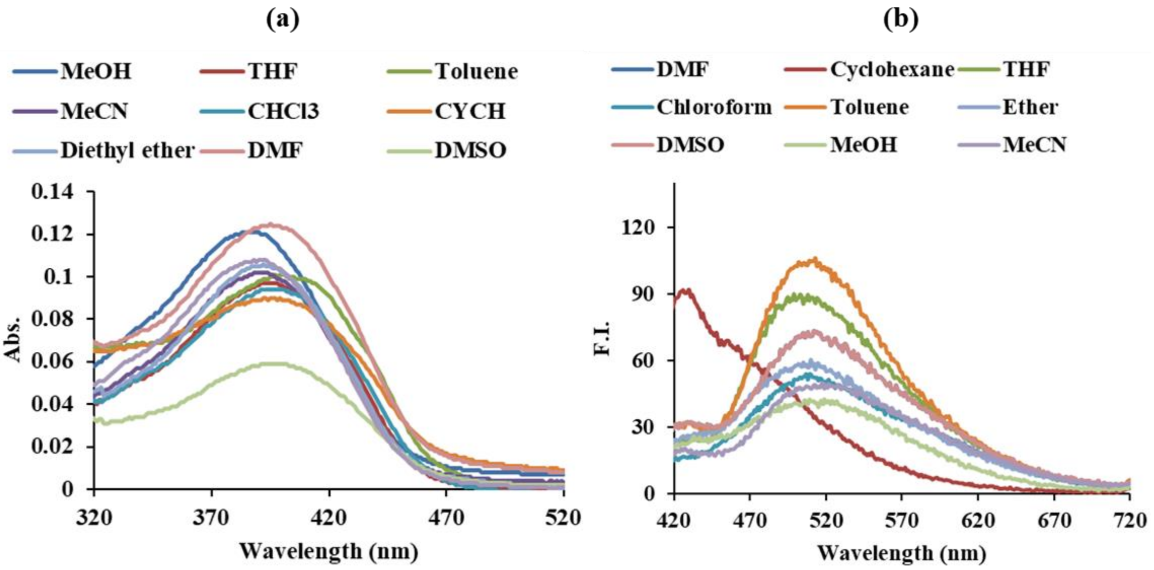


Figure 3.1. (a) Absorption and (b) emission spectra of probe **1** in different solvents.

3.1.1 Sensing properties of probe 1

The photophysical behavior of probe **1** (10 µM; 5/95 (H_2O/CH_3CN); v/v) was examined towards different anions such as CN^-, SCN^-, Cl^-, F^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$, and CH_3COO^- through absorption and emission spectroscopy. The absorption peak of probe 1 at 390 nm was not altered significantly for anions except for CN^- ions (Figure 3.2). Further, the quantitative estimation of CN^- was performed using titration experiment. The incremental addition of CN^- ions (0-280 µM) to probe **1** increased the absorption intensity at 390 nm along with rise of new absorption peak at 486 nm with an isobestic point at 425 nm. The spectral red shift of 96 nm was accompanied with colour change from colourlesss to orange (Figure 3.2).

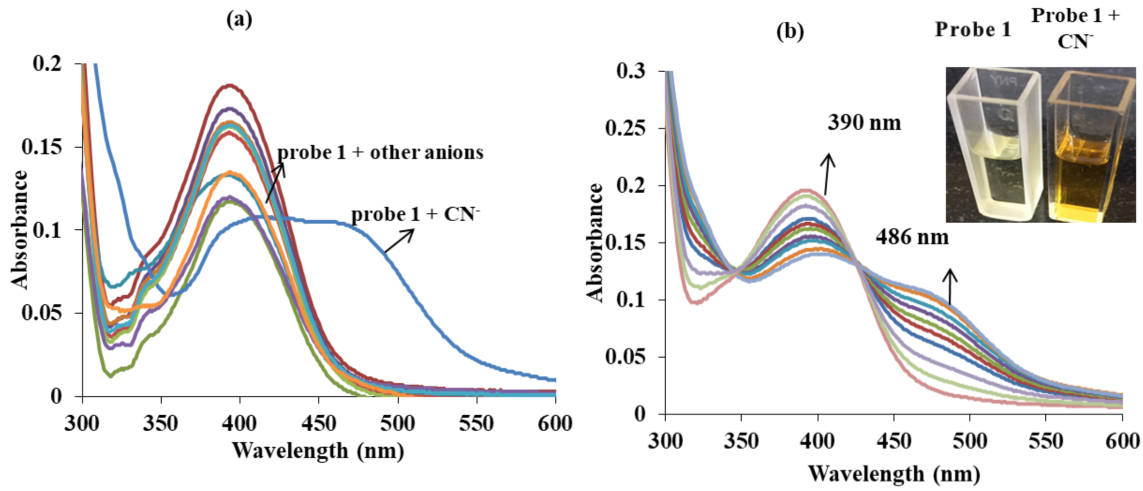


Figure 3.2 Absorption spectra of probe **1** (10 µM; 5/95 (H_2O/CH_3CN); v/v) in the presence of (a) different anions and (b) incremental addition CN^- ions.

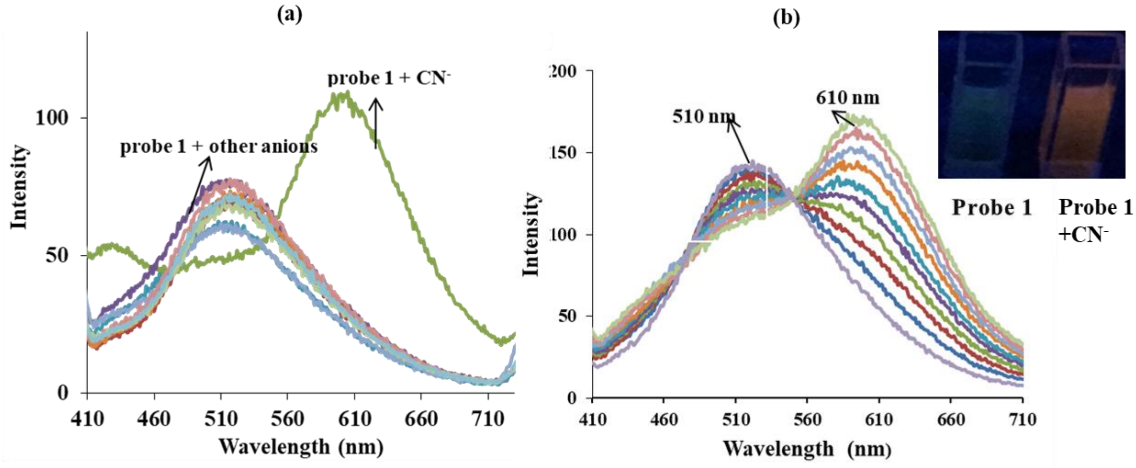


Figure 3.3. Emission spectra of probe **1** (10 µM; 5/95 (H_2O/CH_3CN); v/v in the presence of (a) different anions and (b) incremental addition of CN^- ions

Likewise, the emission behaviour of probe **1** was also measured towards anions. Upon excitation at 390 nm, the emission peak of probe **1** at 510 nm was red shifted by 100 nm to 610 nm. No other anions changed the emission response of probe **1** significantly (fig 3.3). Further, the incremental addition of CN^- ions (0-280 µM) decreased the emission intensity at 510 nm along with rise of emission peak at 610 nm, with an isoemission point at 545 nm. The spectral changes were also accompanied with colour change from light green to red. Thus, the absorption and emission changes of probe **1** facilitated the chromo-fluorescent detection of CN^- ions (Fig3.3(b).

3.1.2 Interference study

In order to determine the sensitivity of probe 1 towards CN^- ions, the spectral measurements were performed in the presence of other ions. It was found that there was negligible interference from anions; however, the presence of HSO_4^- interfered the detection of CN^- ions (Figure 3.4).

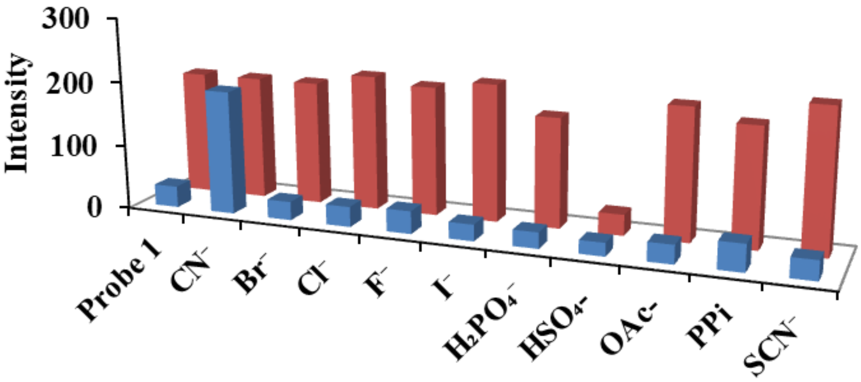


Figure 3.4. Relative intensity of probe **1** (10 µM) in H_2O/CH_3CN::5:95 (λ_{ex} = 390 nm) with different competing anions in the absence and presence of CN^-, at λ = 610 nm, where blue bar represents the emission intensity change of probe 1 with different anions and red bars represents probe **1** with CN^- plus different relevant competing ions.

3.1.3 Stoichiometry, binding constant and detection limit

The stoichiometry of probe **1** towards CN- was determeined by Job plot. The experiment was performed by measuring the spectral response for diffeent mole fraction of CN^- ions. The mole fraction of CN^- ions vs spectral intensity graph displayed maxima at 0.7 mole fraction of CN- ions and thus, described as 1:2 (probe 1:CN^-) stoichiometry (Figure 3.5). Further, Benesi-Hildebrand equation was used to calculate the binding constant for probe 1.CN^- and determined to be 6.4×10^4 M^{-1} (Figure 3.5). The limit of detection was measured for linear response of probe 1 towards CN- ions by standard IUPAC equation and determined to be 3.5 nM (Figure 3.5).

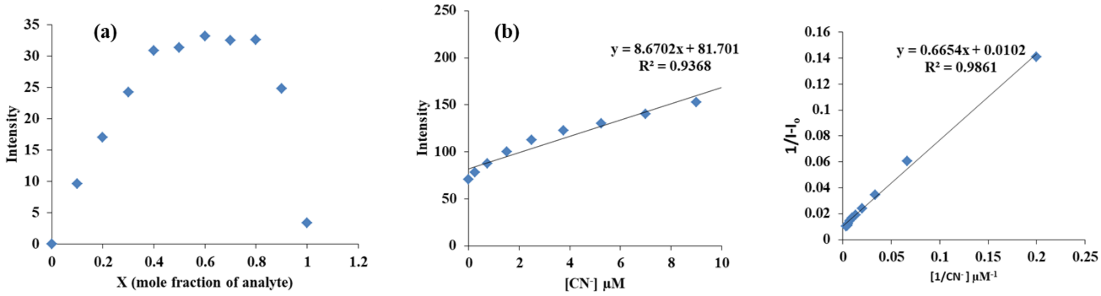


Figure 3.5. (a) Job’ s plot of probe **1** in H_2O/CH_3CN (10:90, v/v) (b) Detection limit of cyanide ions. (c) The stability constant for probe **1.**

3.1.4 Plausible mechanism

Probe **1** contained anthraquinone unit joined through the S-O linkage of sulphonic unit of dansyl unit. The addition of CN^- ions attack the electrophilic S center and thus cleave the S-O bond. The cleavage of probe **1,** generate its precursor (compound **2**) in its deprotonated form. The reason behind this bond scission was the presence of anthraquinone unit and electronegative negative oxygen atoms. The anthraquinone unit and oxygen atoms withdraw the electron density from the S center and trigger it for the nucleophilic substation by introducing CN^- ions. The cleavage of probe **1** to deprotonated compound **2** was confirmed by measuring the emission spectra compound 2. The overlap of spectra suggested the cleavage of probe **1** to compound **2**. The possible mechanism was presented in scheme 3.1.

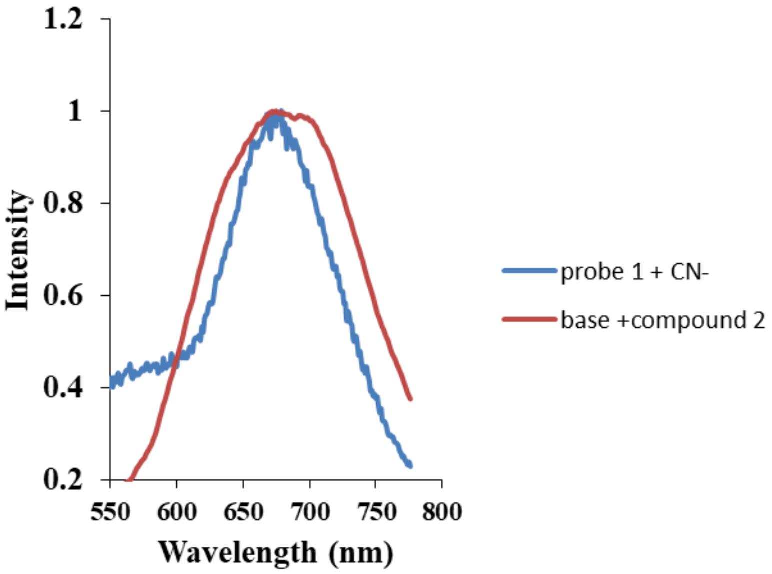
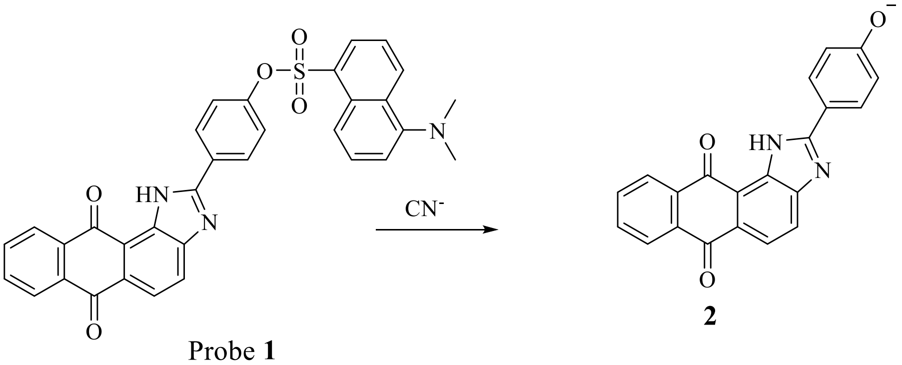


Fig.3.6 Emission spectra of compound 2 on addition base and probe **1** + CN^-



Probe **1**

2

Scheme 3.1 Possible mechanism of detection of CN^- ions.

3.2 *Photophysical studies of probe 2*

The photophysical properties of probe **2** were measured using absorption and emission spectroscopy. The probe **2** (10 µM, MeCN) displayed an absorption peak at 380 nm. Upon excitation at 370 nm, the emission peak was observed at 520 nm, with stokes shift of 150 nm. The designed probe 2 contained the $-N(CH_3)_2$ and coumarin moiety as electron donor and electron accepter units, which could raise electron density shift. Therefore, spectral measurements were extended to different polarity systems (varying polarity from non-polar toluene to polar DMSO). It was noted that the absorption and emission spectral shape and peaks did not change significantly. It described that no significant electron density shift occurred and probe 1 has neutral nature in different environment.

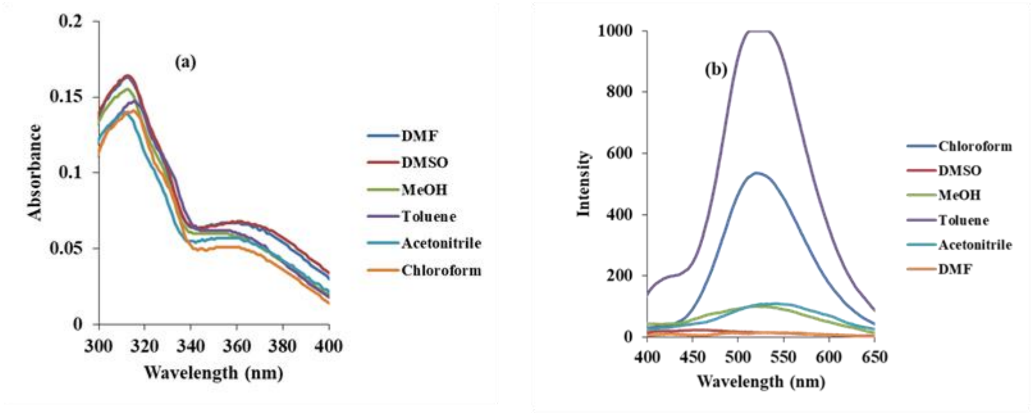


Figure 3.6. Effect of diferent solvents on absorption (a) and emission spectra (b) of probe **2**

3.2.1 Spectral response of probe 2 on varying pH

The coumarin and dansyl units have been used as versatile candidate in aqueous medium such as fluorescent markers, sensors etc. Therefore, the absorption and emission spectroscopy measurements were further extended to acidic and basic medium in pure aqueous medium. Probe 2 (10 µM, H_2O, pH=7.2) displayed absorption peak at 370 nm, 320 nm and 270 nm. On decreasing and increasing the pH of solution of probe 2, the absorption intensity was decreased at 370 nm, 320 nm and 270 nm (Figure 3.7). This cannot be due to diluton effect as similar change was not observed in case of emission .

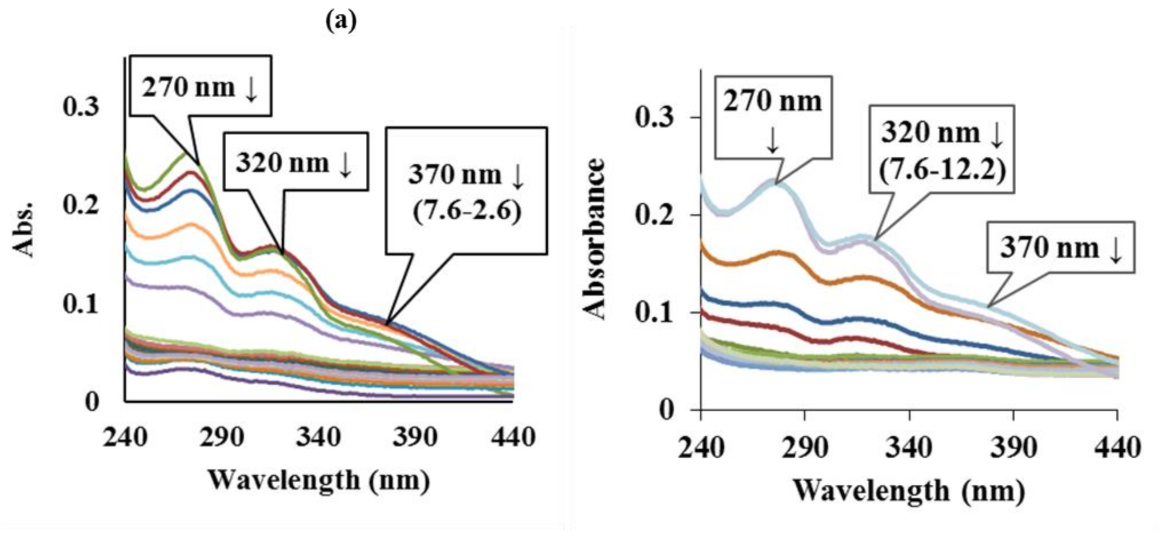


Figure 3.7. Effect of pH on absorption spectra of probe **2**.

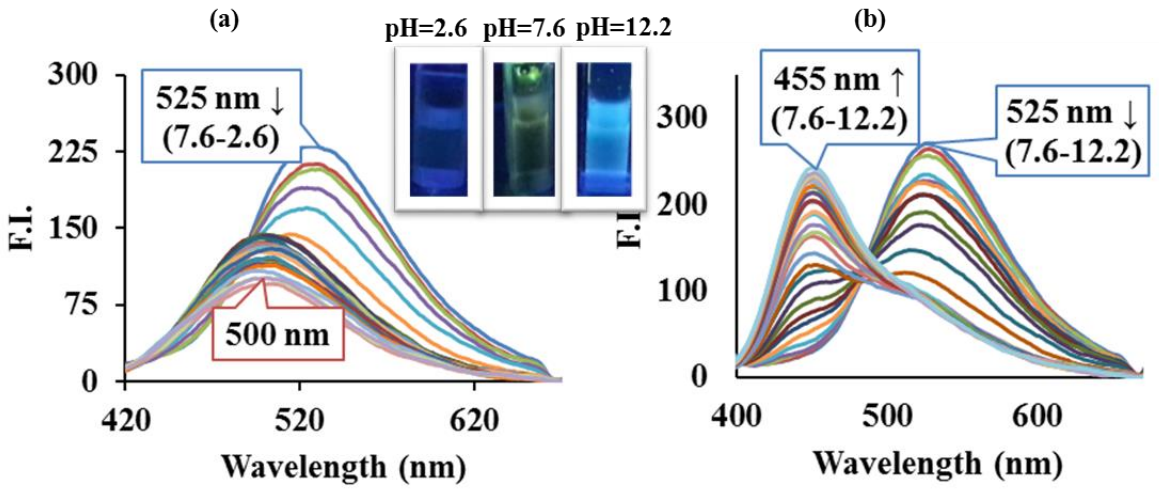


Figure 3.8. Effect of pH on the emission spectra of probe **2**.

Likewise, the emission response of probe **2** was also measured for varying the pH. On decreasing the pH (7.2-2.6) of solution of probe 2 (10 µM, H_2O), the emission peak of probe 2 at 525 nm was decreased in intensity and emission was blue shifted to 490 nm (Figure 3.8). The hypochromic blue shift could be due to protonation of $–N(CH_3)_2$ unit. On the other hand, on increasing the pH (7.2-12.1), the quenching of probe's emission peak at 525 nm and concomitant rise of new emission peak at 450 nm was observed, with an isoemission point 490 nm (Figure 3.8).

3.2.2 *Possible mechanism of interactions*

The probe contained basic –$N(CH_3)_2$ unit and highly nucleophilic S-center. Therefore, the mechanism of interaction of H^+ ions and OH^- ions in acidic and basic medium was understood. At low pH value, the excess of H^+ ions could be interacted to –$N(CH_3)_2$ unit, while, high pH value the presence of OH^- ions could have interacted to S- center could lead to cleavage of probe 2 to compound **3**. This lead to very intense ICT in the compound. The mechanism was supported by overlapping of emission spectra of compound **3** to probe **2** at pH 12.2 (Figure 3.9). The possible interactions were presented in scheme 3.2.

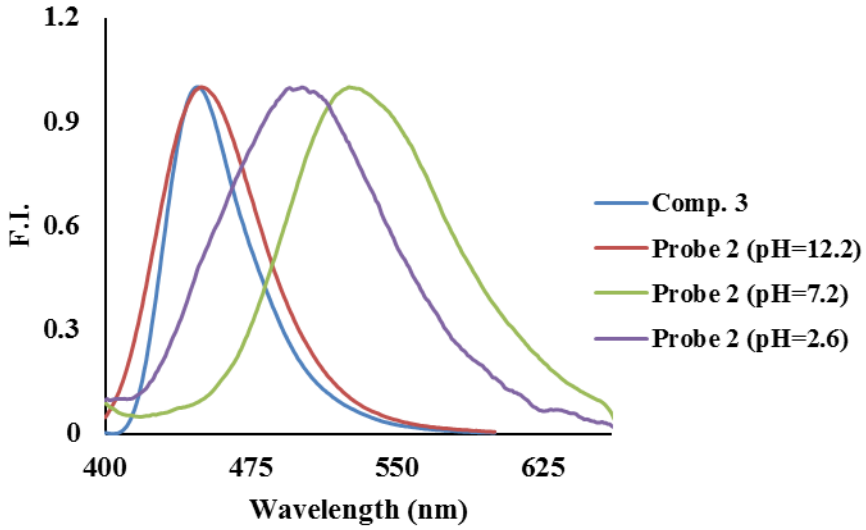
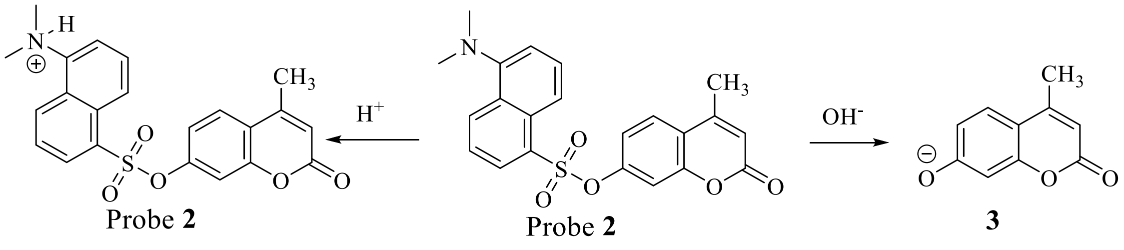


Figure 3.9. Emission of compound **3**, and probe **2** at different pH



Scheme 3.2. Possible mechanism of interaction of probe **2**

3.2.3 *Sensing properties of probe 2*

The photophysical behavior of probe **2** (10 µM; 1:9 (H_2O/CH3CN); v/v) was examined towards different anions such as CN^-, SCN^-, Cl^-, F^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$, and CH_3COO^- through absorption and emission spectroscopy. The absorption peak of probe **2** at 370 nm, 320 nm, and 270 nm was not altered significantly for anions. However, the rise of absorption intensity was observed (Figure 3.10). On the other hand, probe **2** displayed significant selectivity towards CN^- ions through emission response. No other change the emission behavior of probe **2** (Figure 3.10). Further, the quantitative estimation of CN^- was performed using titration experiment. On incremental addition of CN^- ions (0-145 µM), the probe's emission peak was remained unaltered, however, new emission peak at 450 nm was emerged. The spectral changes were also accompanied with color change from yellow to blue (Figure 3.10). Thus, the absorption and emission changes of probe **2** facilitated the naked-eye detection of CN^- ions.

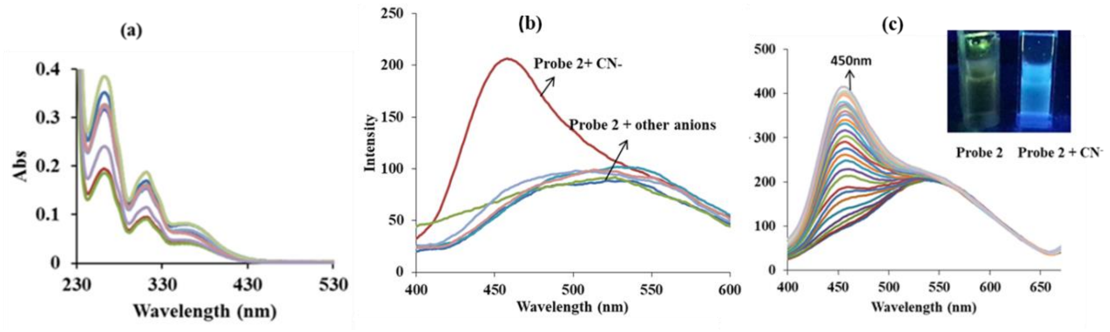


Figure 3.10. (a) Absorption and (b) emission response of probe **2** in the presence of different ions and (c) emission response of probe **2** with incremental addition of CN^- ions; inset: color changes under UV light

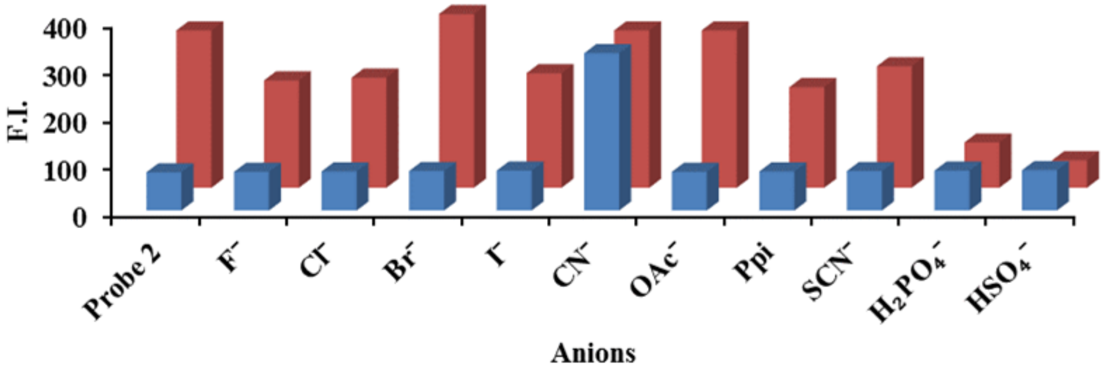


Figure 3.11. Relative intensity of probe **2** (10 µM) in H_2O/CH_3CN::1:9) with different competing anions in the absence and presence of CN^-, where blue bar represents the emission intensity change of probe **2** with different anions and red bars represents probe **2** with CN^- plus different relevant competing ions.

3.2.4 Interference Study

In order to determine the sensitivity of probe **2** towards CN^- ions, the spectral measurements were performed in the presence of other ions. It was found that there was negligible interference from anions; however, the presence of HSO_4^- and $H_2PO_4^-$ interfered the detection of CN^- ions (fig 3.3). The acidic nature of HSO_4^- and $H_2PO_4^-$ ions could lead to protonation of compound **3**.

3.2.5 Stoichiometry, binding constant and detection limit

The stoichiometry of probe **2** towards CN^- was determeined by Job plot. The experiment was performed by measuring the spectral response for different mole fraction of CN^- ions. The mole fraction of CN^- ions vs spectral intensity graph displayed maxima at 0.5 mole fraction of CN- ions and thus, described as 1:1 (probe 1:CN^-) stoichiometry (Figure 3.12). Further, Benesi-Hildebrand equation was used to calculate the binding constant for probe 1.CN^- and determined to be 6.66×10^6 M^{-1} using fluorescence titration at 450 nm (Figure 3.12). The limit of detection was measured for linear response of probe 1 towards CN- ions by standard IUPAC equation and determined to be 17 nM (Figure 3.12).

3.2.6 Plausible mechanism

The addition of CN^- ions could have the very similar effects as that of OH^- ions. The contained coumarin unit as electron sinker and electronegative oxygen atoms promote the more electron deficiency at S-center. Therefore, the presence of CN- ions to probe **2** causes the cleavage of S-O bond which leads to the formation of compound **3.** The possible mechanism was presented in scheme 3.3. It did not show any change with any other anion which can be their nucleophic character and solvation power towards the solvent which do not allow to cleave the bond.

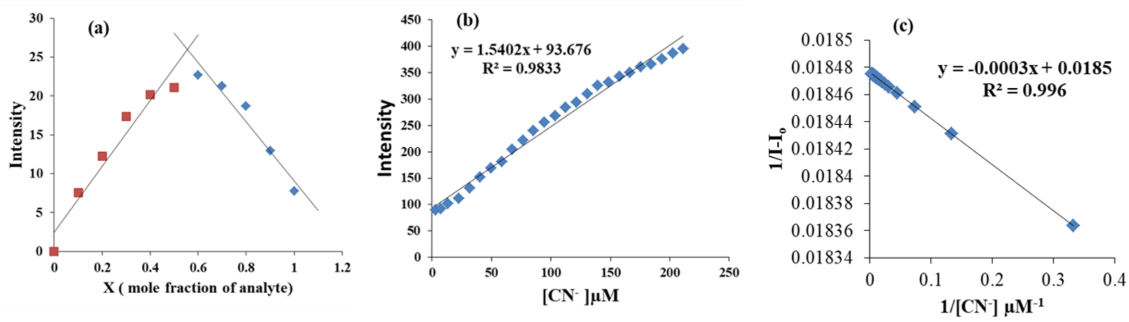
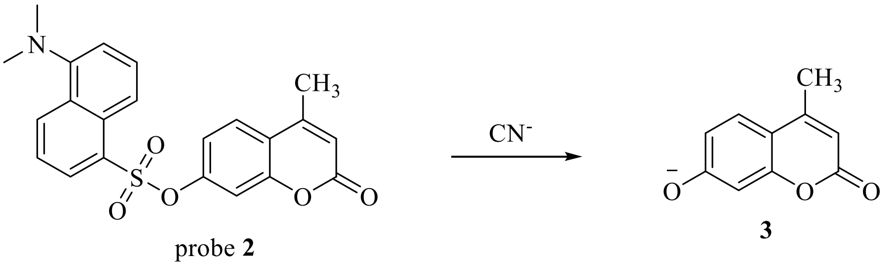


Figure 3.12. (a) Job's plot, (b) detection limit plot and (c) stability constant plot of probe **2**.CN$^-$.



Scheme 3.3. Possible mechanism of interaction of probe **2** towards CN$^-$

3.3 Photophysical studies of probe 3

The photophysical properties of probe **3** were measured using absorption and emission spectroscopy. The probe **3** (10 µM, CH_3CN/H_2O, (9:1, v/v)) displayed an absorption peak at 330 nm. Upon excitation at 330 nm, the emission peak was observed at 466 nm, with stokes shift of 330 nm. The designed probe **3** contained the -$N(CH_3)_2$ and coumarin moiety as electron donor and electron accepter units, which could raise electron density shift. Therefore, spectral measurements were extended to different polarity systems (varying polarity from non-polar (toluene) to polar (DMF). It was noted that the absorption and emission spectral shape and peaks did not change significantly. It described that no significant electron density shift occurred and probe **3** has neutral nature in different environment.

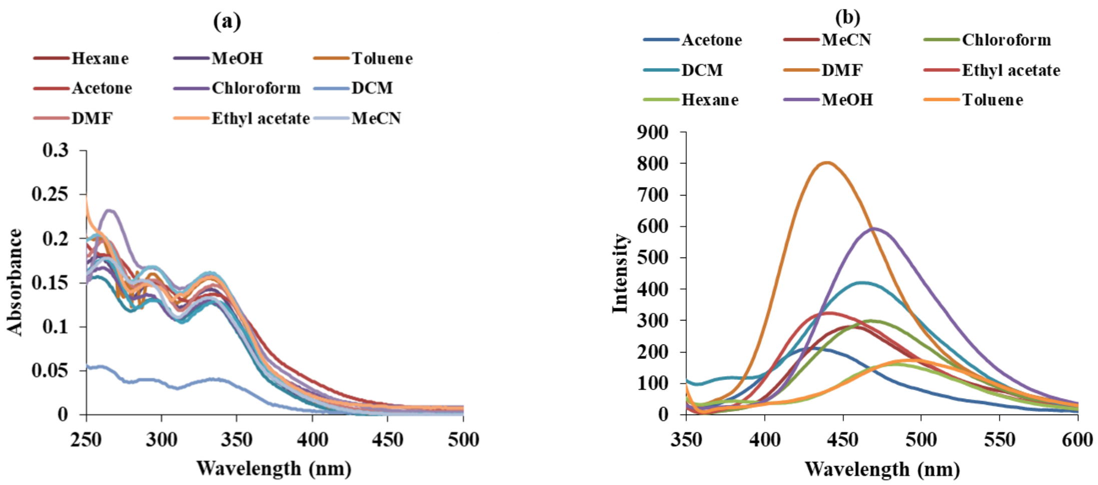


Figure 3.13 (a) The absorption spectra (b) the emission spectra of probe **3** in different solvents.

3.3.1 Spectral response of probe 3 on varying pH

The absorption and emission spectroscopy measurements were further extended to acidic and basic medium in pure aqueous medium. Probe **3** (10 µM, H_2O) displayed absorption peak at 344 nm, 299 nm and 272 nm. On lowering and raising the pH range of probe **3** solution, the absorption intensity was decreased at 344 nm, 299 nm and 272 nm (Figure 3.14).

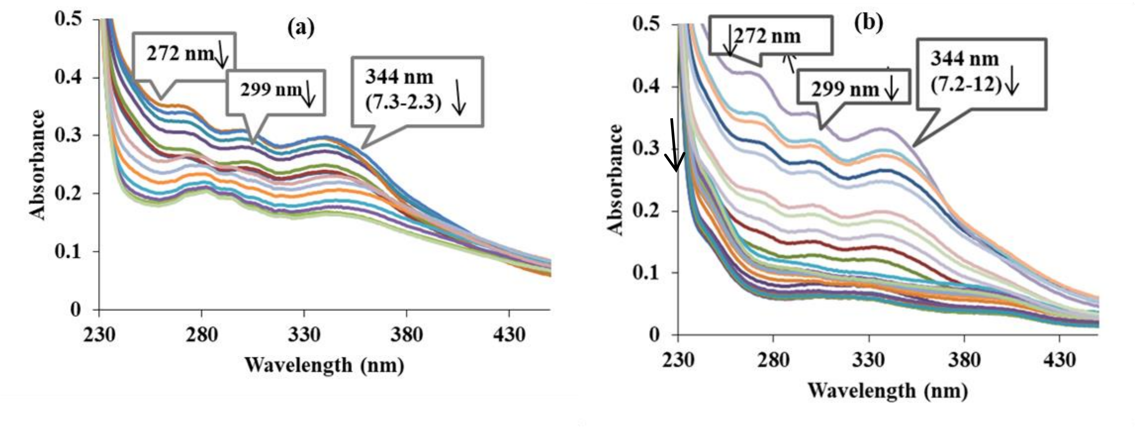


Figure 3.14. Effect of pH on absorption spectra of probe **3**

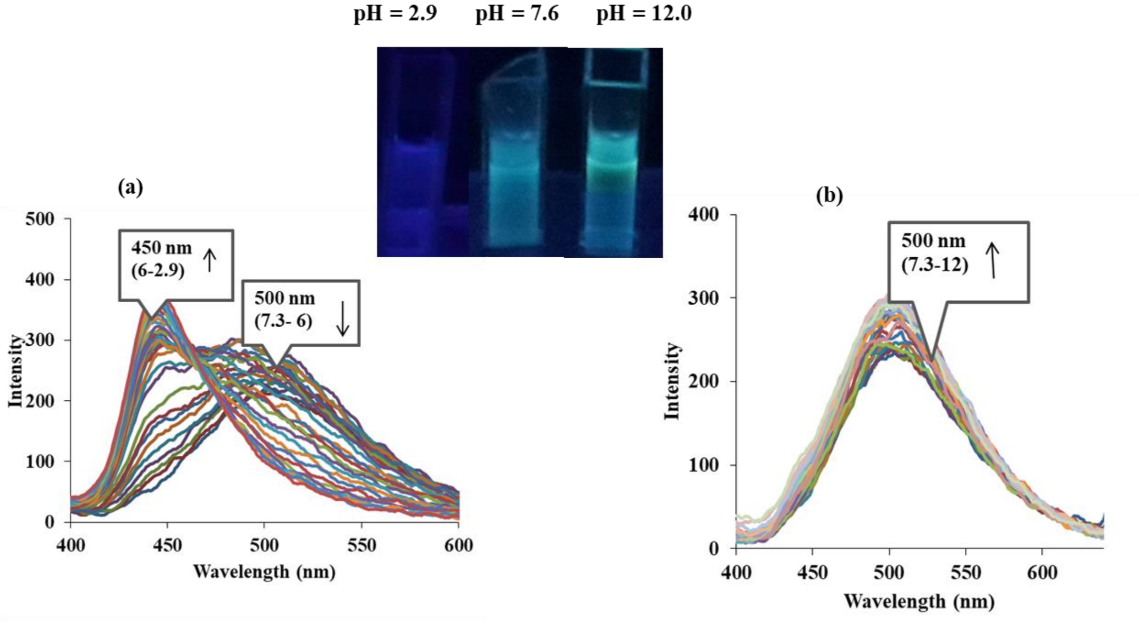


Figure 3.15. Effect of pH on emission spectra of probe **3**.

Similarly, the emission response of probe **3** was also measured. On decreasing the pH (7.2-2.9) of solution of probe **3** (10 µM, H_2O), the emission peak of probe 2 at 500 nm was decreased in intensity and emission was blue shifted to 450 nm (Figure 3.16). The hyperchromic blue shift could be due to protonation of $–N(CH_3)_2$ unit. On the other hand, on increasing the pH (7.2-12.1), mere enhancement of probe's emission peak at 500 nm was observed (Figure 3.16).

3.3.2 Sensing properties of probe 3

Probe **3** exhibited absorption spectra at 330 nm and emission spectra at 466 nm (CH_3CN : H_2O, (90:10), v/v). Further, probe 3 was evaluated for its sensing properties towards anions. However, no change in absorption and emission spectra was observed when anions were added to probe **3** (Figure 3.16). The reason could be presence of good electron donating in the form of ester on coumarin moiety, which pushes electron density towards S-center. Therefore, reduce the electrophilic nature of S-center at probe **3**, and resulted in insignificant spectral changes in the presence of anions.

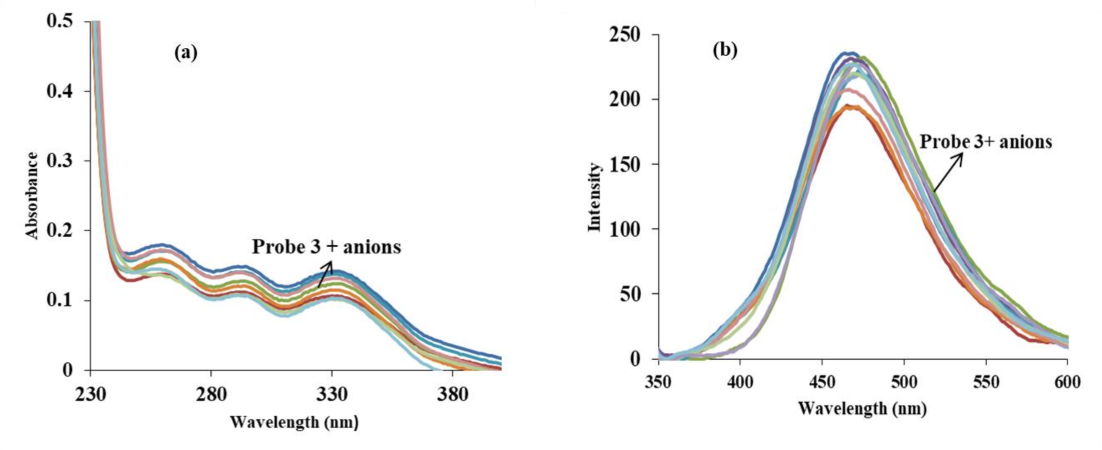


Figure 3.16. (a) Absorption and (b) emission spectra of probe **3** (MeCN:Water, 90:10, v/v).

3.3.3 Comparison of coumarin based Probe 2 and Probe 3

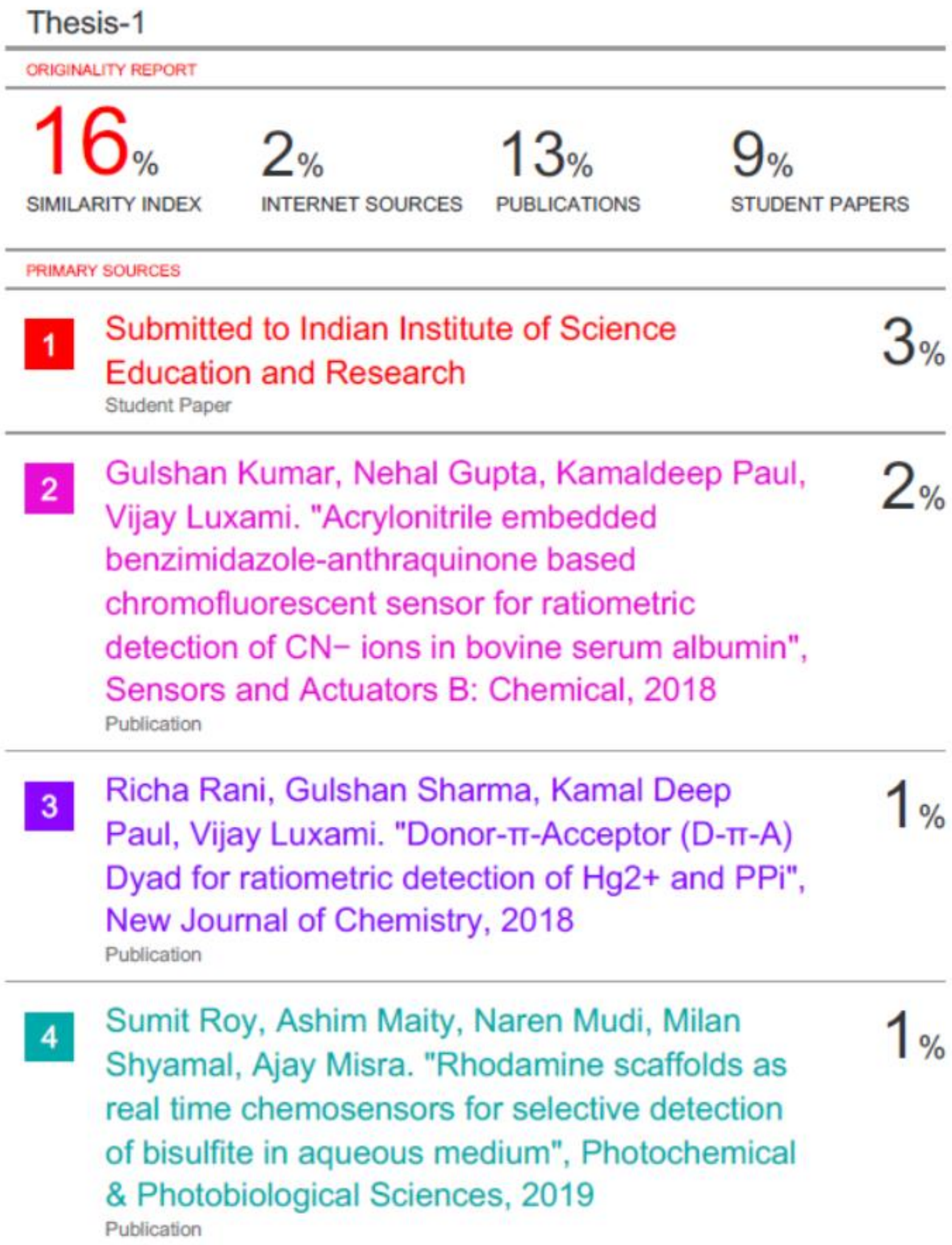
In MeCN : Water (90 : 10, v/v), Probe **2** and probe **3** exhibited absorption maxima at 360 nm and 330 nm respectively. Similarly, the emission spectra was observed at 508 nm and 466 nm. There was no change in absorption spectra of probe **2** and probe **3** on addition of CN^-. However, the emission spectra of Probe **2** showed a blue shift of ~ 53 nm, when CN^- ions were added accompanied by a hyperchromic shift. The fluorescence changed from green to blue. The acidic and basic conditions influence the absorption and fluorescence of probe **2** and **3**. The absorption band of both the probes quenched on increasing or decreasing pH. However, the emission band of probe 2 started to quench on addition of acid and there was a small blue shift at pH 8.1 but in case of basic pH a blue shift of ~50 nm was observed and as the band showed hyperchromic shift at 450 nm with increasing pH. On the other side, probe **3** did not show any significant change in fluorescence on addition of base but decrement in pH caused the band at 500 nm to quench and a intense blue shifted band appeared at 450 nm.

3.4 Conclusion

Anthraquinone and coumarin based dyads were synthesized with dansyl chloride based on S-O bond scission that show ICT on bond cleavage and impart obvious color changes which can be observed with naked eye. The absorption spectra and emission spectra of probe **1** were seen with a red shift on addition of cyanide ions from 390 nm to 450 nm in absorption and 510 nm to 610 nm in emission in MeCN : water (90:5) respectively. There was a visible as well as fluorescence color change. Probe **2** had emission spectra blue shifted, on addition of cyanide from 520 nm to 450 nm accompanied by change in fluorescence from green to blue. Probe **3** gave absorption at 330 nm and emission at 466 nm. It did not show any sensing property towards anions in MeCN : Water (90:10, v/v). This helped to formulate that presence of different substituents influence the sensing ability of anions.

References

1. M. H. Lee, J. S. Kim and J. L. Sessler, *Chem. Soc. Rev.*, 2015, **44**, 4185-4191.
2. T. L. Mako, J. M. Racicot and M. Levine, *Chem. Rev.*, 2018, **119**, 322-477.
3. F. Huang and E. V. Anslyn, ACS Publications, 2015, **115**, 6999-7000.
4. G. Resnati, E. Boldyreva, P. Bombicz and M. Kawano, *IUCrJ*, 2015, **2**, 675-690.
5. E. Mattia and S. Otto, *Nature Nanotechnology*, 2015, **10**, 111.
6. S. Sasaki, G. P. Drummen and G.-i. Konishi, *J. Mater. Chem. C*, 2016, **4**, 2731-2743.
7. V. S. Padalkar and S. Seki, *Chem. Soc. Rev.*, 2016, **45**, 169-202.
8. A. C. Sedgwick, L. Wu, H.-H. Han, S. D. Bull, X.-P. He, T. D. James, J. L. Sessler, B. Z. Tang, H. Tian and J. Yoon, *Chem. Soc. Rev.*, 2018, **47**, 8842-8880.
9. C. K. Moon, K. Suzuki, K. Shizu, C. Adachi, H. Kaji and J. J. Kim, *Adv. Mater.*, 2017, **29**, 1606448.
10. P. B. Pati, *Sens. Actuators, B*, 2016, **222**, 374-390.
11. N. L. Ferreira, L. M. de Cordova, A. D. Schramm, C. R. Nicoleti and V. G. Machado, *J. Mol. Liq.*, 2019, **282**, 142-153.
12. P. R. Lakshmi, R. Manivannan, P. Jayasudha and K. P. Elango, *Anal. Methods*, 2018, **10**, 2368-2375.
13. G. Kumar, N. Gupta, K. Paul and V. Luxami, *Sens. Actuators, B*, 2018, **267**, 549-558.
14. A. Pandey, A. Kumar, S. Vishwakarma and K. K. Upadhyay, *Chemistry Select*, 2018, **3**, 3444-3450.
15. L. Wang, X. F. Yang and M. Zhao, *J Fluoresc*, 2009, **19**, 593-599.
16. X.-F. Yang, L. Wang, H. Xu and M. Zhao, *Anal. Chim. Acta*, 2009, **631**, 91-95.
17. Y. Xu, X. Dai and B.-X. Zhao, *Spectrochim. Acta, Part A*, 2015, **138**, 164-168.
18. Z. Yang, Z. Liu, Y. Chen, X. Wang, W. He and Y. Lu, *Org. Biomol. Chem.*, 2012, **10**, 5073-5076.
19. Q. Zhang, Y. Zhang, S. Ding, H. Zhang and G. Feng, *Sens. Actuators, B*, 2015, **211**, 377-384.
20. H. G. Im, H. Y. Kim, M. G. Choi and S.-K. Chang, *Org. Biomol. Chem.*, 2013, **11**, 2966-2971.
21. S. K. Asthana, A. Kumar, Neeraj and K. K. Upadhyay, *Tetrahedron Lett.*, 2014, **55**, 5988-5992.
22. S. Shweta, A. Kumar, N. Neeraj, S. K. Asthana and K. K. Upadhyay, *New J. Chem.*, 2017, **41**, 5098-5104.
23. J. Ren, W. Zhu and H. Tian, *Talanta*, 2008, **75**, 760-764.
24. L. Xiong, J. Ma, Y. Huang, Z. Wang and Z. Lu, *ACS Sens.*, 2017, **2**, 599-605.
25. H. Wang, X. Wu, S. Yang, H. Tian, Y. Liu and B. Sun, *Food Chem.*, 2019, **286**, 322-328.



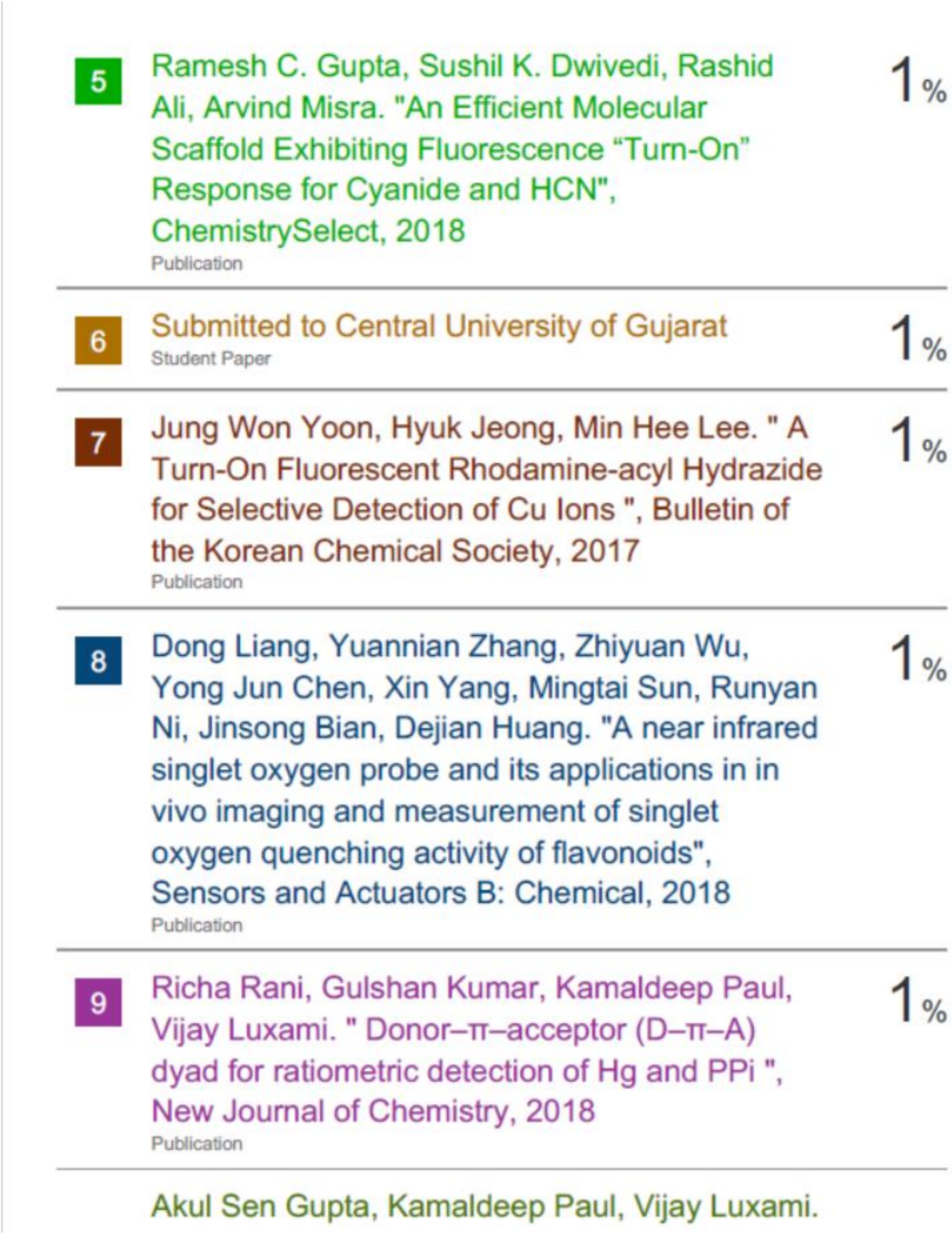
Thesis-1

ORIGINALITY REPORT

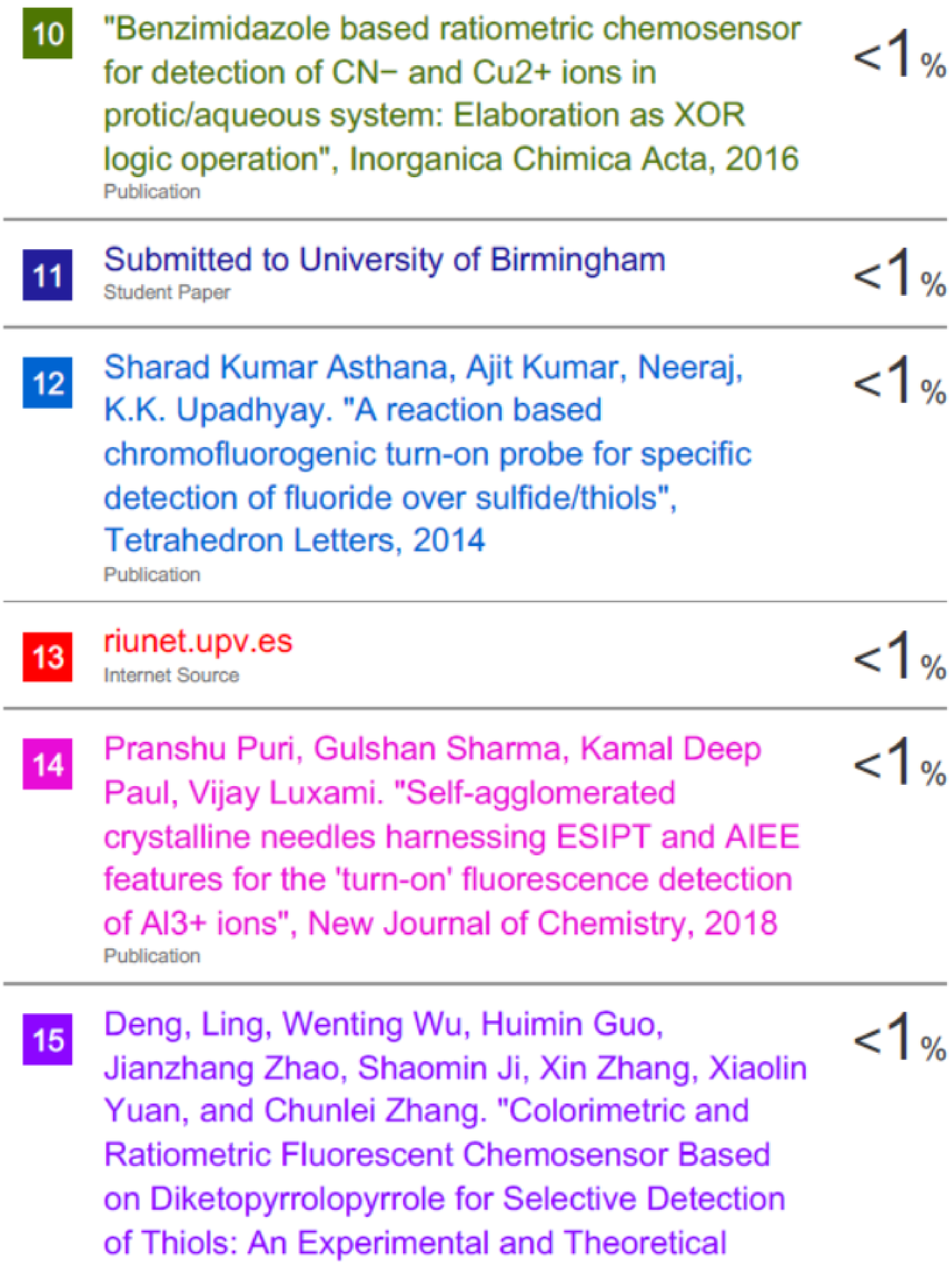
16%	2%	13%	9%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

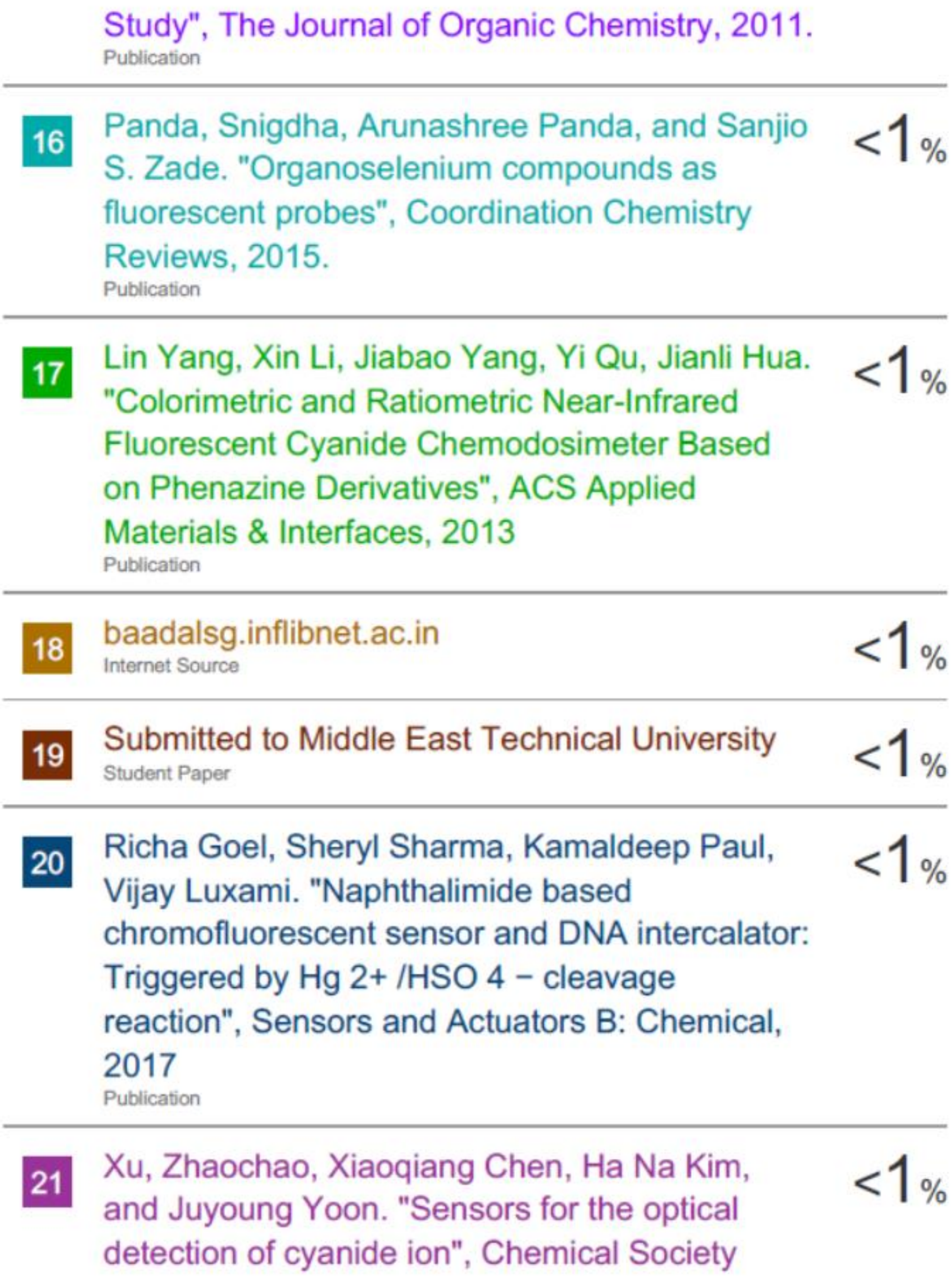
1	Submitted to Indian Institute of Science Education and Research Student Paper	3%
2	Gulshan Kumar, Nehal Gupta, Kamaldeep Paul, Vijay Luxami. "Acrylonitrile embedded benzimidazole-anthraquinone based chromofluorescent sensor for ratiometric detection of CN− ions in bovine serum albumin", Sensors and Actuators B: Chemical, 2018 Publication	2%
3	Richa Rani, Gulshan Sharma, Kamal Deep Paul, Vijay Luxami. "Donor-π-Acceptor (D-π-A) Dyad for ratiometric detection of Hg2+ and PPi", New Journal of Chemistry, 2018 Publication	1%
4	Sumit Roy, Ashim Maity, Naren Mudi, Milan Shyamal, Ajay Misra. "Rhodamine scaffolds as real time chemosensors for selective detection of bisulfite in aqueous medium", Photochemical & Photobiological Sciences, 2019 Publication	1%



5	Ramesh C. Gupta, Sushil K. Dwivedi, Rashid Ali, Arvind Misra. "An Efficient Molecular Scaffold Exhibiting Fluorescence “Turn-On” Response for Cyanide and HCN", ChemistrySelect, 2018 Publication	1%
6	Submitted to Central University of Gujarat Student Paper	1%
7	Jung Won Yoon, Hyuk Jeong, Min Hee Lee. " A Turn-On Fluorescent Rhodamine-acyl Hydrazide for Selective Detection of Cu Ions ", Bulletin of the Korean Chemical Society, 2017 Publication	1%
8	Dong Liang, Yuannian Zhang, Zhiyuan Wu, Yong Jun Chen, Xin Yang, Mingtai Sun, Runyan Ni, Jinsong Bian, Dejian Huang. "A near infrared singlet oxygen probe and its applications in in vivo imaging and measurement of singlet oxygen quenching activity of flavonoids", Sensors and Actuators B: Chemical, 2018 Publication	1%
9	Richa Rani, Gulshan Kumar, Kamaldeep Paul, Vijay Luxami. " Donor–π–acceptor (D–π–A) dyad for ratiometric detection of Hg and PPi ", New Journal of Chemistry, 2018 Publication	1%
	Akul Sen Gupta, Kamaldeep Paul, Vijay Luxami.	

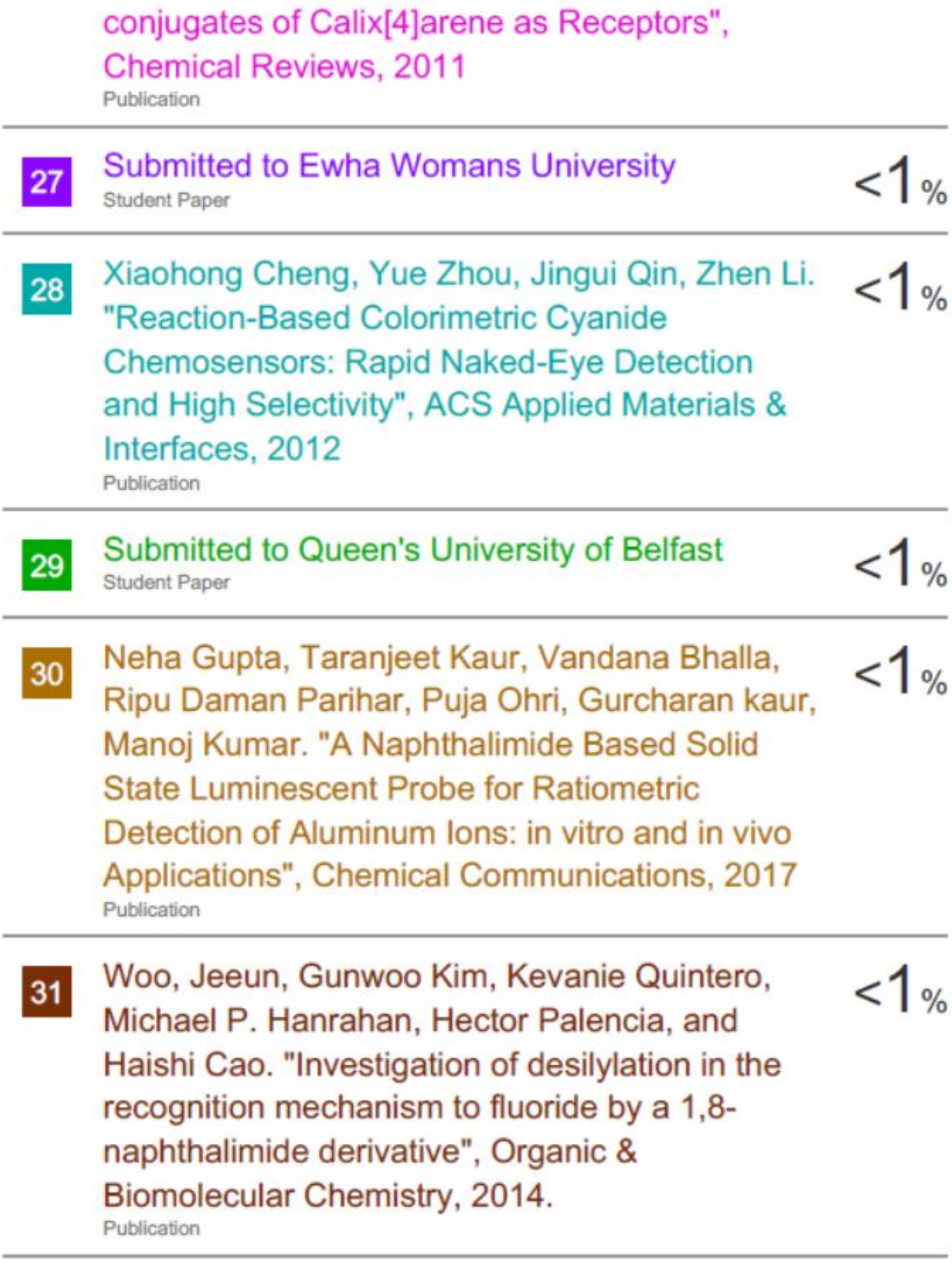


10	"Benzimidazole based ratiometric chemosensor for detection of CN− and Cu2+ ions in protic/aqueous system: Elaboration as XOR logic operation", Inorganica Chimica Acta, 2016 Publication	<1 %
11	Submitted to University of Birmingham Student Paper	<1 %
12	Sharad Kumar Asthana, Ajit Kumar, Neeraj, K.K. Upadhyay. "A reaction based chromofluorogenic turn-on probe for specific detection of fluoride over sulfide/thiols", Tetrahedron Letters, 2014 Publication	<1 %
13	riunet.upv.es Internet Source	<1 %
14	Pranshu Puri, Gulshan Sharma, Kamal Deep Paul, Vijay Luxami. "Self-agglomerated crystalline needles harnessing ESIPT and AIEE features for the 'turn-on' fluorescence detection of Al3+ ions", New Journal of Chemistry, 2018 Publication	<1 %
15	Deng, Ling, Wenting Wu, Huimin Guo, Jianzhang Zhao, Shaomin Ji, Xin Zhang, Xiaolin Yuan, and Chunlei Zhang. "Colorimetric and Ratiometric Fluorescent Chemosensor Based on Diketopyrrolopyrrole for Selective Detection of Thiols: An Experimental and Theoretical	<1 %

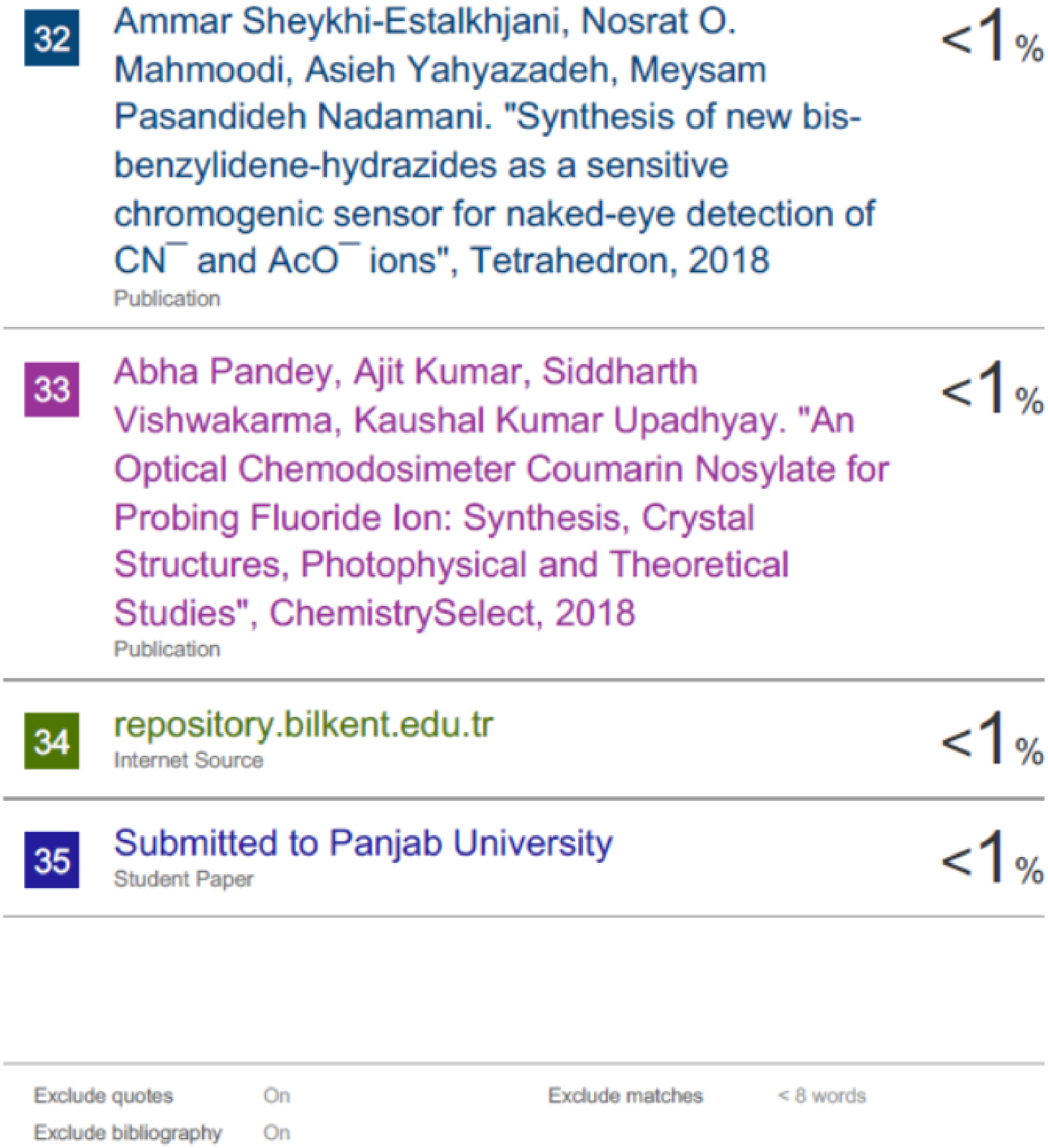


	Study", The Journal of Organic Chemistry, 2011. Publication	
16	Panda, Snigdha, Arunashree Panda, and Sanjio S. Zade. "Organoselenium compounds as fluorescent probes", Coordination Chemistry Reviews, 2015. Publication	<1%
17	Lin Yang, Xin Li, Jiabao Yang, Yi Qu, Jianli Hua. "Colorimetric and Ratiometric Near-Infrared Fluorescent Cyanide Chemodosimeter Based on Phenazine Derivatives", ACS Applied Materials & Interfaces, 2013 Publication	<1%
18	baadalsg.inflibnet.ac.in Internet Source	<1%
19	Submitted to Middle East Technical University Student Paper	<1%
20	Richa Goel, Sheryl Sharma, Kamaldeep Paul, Vijay Luxami. "Naphthalimide based chromofluorescent sensor and DNA intercalator: Triggered by Hg 2+ /HSO 4 − cleavage reaction", Sensors and Actuators B: Chemical, 2017 Publication	<1%
21	Xu, Zhaochao, Xiaoqiang Chen, Ha Na Kim, and Juyoung Yoon. "Sensors for the optical detection of cyanide ion", Chemical Society	<1%

	Reviews, 2010. Publication	
22	Ji-Ting Hou, Hyeong Seok Kim, Chong Duan, Myung Sun Ji, Shan Wang, Lintao Zeng, Wen Xiu Ren, Jong Seung Kim. "A ratiometric fluorescent probe for detecting hypochlorite in the endoplasmic reticulum", Chemical Communications, 2019 Publication	<1 %
23	Sasiwimon Kraithong, Rapeepat Sangsuwan, Nattawan Worawannotai, Jitnapa Sirirak et al. " Triple detection modes for Hg sensing based on a NBD-fluorescent and colorimetric sensor and its potential in cell imaging ", New Journal of Chemistry, 2018 Publication	<1 %
24	www.physoc.org Internet Source	<1 %
25	Shan Wang, Liyan Chen, Paramesh Jangili, Amit Sharma, Wei Li, Ji-Ting Hou, Caiqin Qin, Juyoung Yoon, Jong Seung Kim. "Design and applications of fluorescent detectors for peroxynitrite", Coordination Chemistry Reviews, 2018 Publication	<1 %
26	Roymon Joseph, Chebrolu Pulla Rao. "Ion and Molecular Recognition by Lower Rim 1,3-Di-	<1 %



	conjugates of Calix[4]arene as Receptors", Chemical Reviews, 2011 Publication	
27	Submitted to Ewha Womans University Student Paper	<1%
28	Xiaohong Cheng, Yue Zhou, Jingui Qin, Zhen Li. "Reaction-Based Colorimetric Cyanide Chemosensors: Rapid Naked-Eye Detection and High Selectivity", ACS Applied Materials & Interfaces, 2012 Publication	<1%
29	Submitted to Queen's University of Belfast Student Paper	<1%
30	Neha Gupta, Taranjeet Kaur, Vandana Bhalla, Ripu Daman Parihar, Puja Ohri, Gurcharan kaur, Manoj Kumar. "A Naphthalimide Based Solid State Luminescent Probe for Ratiometric Detection of Aluminum Ions: in vitro and in vivo Applications", Chemical Communications, 2017 Publication	<1%
31	Woo, Jeeun, Gunwoo Kim, Kevanie Quintero, Michael P. Hanrahan, Hector Palencia, and Haishi Cao. "Investigation of desilylation in the recognition mechanism to fluoride by a 1,8-naphthalimide derivative", Organic & Biomolecular Chemistry, 2014. Publication	<1%



32	Ammar Sheykhi-Estalkhjani, Nosrat O. Mahmoodi, Asieh Yahyazadeh, Meysam Pasandideh Nadamani. "Synthesis of new bis-benzylidene-hydrazides as a sensitive chromogenic sensor for naked-eye detection of CN^{-} and AcO^{-} ions", Tetrahedron, 2018 Publication	<1 %
33	Abha Pandey, Ajit Kumar, Siddharth Vishwakarma, Kaushal Kumar Upadhyay. "An Optical Chemodosimeter Coumarin Nosylate for Probing Fluoride Ion: Synthesis, Crystal Structures, Photophysical and Theoretical Studies", ChemistrySelect, 2018 Publication	<1 %
34	repository.bilkent.edu.tr Internet Source	<1 %
35	Submitted to Panjab University Student Paper	<1 %

Exclude quotes	On	Exclude matches	< 8 words
Exclude bibliography	On		