“COUMARIN

BASED

FLUORESCENT

CHEMOSENSORS”

Name: Prachi Vishwas Dessai

Class: M.Sc. Part II Analytical Chemistry

Roll No: 20P0490014

COUMARIN BASED FLUORESCENT CHEMOSENSORS

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By

Ms. Prachi Vishwas Dessai

20P0490014

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School Of Chemical Sciences

Goa University

Goa 403206

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COUMARIN BASED FLUORESCENT CHEMOSENSORS

INTRODUCTION

Coumarin compounds have the unique 2H-chromen-2-one motif. Coumarin derivatives are widely found in nature, especially in plants and are constituents of several essential oils. Up to now, thousands of coumarin derivatives have been isolated from nature or produced by chemists. In recent years, coumarin has received increasing interest as fluorescent chemosensor, because of their less toxicity, good structural flexibility, good photo-stability, strong and stable fluorescence emission, and large stokes shifts production. The carbonyl group of coumarin take part in coordination with metal ions. Coumarin derivatives are insoluble in water, so, multy-hydroxy alcohol introduced to increase the water solubility and selectivity of the sensor.

In recent years, fluorescent sensors have attracted more and more attention due to their advantages over other techniques, including ease of detection, sensitivity, and instantaneous response. The development of fluorescent chemosensors, possessing high sensitivity and selectivity, for environmentally and biologically important, heavy and transition metal cations has evolved into a growing field of research, due to the significant advantages they offer.

a) Conventional sensing methods, such as, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS) and electrochemical methods are costly and require professional operators.
b) Compared to sophisticated instrumentation, fluorescent chemosensors, for analyte detection and analysis have shown to be promising alternatives due to the simple equipment required, cost-effective synthetic procedures and analysis, rapid response times, low detection limits, high resolution and good selectivity and sensitivity.
c) A typical chemosensor consists of two distinct components: a receptor and signalling unit (fluorophore), which connected either by chemical bonds or by spacer units.

The fluorophore unit is the site of excitation and emission, and the receptor subunit is responsible for recognizing and binding to an analyte of interest. With high selectivity and efficiency via a reversible/non-reversible covalent or non-covalent interaction. Recently, coumarin have been used in fluorescent chemosensors due to their high optical activities, high light stabilities, high quantum yields, wide Stokes shifts, ease of tuneability, and low toxicity properties. Furthermore, the carbonyl group of coumarin can take part in coordination with metal ions, if necessary. This is advantageous for the design of chemosensors as the response will be fast and efficient when analytes are bound to the host probes. Both nitrogen and oxygen atoms are donor atoms which readily combine with transition metal cations.[1]

LITERATURE REVIEW

1. A Coumarin-Based Fluorescent Chemosensor for Zn^{2+} ions

This chemosensor exhibits a high selectivity towards Zn^{2+} ions by utilizing a chelation enhanced fluorescence (CHEF) mechanism. It also exhibits lower background fluorescence due to intramolecular photo induced electron transfer. This sensor was developed by incorporating a semicarbazide at the 8th position of Coumarin ring by a “C=N” bond, which quench the excited state emission of Coumarin fluorophore via photo induced electron transfer (PET). Zn(II) has a closed-shell d^{10} electronic configuration, it has been anticipated that its coordination would alleviate PET and provide fluorescence “turn-on”. Upon mixing with Zn^{2+} in aqueous ethanol solution, the sensor showed a”turn-on” fluorescence. The fluorescence of chemosensor largely enhanced and it increases linearly with the concentration of Zn^{2+}. This enhancement is due to the formation of a 1:1 complex of chemosensor and Zn^{2+} (chemosensor-Zn^{2+}) in ethanol aqueous media. The chemosensor does not show fluorescence enhancement for other metal ions. This chemosensor was applied for the determination of Zn^{2+} in water sample.[2]

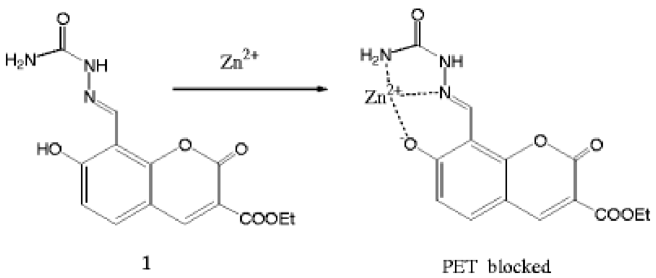


Fig.1 the binding model of chemosensor with Zn^{2+}.

2. coumarin-based fluorescent chemosensor for Cu^{2+} ions

The chemosensor synthesized by the combination of coumarin and semicarbazide, which selectively indicates Cu^{2+} via a fluorescent property. This probe demonstrated an “on-off” fluorescence response at 492nm in the presence of Cu^{2+}. The binding ratio of chemosensor probe to Cu^{2+} is 1:1.

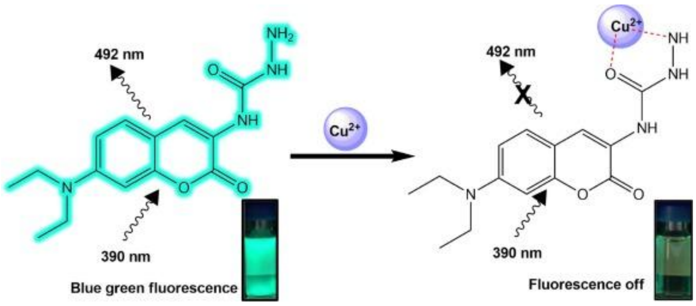


Fig.2 sensing mechanism of Cu^{2+} ions by chemosensor.

This chemosensor is highly selective and sensitive towards Cu^{2+} over other metal ions in CH_3CN/H_2O (1:1, v/v). The fluorescence changes are from static quenching due to the formation of chemosensor-Cu^{2+} complex. It showed a promising potential for application in real sample analysis.[3]

3. Coumarin-based fluorescence chemosensor for Al^{3+} ions

The chemosensor for the detection of Al^{3+} is a derivative of coumarin, which has been synthesized by the condensation of 8-hydroxycoumarin with niacin hydrazide. This chemosensor exhibited a remarkable fluorescence enhancement towards Al^{3+} with high selectivity and sensitivity, in EtOH-HEPES (95:5, v/v, pH=7.40), this was attributed to the photoinduced electron transfer (PET) and –C=N isomerisation mechanism. The stoichiometric binding between chemosensor and Al^{3+} was 1:1.

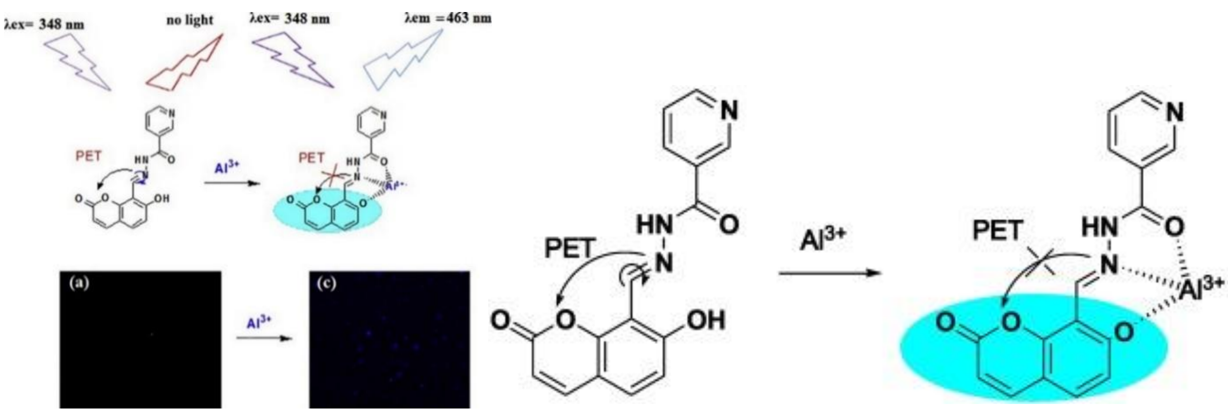
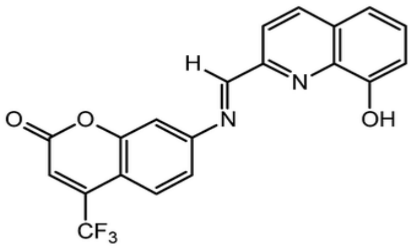


Fig.3 Mechanism of the sensor for detection of Al3+.

The sensor has a good potential application because of its excellent selectivity and high sensitivity, wide range of pH (2-11) and very low detection limit and more importantly, due to its low toxicity, bio-imaging study revealed that the chemosensor could successfully applied to monitor Al^{3+} in live cells. This result indicates that it can be a good chemosensor for selectively recognising Al^{3+} in biological environment.[4]

4. Coumarin based fluorescent probe for Zn^{2+} and Cu^{2+} ions

Coumarin based Schiff-base fluorescent probe-(*E*)-7-(((8-hydroxyquinoline-2-yl) methylene) amino)-4-(trifluoromethyl)-2*H*-chromen-2-one (**$H_{12}L$**), which selectively and sensitively recognized both Zn^{2+} and Cu^{2+} using fluorescence spectroscopy. This chemosensor shows fluorescence "turn on-off" response for Zn^{2+} and Cu^{2+} using steady state absorption and fluorescence spectroscopy. This chemosensor exhibits a very good fluorescence sensing ability to Zn^{2+} over a wide pH range and provides a new approach with economically cheap and less complicated synthetic route for selective, sensitive and quantitative detection of these three most abundant and essential traces elements in the human body.[5]

- 

(*E*)-7-(((8-hydroxyquinolin-2-yl)methylene)amino)-4-(trifluoromethyl)-2*H*-chromen-2-one

Fig. 4 chemosensor for detection of Zn^{2+} and Cu^{2+}.

5. Coumarin-based chemosensor for Fe^{3+} ions

Chemosensor, which is a coumarin derivative bearing three hydroxyls, displays high selectivity for Fe^{3+} in HEPES aqueous buffer. The binding property of this chemosensor towards metal ions examined through the changes in fluorescence intensity. It exhibits high selectivity for Fe^{3+} in HEPES aqueous buffer (pH 7.2), and the selectivity was not affected by the presence of representative alkali metals, alkali earth metals and other transition-metal salts. The addition of Fe^{3+} to the HEPES aqueous buffer (PH 7.2) of chemosensor, decreases the emission intensity dramatically.[6]

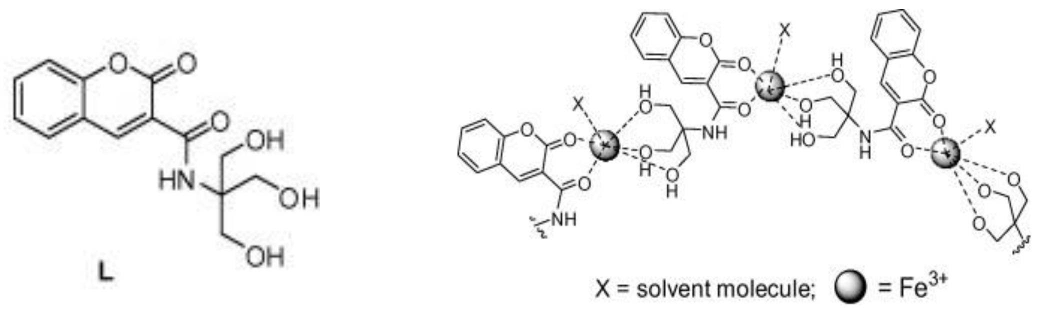


Fig. 5 chemosensor for detection of Fe3[+].

6. Coumarin-based fluorescence chemosensor for aluminium (III) ions

The coumarin based fluorescence chemosensor containing L-histidine for aluminium is water-soluble; it shows high sensitivity and selectivity for Al^{3+} recognition in comparison to other metal ions in pure aqueous solution. The sensor exhibited 1:1 coordination with Al^{3+} with enhancement of emission based on the photo-induced electron transfer (PET) mechanism. These fluorescent experiments performed in a pure aqueous solution, which is different from other probes, determined in organic solvents or mixed solutions. This chemosensor is a weakly fluorescent molecule. Upon addition of 10.0 equivalent of Al^{3+} to the solution of chemosensor, an outstanding enhancement of the fluorescence intensity. However, at the same concentration, other common metal ions did not produce significant fluorescence changes. These observations indicated that, sensor has an excellent selectivity towards Al^{3+} in aqueous solution (Tris–HCl, 0.1 mM, pH 7.2) as a fluorescence "off–on" probe. It has potential application in detection and analysis of various Aluminium related issues in environmental, biological and medical areas.[7]

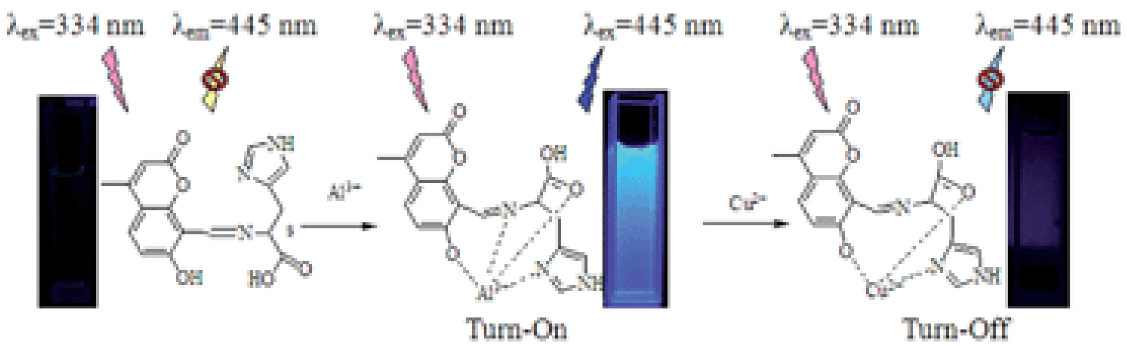


Fig. 6 mechanism of the chemosensor for the detection of Al^{3+}.

7. **Coumarin-based fluorescent chemosensor for Zn^{2+} and AcO^{-} ions**

Coumarin based fluorescent chemosensor displayed highly sensitive "off-on-off" response to Zn^{2+} and AcO^{-} in mixed aqueous solution(DMF/H_2O = 3:7, HEPES buffered, pH = 7.2). It is a fluorophore for the recognition of Zn^{2+} and AcO^{-} in water and an excellent cell-permeable for the imaging of Zn^{2+} and AcO^{-} in living cells. Sensor specifically binds to Zn^{2+} in the presence of other competing cations and evident changes occurs in UV-Vis and fluorescence spectra in HEPES buffer. Interaction of chemosensor with Zn^{2+} led to complete enhancement of fluorescence intensity through a 1:1 binding mode. The enhancement fluorescence of the in situ generated **chemosensor**-Zn^{2+} quenched upon the addition of AcO^{-}, realizing the detection of AcO^{-} by utilizing the Zn^{2+} displacement approach. This "OFF-ON-OFF" response provided a convenient and practical way to detect both Zn^{2+} and AcO^{-} in environmental and biological samples.chemosensor and the resultant complex **chemosensor**-Zn^{2+} exhibit low cytotoxicity and cell-membrane permeability, which makes them capable of Zn^{2+} and AcO^{-} imaging in living Hep G2 cells.[8]

Fig. 7 chemosensor for the detection of Zn^{2+} and AcO^{-}.

8. **Coumarin-based fluorescent probe for Cu(II) ions**

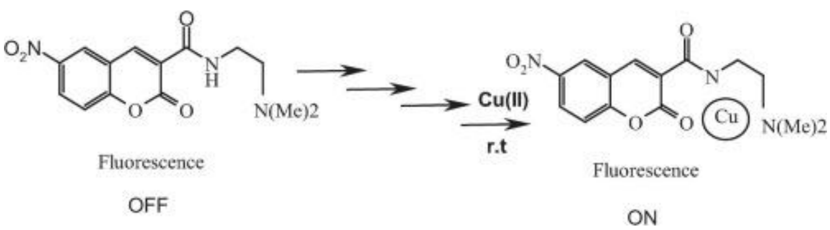


Fig. 8 chemosensor for detection of Cu^{2+}.

Nitro-3-carboxamide is a coumarin derivative, used as fluorescent chemosensor for the detection of Cu^{2+}. This probe has the selectivity for Cu^{2+} over other metal ions in aqueous solution. The fluorescence of 6-nitro-N-[2-(dimethylamino)ethyl]-2-oxo-2H-chromene-3-

carboxamide is the highest in the presence of Cu^{2+} ions. Indicating 1:1 stoichiometry between the sensor and Cu2+. In this structure, Cu2+ binds with an oxygen atom of a carbonyl group, a nitrogen atom of an amide, a nitrogen atom of an amine, and two oxygen atoms of a nitrate. 3-Cu(II) in aqueous solution (HEPES:DMSO) 9:1, v/v).[9]

9. Coumarin Based Fluorescent Sensor for Cu^{2+} and S^{2-} ions

The 6, 7-dihydroxy3-(3-chlorophenyl) coumarin (CFHC), is a fluorescent chemosensor for the detection of Cu^{2+} and S^{2-} ions. The binding behaviours of CFHC for cations investigated by UV-vis and fluorescence spectroscopy. CFHC showed an effectively selective 'turn-off', fluorescence quenching for Cu2+ ion over other metal ions to form new complex CFHC-Cu2+. This complex indicated high sensitivity and selectivity for sulfide over other possible competitive anions, resulting in fluorescence enhancement in CH3CN/H2O (v/v, 9/1) at 455 nm.

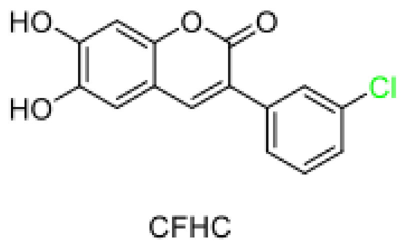


Fig 9 A selective visual fluorescence change upon addition of a selective visual fluorescence change upon addition of Cu2+ ion to CFHC solution over other various metal ions various metal ions(5.0 eq.) to CFHC solution.

Interactions of CFHC with Cu^{2+} induced complete quenching of fluorescence intensity through a 1:1 binding mode. The complex formation of CFHC-Cu^{2+} gave rise to colour changes from blue to colourless. The coumarin based chemosensor showed "off-on-off" fluorescence for Cu^{2+} and S^{2-} ions in aqueous solution. The complex formed also indicated high sensitivity to S^{2-} anions by Cu^{2+} displacement approach.[10]

10. Coumarin-Based Chemosensor for Cu^{2+} ion

N'-{[7-(diethylamino)- 2-oxo-2H-chromen-3-yl]carbonyl}pyridine-3-carbohydrazide and N'-benzoyl-7-(diethylamino)-2-oxo-2H-chromene-3- carbohydrazide, are the two coumarin based fluorescent chemosensors for the detection of Cu^{2+} in aqueous solution. These two probes showed an instant "turn-off" fluorescence response to Cu^{2+} over other metal ions in ethanol-water mixture (1:100 ratio) based on intramolecular charge transfer (ICT). The N'-{[7-(diethylamino)- 2-oxo-2H-chromen-3-yl]carbonyl}pyridine-3-carbohydrazide chemosensor coordinates with Cu^{2+} in 1:1 stoichiometry.[11]

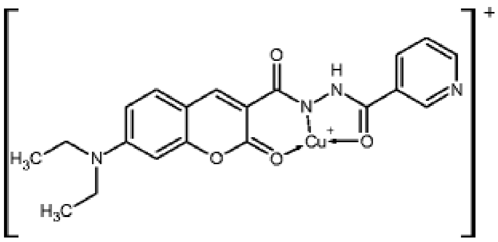


Fig. 10 Coordination mode of Cu^{2+} ion to N'-{[7-(diethyl amino) - 2-oxo-2H-chromen-3-yl] carbonyl} pyridine-3-carbohydrazide.

11. Coumarin-based fluorescent chemosensor for F^- detection

Receptor based on coumarin thiocarbohydrazone (CTC) is a fluorescent chemosensor for the detection of fluoride ions in CH_3CN/DMSO. CTC binds with the fluoride ion in 1:1 ratio. It shows specific sensitivity and selectivity towards fluoride giving rise to ON-OFF-ON fluorescence response. During the addition of fluoride ions, the emissions quenched or "switched OFF" by 70%, this is due to the formation of receptor-anion (host-guest) hydrogen bonded complex. The remaining fluorescence signal is due to poorly emissive excited state tautomer $[CTC\cdots H–F]^{-*}$ or intramolecular charge transfer. Upon addition of further fluoride anion the fluorescence gradually increased i.e. "switched ON", because of the formation of deprotonated species. The phenomenon of reappearance of fluorescence of the compound CTC is because of the electronic reconfiguration of the fluorophore due to the generation of negative charge on it. Initially it showed GREEN fluorescence, after the addition of fluoride the green fluorescence turned off. On Further addition of fluoride ions the new cyan coloured fluorescence developed, thus giving rise to an ON^1-OFF-ON^2 fluorescent response against fluoride. Except F^-, there was no unique fluorescence response with respect to other anions.[12]

Fig. 11 proposed binding fashion of compound CTC with F^- anion in solution. In the case of CTC deprotonation occurred and the overall sensing mechanism and a qualitative sketch of the ON^1–OFF–ON^2 behaviour of CTC in CH_3CN/DMSO upon addition of different amount of TBAF or fluoride ions.

12. Coumarin based fluorescent chemosensor for Cu^{2+} and PPi

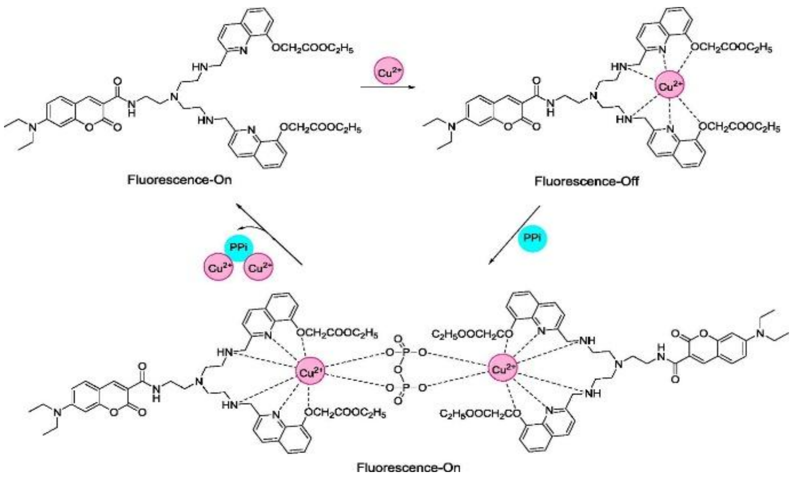


Fig 12 the mechanism showing fluorescence "ON-OFF" behaviour for Cu^{2+} and "OFF-ON" response for PPi.

The chemosensor 1 with coumarin as the fluorophore and tren and quinoline as the receptors, for the recognition of Cu^{2+} and PPi, showed "ON-OFF" fluorescence quenching response towards Cu^{2+}. The quenching efficiency reached a maximum of 99.6% with the addition of Cu^{2+}. The chemosensor 1-Cu^{2+} complex showed an "OFF-ON" fluorescent enhancement response towards PPi over many anions, especially HPO_4^{2-} and $H_2PO_4^-$. The chemosensor 1 showed a 1:1 binding stoichiometry to Cu^{2+} and chemosensor 1-Cu^{2+} showed 2:1 binding stoichiometry to PPi in CH_3CN/HEPES buffer medium (9:1 v/v, pH = 7.4). The stable pH range of sensor **1** to Cu^{2+} and **1**-Cu^{2+} to PPi was from 4 to 8. The detection limits were 1.9×10^{-6} M to Cu^{2+} and 5.96×10^{-8} M to PPi, indicating high sensitivity.[13]

13. Coumarin-based fluorescence chemosensor for Fe^{3+}

The coumarin based chemosensor [7-diethylamino-2-oxo-2H-chromene-3-carboxylic acid (6-amino-pyridin2-yl)-amide, CFe1] for the detection of Fe^{3+} showed good selectivity and fast response. Chemosensor (CFe1) in the presence of $Fe^{3=}$ and ethylenediaminetetraacetic acid (EDTA) makes the blue solution fade to colourless, which is due to the formation of CFe1-Fe^{3+} complex. The fluorescence reduction upon addition of Fe^{3+} is due to the excitation energy transfer from the ligand to the metal d-orbital or the charge transfer from ligand to metal. It can serve as a tool in Fe^{3+} related chemical, biological and environmental investigation.[14]

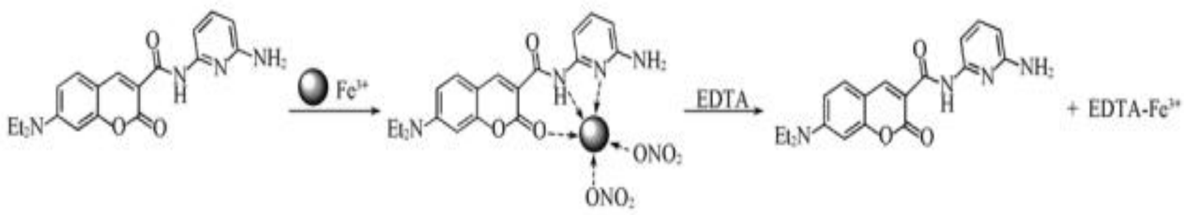


Fig. 13 mechanism of CFe1-Fe^{3+} complex formation.

14. Coumarin based fluorescent chemosensor for detection of zinc ion

The chemosensor based on 4-hydroxycoumarin skeleton for the detection of zinc ions, displays highly selective and sensitive fluorescence enhancement to Zn^{2+} over other metal ions, in living biological samples and water resources. The detection limit for the fluorescent chemosensor **1** toward Zn^{2+} was 3.58×10^{-8} M.

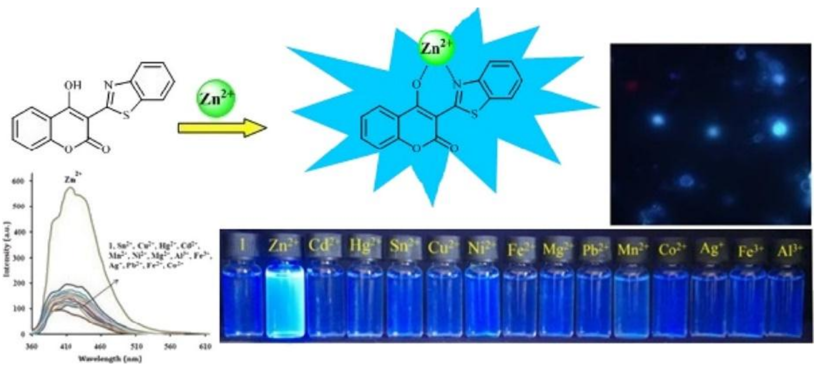


Fig. 14 chemosensor showing fluorescence for Zn^{2+} ions.

This chemosensor shows drastic change in fluorescent intensity, from dark blue to brilliant blue fluorescence for Zn^{2+}, in an aqueous solution of acetonitrile (CH_3CN/H_2O, 95:5, v/v) because of highly efficient PET process. The fluorescent intensity increases with increasing concentration of Zn^{2+}. The fluorescence response to Zn^{2+} can be seen by naked eyes[15].

15. Coumarin-based fluorescent chemosensor for Cu^{2+} ion

Coumarin based fluorescent chemosensor, 3-acetoacetyl-7-diethylaminocoumarin showed "turn-off" fluorescence for the detection of Cu^{2+} in aqueous solution. This chemosensor exhibits highly selective and sensitive absorbance and fluorescence sensing ability for Cu^{2+} over other metal ions. Addition of Cu^{2+} to the aqueous solution of chemosensor gave rise to absorbance change and fluorescence quenching. The fluorescence"turn-off" is due to the 1:1 stoichiometric complex between chemosensor and Cu^{2+} ion.[16]

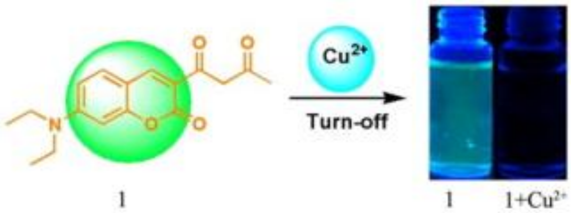
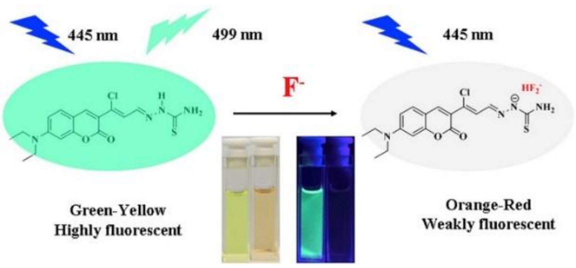


Fig. 15 the chemosensor showing fluorescence "turn-off" for Cu^{2+}.

16. Coumarin-based fluorescent chemosensor for detection of fluoride ion

The coumarin based fluorescent chemosensor having thiosemicarbazone as binding unit, is used for the detection of fluoride anion. The addition of F^- to the solution of chemosensor in tetrahydrofuran resulted in evident naked-eye colour change from green-yellow to orange-red under daylight and obvious fluorescence quenching within 3s. The colorimetric and fluorescent sensor performed high selectivity, short response time and excellent sensitivity toward F^- over other in THF solution with the low detection limit of 2.16×10^{-7} mol/L.



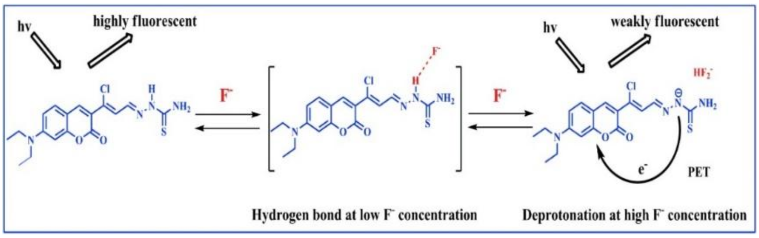


Fig. 16 sensing mechanism for fluoride ions.

The interaction between chemosensor and fluoride ion: F^- interacts with chemosensor through hydrogen bonding at lower fluoride ion concentration, but at higher concentration, it induces the deprotonation of N-H proton at high fluoride ion concentration. After deprotonation, the electron transfer effect of the PET transition would be enhanced due to the increase of electron density on the nitrogen, which leads to quenching of the fluorescence. Upon treatment with F^-, the color change from light green to dark was observed, which is attributed to the enhancement in the electron transfer effect of the PET process through the deprotonation of N-H active proton.[17]

17. coumarin based chemosensor for Cu (II) ions

N'-acetyl-2-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)acetohydrazide **(HMC1)** is a chemosensor for the detection of Cu^{2+} ions based on fluorescence quenching . It is designed by photo-induced electron transfer mechanism. Its fluorescence quenched by Cu^{2+} ions. This chemosensor used as intracellular "turn-off" fluorescent chemosensor for Cu^{2+} in living cells. The fluorescence of the chemosensor remains constant at 380nm throughout different pH values and after quenching of the probe by the addition of Cu^{2+} ions, the fluorescence intensity decreases in steady manner at different pH values.[18]

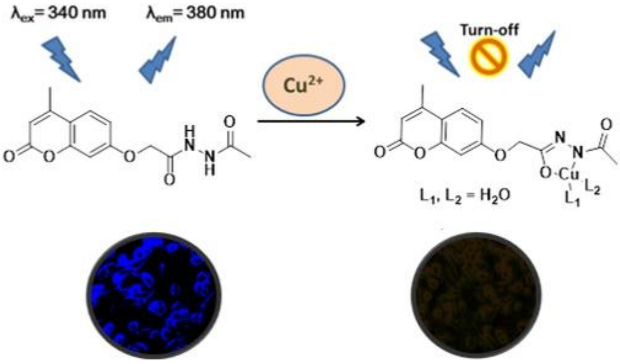


Fig. 17 presense of Cu^{2+} ion shown by fluorescence turn off.

18. Coumarin based fluorescent for Zn^{2+} ions

Chemosensor, 4-hydroxy-3-(1-(quinolin-8-ylimino) ethyl)-2H-chromen-2-one (HL) is a sensitive and selective "turn-on" type chemosensor for the detection of Zn^{2+} ions. It shows increase in luminescence intensity when coordinated with Zn^{2+} ion. This is the main characteristics of photo-induced electron transfer (PET) based sensor mechanism. In fluorescence "OFF" mode i.e., in the absence of Zn^{2+}, there is delocalisation of the lone pair present on nitrogen of immine group, in the coumarin ring; this causes non-radiative decay of the excited state, which leads to fluorescence quenching. However, in "ON" mode chemosensor (HL) coordinates with the Zn^{2+} ion through –O, immine-N and N atom in the quinoline moiety.[19]

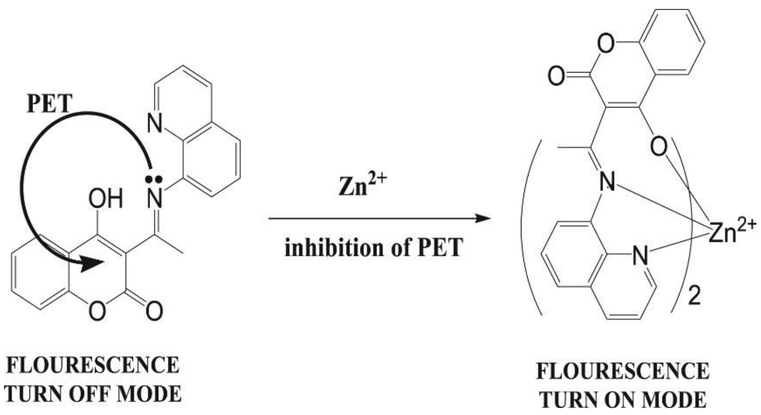
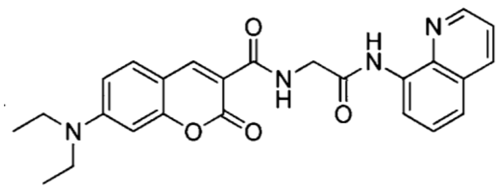


Fig. 18 PET phenomenon leading to fluorescence quenching in the chemosensor HL.

19. Coumarin-based fluorescent probe for Cu^{2+} ion

The 7-N,N-diethylaminocoumarin-4-N-2-amino-N-(quinolin-8-yl)acetamide (CAQA) is a coumarin based chemosensor for the detection of Cu^{2+} ion in aqueous acetonitrile solution. It possesses high sensitivity and selectivity towards Cu^{2+} and gives "ON-OFF" fluorescence. The 1:1 complex is formed between the chemosensor and Cu^{2+} ion (CAQA- Cu^{2+}).[20]



CAQA

Fig. 19 structure of chemosensor CAQA for the detection of Cu^{2+} ions.

20. A coumarin-derived Cu2+-fluorescent chemosensor

The coumarin based chemosensor (E)-N'-((7-(diethylamino)-2-oxo-2H-chromen-3-yl)methylene)- 3,4,5-trimethoxybenzohydrazide (FCBH) for the detection of Cu^{2+} ion, has excellent selectivity for Cu^{2+} over other metal ions. It shows a reversible fluorescence quenching response towards Cu^{2+} in the presence of CN^{-}, via 1:1 binding mode in aqueous solution. The addition of Cu^{2+} causes a visible colour change from greenish yellow to red, as well as green fluorescence quenching. Upon addition of Cu^{2+}, deprotonation of chemosensor FCBH occurs and 1:1 metal-ligand complex formed. The quenched fluorescence of FCBH-Cu^{2+} complex restored upon addition of CN^{-} ions.[21]

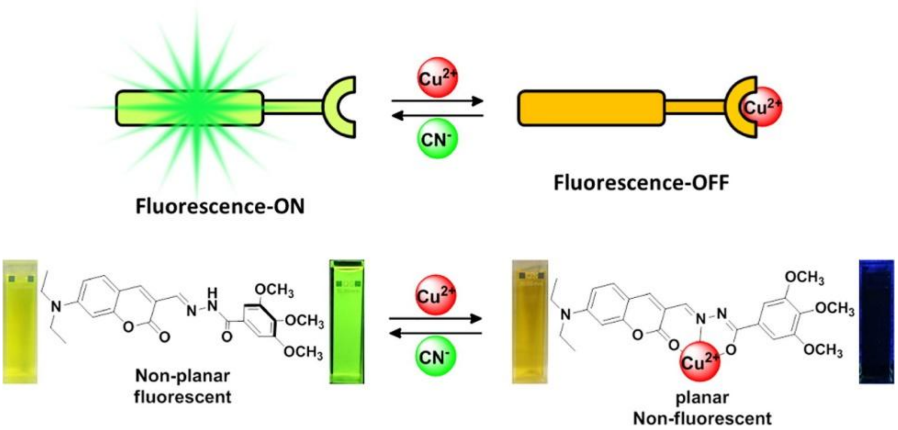


Fig. 20 Proposed mode of complexation between **FCBH** and Cu^{2+}. Observed naked-eye (left) and fluorescence (right) changes upon **FCBH**-Cu^{2+} complexation and subsequent treatment with CN^{-} ions.

21. Coumarin-Based Fluorescent Probe for Hypochlorites

The coumarin based chemosensor (C1) for the detection of hypochlorite anion taking advantage of the oxidation property of hypochlorite and different coordination properties of Cu^{+} and Cu^{2+} ions, in HEPES:CH_3CN (9:1 v/v, pH=7.4) solution. Upon addition of hypochlorite anions, strongly green fluorescence was observed and non-fluorescence was observed due to formation of C1-Cu^{2+} complex, C1 acts as "switching off" fluorescent chemosensor for Cu^{2+} ions.[22]

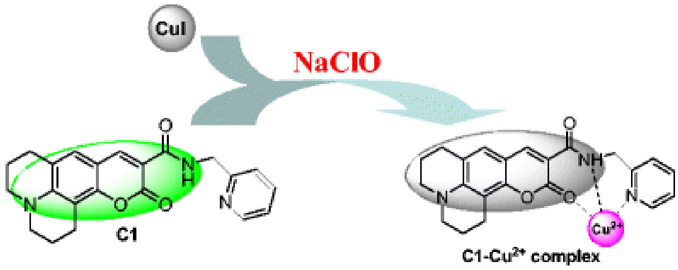


Fig.21 chemosensor C1 for the detection of hypochlorite.

CONCLUSION

Coumarin due to its excellent biocompatibility, strong and stable fluorescence emission, and good structural flexibility, has found wide applications in the development of fluorescent chemosensors in the field of molecular recognition, molecular imaging, bioorganic chemistry, analytical chemistry, material chemistry, as well as in the biology and medical science communities. Many coumarin based fluorescent chemosensors produced for the detection of metal ions. The presence of metal ions detected by the change in fluorescence intensities. The chemosensors forms complex with the metal ions in different stoichiometry by photo-induced electron transfer (PET) mechanism.

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