

Investigation on synthesis and chromogenic receptor interactions of nano hybrid chromone derivatives

Project Report-1
Masters of Sciences

In

Chemistry (Hons.)

By

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Under the guidance

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April 2017

DECLARATION

I hereby declare that the dissertation entitled, "Investigation on synthesis and chromogenic receptor interactions of nanohybrid chromone derivatives", submitted for M.Sc Degree to Department of Chemistry, Lovely Professional University is entirely original work and all ideas and references have been duly acknowledged. The dissertation had not been formed the basis for the award of any other degree.

Date:

Anjali Mehan

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Certificate

This is to certify that the pre-dissertation project entitled “**Investigation on synthesis and chromogenic receptor interactions of nanohybrid chromone derivatives**” submitted by **Anjali Mehan** to the Lovely Professional University, Punjab, India is a documentation of genuine literature review of coming research work approved under my guidance and is commendable of consideration for the honor of the degree of Master of Science in Chemistry of the University.

Supervisor

Dr. Gurbinder Singh

Assistant Professor

Acknowledgment

Through this column, I would first like to thank God for giving me the strength in making this research journey a success.

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Contents	Page no.
Introduction	6-7
Review of Literature	8-12
Objectives Of The Study	13
Methodology	14-20
Result and Discussion	21-26
Conclusion	27
References	28-29

INTRODUCTION

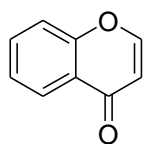
Ligand receptor interactions involved in the living system play an important role in the various biological process involving the cell growth mechanism, signal processing and movement of various types of solutes across biological membrane, these also play a role in the binding abilities of various types of drug molecules and chemical species present which may have detrimental effects in the living system. The present investigation is aimed to synthesize new anion receptors that have the capability of detection of anionic species optically or electrochemically of particular biological and environmental standards such as cyanide, chloride, fluoride, hydrogen, bromide, sulphate etc^{1a}. These receptors are having tendency to alter the chemical composition, chemical and physical properties of the analyte in the direct interaction between ligand and chemical entities, various types of changes can be chemical properties changes like frontier orbital energy change and variation in electron distribution, in these ligand receptor interactions selectivity is the main aspect of receptors due to which it directly binds with an analyte even in the presence of interfering molecules¹¹. Cation recognition in an aqueous medium is tremendously crucial issue, as their presence in excess amount in the environment is the reason for major health problems like break down of the central nervous system^{1d}.

Sensors respond to particular moiety and change its chemical stimuli into recordable signals. Nanoparticles based sensors are among the finest for the detection of anions/cations in an aqueous medium due to their large surface area and small particle size (1-100nm) and also have definite target binding sites². Detection of metals, biomolecules and anions in an aqueous medium is one of the most challenging detections. Chemosensors with desired selectivity and sensitivity are in big demand for detection of these analytes^{1b}. Fluorescent organic nanoparticles being highly selective and sensitive with easy methods of operation are also significant for the recognition of metal ions^{1c}.

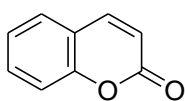
Chemosensors are widely used as sensors as it binds non-covalently with particular analyte. Development of chemo-sensor receptor design is one of the important steps; therefore anionic chemosensors must have ability to take part in H-bonding such as urea, amides and thiourea. Anionic receptors cannot work under aqueous conditions due to presence of water molecules that are ready to interact with anionic receptors so the receptors that are based on metal complexes work precisely under aqueous conditions. Sensitivity of sensors relies on a particular analyte. An intense change in the photophysical properties should be observed due to a little concentration change of an analyte¹¹.

REVIEW OF LITERATURE

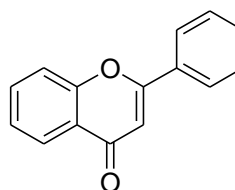
Chromone is the basic structure for the heterocyclic compounds. There are many organic compound synthesized and processed into organic nanoparticles are based on a chromone fluorophore¹. Chromones, coumarins and flavonoids are naturally occurring compounds and have medicinal properties. Chromone derivative are widely distributed in plants, and their biological activity and pharmacological properties have prompted research into their chemical properties².



(a)



(b)



(c)

Chromones with heteroatom oxygen have various properties like it act as an antibacterial, antifungal, anticancer and antiviral also³. Several reported chromone derivatives also act as kinase inhibitors that bind to benzodiazepine receptors and as resourceful mediator in the treatment of cystic fibrosis⁴. A group of various naturally occurring pigments that are widely distributed in the plant kingdom are represented by flavonoids. It is one of the important components of human diet as its high content is found in fruits and vegetables⁵. For the detection or sensing of heavy metal ions chromone derivatives act as fluorescent probes. Metal ions are highly variable in size and the fluorescence is variable depends upon viscosity and polarity⁶.

Belonging to normal and tautomeric excited state 3-hydroxychromone derivatives with a fused furan heterocyclic (2-aryl-3-hydroxyfurano [3, 2] chromones) compounds exhibit two intensive fluorescence emission bands⁷. 7-methoxychromone-3-carbaldehyde-(indole-2-formyl) hydrazone is simple chromone Schiff-base receptor⁸. Optical chemosensor receptor based on chromone shows intense selectivity for fluoride ions upon its addition, a dramatic colour change has been observed from yellow to deep red in acetonitrile⁹. A longest wavelength fluorescent dye is chromone, in both fluorescent and absorption spectra it exhibits strong red shift, its new derivative is 3-hydroxychromone derivative¹⁰.

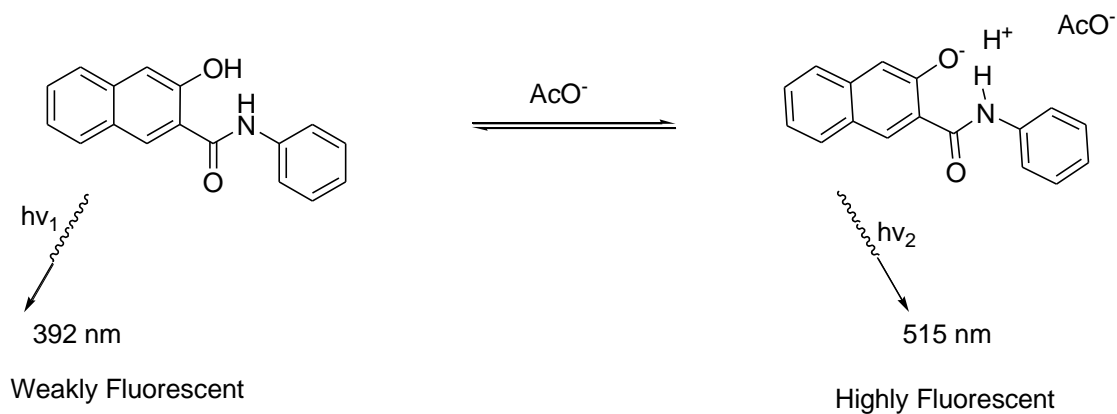
Chemosensors are being synthesized according to requirement. In the development of chemosensors the important step is the design of receptors or binding site¹¹.

Chemo sensors are based on receptor of metal complexes of fluorescent organic nanoparticles with ferric ions¹². To measure fluoride at two different concentration ranges polymeric sensors are used to detect either by absorbance or emission signalling¹³. There are various analytical techniques to determine metal ions but use of fluorescent organic nanoparticles is highly significant¹⁴. White light emitting dyes, which is used as fluorescent material used to identify H₂S¹⁵. Schiff bases, triazoles, secondary and tertiary amines fluorescent probes have been developed to detect anions like Al³⁺,¹⁶.

Receptor is a moiety that interacts directly with the analyte and changes its physical and chemical properties, receptor with a unique combination of sp² nitrogen and carbonyl groups from amide linkages¹⁷. Fluorescent receptor which is imine-linked bearing both the hydrogen bond donor and acceptor motifs as detection sites in the propose of the receptor¹⁸. Hybrid nanoparticles are production of dipodal naphthalimide based receptor and of organic nanoparticles¹⁹.

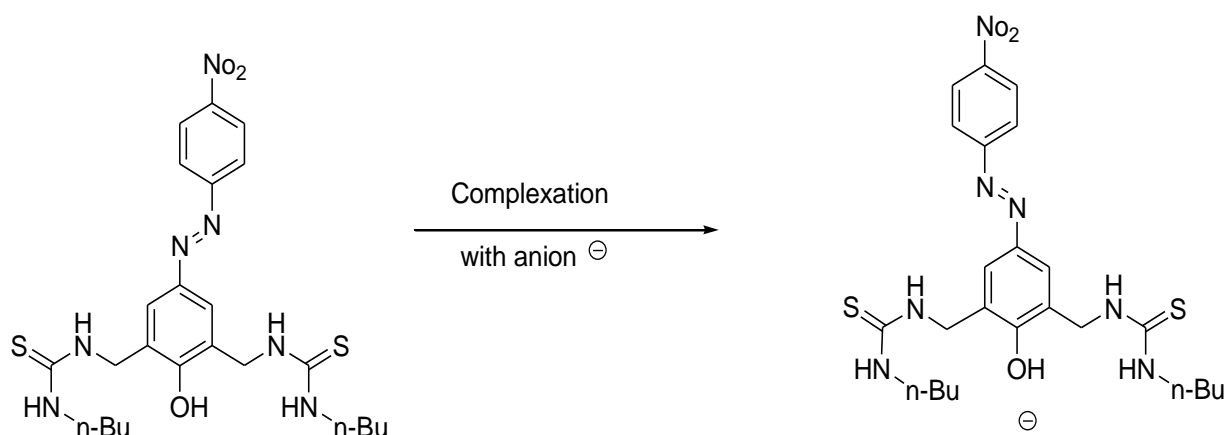
Over intake of heavy metal ions causes harmful diseases. Due to the sensing ability of Lawson azo dye based fluorescent receptor metals ions can be detected²⁰. Receptors are also having binding capability with metal ions; receptors like heteroditopic are highly capable of binding Hg²⁺ even in the existence of other ions in the water bodies²¹. There are different types of artificial tripodal receptors for the selective detection and sensing of cations and anions²². The detection of heavy metal ions is highly sensitive and selective in semi-aqueous system as they are variable in size. The fluorescent receptor was enhanced correspondingly with the addition of heavy metal ions over other cations²³. For the detection of cations like Hg²⁺ in water bodies, ZnO Nanoparticles are used with organic receptors²⁴.

Today, positively charged receptors such as pyridinium, ammonium and imidazolium/benzimidazolium are of greatest interest. Subunits of these positively charged receptors binds with anions through charge-charge interactions and through alternative hydrogen bonds²⁵. Excess of Al³⁺ and Zn²⁺ has neurotoxic effects in organisms. The detection of these metal cations is difficult due to bad coordination ability. Fluorescent probe containing chromone and rhodamine moieties are able to detect these cations²⁶.

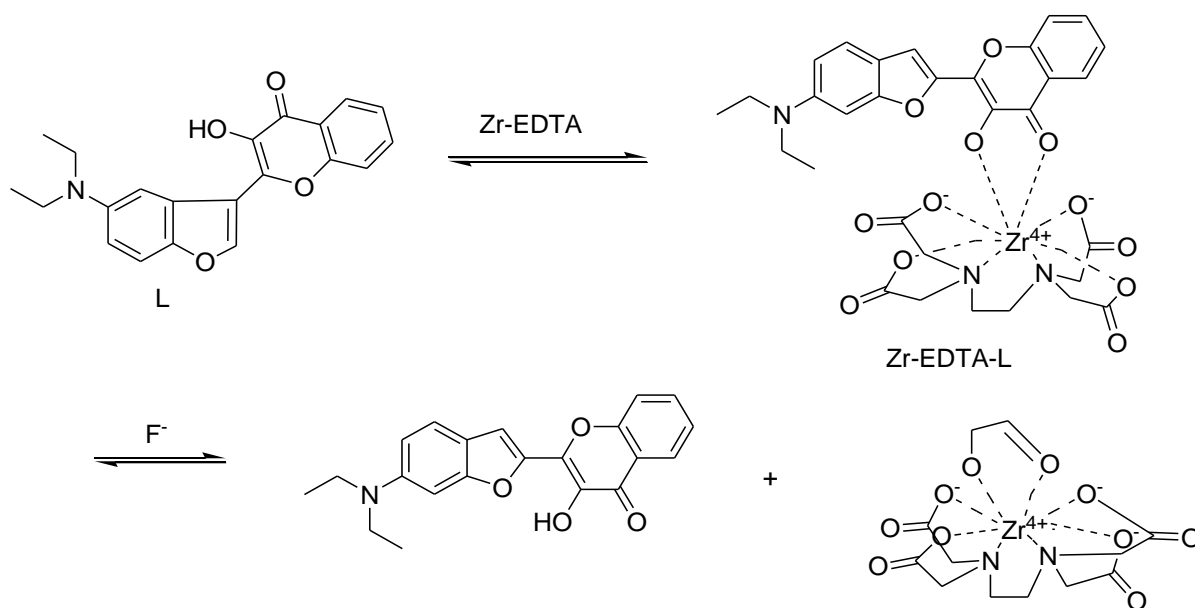


The detection and sensing of anions via artificial receptors are field of recent interests as they are extremely sensitive and uncomplicated to signal²⁷.

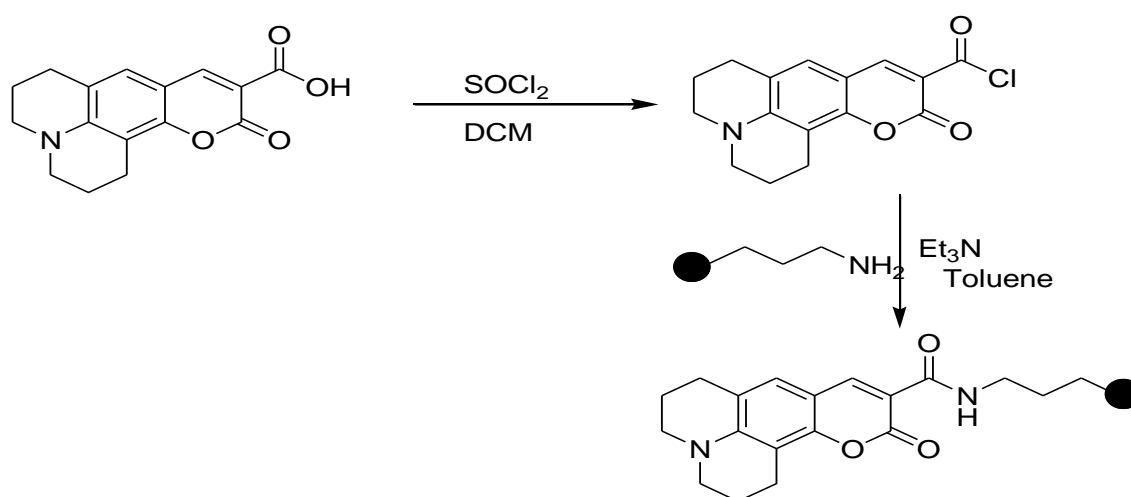
Optical sensors consist of two parts, one is the anion-binding part and the other is the chromophores which are either covalently attached or intermolecularly linked induced changes into optical signals²⁸.



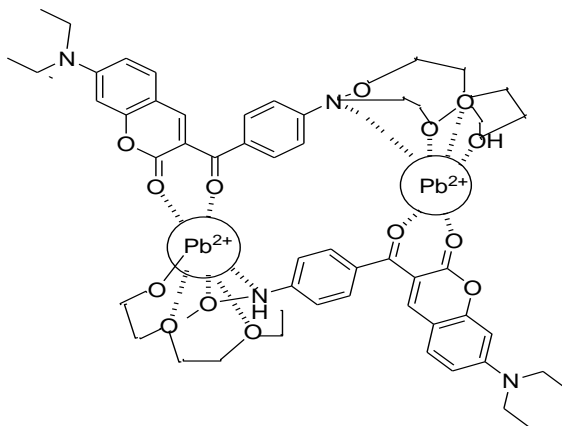
Zr-EDTA and 3-hydroxyflavone act as resourceful fluoride sensor receptors capable of selective interactions with water-soluble anions example F^- , Cl^- .²⁹



Fluorescent sensors are tool for the detection of H_2S and also for bio imaging, its response to H_2S in living cells as well as in solutions is with turn on signals. There are multiple fluorescent sensors have been developed but three channel fluorescent sensor which gives signals in three different channels are more consistent³⁰.



The presence of Pb^{2+} in sources can lead to poor health and environmental issues like anemia, memory loss, and retardation. The cellular role of polypeptide capable of scaffolds selective fluorescent sensors have been developed for the sensing of this injurious metal ion³¹.

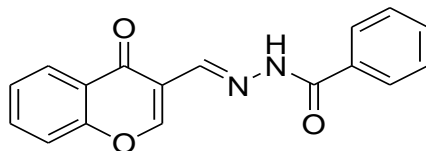


OBJECTIVES OF THE STUDY

- A new class of compounds are synthesized which have differentiable properties from their bulk materials.
- The nano compounds so synthesized have been used for studies of the ligand behaviour where in key structural features of chromone nucleus can be explored to study the interaction behaviour.
- Nano synthesized compounds have been reported to have visual characterization of some of the important cations, synthesis of chromone based derivatives resembling to naturally occurring flavones used for those types of detection studies which have the minimum utilization of toxic chemical substances.

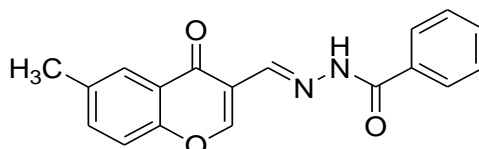
METHODOLOGY

Preparation of N'-((4-oxo-4H-chromone-3-yl) methylene) benzohydrazide



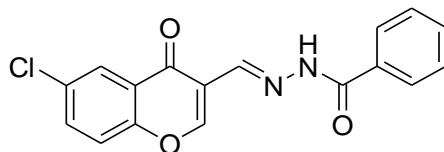
To the clear solution of benzhydrazide (0.19 gm, 0.143 mol) in methanol (15 ml) in RBF was added zinc perchlorate (5mg), and stirred the contents on magnetic stirrer for 10 minute under anhydrous conditions. To the stirred solution 3-formylchromone (0.25 gm, 0.137 mol) dissolved in methanol (5 ml) was added and stirred on magnetic stirrer for 4 h. Progress of the reaction was monitored using TLC (chloroform). After the completion of reaction TLC, solvent was evaporated under reduced pressure to obtained solid mass which was further triturated with diethyl ether (5×2 ml) and product was dried to obtained white solid (0.38 gm, 87%); m.p. 149-150° C, I.R data (KBr, cm^{-1}) N-H 3475, C-H 3088, C=O 1678, C=N 1562, C-H 1408, C-O 1134, C-N 1020.

Preparation of N'-((6-methyl-4-oxo-4H-chromone-3-yl) methylene) benzohydrazide



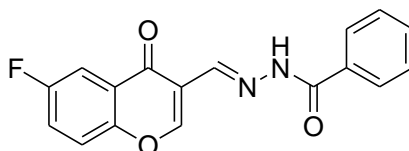
To the clear solution of benzhydrazide (0.18 gm, 0.13 mol) in methanol (10 ml) in RBF was added zinc perchlorate (5 mg) and the solution was stirred for 10 minute under the anhydrous conditions. To the stirred solution 6-methyl-3-formylchromone (0.25 gm, 0.13 mol) dissolved in methanol (5 ml) was added and stirred on magnetic stirrer for 5 h. Progress of the reaction was monitored using TLC (chloroform). After the completion of reaction TLC, solvent was evaporated under reduced pressure to obtained solid mass which was further triturated with diethyl ether (5×2 ml) and product was dried to obtained light orange coloured solid (0.26 gm, 97%); m.p. 88-89° C, I.R data (KBr, cm^{-1}) N-H 3475, C-H 3205, C=O 1639, C=N 1577, C-H 3064, C-O 1151, C-N 1317.

Preparation of N'-((6-chloro-4-oxo-4H-chromone-3-yl) methylene) benzohydrazide



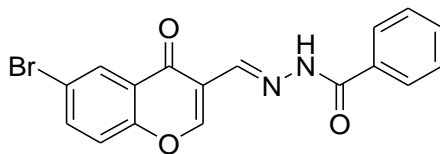
To the clear solution of benzhydrazide (0.16 gm, 0.12 mol) in methanol (10 ml) in RBF was added zinc perchlorate (5 mg) and the solution was stirred for 10 minute under the anhydrous conditions. To the stirred solution 6-chloro-3-formylchromone (0.25 gm, 0.17 mol) dissolved in methanol (5 ml) was added and stirred on magnetic stirrer for 4 h at room temperature. Progress of the reaction was monitored using TLC (chloroform). After the completion of reaction TLC, solvent was evaporated under reduced pressure and crude product was obtained, which was further triturated with diethyl ether (5×2 ml) and product was dried to obtained yellow coloured solid (0.30 gm, 77%); m.p. 102-104° C, I.R data (KBr, cm^{-1}) N-H 3416, N-H 3271 C-H 2800, C=O 1676, C=N 1531, C-H 1491, C-O 1120, C-Cl 707.

Preparation of N'-((6-fluoro-4-oxo-4H-chromone-3-yl) methylene) benzohydrazide



To the clear solution of benzhydrazide (0.07 gm, 0.52 mol) in methanol (10 ml) in RBF was added zinc perchlorate (5 mg) and the solution was stirred for 10 minute under the anhydrous conditions. To the stirred solution 6-fluoro-3-formylchromone (0.1gm, 0.51 mol) dissolved in methanol (5 ml) was added and stirred on magnetic stirrer for 5 h at room temperature. Progress of the reaction was monitored using TLC (chloroform). After the completion of reaction TLC, solvent was evaporated under reduced pressure and solid mass was obtained, which was further triturated with diethyl ether (5×2 ml) and product was dried to obtained light green coloured solid I.R data (KBr, cm^{-1}) N-H 3641, C-H 3269, C-H 3047, C=O 1678, C=C 1645, C=N 1573, C-H 1475, C-O 1149, C-F 891.

Preparation of N'-((6-bromo-4-oxo-4H-chromone-3-yl) methylene) benzohydrazide



To the clear solution of benzhydrazide (0.06 gm, 0.47 mol) in methanol (10 ml) in RBF was added zinc perchlorate (5 mg) and the solution was stirred for 10 minute under the anhydrous conditions. To the stirred solution 6-bromo-3-formylchromone (0.1gm, 0.51 mol) dissolved in methanol (5 ml) was added and stirred on magnetic stirrer for 5 h at room temperature. Progress of the reaction was monitored using TLC (chloroform). After the completion of reaction TLC, solvent was evaporated under reduced pressure and solid mass was obtained, which was further triturated with diethyl ether (5×2 ml) and product was dried to obtained yellow coloured solid I.R data (KBr, cm^{-1}) N-H 3743, C-H 3031, C-H 2809, C=O 1712, C=N 1649, C-O 1209, C-Br 552.

Preparation of Gold nanohybrids: By using reprecipitation method, stock solutions of amount 1 mL of 3-formyl chromone and its derivatives were prepared by injecting these organic compounds with a micro syringe into 100 mL de-ionized water at a stable rate under continuous and vigorous stirring. The prepared solution was then sonicated for half an hour at stable temperature to ensure the formation of organic nanoparticles. By using Dynamic Light Scattering (DLS) size analyzer, we can find out the size distribution of formed particles.

Reduction product of HAuCl_4 using ascorbic acid was used in a particular ratio to prepare gold nanohybrids. By using de-ionized water 250 mL aqueous solutions of 1mM of HAuCl_4 and ascorbic acid were prepared from stock solutions of HAuCl_4 (0.001M) and ascorbic acid (0.001 M). The solutions were equilibrated at ambient temperature for 2 hours and were then mixed along with organic nanoparticles to attain gold nanohybrids. The emergence of pink color in the solution confirmed the formation of gold nanohybrids. By a variety of factors we can control the size distribution of the hybrid nanoparticles in the solution such as the order in which we added reagents, the ratio of three components i.e.

ascorbic acid, gold and the nanoparticles prepared, also the physical conditions provided i.e. temperature.

Interaction of Gold nanoparticles solution (N'-((4-oxo-4H-chromone-3-yl) methylene) benzohydrazide) with Alkali metal

1 molar of 10 ml solution of $K_2Cr_2O_7$ was taken and its 80 μM was added to 20 μM of gold nano hybrid solution and characterised by UV-Visible spectroscopy to find out the interaction of nano hybrid organic compound with alkali metal.

Interaction of Gold nanoparticles solution (N'-((4-oxo-4H-chromone-3-yl) methylene) benzohydrazide) with Alkaline earth metals

1 molar of 10 ml solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $CaCO_3$ was taken and its 80 μM was added to 20 μM of gold nano hybrid solution and characterised by UV-Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((4-oxo-4H-chromone-3-yl) methylene) benzohydrazide) with Heavy metals

1 molar of 10 ml solution of $Co(NO_3)_2$, $ZnCl_2$, $NiCO_3$, $Pb(CH_3COO)_2 \cdot 3H_2O$, KBr , $CuCl_2 \cdot H_2O$ was taken and its 80 μM was added to 20 μM of gold nano hybrid solution and characterised by UV-Visible spectroscopy.

AT 0.1M CONCENTRATION

Interaction of Gold nanoparticles solution (N'-((4-oxo-4H-chromone-3-yl) methylene) benzohydrazide) with Heavy metals and Alkaline earth metals

0.1 molar of 10 ml solution were prepared. For better interaction we made solution little acidic by adding 0.01 ml conc. HCl to each of the test tube, with the change in pH the solution become more soluble, its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV- Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((4-oxo-4H-chromone-3-yl) methylene) benzohydrazide) with Sulfate ions

0.1 molar of 10 ml solution of MgSO_4 , MnSO_4 , AlSO_4 , FeSO_4 , $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2$, $\text{K}_2\text{S}_2\text{O}_8$, Ag_2SO_4 were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV- Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-methyl-4-oxo-4H-chromone-3-yl) methylene) benzohydrazide) with Heavy metals and Alkaline earth metals

0.1 molar of 10 ml solution were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of Gold nanohybrid solution and characterised by UV- Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-methyl-4-oxo-4H-chromone-3-yl) methylene) benzohydrazide) with sulfate ions

0.1 molar of 10 ml solution of MgSO_4 , MnSO_4 , AlSO_4 , FeSO_4 , $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2$, $\text{K}_2\text{S}_2\text{O}_8$, Ag_2SO_4 were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV- Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-fluoro-4-oxo-4H-chromone-3-yl)methylene) benzohydrazide) with Heavy metals and Alkaline earth metals

0.1 molar of 10 ml solution were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV- Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-fluoro-4-oxo-4H-chromone-3-yl)methylene) benzohydrazide) with sulfate ions

0.1 molar of 10 ml solution of MgSO_4 , MnSO_4 , AlSO_4 , FeSO_4 , $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2$, $\text{K}_2\text{S}_2\text{O}_8$, Ag_2SO_4 were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanoparticle solution and characterised by UV-Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-bromo-4-oxo-4H-chromone-3-yl)methylene) benzohydrazide) with Heavy metals and Alkaline earth metals

0.1 molar of 10 ml solution were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV- Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-bromo-4-oxo-4H-chromone-3-yl)methylene) benzohydrazide) with sulfate ions

0.1 molar of 10 ml solution of MgSO₄, MnSO₄, AlSO₄, FeSO₄, (NH₄)₂Ni (SO₄)₂, K₂S₂O₈, Ag₂SO₄ were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV-Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-chloro-4-oxo-4H-chromone-3-yl)methylene) benzohydrazide) with Heavy metals and Alkaline earth metals

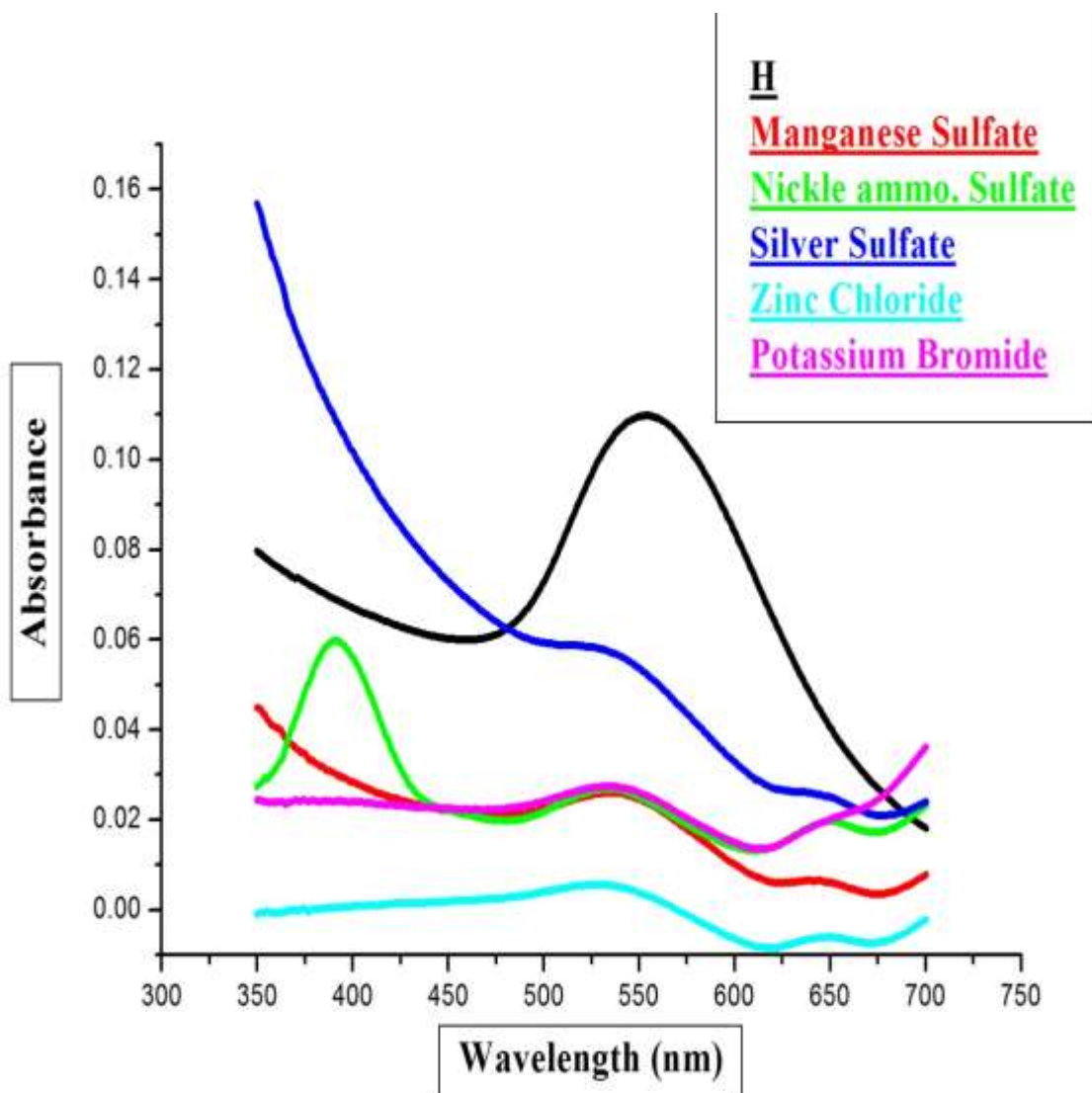
0.1 molar of 10 ml solution were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV- Visible spectroscopy.

Interaction of Gold nanoparticles solution (N'-((6-chloro-4-oxo-4H-chromone-3-yl)methylene) benzohydrazide) with sulfate ions

0.1 molar of 10 ml solution of MgSO₄, MnSO₄, AlSO₄, FeSO₄, (NH₄)₂Ni(SO₄)₂, K₂S₂O₈, Ag₂SO₄ were prepared. To make it acidic 0.01 ml conc. HCl was added to the each test tube and its 80 μM was added to 20 μM of gold nanohybrid solution and characterised by UV-Visible spectroscopy.

RESULT AND DISCUSSION

Characterization by UV-Visible Spectroscopy: In order to investigate the ligand binding interaction of organo nanomaterials with various types of metal ions, the studies were taken up in two different concentrations of 1.0M and 0.1M. Initially the studies were carried with Au-chromone nanoparticles, where in the interactions of different Alkali and Alkaline earth metals were carried which were further extended to some of transition metals. The metals show significant interaction behaviour studies where the Cation species of these metal ions were detected. In these investigations Mg, Ni, Ag exhibited higher interactions with 3-formyl chromone nanoparticles. In order to investigate the effect of different substitutions attached over chromone ring moiety, these investigations were extended further with substituent like (Cl, F, Br and CH₃) at C₆-position of chromone. Results for these investigations are described in Fig: 1 and graph is given below.

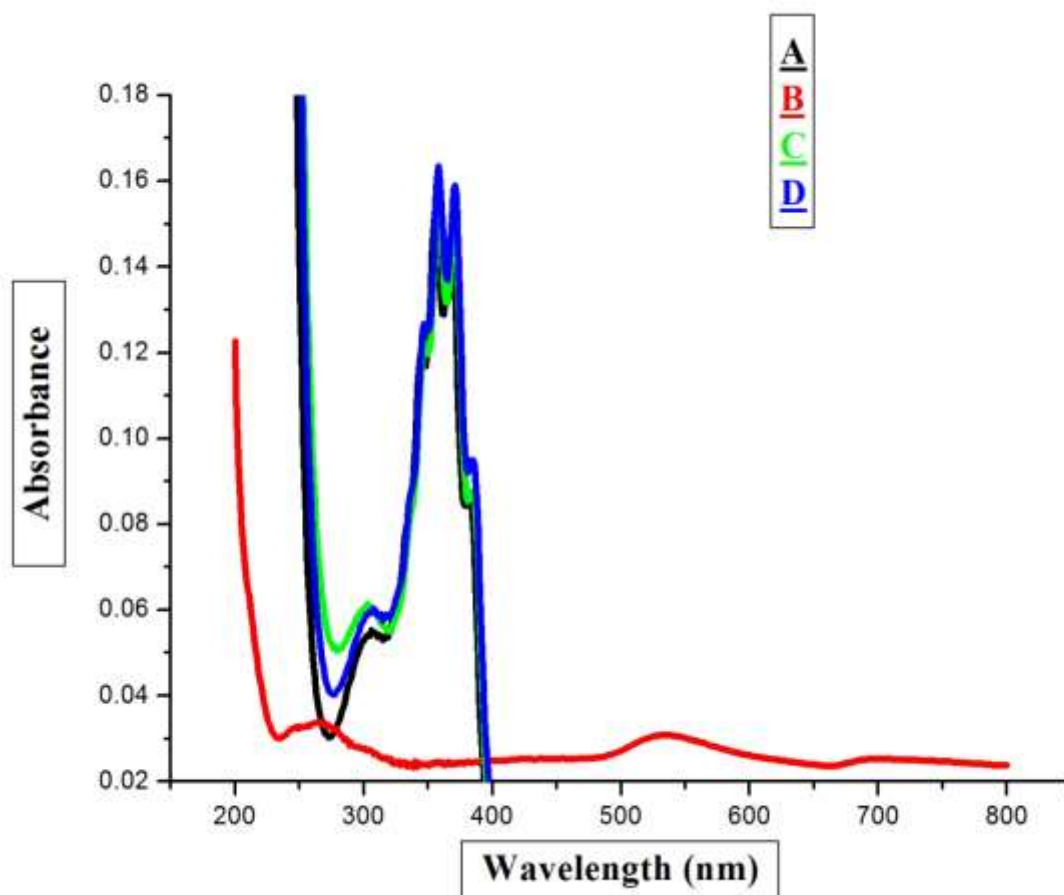


(Fig: 1): overlay of 3-formyl Chromone organic nanohybrid

From the above graph we conclude that after taking UV of so many alkali metals, alkaline earth metals, Heavy metals and sulfate ions. The interactions are shown by Manganese Sulfate, Nickel Sulfate, Silver Sulfate, Zinc Chloride and Potassium Bromide. Metals have the tendency to gain electrons to make its octet complete and the ligands have the tendency to donate electrons to the vacant orbitals of the metals. Here 3-formyl Chromone is behaving as a ligand and it is doped with the organic Gold nanoparticle.

In the further studies of their interaction with the other metals we cannot consider its electron donating and accepting property, when they interact with other metals the oxo group of the ligand and two amine groups are in conjugation, due to which a cavity forms in between into which other metals get attached and with the different absorbance values of different metals we come to know which metal is showing better results with the organic nanohybrid chemosensor. From this graph we see that Manganese Sulfate is showing Absorbance at around 600-650 nm. Nickel amm. Sulfate and Silver Sulfate is also showing absorbance near to this range but after its further study with Chromone derivatives we found that Manganese is giving effective results rest both of them have negative peaks.

INTERACTION OF METALS WITH THE CHROMONE DERIVATIVES



(Fig: 2): Overlay of Chromone derivatives with Manganese Sulfate at 0.1 concentration

From the above graph we conclude that among Chromone derivatives Floro group is showing strongest interaction and rest are in the order as follows:



Absorbance value for Floro derivative is at around 430-500, 350-450 nm for chloro derivative, 400 nm for bromo and around 250 nm for methyl group derivative of chromone.

Characterized by Fluorescence Spectrometer

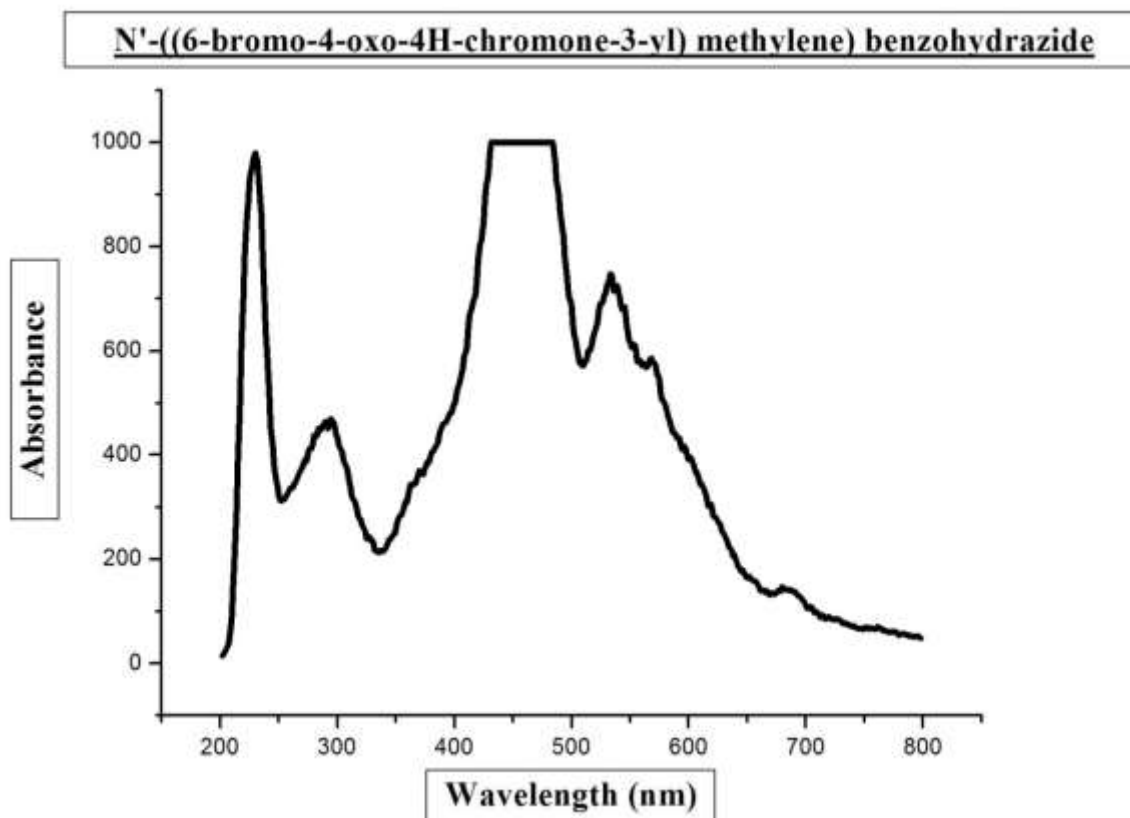


Fig: 3 Fluorescence spectra of N'-((6-bromo-4-oxo-4H-chromone-3-yl) methylene) benzohydrazide

So far we concluded that Fluoro derivative of chromone is showing appropriate results but with the Fluorescence studies we come to know that counter ion effect comes when we dope strong and stable metals with chromone derivatives as gold is one of the strongest metals, Bromo derivative in the above graph is not showing appropriate results but some florescence is there rest all derivatives is not showing any florescence due to quenching of signals by gold metal. When we dope gold nanoparticles with chromone derivatives there is formation of strong bond between them.

There are very few free electrons to excite, so the fluorescence signals are weak. As we said counter ion effect is there, from that we mean if we add a little amount of anions into the nanohybrid solution, then that anion will make bond with gold and the ligand will be free to show fluorescence.

CONCLUSION

Present investigations were aimed at selective synthesized identification of nanohybrid chromone derivatives. These studies provide a significant route for the identification of various metal ions present in the aqueous system. A major advantage of such study involves identification heavy metals with small concentration, presence of these metals in excess can act as a potential threat to the living system and may pose as a danger towards various health ailments and hazards. The present study can act as a good lead for the development of new methods for detection of these ions in solutions. Spectroscopic estimations of these compounds are highly efficient system and used of nanostructured chromone complexes provides an edge where the system can be developed even for the estimation of compounds in ppm concentration.

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