Synthesis and Photophysical Studies of Thiazolidin-2,4-dione Derivatives

A

Thesis submitted

in partial fulfillment of the requirements for the award of the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

By

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July, 2014

Candidate's Declaration

I hereby declared that the work which is being presented in the dissertation entitled "Synthesis and Photophysical Studies of Thiazolidin-2,4-dione Derivatives" in the partial fulfillment of the requirements for the award of the degree of Masters of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January to July 2014 under the supervision of **Dr. Kamaldeep Paul**. My thesis has not previously formed the basis for any degree, diploma, or other similar title or recognisation.

Place: Patiala

Charanpreet Kaur
Charan Preet Kaur

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

Kamaldeep Paul
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18/7/14
Prof. Bonamali Pal
Head of the Department
School of Chemistry and Biochemistry
Thapar University

CERTIFICATE

This is to certify that the project entitled "Synthesis and Photophysical Studies of Thiazolidin-2,4-dione Derivatives" being submitted by **Mrs. Charan Preet Kaur** in the partial fulfillment of the requirement for the award of the degree of Masters of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala is a bonafide work carried under the supervision of **Dr. Kamaldeep Paul** and no part of this project has been submitted for the award of any other degree by me.

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Acknowledgement

I would like to convey my sincere gratitude to my research guide Dr. Kamaldeep Paul, Assistant Professor, School of Chemistry and Biochemistry for his guidance and suggestions which helped me immensely during this course. I am extremely indebted to him for giving me chance to work on such an interesting topic.

I am grateful to Prof. Bonamali Pal, Head, School of Chemistry and Biochemistry, Thapar University, Patiala for approving this project and also Dr. Vijay Luxami, Assistant Professor, School of Chemistry and Biochemistry for her fruitful suggestions throughout my project work.

I am also thankful to Ph.D Research Scholars, Alka Sharma, Meenakshi Verma, Prinka Singla, Richa Goel, Richa Rani, Akul and Alka Rani for their guidance and support.

I greatly acknowledge SAI Labs, Thapar University for NMR facility.

Last but not the least, I express my gratitude to Almighty God and my parents for their encouragement through the entire process.

Charanpreet Kaur.

Date: 18 July, 2014

Charan Preet Kaur

Place: Patiala

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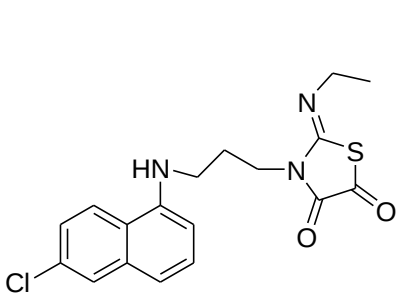
ABSTRACT

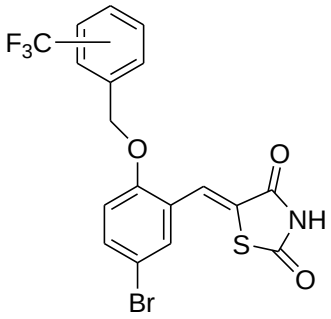
Thiaaolidin-2,4-dione(1) and its derivative-5-(2- hydroxy benzylidene) thiazolidine-2,4-dione(2) 5-(4- bromo -2- hydroxylbenzylidene)thiazolidine -2,4-dione (3)5-(4- chloro-2-hydroxybenzylidene)thiazolidine-2,4-dione(4) 3-(2,4- dioxothiazolidin-5-ylidne) methyl)-4-hydroxybenzaldehyde(5) have been synthesized.Compound (2) acts as selective chemosensor for Cu^{2+} ions amongst ions and for cyanide ions amongst another anions of biological importance.

INTRODUCTION AND REVIEW OF LITERATURE

Compounds produced from natural sources play a major role in drug therapy. Small molecule libraries based on natural products as templates[1] e.g. camalexins formed as phytoalexins in leaves of camelina sativa in response to injection by fungi plays an important role. Alternaria brassicae, was elucidated to be (3-indolyl)-2 thiazoles[2]. These thiazolidine derivatives have been reported to show a variety of biological activities like antimicrobial[3] and cytotoxlc activities. Bis (Indolyl) thiazoles are also founded as new anti tumor agents. Novel thiourea thiazolidinedione used as potent antimalarials. Malaria is devastating disease caused by parasite plasmodium which afflicts more than 40% of the world population causing an estimated mortality of 1.5-2.7 million people annually[4]. This epidemic is deadly caused by parasite *plasmodium falciparum* due to its resistance to antimalarial drug. This *P. falciparum* affects mainly pregnant women and children under the age of five[5]. It acts by binding to heme molecule released from the hemoglobin that is digested by malaria parasite as they grow. Among, old and new drug targets of malaria, host heme molecules remains one of the most attractive target. Based on these observation, modification of 1,4-diaminoalkyl chain of chloroquine has been done and promising results against resistant strains of plasmodium were obtained. Urea derivatives have also been identified as inhibitors of β- hematin formation[6], while imidazolidinedione with prophylactic antimalarial activity[7].



1

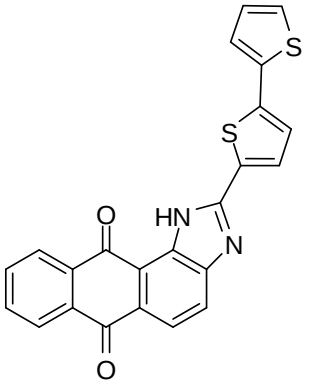


2

Thiazoliclinedione (TZD) derivatives (**1**) named Glitazones marketed in 1990 have antihyperglycemic and antiobesity effects. Their activities were affected via ortho and para substitution by CF_3 group. Compound **2** significantly suppress weight gain and improved blood parameters such as TG, total cholesterol. TZD is also used for the treatment of type 2 diabetic disease that is associated with ageing and obesity. Currently, several drugs are available in the treatment of insulin resistance such as metformin, berberine, TZD etc. Among these TZD based drugs are the most powerful medicine. Inhibition of human

immunodeficiency virus type I wild type and mutant reverse transcriptase by the phenyl ethyl thiazolyl thiourea. A new class of potent and selective inhibitors of HIV reverse transcriptase (RT) has recently been identified. The prototype compound trovirdine and MSC-127 caused inhibition of wild type HIV viruses. Thus, depending on the substituent's thiazolyl compounds have different biological properties such as antibacterial, antifungal[8], antidiabetic,[9,10] Cardiotonic[11] and anti convulsant[12] properties. Also, it has been shown that the introduction of arylidene moieties at different positions of the thiazolidine ring enhanced antimicrobial activity.[13,14]

Chemosensors using color and/or fluorescence intensity have been developed to be useful tools for sensing various analytes. A typical optical chemosensor has a receptor (the recognition site), linked to a fluorophore (the signal source), that translates the recognition event into the fluorescence signal. A large number of small anions and cations, which play vital roles in human life, exist within organisms and in the external environment. Consequently, the detection of such anions and cations are of great interest and importance to many chemists, biologists and environmentalists.



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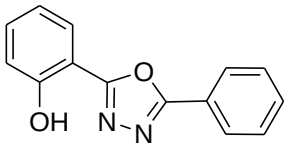

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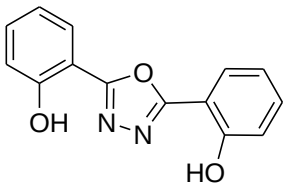
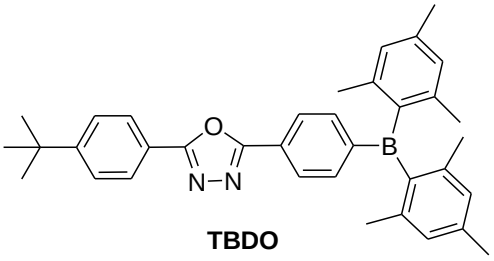


3

Batista and co-worker[15] reported bithienyl, imidazo, anthraquinone based fluorescent chemo sensor. A red shift with an enhancement of the fluorescence emission intensity on the addition of fluoride ion was observed. The deprotonation of the NH in the imidazole ring with fluoride ion was responsible for a significant color change from yellow to pink. Upon the addition of metal ions such as Hg^{2+}, Cu^{2+} original yellow color of receptor with a quenching of florescence intensity. This reversible colorimetric reaction upon metal complexation gives rise to an off-on-off (yellow-pink-yellow) system. In the fluorescence spectra large quenching of intensity of the band at 375 nm was observed on the addition of fluoride ion. The further addition of F^- ion slowly shifted the band to 434 nm.

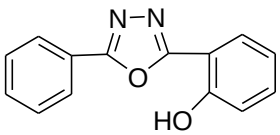
Hui Tong and Co-workers[16] reported the new electro neutral anion chemosensors **2** and **3** for phosphate and fluoride ions with high fluoride/chloride and phosphate/chloride selectively. In non-polar solvents (hexane), compound exhibits a strong long wavelength fluorescence (498 nm) and short-wave length fluorescence (354 nm). In polar solvents (acetonitrile and DMF), it events a strong intermediate wavelength light around 448 nm and weak short wavelength light (354 nm).

Hong *et. al.*[17] have used compounds containing three coordinated groups exhibit intersecting fluoresence emission thiophene,[18] fluorena,[19] napthyl phenyl amine[20] etc. were introduced.



TBDO

(4)



5

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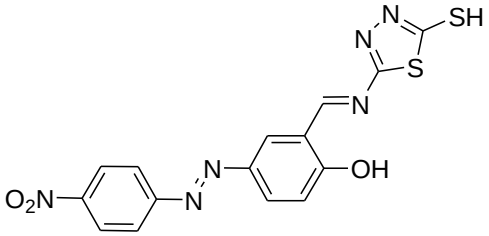
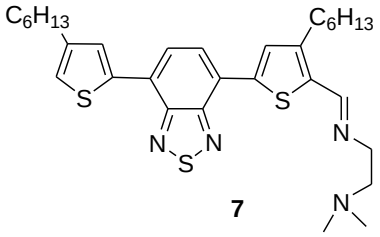
In THF solution, TBDO showed strong absorption band at 331 nm due to transitions when excited at 330 nm, it exhibits good blue, emission at 425 nm. TBDO stands for a fluoride sensor which showed unique blue shift absorptions and fluorescence quenching properties after the addition of fluoride anion. So, addition of tetrabutyl ammonium fluoride (TBAF) to the TBDO solution leads to a significant blue shifted absorption from 330 nm to 310 nm. Also, emission bands of TBDO centered at 425 nm gradually decrease. The selectivity of the interacting was also investigated using anions such as AcO^-, Cl^-, Br^-.

Ruifa Jin. *et.al.* [21] used 2-(2-hydroxyl phenyl)-5-phenyl-1,3,4-oxadiazole (HOXDI) **5** acted as both colorimetric and fluorescence sensor for $F^-/H_2PO_4^-$. Color change allowed their detection with naked eyes. Different signaling mechanisms have been suggested for $F^-/H_2PO_4^-$ chemosensors such as photo induced electron transfer[22] (PET), excited state photon transfer[23] (ESPT), intermolecular charge transfer[24] (ICT) and metal ligand charge transfer[25] (MLCT) etc.

Jun-Qiang *et. al*[26] used novel sensor **6** having acetate selective property based on azophenol and mercapto thiadiazole moiety. Sensor **6** has single selectivity and sensitivity in the recognition for AcO^- anion over other anions by naked eyes and UV- vis spectra changes in aqueous solution.



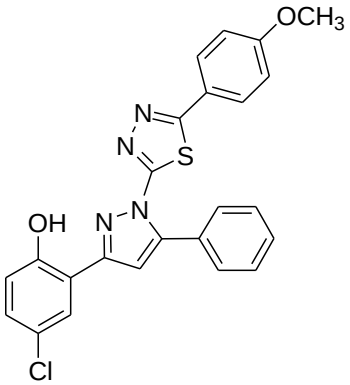
6



7

Palas *et. al.*[27] studied D-A-D system (donor–acceptor–donor), system of benzo [2,1,3]thiadiazole acceptor and thiophene donor with azomethine pendant arm. Such D-A systems displayed strong color as well as high absorption coefficient due to effective intramolecular orange transfer. The alternation in the strength of the donor or acceptor can create a color change. The pendant arm attached to the azomethine thienyl group act as metal binding site. Therefore, upon binding to metal ion, the electron donation capability of thienyl azomethine moiety was increased due to MLCT (metal ligand charge transfer which leads to stronger ICT. A bathochromic shift in absorption spectra upon addition of metal ions is thus expected.

Sheng Qing *et. al.*[28] synthesized pyrazoline derivatives by the reaction of chalcone and 5-aryl-2-hydrazinyl-1,3,4-thiadiazole. These possess stronger fluorescence and have higher hole-transport efficiency and excellent emitting property. 1- and 3-positions of pyrazoline ring influenced the photophysical properties in different ways[29,30,31] by modifying the substituent at 1- and 3-position so that new structures were synthesized. It is found that charge transfer process exists between the nitrogen atom at 1-position and the carbon atom present in 3-position in pyrazoline moiety. The fluorescence spectra of compound **8** for detecting Cu^{2+} were studied and showed that **8** exhibited Cu^{2+} selective and sensitive chromogenic signaling behavior over other common physiologically important metal ions.



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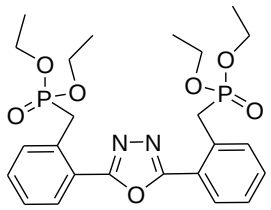
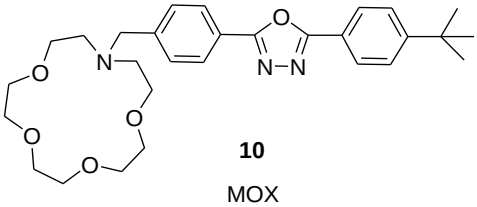


9

Yanqin Z hang *et. al.*[32] synthesized novel phosphoric acid functionalized sensor 2,5-bis[2- phosphoric acid methyl) phenyl-1,3,4-oxadiazole (**9**) as selective sensor for Fe^{3+} ions.

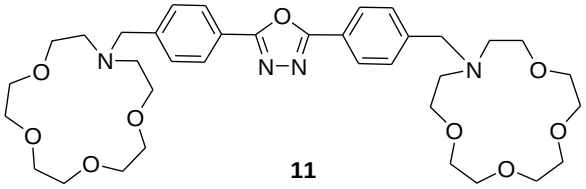
It showed fluorescence change with high selectivity and sensitivity towards Fe^{3+} in DMF-H_2O solution.

Novel Fluoroionophores MoX and BOX[33] incorporating one and two monoaza-15-crown-5, respectively on photoemittive diaryl-1,3,4-oxadiazoles is reported. Neither absorption nor emission spectra of both BOX and MOX was quiet changed in presence of alkali met of ions. However, for alkaline earth metals BOX served as a sensitive Mg^{2+} sensor in biological system.



10

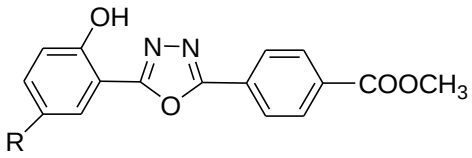
MOX



11

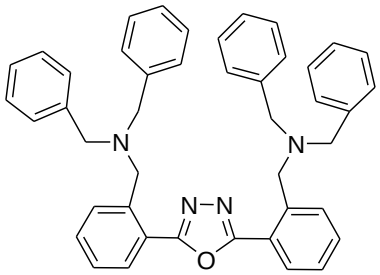
BOX

J. Ma *et al.*[34] used oxadiazole-based compounds for sensitive ion sensing[17] and optical data storage materials[18]. The compounds **12-13** having adjacent phenolic hydroxyl and 1,3,4-oxadiazole units were resulting intramolecular hydrogen bond that is strong enough to hinder the association of most anions but not F^-, with the phenolic hydroxyl hydrogen. Thus, both molecules display same color changes from colorless to yellow but different optical shifts upon addiction of F^-.



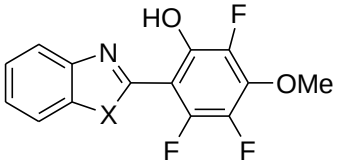
R=Cl (12)

R=H (13)

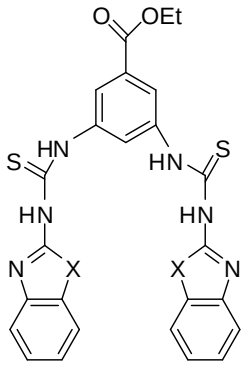


14

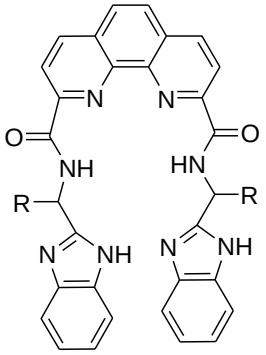
A fluorescent sensor **14** based on a 1,3,4-oxadiazole chromospheres and the N, N-bis (2-pyridymethyl)amine displayed a remarkable fluorescence sensing effect for determination of Cu^{2+} and protons. It showed on-off-on "switch for proton and ' on–off' switch towards Cu^{2+}. Kiyoshi *et al.*[36] synthesized 2-(3,5,6-trifluoro-2-hydroxy-4-methoxy phenyl) benzoxazole **15** and benzothiazole analogue **16** from the corresponding 2-penta fluoro phenyl benzazoles. Benzoxazole **15** applicable to fluorescent probe sensing Mg^{2+} and **16** was suitably used for sensing of Zn^{2+}.



X=O**(15)**,
X=S **(16)**



X=NH **(17)**,
X=S **(18)**



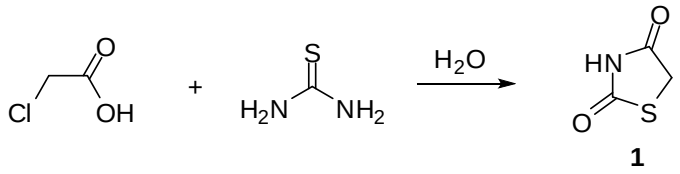
R=H **(19)**,
R=CH_3 **(20)**

Gangwoo Lee *et. al*.[37] used receptor bearing an array of hydrogen bond donors from benzimidazole and thiourea moieties. The receptor showed changes in fluorescence intensity only with PO_4^{3-} in DMSO/H_2O and no significant response to any of other anion. The receptor acts as a selective sensor for PO_4^{3-} even in presence of other anions in 20% DMSO.

Emma B. Veale *et.al* [38] used neutral sensors **19** and **20** containing benzimidazole receptor and 1-10-phenanthroline fluorophore respectively showed both positive and negative fluorescence responses depending upon the anions being detected. Binding to more basic anion such as F^- and ACO^- gave rise to quenching in the fluorescence emission while it showed an enhancement upon interaction with Cl^-, Br^-, I^-.

RESULT AND DISCUSSIONS

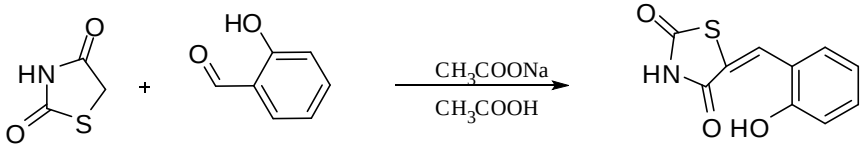
Keeping in mind biological importance five membered heterocyclic moieties, new thiazolidine-2,4-dione derivatives have been synthesized. Compounds **2-5** were synthesized according to the schemes **1-5**. A mixture of $ClCH_2COOH$ (0.106 mol) and thiourea (0.106 mol) in 10 ml water was heated for 40 hrs. The solid product was filtered and washed water. The crude product was crystallized from water to give pure compound **1** with 82% yield with Mpt = 110-115 ^oC.



1

Scheme-1

A mixture of compound **1** (0.001 mol) and salicaldehyde (0.001 mol) was heated at 100˚C in the presence of 1 ml glacial acetic acid and sodium acetate (0.001 mol) for 10 hrs. The product thus formed was treated with concentrated HCl to acidic pH and then stirred for half an hour and solid thus formed was filtered to get pure compound **2**. ^1H NMR of this compound showed 1H broad singlet at δ 10.12 of NH, 1H singlet at δ 7.81 of CH, 1H doublet at δ 7.33, 1H triplet at δ 7.25 and 2H multiplet at δ 6.97-6.90 of aromatic-H (**Fig. 1**). On the basis of NMR spectrum, this compound has confirmed the structure of 5-(2-hydroxybenzylidene)thiazolidine-2,4-dione (**2**).



1 **2**

Scheme-2

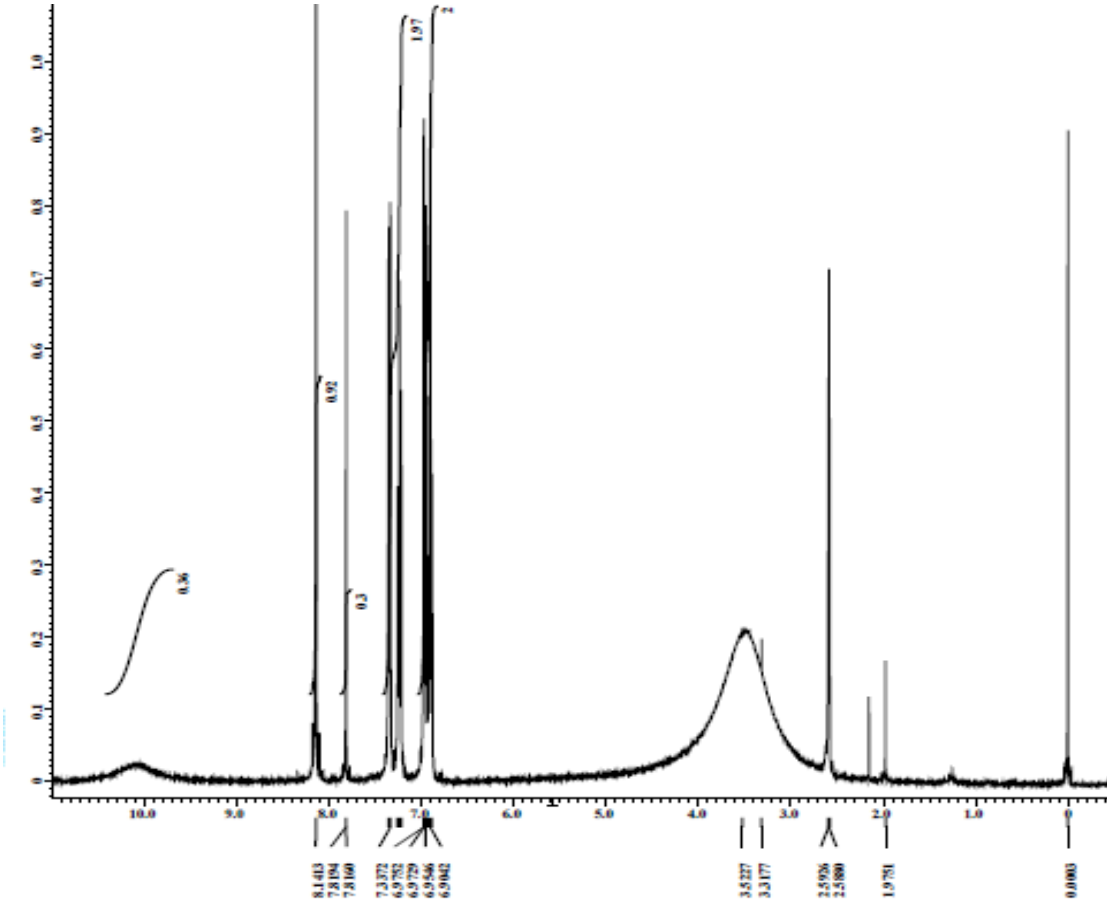
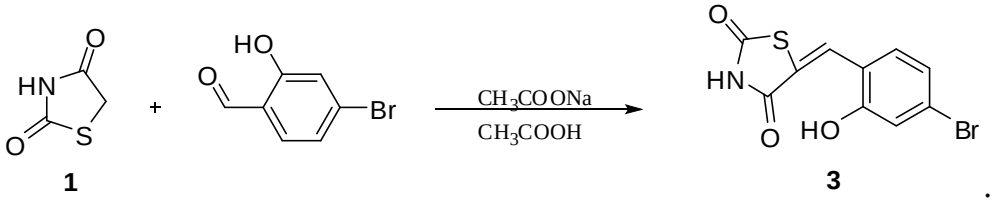


Figure 1: ^{1}H NMR spectrum of 5-(2-hydroxybenzylidene)thiazolidine-2,4-dione (2)

Similarly, mixture of compound **1** (0.004 mol) and 4-bromo-2-hydroxy benzaldehyde (0.0047 mol) was heated at 100 ^{o}C in the presence of sodium acetate (0.0064 mol) and acetic acid (1-2 ml) for18 hrs. The crude product then formed was purified by column chromatography using hexane : ethyl acetate as eluants to get pure compound **3**. ^{1}H NMR of this compound showed 1H broad singlet at δ 10.73 of NH, 1H singlet at δ 7.87 of CH, 2H singlet at δ 7.35 and 1H doublet at δ 6.85 of aromatic-H **(Fig. 2)**. On the basis of NMR spectrum, this compound has confirmed the structure of 5-(4-bromo-2-hydroxybenzylidene)thiazolidine-2,4-dione (**3**).



1 **3**

Scheme-3

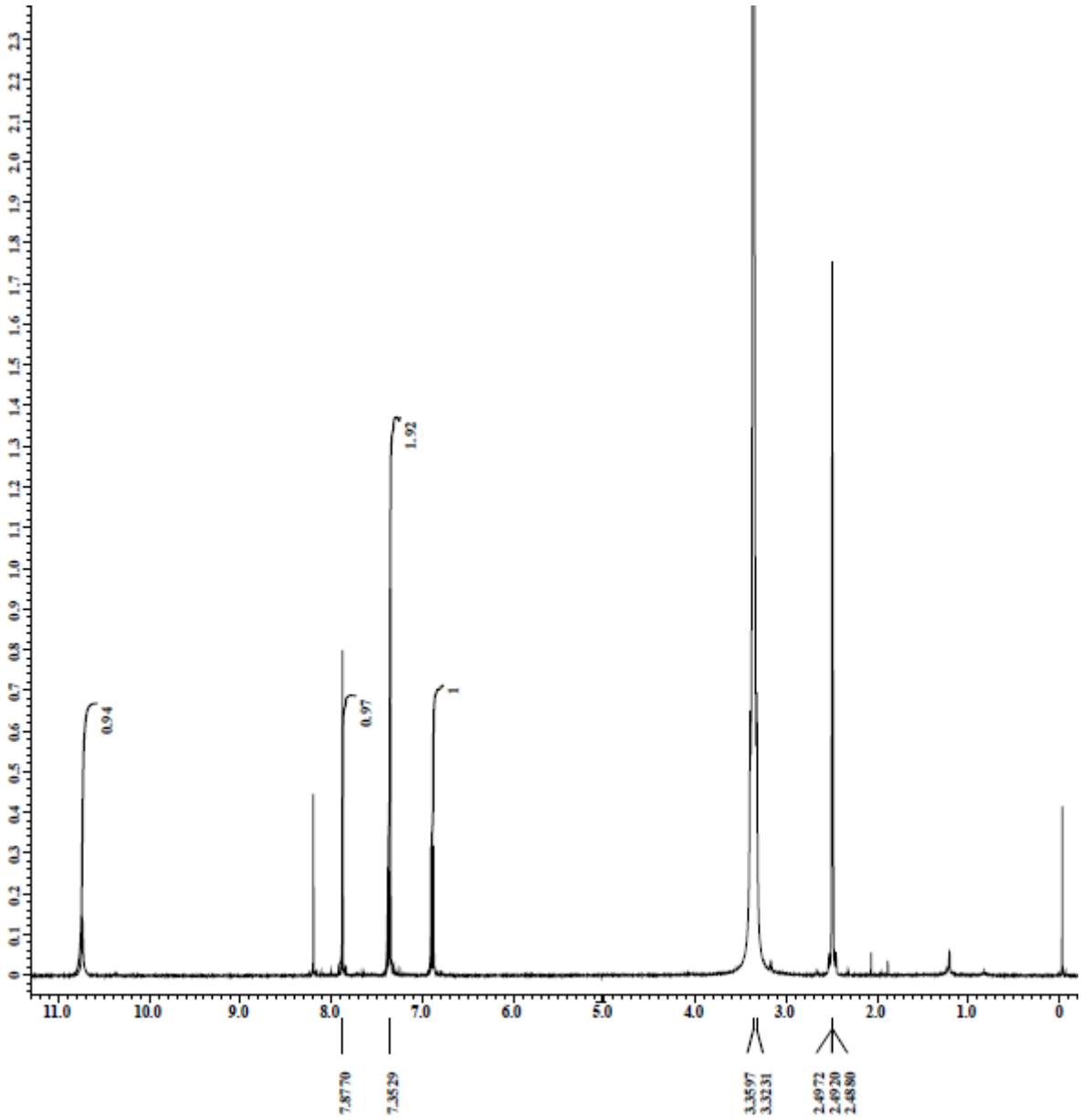
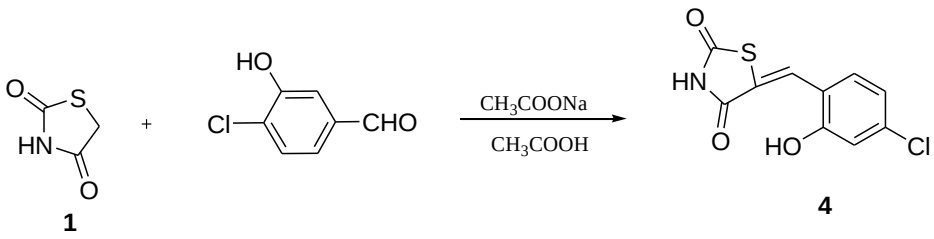


Figure 2: ^{1}H NMR spectrum of 5-(4-bromo-2-hydroxybenzylidene)thiazolidine-2,4-dione (3).

Similar to the above procedure, mixture of compound **1** (0.004 mol) and 4-chioro-2-hydroxy benzaldehyde (0.0047 mol) was heated in the presence of sodium acetate (0.0064 mol) and acetic acid (1-2 ml) for 18 hrs. The solid formed in the reaction directly scratched to get pure product (**4**). ^{1}H NMR of this compound showed 1H singlet at δ 7.57 of CH, 1H singlet at δ 7.35 1H singlet at 7.13 and 1H doublet at δ 6.86 of aromatic-H (**Fig. 3**). On the basis of NMR spectrum, this compound has confirmed the structure of 5-(4-chloro-2-hydroxybenzylidene)thiazolidine-2,4-dione (**4**).



Scheme-4

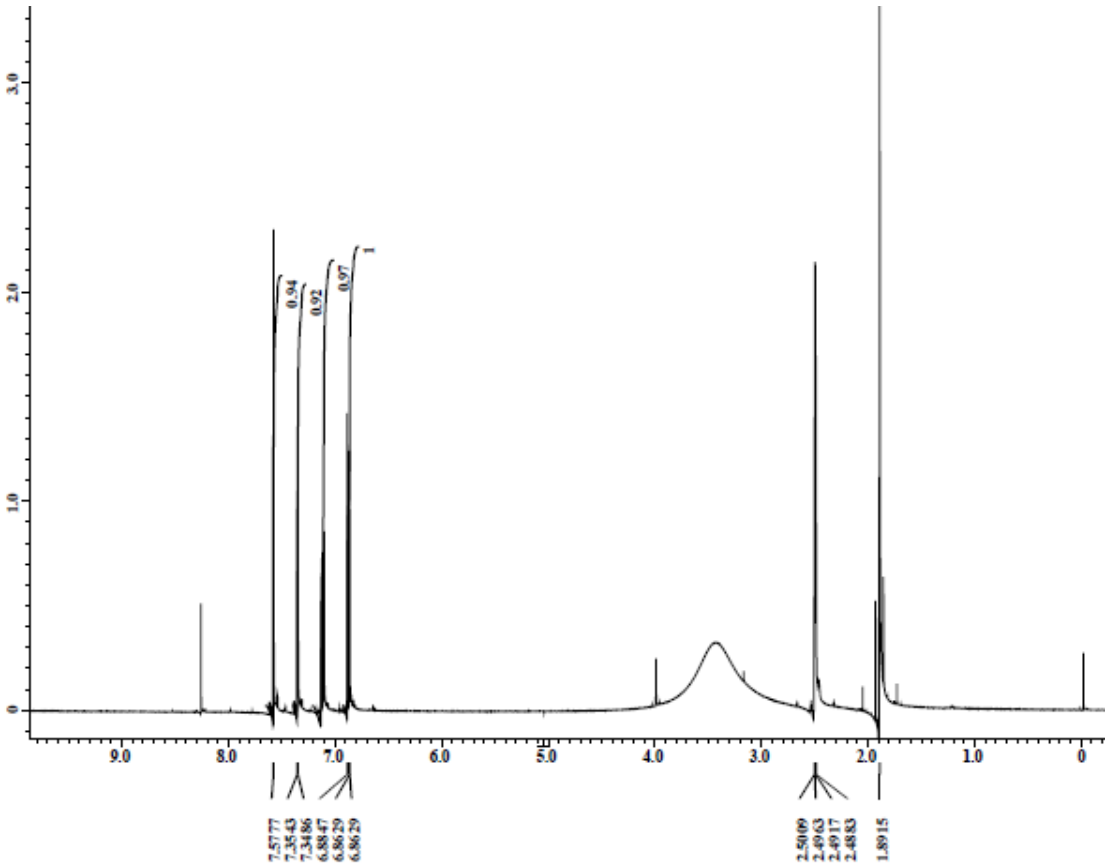
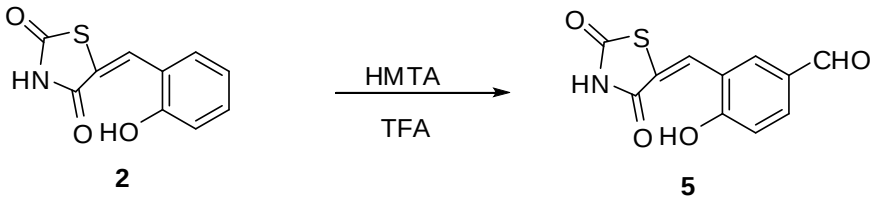


Figure 3: ^{1}H NMR spectrum of 5-(4-chloro-2-hydroxybenzylidene)thiazolidine-2,4-dione (4)

Similarly, compound **2** (0.001 mol) was treated with hexamethylenetetramine (HMTA) in the presence of trifluoroacetic acid (0.5 ml) in toluene : acetic acid (1:1) and refluxed for 24 hrs. The reaction mixture was cooled to room temperature and neutralized with saturated solution of Na_2CO_3 and mixture was extracted with three times with $CHCl_3$ and organic layer was dried over sodium sulphate, filtered and concentrated to get pure compound **5**. ^{1}H NMR of this compound showed 1H broad singlet at δ 11.65 of NH, 1H singlet at δ 7.87 of aldehyde (CHO), 1H singlet at δ 7.90 of CH, 1H singlet at δ 6.85, 1H doublet at δ 7.18 and 1H doublet at δ 6.75 of aromatic-H (**Fig. 4**). On the basis of NMR spectrum, this compound has

confirmed the structure of 3-((2,4-dioxothiazolidin-5-ylidne)methyl)-4-hydroxybenzaldehyde (**5**).



2 **5**

Scheme-5

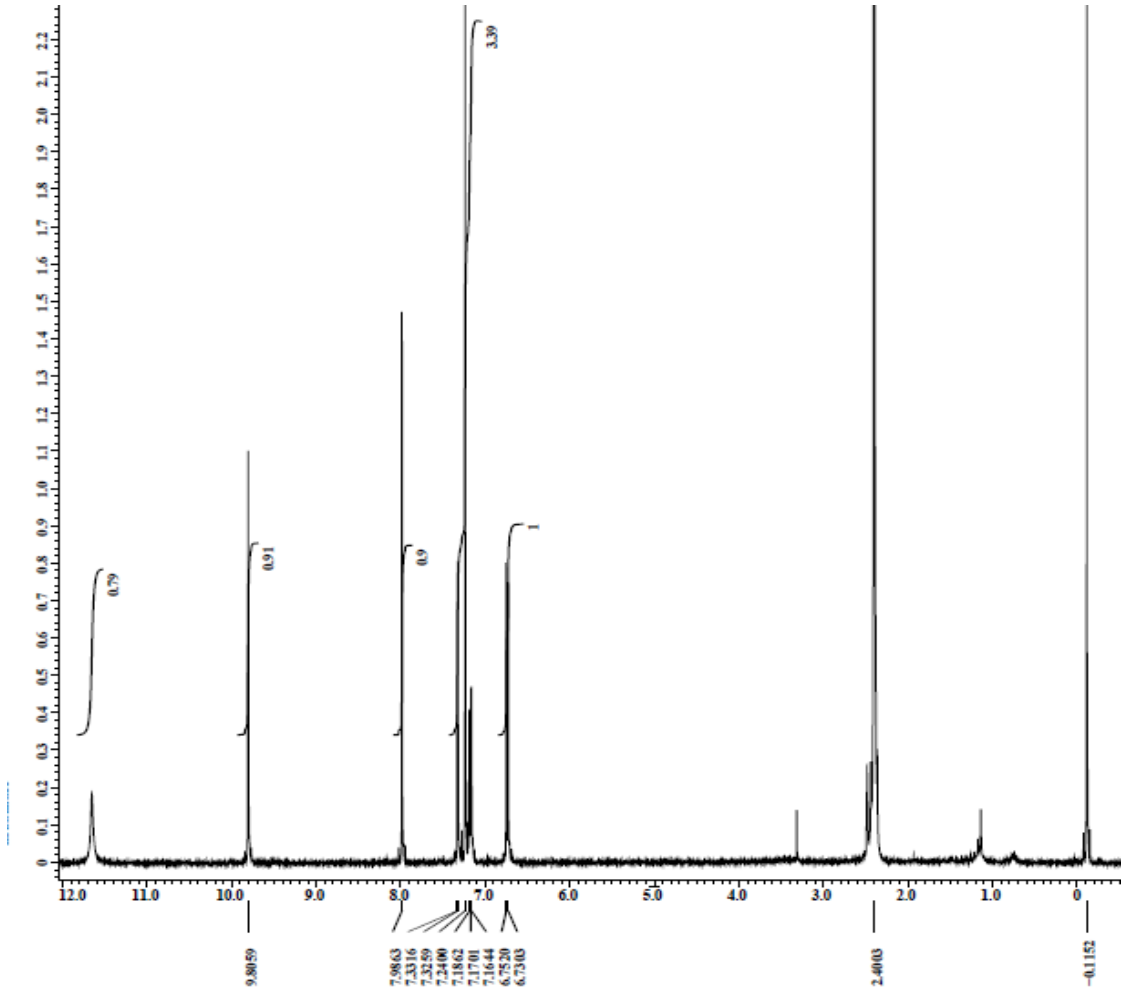


Figure 4: ^{1}H NMR spectrum of 3-((2,4-dioxothiazolidin-5-ylidne)methyl)-4-hydroxybenzaldehyde (5).

Photophysical Studies

The compound **2** (20 µM, CH_3CN) shows an absorption spectrum having λ_{max} at 350 nm (ϵ = 15000 mol^{-1} Cm^{-1} on addition of different metal ions, viz Na^{+}, Li^{+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, Fe^{2+}, etc. to solution of **2**, there is no significant change in its UV visible spectrum except in case of addition of Cu^{2+} ions. The addition of Cu^{2+} caused appearance of new absorption band at 310 nm appeared **Figure 5**.

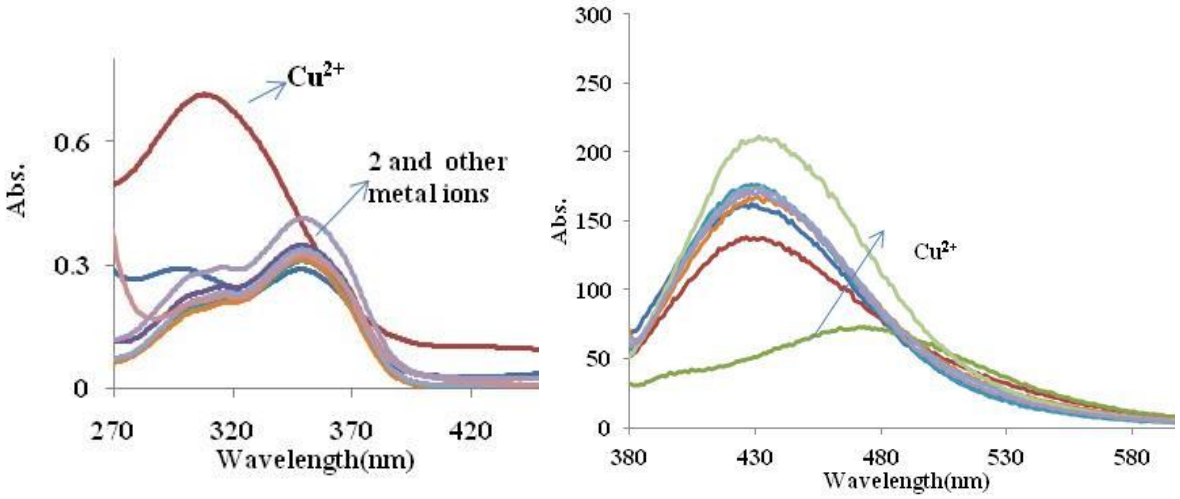


Figure 5: Effect of metal ions on (a) absorption spectra (b) emission spectra of compound 2 (20 µM, CH_3CN).

Upon excitation of compound **2** (20 µM, CH_3CN) at λ_{max} = 350 nm showed emission at 420 nm. On addition of different metal ions like Na^{+}, Li^{+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, Fe^{2+}, etc. to solution of **2** caused no significant changes except addition of Cu^{2+} ions. The addition of Cu^{2+} ions caused emission quenching at 420 nm.

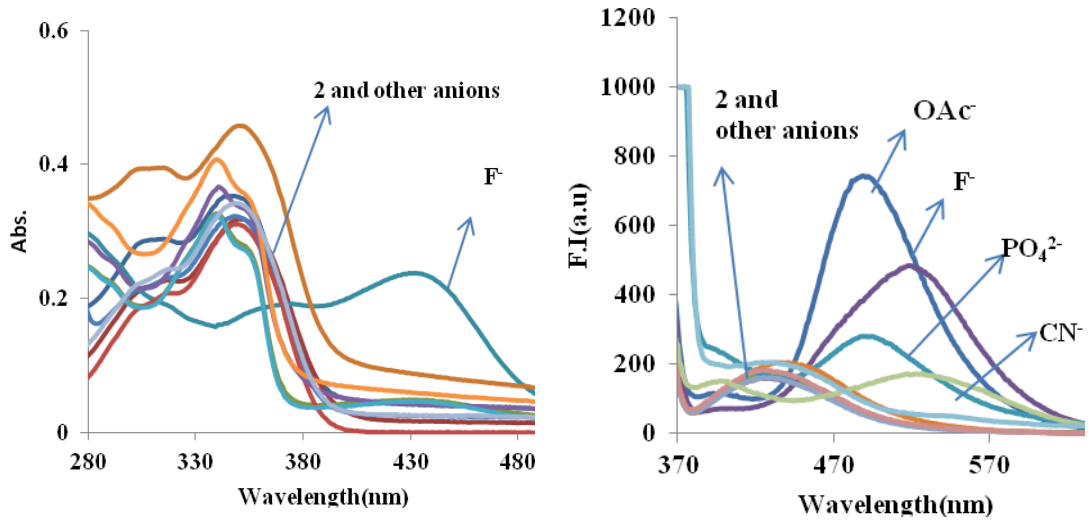


Figure 6: Effect of anions on (a) absorption spectra (b) emission spectra of compound 2 (20 µM, CH_3CN).

Upon changing the solvent from acetonitrile to acetonitrile –water (1:1) and addition of different anions, viz F^-, Cl^-, Br^-, I^-, NO_3^{2-}, SO_4^{2-}, HSO_4^-, CH_3COO^-, CN^- etc. to compound (20 µM) caused no significant change in its UV visible spectrum except in case of addition of CN^- ions to solution of **2**.

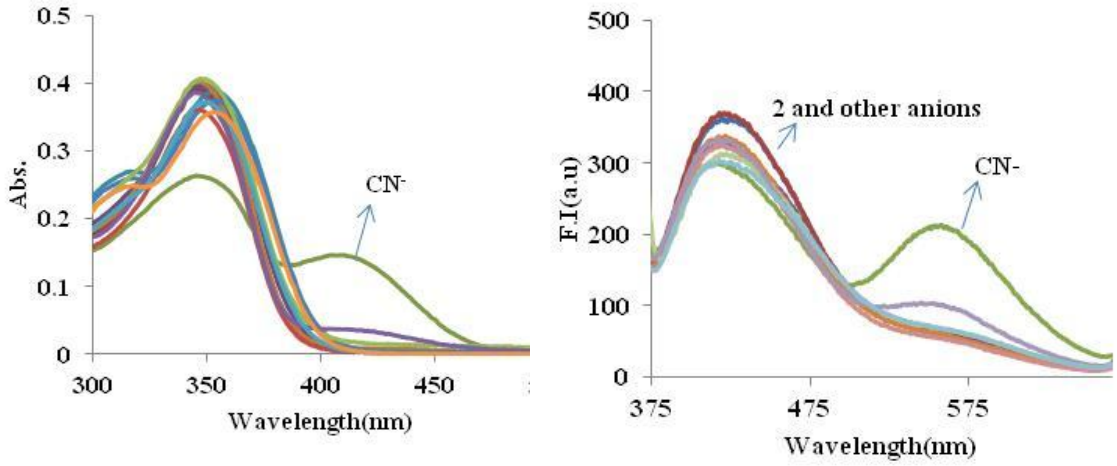
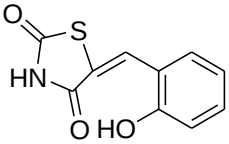


Figure 7: Effect of anions on (a) absorption spectra (b) emission spectra of compound 2 (20 µM, $CH_3CN:H_2O$(1:1).

Similarly in case of emission studies showed that addition of different anions to compound 2 caused selective changes only in the presence of cyanide ions (**Figure 7**). Hence this molecule is selective for cyanide ions in mixed aqueous system.

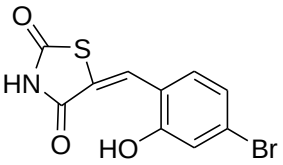
EXPERIMENTAL

Melting points were determined in open capillaries. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-400 MHz, NMR spectrometer using $CDCl_3$ and DMSO-d_6 as solvent. Chemical shifts are given in ppm with TMS as an internal reference. J values are given in Hertz. Signals are abbreviated as Singlet s; doublet, d; doublet-doublet,dd; triplet,t; multiplet,m. Column Chromatography were performed with Silica-120 mesh and reactions were monitored by thin layer chromatography (TLC) with silica plates coated with silica gel HF-254. All the chemicals viz. salicaldehyde, 4-bromo-2-hydroxy benzaldehyde, 4-chloro-2-hydroxy benzaldehyde, were purchased from Aldrich and spectrochem and were used without further purification.



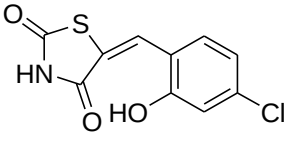
2

A mixture of compound **1** (0.117 g, 0.001 mol) and salicaldehyde (0.112 g, 0.001 mol) was heated at 100˚C in the presence of 1 ml glacial acetic acid and sodium acetate (0.001 mol) for 10 hrs. The product thus formed was treated with HCl to acidic pH and then stirred for half an hour and solid thus formed was filtered to get compound **2**. Yield: 80%; M.pt. = 235-237 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.12 (bs, 1H, NH), 7.81 (s, 1H, CH), 7.33 (d, 1H, J = 8.01 Hz), 7.25 (t, 1H, J = 7.08 Hz, ArH), 6.97-6.90 (m, 2H, ArH).



3

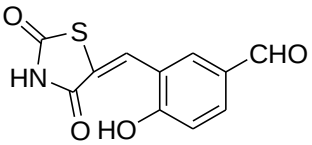
A mixture of compound **1** (0.5 g, 0.004 mol) and 4-bromo -2-hydroxy benzaldehyde (0.9449 g, 0.0047 mol) was heated at 100 ^{o}C in the presence of sodium acetate (0.525 g, 0.0064 mol) and acetic acid (1-2 ml) for18 hrs. The product thus formed was purified by column chromatography using hexane : ethyl acetate as eluants to get pure compound **3**. Yield: 62%; M.pt. 245-250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.73 (bs, 1H, NH), 7.87 (s, 1H, CH), 7.35 (s, 2H, ArH), 6.85(d, 1H, J = 8.24 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.8, 167.6, 167.3, 156.4, 131.8, 130.2, 127.8, 126.2, 123.2, 122.3, 119.3.



4

A mixture of compound **1** (0.5 g, 0.004 mol) and 4-chioro-2-hydroxy benzaldehyde (0.736 g, 0.0047 mol) was heated in the presence of sodium acetate (0.525 g, 0.0064 mol) and acetic acid (1-2 ml) for 18 hrs. The solid formed in the reaction directly scratched to get pure product. Yield: 56%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.57 (s, 1H,

CH), 7.35 (d, 1H, *J* = 2.28 Hz, ArH), 7.13 (d, 1H, *J* = 8.28 Hz, ArH), 6.86 (d, 1H, *J* = 8.72 Hz, ArH); ^{13}C NMR (100MHz, DMSO-d_6): δ 176.2, 174.2, 173.6, 155.9, 129.9, 129.0, 127.1, 123.2, 123.1, 117.3.



5

A mixture of compound **2** (0.222 g, 0.001 mol) was reacted with hexamethylenetetraamine in the presence of trifluoroacetic acid (0.5 ml) and toluene : acetic acid (1:1) and refluxed for 24 hrs. The reaction mixture was cooled to room temperature and neutralized with satd. solution of Na_2CO_3 and mixture was extracted three time with $CHCl_3$ and organic layer was dried over sodium sulphate, filtered and concentrated to get pure compound **5.** Yield: 35%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.65 (bs, 1H, NH), 9.80 (s, 1H, CHO), 7.90 (s, 1H, CH), 7.33 (s, 1H, ArH), 7.18 (d, 1H, = 2.28 Hz, ArH), 6.75 (d, 1H, *J* = 8.80 Hz, ArH).

General procedure for UV-Vis and Fluorescence Spectroscopy

The solvents used were of analytical grade. UV-Visible spectrum of various compounds were recorded at Analytical Jena SPECORD 205 UV-Visible spectrophotometer having slit widths of 1.0 cm. Absorption scans were saved having name as ACS 1 File and further processed in Excel so that graphs can be shown. Acetonitrile was used for preparing stock solution of chemosensor **2**. For preparing the desired solution; aliquot was transferred to measuring flask and solution was made in doubly distilled ACS.

CONCLUSIONS

1. Thoazolidin-2,4-dione and its derivatives have been synthesized in moderate to good yields.
2. Duff reaction was successfully performed regioselectively at the para position.
3. Compound **2** acts as selective chemosensor for Cu^{2+} ions amongst metal ions.
4. Compound **2** behaved as selective cyanide sensor in mixed aqueous system amongst another anions of biological importance

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