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Unveiling the Synthesis and Photophysical Properties of 2,2'-[Iminobis(2,1-ethanediyliminomethylene)]diphenol and Its Zinc Complexes†

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Abstract: Background: In recent years, in situ reaction monitoring has grown in use for this purpose. ReactIR is one of the in-situ reaction monitoring techniques used to understand chemical reactions. The reductive amination of Schiff base formed in situ by treating salicylaldehyde and diethylene triamine by using sodium borohydride in methanol was completed within 28 minutes, which was monitored by ReactIR. Materials and Methods: Zinc complexes of diethylene triamine, Schiff base, and their reductive amination products were synthesized using 1:1, 1:2, and 1:3 mole ratios of ligand-zinc chloride at room temperature. Results and conclusion: The formation of the product was confirmed by IR spectra. All these complexes showed photoluminescence in the blue region.

Keywords: Photoluminescence; Schiff bases; Sodium borohydride; Reductive amination; Salicylaldehyde

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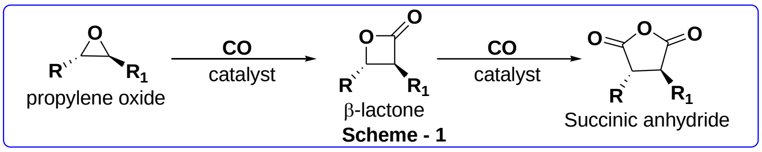
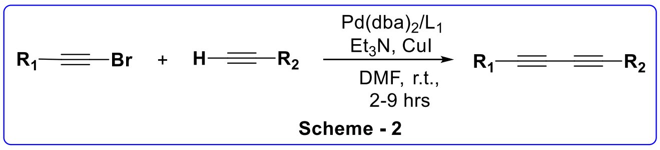
1. Introduction

In modern science, the chemist does not use the traditional synthesis protocols for the design and synthesis of the desired product. Cost-effective and quick synthesis of the molecules with minimum impurities was the biggest challenge for them. When the actual reaction takes place, energy and temperature change and intermediate formed or not without changing the reaction conditions or in a given short period were very difficult with traditional methods. In some of the chemical reactions, after completion of the reaction, the impurity profile or in some cases the desired product undergoes degradation and forms new unexpected products. Therefore, various new methodologies and techniques were developed to detect and analyze chemical reactions such as HPLC. It gives quantitative information regarding the reaction components at any time, but the only condition is that the reaction is sampled and then analyzed. The chemist should wait for sample analysis which was time-consuming and therefore, during the waiting period, there may be certain changes in reaction composition.

In recent years, *in situ* reaction monitoring has grown in use for this purpose. ReactIR is one of the in situ reaction monitoring technique used to understand chemical reactions. It's taken spectra of all chemical species present in the reaction mixture and translated it into a quantitative manner so chemists, easily predict participation of catalyst or solvent in reaction, changes in concentration of reactants, new peaks for intermediate and products, etc. This helps to predict the mechanism, pathway and kinetic determination. It is also used to predict exact stoichiometry of reactants and catalyst (if used), reaction time, the external addition rate of reactant or catalyst, thermal and energetic predictions, etc. of the reaction which help to design a cost-effective reaction. The numbers of reactions are monitored and determined their reaction steps, mechanism, kinetics and thermal study by using ReactIR techniques, catalytic double carbonylation of epoxides to Succinic anhydride (Scheme 1) [1], palladium-catalyzed cross-coupling reaction of haloalkyne and terminal alkynes using phosphine-olefin ligand (Scheme 2) [2], etc.



Scheme 1. ReactIR techniques, catalytic double carbonylation of epoxides to Succinic anhydride.



Scheme 2. : palladium-catalyzed cross-coupling reaction of haloalkyne and terminal alkynes using phosphine-olefin ligand.

Two methods are most commonly used for direct reductive amination which are differing from a reducing agent. The first method is catalytic hydrogenation with metals such as platinum, palladium, nickel, etc., the catalyst [3,4] used for the reduction is economical and the reductive amination method is effective, particularly in large scale reactions. But such reactions may give a mixture of products and low yields depending on the molar ratio and the structure of the reactant [5]. The second method utilizes hydride reducing agents, particularly sodium borohydride or its derivatives such as sodium cyanoborohydride ($NaBH_3CN$) and triacetoxyborohydride for reduction [6,7]. The sodium cyanoborohydride is successfully used because of its stability in relatively strong acidic conditions (~ pH = 3) and higher stability in hydroxylic solvents such as methanol. It has different selectivities at different pH scales [8]. At pH = 3-4, it reduces ketones, but this become slow at higher pH. At pH 6-8, the more basic imines are protonated preferentially and reduce faster than aldehydes and ketones [8]. The other hydride reducing reagents reported for the reductive amination are - boron-pyridine (BH_3-Py) [9a], $Ti(OiPr)_4/NaBH_3CN$ [9b], borohydride exchange resin [9a], Zn/AcOH [9b], $NaBH_4$/Mg(ClO4)2 [9c], $Zn(BH_4)_2/ZnCl_2$ [9d], etc. Some reports of electrochemical reductive amination have been also reported [10].

In most of the metal complexes or metal-doped organic compounds, metal ions with d^0 to d^{10} configurations were acting as sensitizers for the organic phosphor. The electrons present in the incomplete filled d-orbitals of metal ions were significantly integrated with the π and π^* orbitals of the organic ligand in the complexes. The singlet and triplet states of the organic ligands were very short-lived and therefore the quantum yields of triplet state formation are very low. Zinc complexes are important as light-emitting materials [11-14] as well as having tunable electronic properties [15,16], ternary complexes as electronic transport and electroluminescent materials [17].

2. Results and Discussion

2.1. Reaction Monitoring Study

The conversion of reductive amination product from diethylene triamine (2) is a ‘two steps reaction’ however the researcher wished to reduce this in single synthetic step or continuous steps without isolation of product to save time. This conversion was carried out in methanol in presence of a catalytic amount of acetic acid at room temperature. The

ATR probe of the instrument was inserted into the reaction mixture which monitored the reaction without analyzing the sample separately.

After the addition of salicylaldehyde (1) into diethylene triamine (2); initially rate of reaction was very high; most of the aldehyde (1) and amine (2) is converted into Schiff base intermediate (3) which was confirmed by monitoring reaction at a wavenumber of the amine (2) at 1233, salicylaldehyde at 828, intermediate (3) at 1024 as shown in Figure 1 and Fig. 2. The reaction is completed within 18 minutes and then add a reducing agent. After the addition of $NaBH_4$; the initial rate of reduction is very slow but it increases sharply after 4-5 minutes and almost intermediate (3) get reduced within 10 minutes after the addition of borohydride. The formation and reduction of the intermediate (3) were also confirmed from the real-time monitoring of 3-dimensional MIR spectral data collected with an *in-situ* ATR probe at periodic intervals throughout the reaction. The absorption intensity at 1024 cm^{-1} was begin to visible initially after the addition of salicylaldehyde and it start to get disappear once reduction stats after the addition of borohydride.

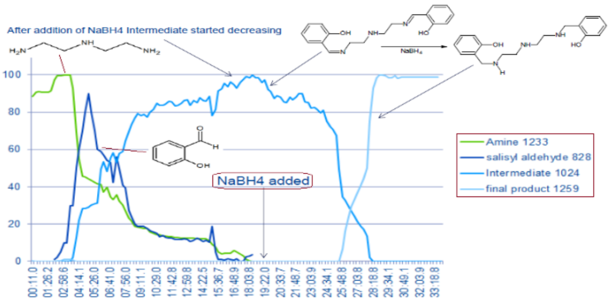


Figure 1. Monitoring reaction by using ReactIR.

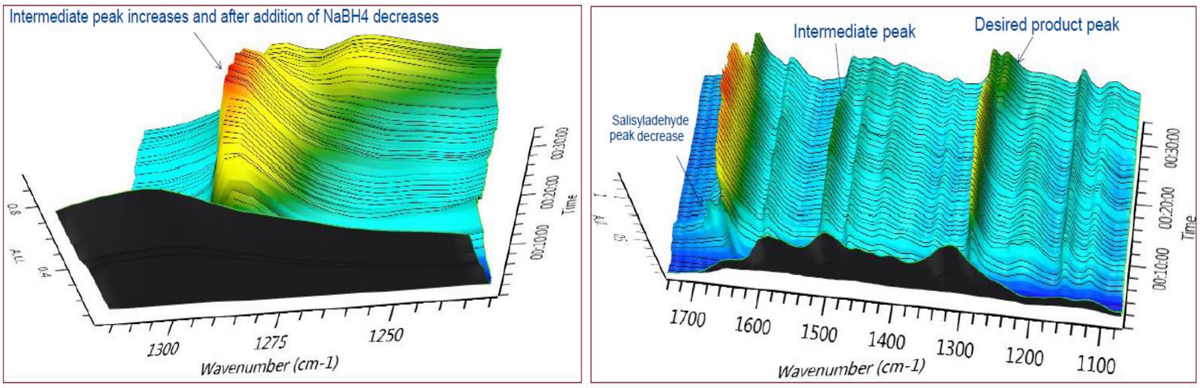


Figure 2. Images of recording of new IR peaks during monitoring the reaction.

2.1.1. Thermal study:

This study suggested that the formation of Schiff base (3) is an exothermic reaction, initially the temperature of the reaction increases sharply after the addition of salicylaldehyde (1) to nearly 45⁰C with a sharp decrease in the concentration of diethylenetriamine (2) and increase the amount of Schiff base (3). The maximum content of the diethylenetriamine (2) reacted with 3 to 4 minutes and the reaction get nearly complete within 18 minutes. After completion of the reaction, *in-situ* reduction of imine bond by using sodium borohydride at slightly acidic pH (6 to 6.5; by adding acetic acid). After the addition of $NaBH_4$; the temperature of the reaction mixture increases by 4-5⁰C with the initiation of the reaction. It was confirmed by the monitoring signal intensity at a different wavenumber of the amine at 1233, aldehyde (1) at 828, intermediate (3) at 1024 and final reductive animation product (4) at 1259 cm^{-1}.

2.2. Synthesis of 2,2'-[iminobis(2,1-ethanediyliminomethylene)]diphenol (4):

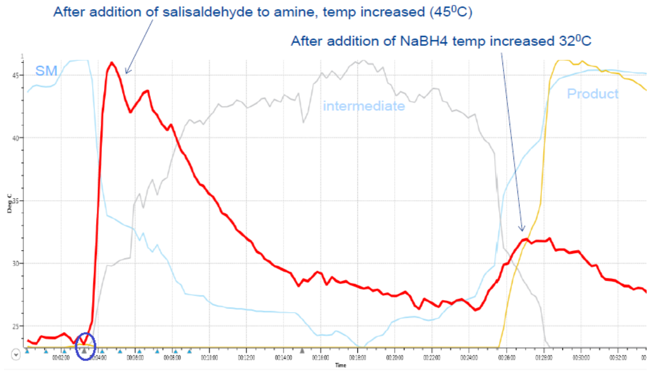
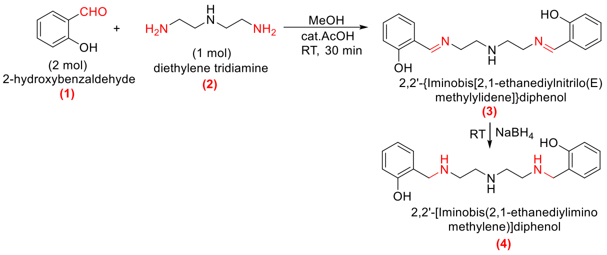


Figure 3. Thermal changes during the progress of the reaction.



Scheme 3. : Reaction scheme employed for the current study.

Dissolve 0.5 moles of salicylaldehyde (1) in 50 ml methanol, add 0.25 mole of diethylenetriamine (2) slowly with constant stirring so that solution turns to yellowish-brown with temperature rise (Figure 3, Scheme 3). Add the catalytic amount of acetic acid and stir the solution at room temperature for 20 minutes so that it becomes yellow. Confirm the formation of the Schiff base (3) by monitoring TLC. Add cold distilled water slowly into the reaction mixture so that it turns to become turbid and orange-yellow colour viscous liquid start to separate. Continue the stirring, add 0.30 mole of anhydrous sodium borohydride in a batch-wise manner. After complete addition, stir the reaction mixture for 15 minutes and pour into ice-cold saturated sodium bicarbonate solution, stir and filter the 2,2′-[iminobis(2,1-ethanediyliminomethylene)]diphenol (4) and recrystallized from aqueous alcohol Figure 4.

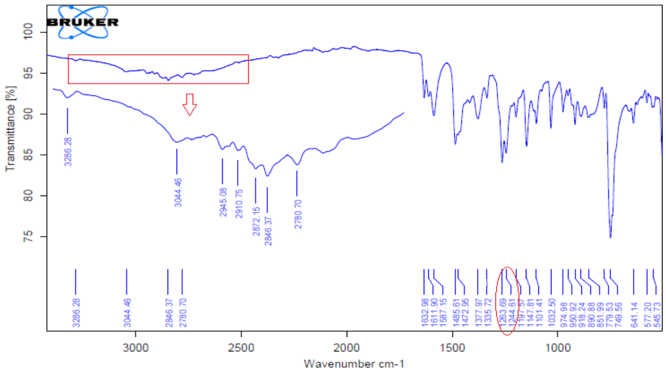


Figure 4. FT-IR Spectra of 2,2′-[iminobis(2,1-ethanediyliminomethylene)]diphenol (4).

Colour – Faint Yellow solid; Yield – 91%; M.P. 122 – 124⁰C.

FT-IR (cm^{-1}): 3286, 3044, 2846, 2780, 1632, 1611, 1587, 1485, 1472, 1377, 1335, 1263, 1244, 1197, 1147, 1101, 1032, 974, 950, 779, 749.

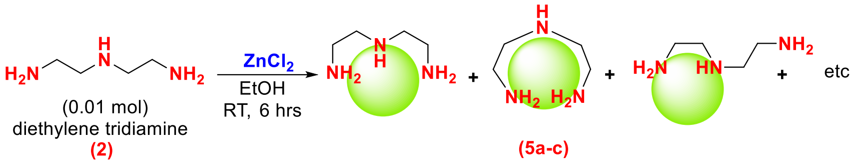
NMR ($CDCl_3$, 61 MHz): 8.41 (bs, 2H, 2OH); 7.69 – 6.52 (m, 8H, Ar-H); 4.18 – 2.51 (m, 12H, -CH_2-N).

CMR ($CDCl_3$, 60 MHz): 50.11, 77.06, 116.24, 117.70, 118.68, 119.36, 131, 132.42.

Broad stretching vibrations of polar –NH and –OH show a broad peak in the range 3300 – 3000 cm^{-1}. The aromatic and aliphatic –C-H stretching vibrations are in the range 2950 – 2780 cm^{-1}. The new peak of amine was observed at 1463 and 1244 cm^{-1} confirm the reduction of the imine bond.

2.3. Synthesis of Metal complexes (5a-c) of diethylene triamine (2):

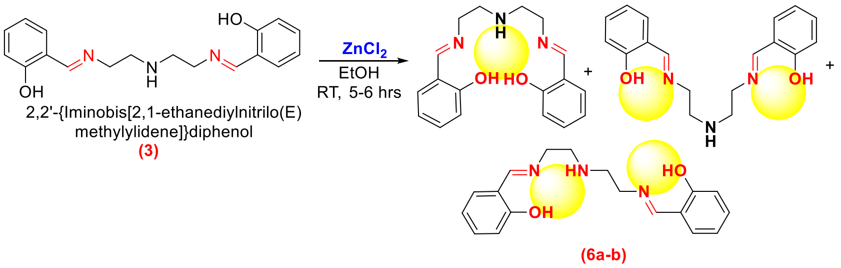
Dissolve 0.01 mole of diethylenetriamine (2) in absolute alcohol, add stoichiometrical amount (0.01, 0.02 and 0.03 mole) of zinc (II) chloride with stirring. Stir the reaction mixture for 5-6 hours at room temperature. Filter the solid Zn-complex (5a-c) Scheme 4 and wash with cold absolute alcohol. The complex of 1:3 stoichiometric ratio was not separated as stable solid or it absorb moisture and get liquefy because of formation of hydrochloride or may be due to the presence of excess unreacted zinc chloride. Add the gel or viscous solid into saturated $NaHCO_3$ and stir for a few minutes, the solid get free and filter. Wash the solid with cold ethanol.



Scheme 4. : Synthesis of Metal complexes (5a-c) of diethylene triamine (2).

2.4. Synthesis of Zn-complex (6a-b) of Schiff base (3):

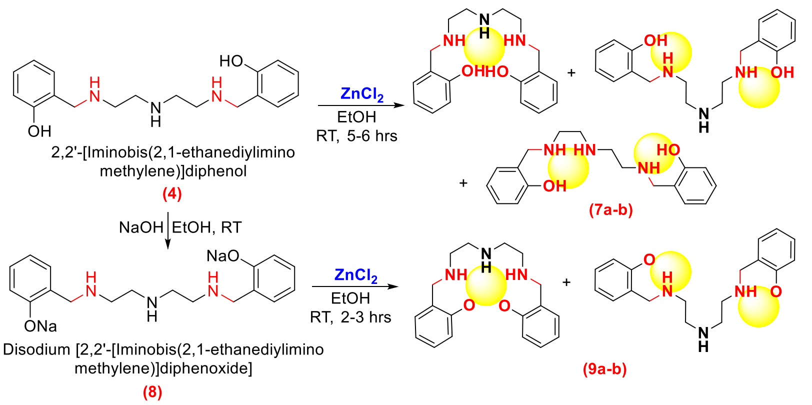
Dissolve 0.5 moles of salicylaldehyde (1) in 50 ml ethanol, add 0.25 mmole of diethylenetriamine (2) slowly with constant stirring so that solution turns to yellowish brown with a rise in temperature. Add the catalytic amount of acetic acid and continue the stirring at room temperature for 20 minutes so that it becomes yellow. Add 0.25/0.50 mmole of zinc (II) chloride with stirring in a single lot. Initially, the color of the solution becomes dark and after some time solid/gel (6a-b) get separated. The gel/viscous solid dissolved in saturated $NaHCO_3$ and stir for a few minutes. Filter the solid complex (6a-b) and wash with cold ethanol Scheme 5.



Scheme 5. : Synthesis of Zn-complex (6a-b) of Schiff base (3).

2.5. The metal complex of Amine and its salt:

Dissolve 0.25 mmol of amine (4) and 0.25/0.50 mmol of zinc (II) chloride in ethanol and stir for 5-6 hours. Complexes get separated in gel/viscous form. The gel/viscous complex is dissolved in saturated $NaHCO_3$ and stirred for a few minutes. Filter the solid complex (7a-b) and wash with cold ethanol Scheme 6.



Scheme 6. : Synthesis of Zn-complex (6a-b) of Schiff base (3).

The complexes of sodium salt were synthesized by repeating the same protocol in presence of 0.50 mmol of sodium hydroxide. First, prepare sodium salt of amine (8) and then add stoichiometric amount zinc chloride, and stir for 3 hours. Filter the complex (7a-b) and wash with water.

The FT-IR spectra were measured by using the Bruker Tensor II model with platinum ATR, while the fluorescence study was done by using Spectrofluorometer model number RF5301. The conductance of all metal complexes was measured by using a digital conductivity meter with a cell constant of 1 cm^{-1}.

The FTIR spectra of all complexes were recorded by using the ATR technique, 5c (1:3 mole ratio), and 7b (1:2 mole ratio; of both cases) showing broad signal nearly at 3500 cm^{-1} indicate the presence of water which was maybe part of complexion or water of crystallization. Other complexes do not contain any water ligand or water of crystallization (SI. tables 1-3).

The ionic character of the Zn-complex was determined by measuring conductance in DMSO. The chlorine ion is the part of a complexion (co-ordination sphere) or associated with complex ion may be predicted from the ionic conductance of the complex. The 9a complex synthesized from Na-salt of (4) with a 1:1 mole ratio of the ligand and $ZnCl_2$ has the least conductance indicate that it was least ionic. All the complexes formed by using 1:1 mole ratio of ligand and $ZnCl_2$ has higher conductance than those synthesized by using a 1:2 mole ratio. The conductance of the 9a complex is less as compared to those synthesized by using amine indicate that $–O^-$ and –OH of the ligands are part of the coordination sphere. The 9a complex does not contain water in the coordination sphere which is confirmed from IR spectra.

2.6. Photophysical properties of Zn(II) complexes:

Photophysical properties of Zn(II) complexes of diethylenetriamine (2), Schiff base (3) and reductively aminated product (4) have been recorded by using Spectrofluorometer model number RF5301. A Xe laser lamp was used for excitation and emission spectra; samples were scanned from the range 220 nm to 800 nm. For fluorescence study of the metal complexes, dimethylformamide is used as solvent and reference material. The absorption of light was due to electronic excitations from bonding (π, n) to non-bonding orbitals (π*).

A. Study Parameters:

Solution concentration: 4 - 5 mg per 10 ml
Emission wavelength (for excitation): 400 nm
Slit width: 3 - 5 nm.
Scan speed: Super
Sensitivity: High

B. Effect of Solvent on fluorescence properties of 6a:

The absorption, excitation and emission of the compounds depended on the substitution pattern, solvent, temperature, pH, etc. The electronic spectra are measured in solvents of different polarities and hydrogen bond donor/acceptor ability, it was found that the position, shape and intensity of the emission spectra were usually affected by solvents. This phenomenon was referred to as solvatochromism [18]. These changes are due to solute-solvent intermolecular forces such as specific electrostatic interactions (hydrogen bonding or electron donor/acceptor interaction) and or non-specific electrostatic interactions [18, 19]. The effect of solvent was studied by measuring excitation and emission spectra of the compound in non-polar, polar aprotic and polar solvents. The excitation maxima, emission maxima and quantum efficiency were shown in the above SI. table.

The excitation and emission spectra of 6a were recorded in different solvents in the wavelength range of 220 – 800 nm SI. tables 4. The excitation spectra were due to electronic transitions from HOMO→LUMO or due to the electronic transitions such as $\pi \rightarrow \pi^*$ (strong) or $n \rightarrow \pi^*$ (weak). For all solvents (except DMF), excitation of the electrons takes place in the same range but emission shows blue shift for both excitation wavelengths except for polar solvents such as ethanol and methanol at 400 nm. The stoke shift was unusually less for 400 nm excitation wavelength indicates that both S_0 and S_1 states do not have intra molecular charge transfer characteristics as like another excitation wavelength (near around 360 nm). The second excitation maxima were blue-shifted for all other solvents as compared to benzene indicate that the molecule was polar and shows specific electrostatic interactions such as H-bonding or dipole-dipole interactions leading to net stabilization of the ground state of the 6a leading to a hypsochromic shift in the spectrum. The excitation second maxima of 6a shows a longer shift in ethanol and methanol because of its higher ability to form H-bonding and solubility; water does not show a marginal longer shift because of less solubility of the 6a (Figures 5, 6). The 6a shows a narrow band shift for the excitation at 400 nm but it was higher for excitation at nearly 360 nm. This observation was indicated that triplet state stabilization was more for the excitation at neatly 360 nm than the 400 nm. The stoke shift was highest in DMF is may be due to charge transfer transitions.

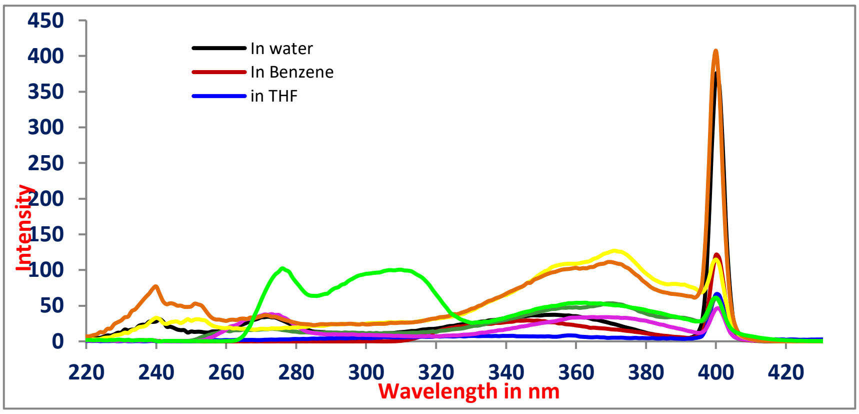


Figure 5. Excitation spectra of 6a.

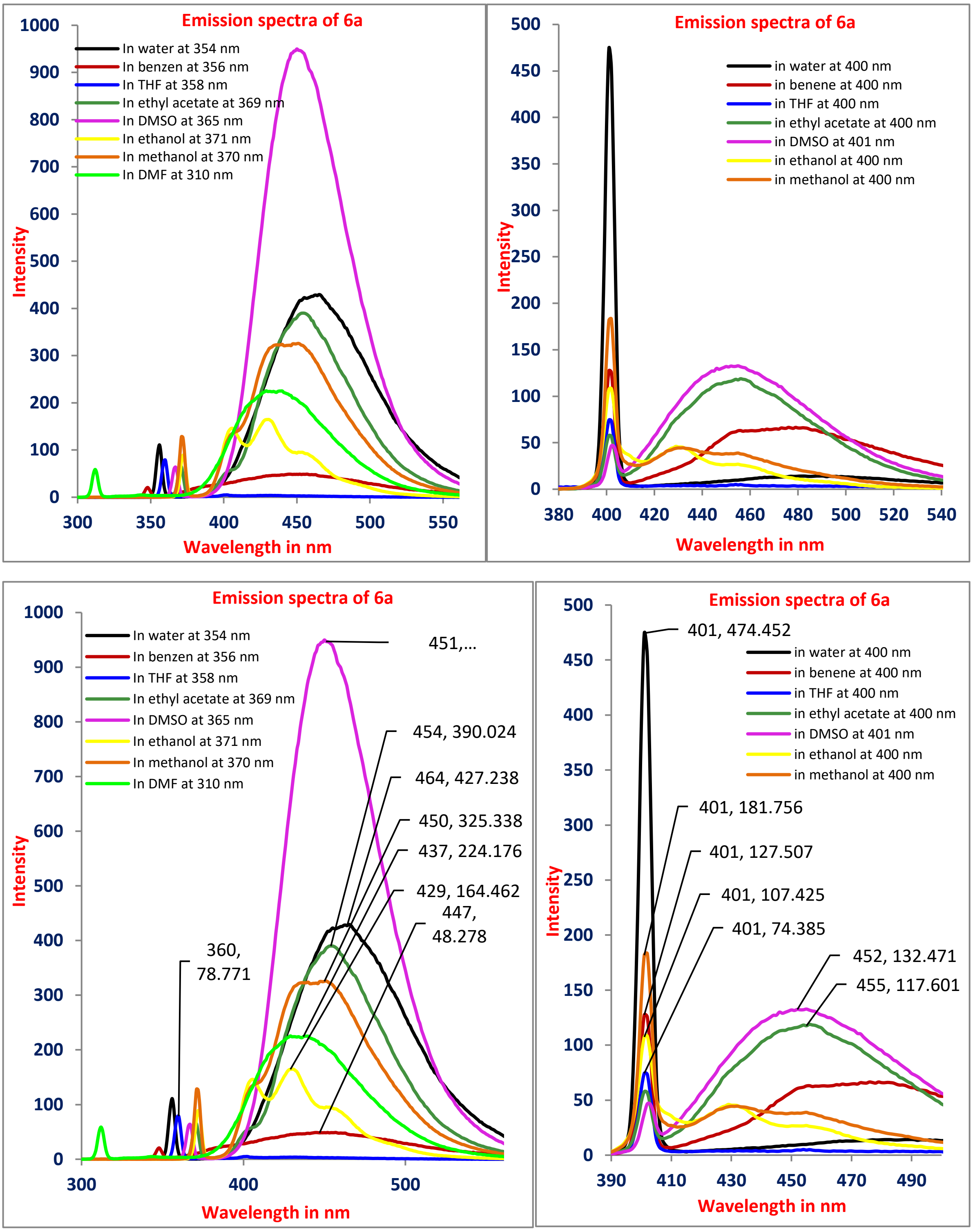


Figure 6. Emission spectra of 6a.

C. Photophysical properties of Zn(II) complexes (5a-c) (SI. table 5, Figure 7, 8)

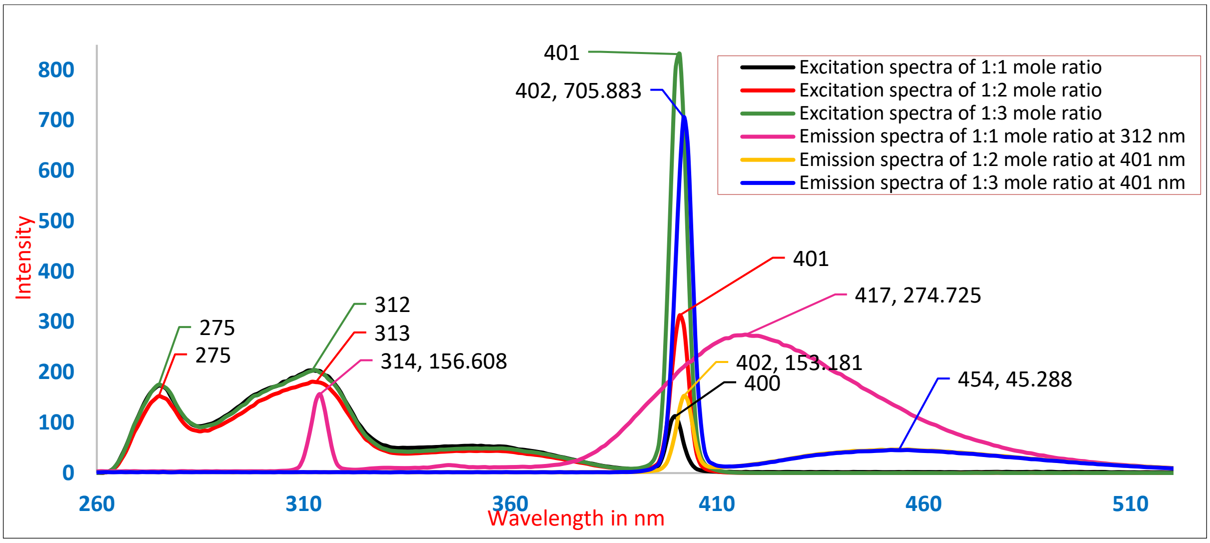


Figure 7. Fluorescence Study of Zn(II)-complex (5a-c).

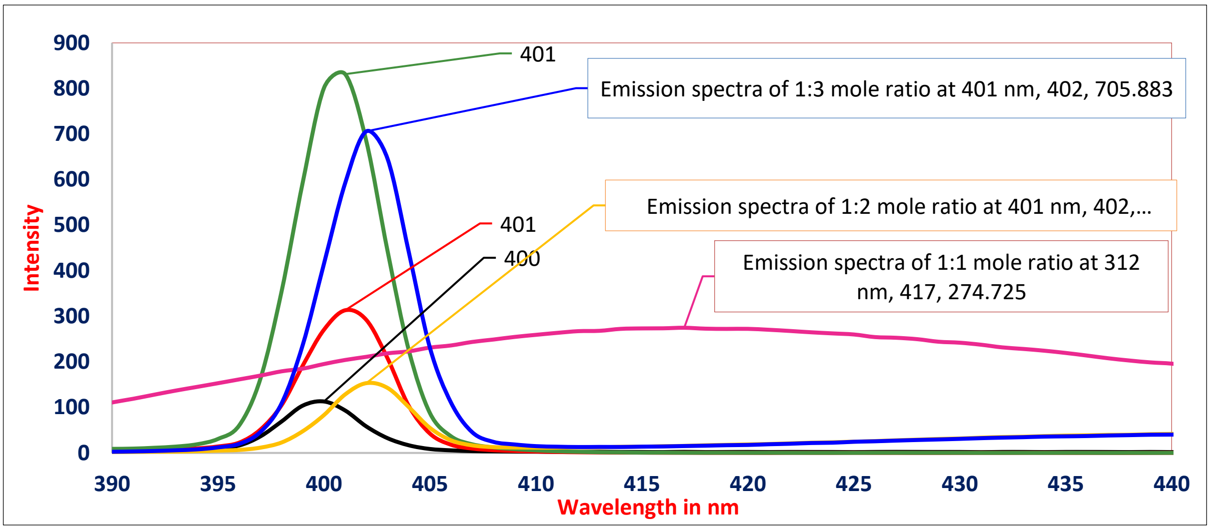


Figure 8. Fluorescence Study of Zn(II)-complex (5a-c).

D. Photophysical properties of Zn(II) complexes (6a-b) (SI. table 6, Figure 9, 10)

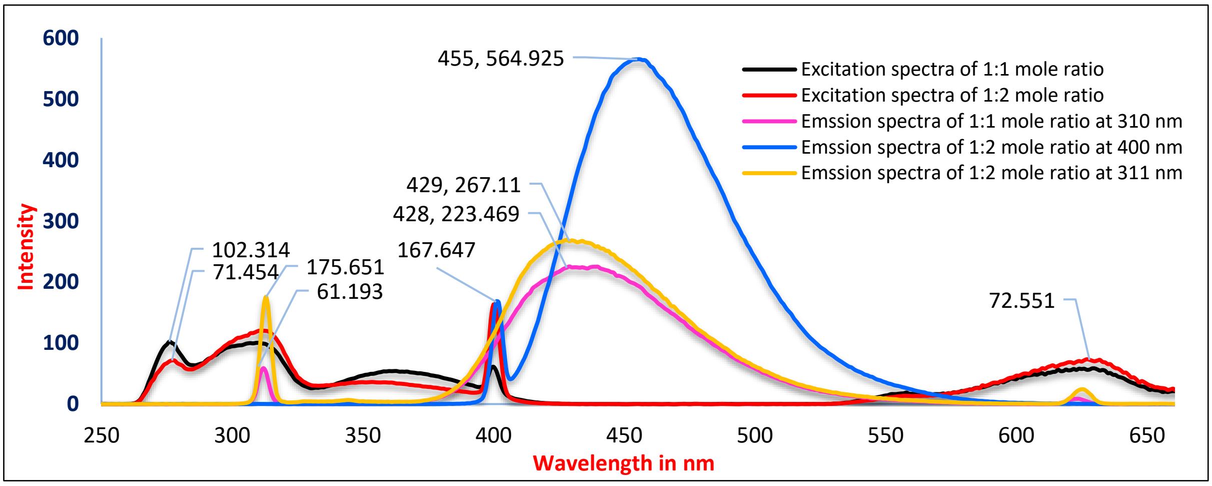


Figure 9. Fluoroscence spectra of Zn(II)-complex (6a-b).

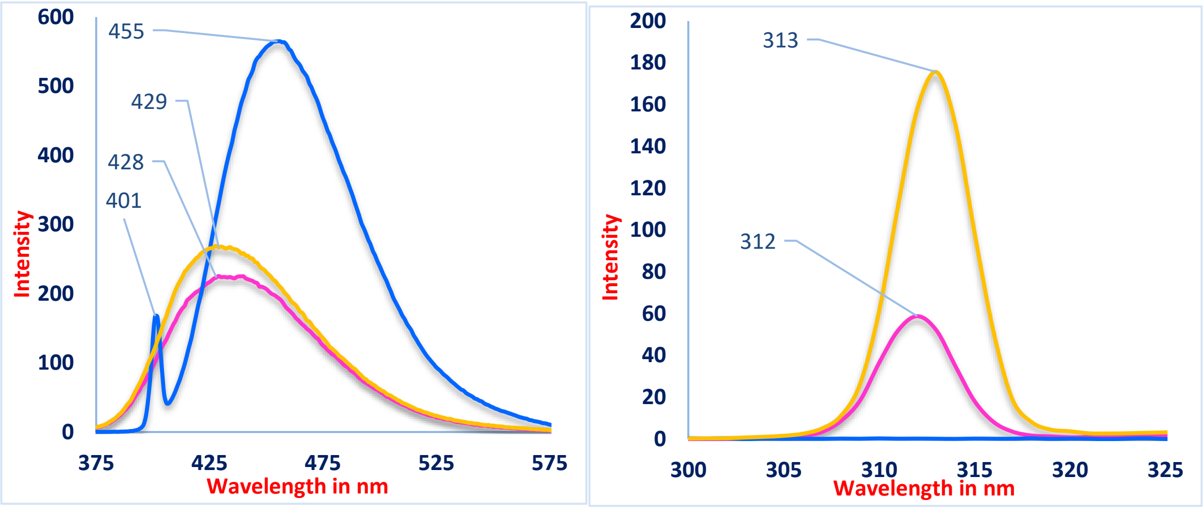


Figure 10. Emission spectra of Zn(II)-complex (6a-b).

E. Photophysical properties of Zn(II)-complexes (7a-b) (SI. table 7, Figure 11, 12):

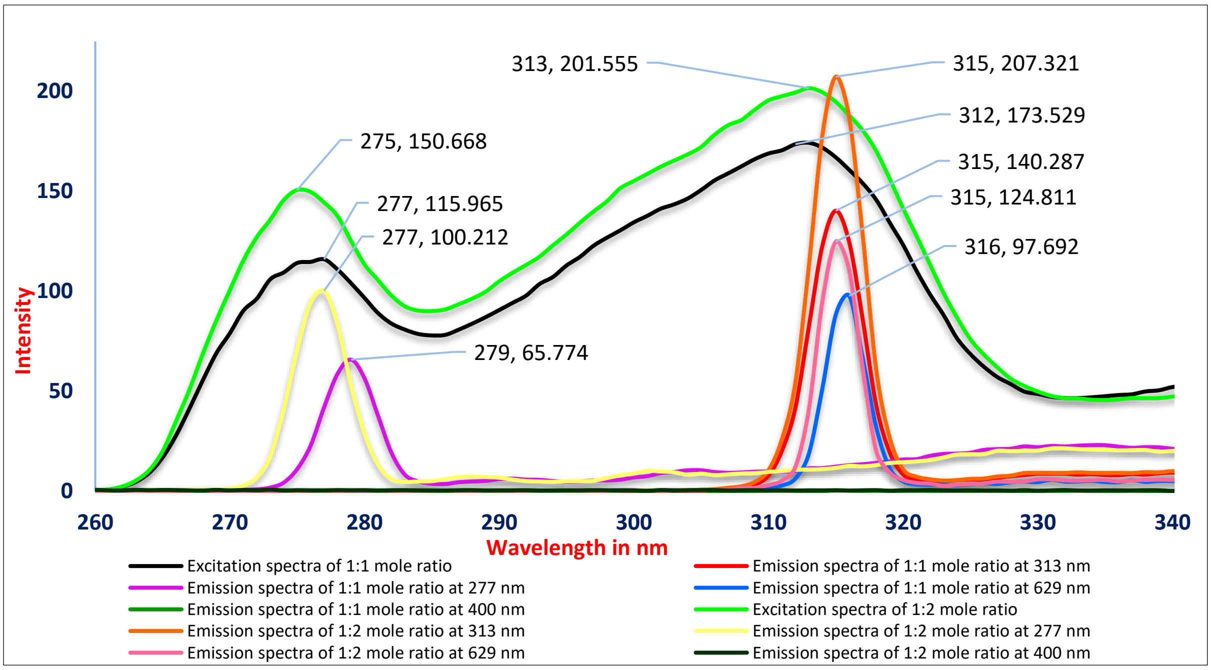


Figure 11. Fluoroscence Spectra of Zn(II) complexes (7a-b).

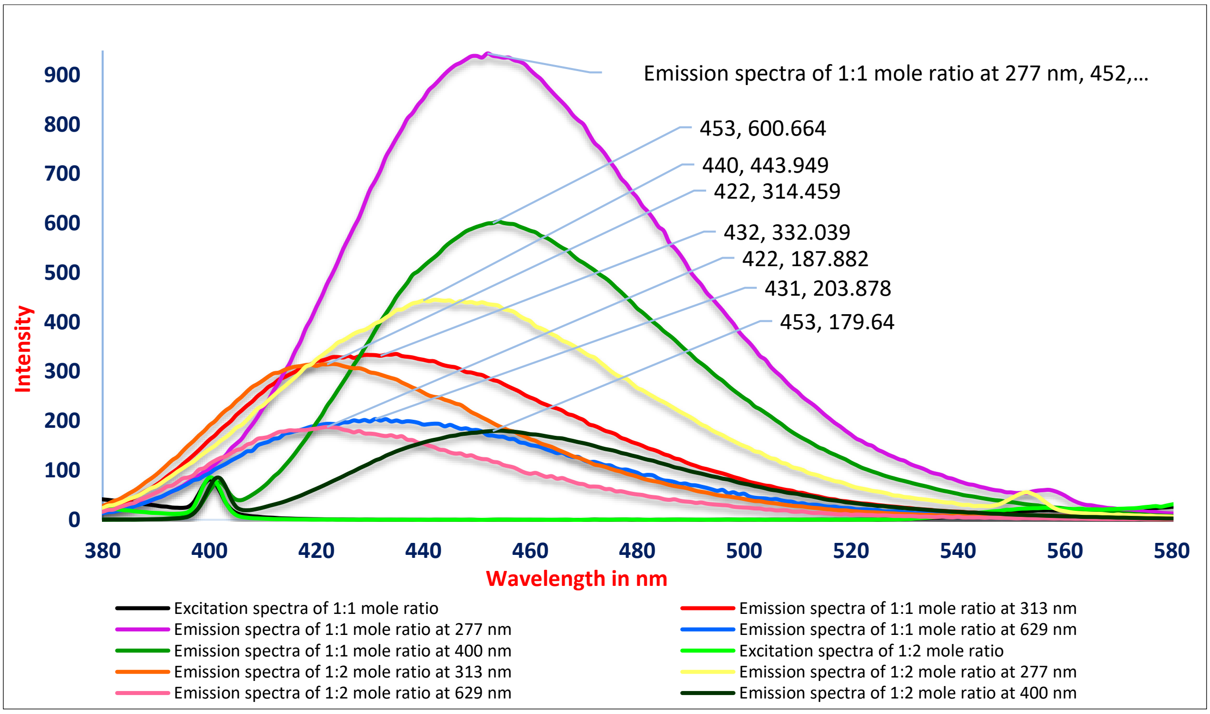


Figure 12. Fluoroscence Spectra of Zn(II)-complexes (7a-b).

F. Photophysical properties of Zn(II)-SATAA complexes: (SI. table 8, Figure 13, 14)

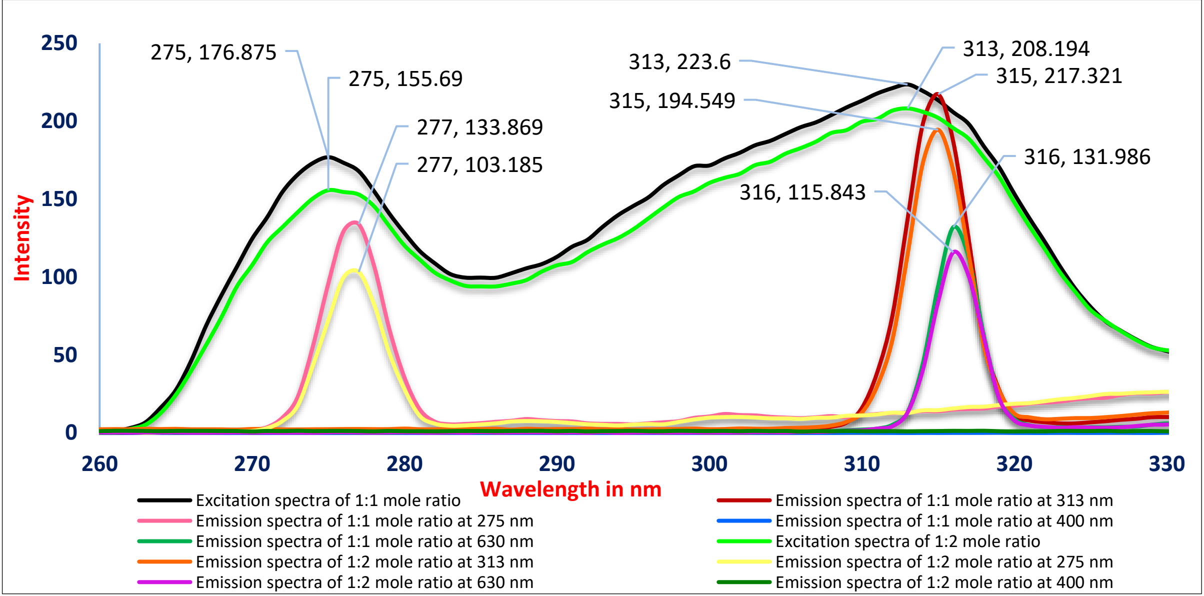


Figure 13. Fluoroscence spectra of Zn(II)-complexes (9a-b).

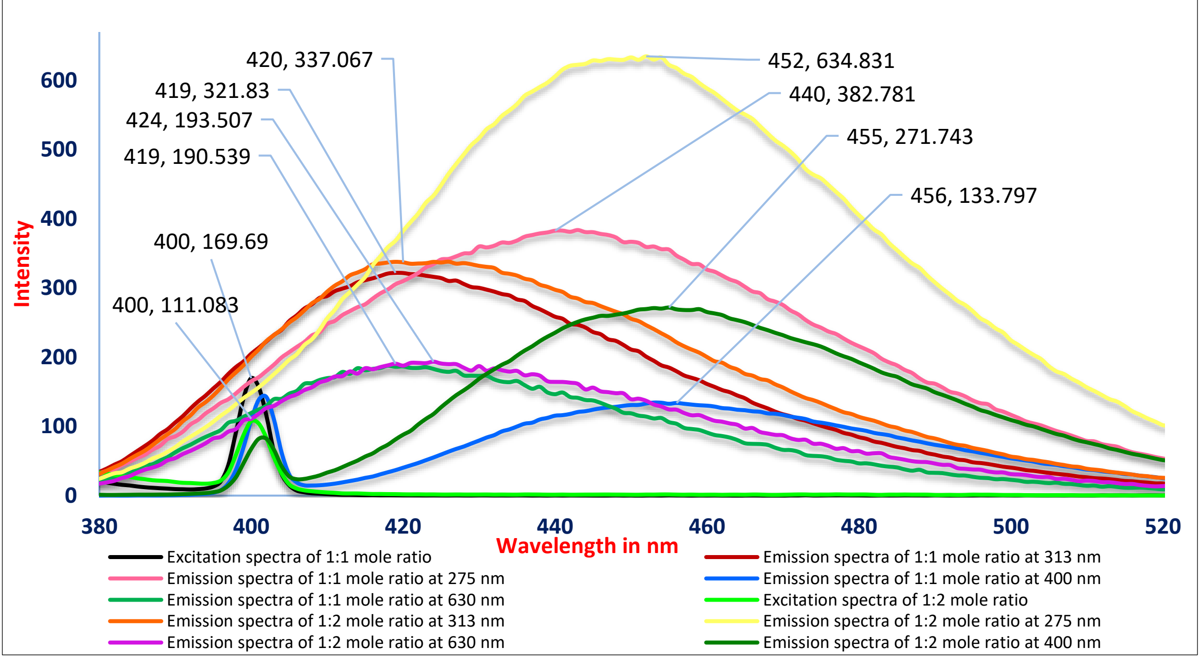


Figure 14. Fluoroscence spectra of Zn(II)-complexes (9a-b).

The luminescence properties of Zn(II) complexes originates from organic ligands rather than LMCT because the d-shell of the central ion is filled [19]. The literature survey suggests that zinc complexes of salicylaldehyde Schiff bases and their derivatives emits light in blue, green and red regions. All Zn(II)-complexes were excited at 220–800 nm to determine wavelength of excitations of electrons and the higher excitation wavelength/s was used to determine emission. All excitation and emission spectrum of all complexes synthesized with various combinations of ligand and zinc chloride were recorded and are shown in the above figs. The complexes showed good laminating properties in solid as well as in solution state. Since there was no d-d transition in the zinc complexes; the emission of light is due to relaxation from higher energy level to lower energy level by intraligand transitions. All complexes, except those synthesized from the sodium salt of amine showing emission in the visible region, this is maybe due to change in donor atom from OH to O^-. The PL properties were changed by changing mole ratio of the ligand and metal as well as the nature of donating atom. A stronger and low energy emission was observed for the 6a-b complexes. All the complexes show redshift with an increase in intensity of emission.

G. Combine the study of Photophysical properties of (4) and Zn(II)-complexes (Figures 15-18):

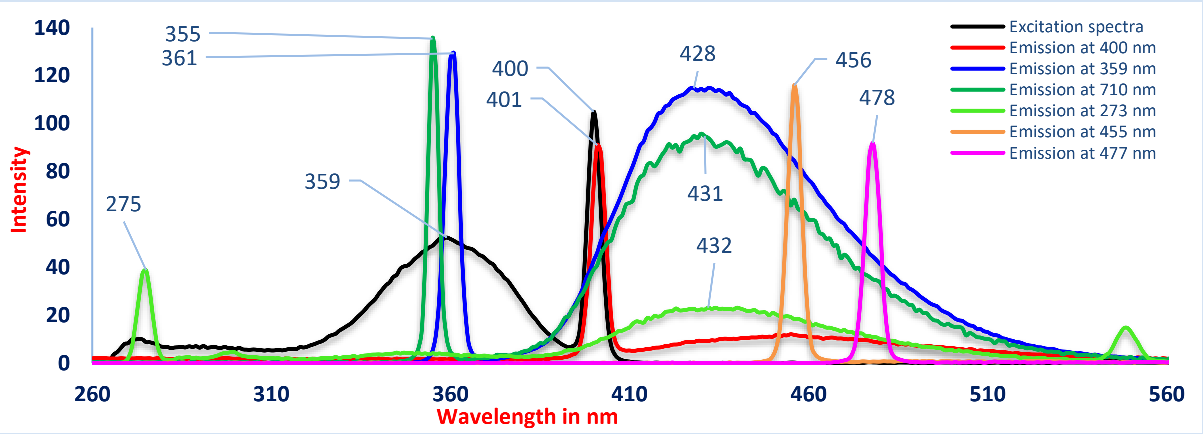


Figure 15. Fluoroscence spectra of 4.

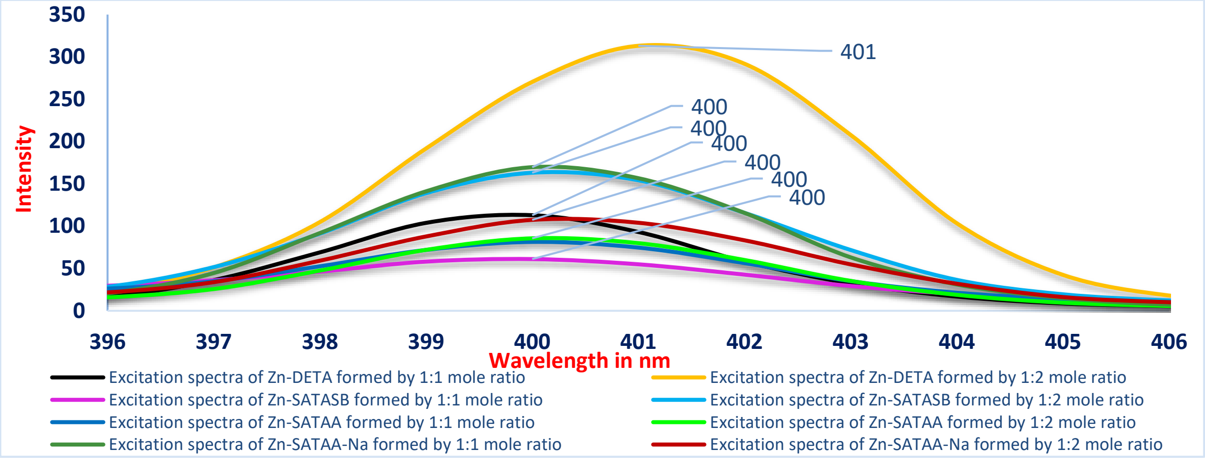


Figure 16. Excitation spectra of different Zn(II) complexes.

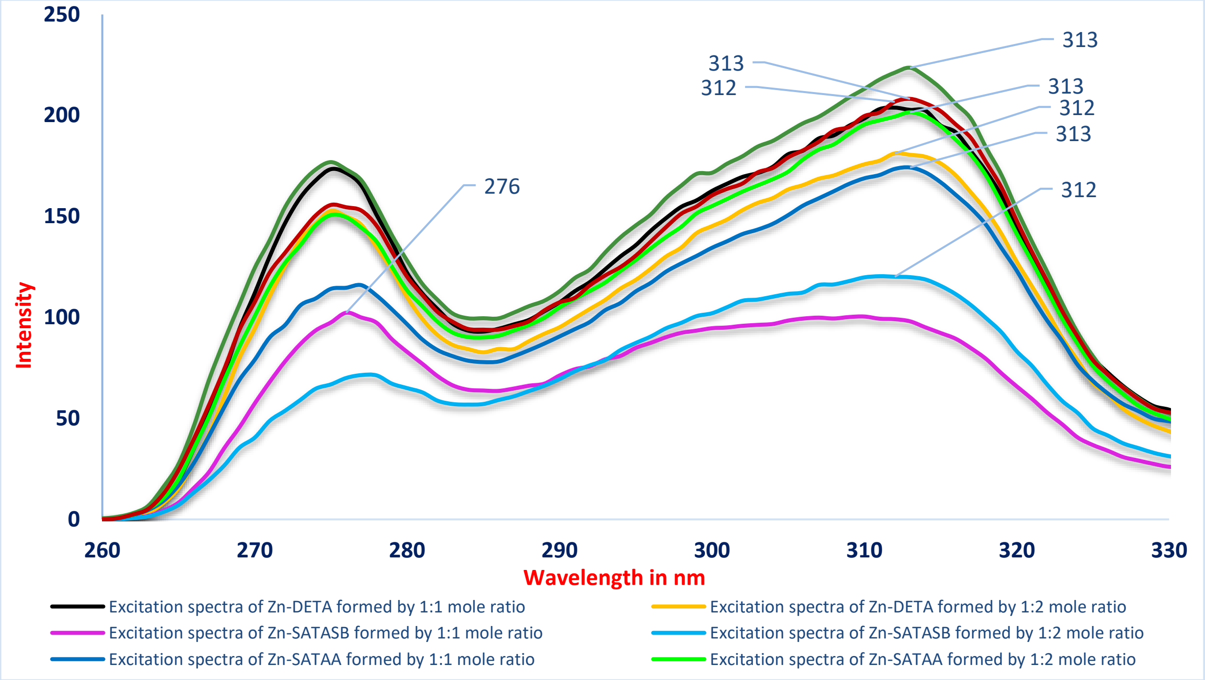


Figure 17. Excitation spectra of different Cu(II) complexes.

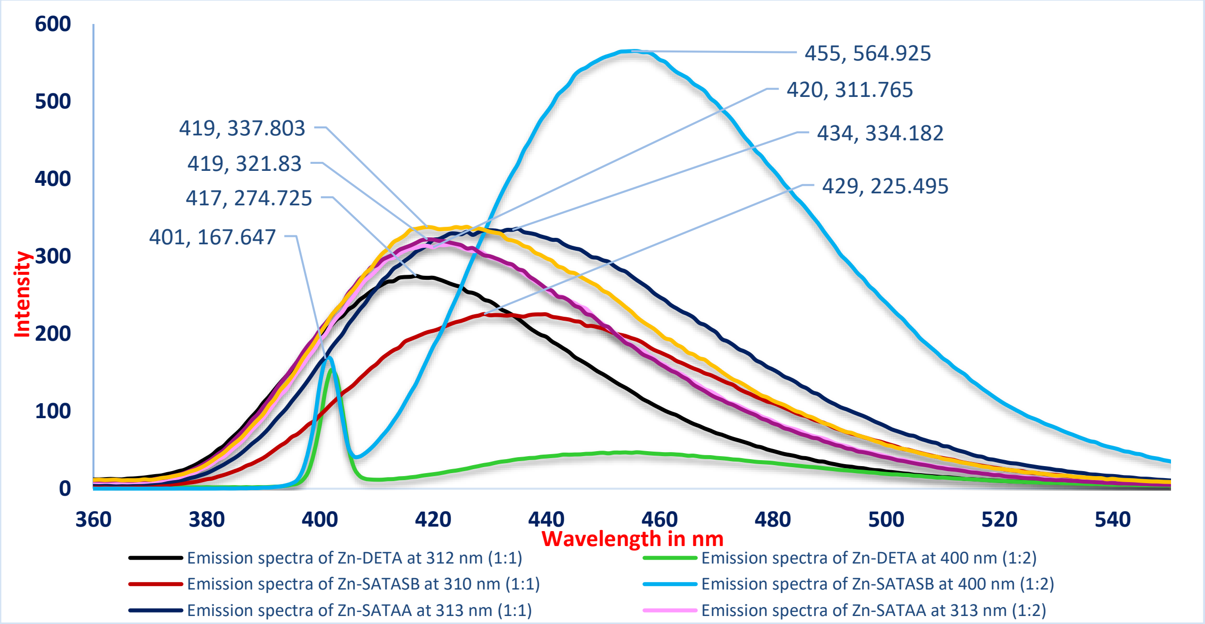


Figure 18. a: Emission spectra of different Zn(II) complexes.

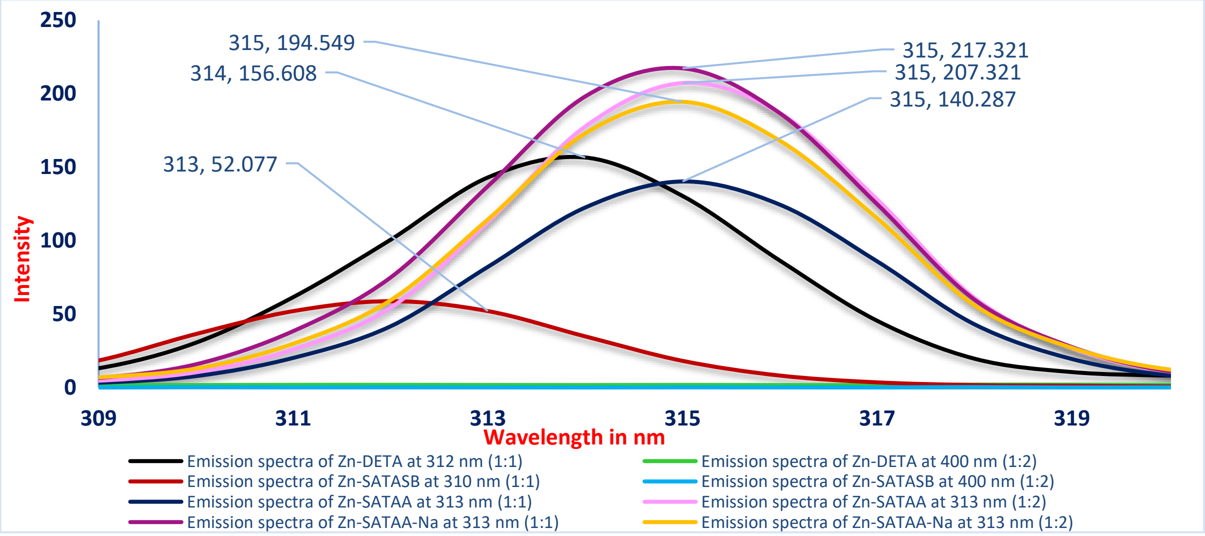


Figure 18. b: Emission spectra of different Zn(II) complexes.

Quantum efficiency of the metal complexes was broadly calculated by using the following equation. It was more than one in all complexes except 5b and 9a-b.

The amine (4) showed strong excitation at 400 nm but weak emission (401 nm) at 400 nm as compared to the excitation at 359 nm. The Zn complexes (7a-b) shows strong excitation at 313 nm. The quantum efficiency of complex 5b formed from diethylene triamine (2) at 401 nm (light of excitation) was least as compared to other complexes. Also, the quantum efficiency of 9a-b was less than 100% as compared to other complexes. It was highest for complexes (6a-b) formed from Schiff base (3). The nature of the complex ions of 7a-b and 9a-b was different due to their synthesis under different reaction conditions (neutral and alkaline) which were confirmed from both conductance measurement and emission spectra.

3. Conclusions

Schiff base (**3**) of diethylene triamine (**2**) and salicylaldehyde (**1**) was synthesized at room temperature in methanol under slightly acidic condition was monitored by the reaction. The result suggests that reaction was completed within 18 minutes and is an exothermic reaction. The Schiff base (**3**) was *in-situ* reduced by using sodium borohydride at room temperature, which gets completed within 8 – 10 minutes. It was also an exothermic reaction. These results indicate that there was no need for heating or reflux the reaction mixture which was reported in different literatures. A series of zinc metal ion complexes were prepared from diethylene triamine (**2**), Schiff base (**3**), reduced amine (**4**) and its sodium salt (**8**) at room temperature in methanol/ethanol. The conductance of the solutions of all complexes in DMSO (50 mg per 100 ml) was measured and was more than zero indicates that chlorine was not a part of the coordination sphere or ion. These are ionic complexes. All the synthesized complexes were emitting blue light expect **9a-b** synthesized from **8**.

Zinc complexes of diethylene triamine (**2**), Schiff base (**3**) and reduced amine (**4**) have received particular attention due to their effective optical properties. These complexes have efficient emission of blue light under the UV light (310 – 313 nm) source. These complexes were emit blue light luminescence (405 – 450 nm) that could be efficiently used for the generation of white light for various optoelectronic applications. The conductance data suggested that **9a-b** complexes have the least conductance is due to their less ionic character.

Supplementary Materials: Not applicable.

Author Contributions: Conceptualization, S.M., BT.; methodology, S.M., BT.; software, S.M.; writing—review and editing, S.M. and BT.; visualization, S.M. and BT.; supervision, BT.

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Conflicts of Interest: The authors declare no conflict of interest.

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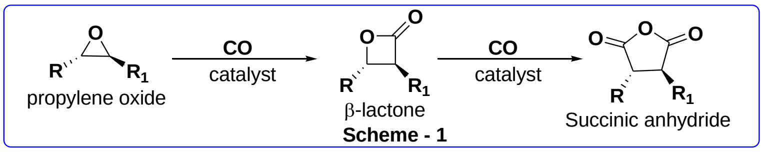
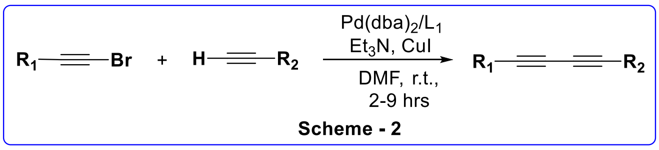


Scheme 1: ReactIR techniques, catalytic double carbonylation of epoxides to Succinic anhydride



Scheme 2 : palladium-catalyzed cross-coupling reaction of haloalkyne and terminal alkynes using phosphine-olefin ligand

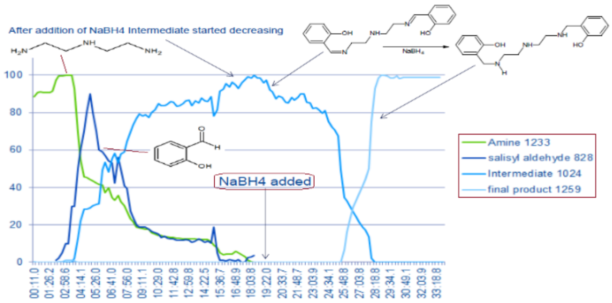


Fig. 1: Monitoring reaction by using ReactIR

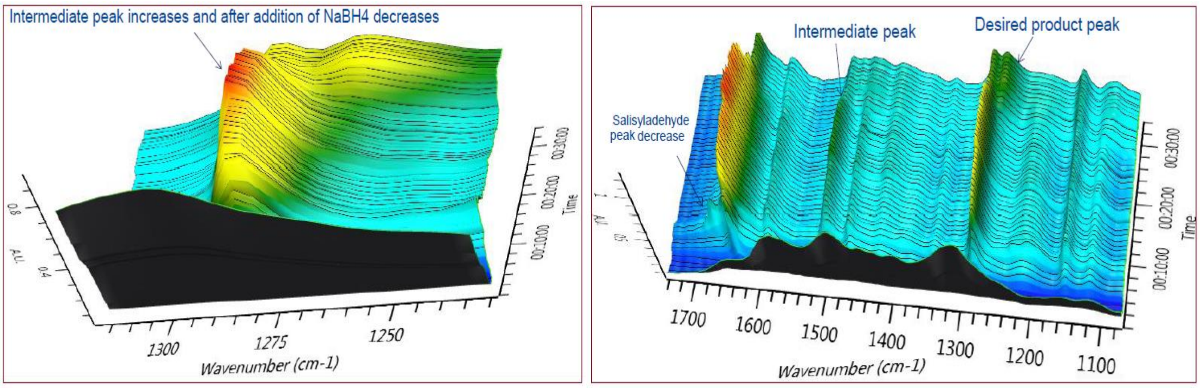


Fig. 2: Images of recording of new IR peaks during monitoring the reaction

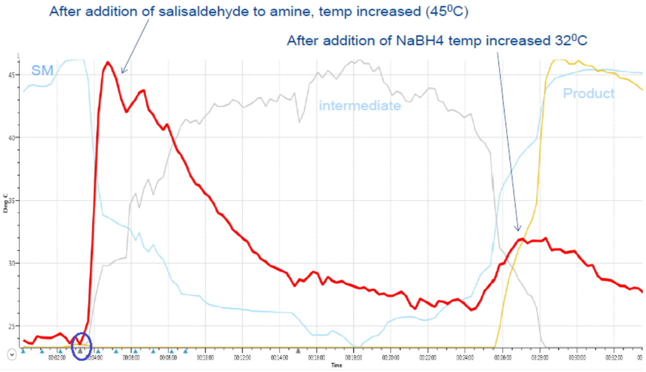


Fig. 3: Thermal changes during the progress of the reaction

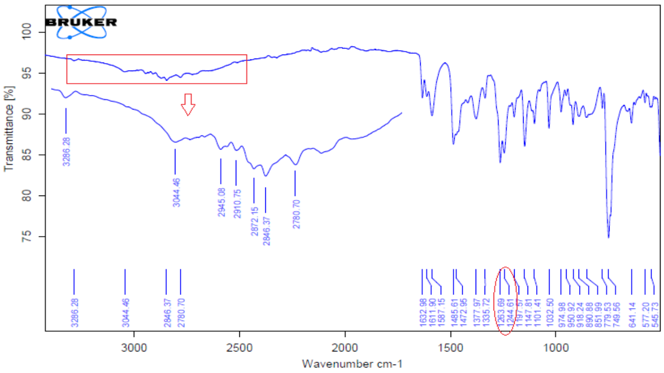
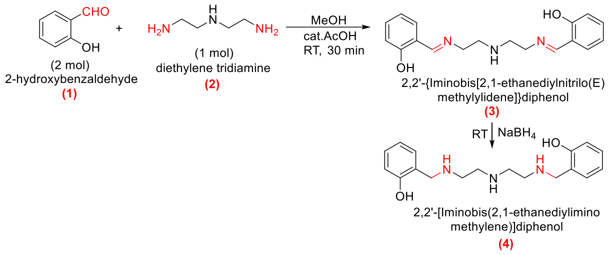
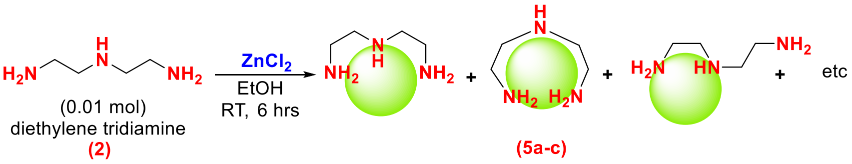


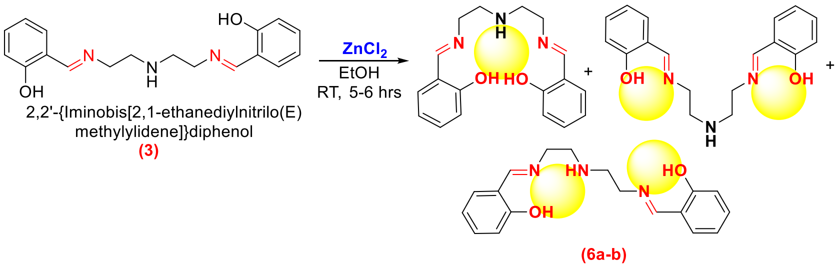
Fig. 4: FT-IR Spectra of 2,2′-[iminobis(2,1-ethanediyliminomethylene)]diphenol (4)



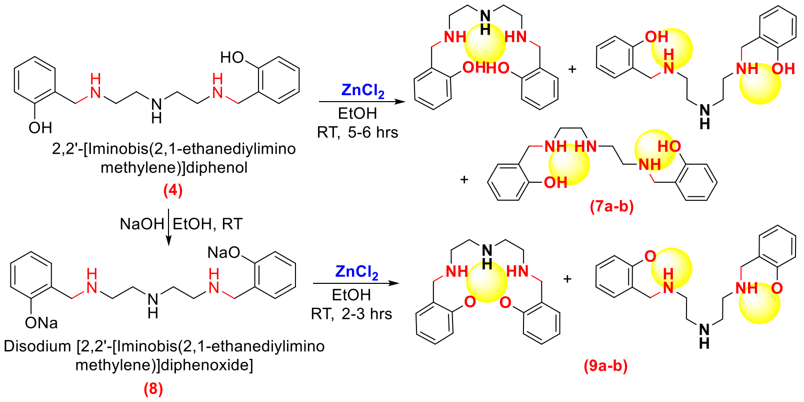
Scheme 3 : Reaction scheme employed for the current study.



Scheme 4 : Synthesis of Metal complexes (5a-c) of diethylene triamine (2)



Scheme 5 : Synthesis of Zn-complex (6a-b) of Schiff base (3)



Scheme 6 : Synthesis of Zn-complex (6a-b) of Schiff base (3)

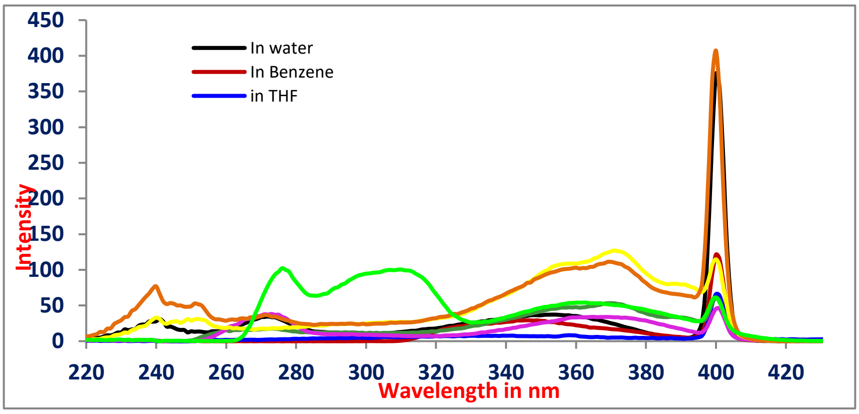
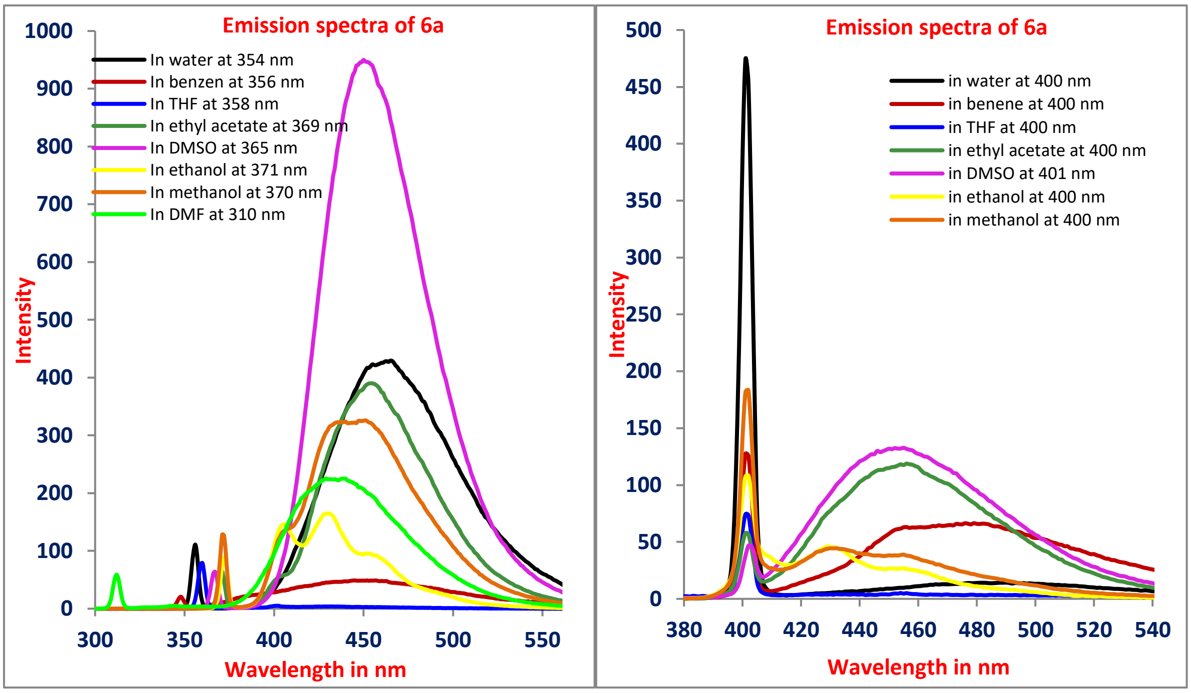


Fig. 5: Excitation spectra of 6a



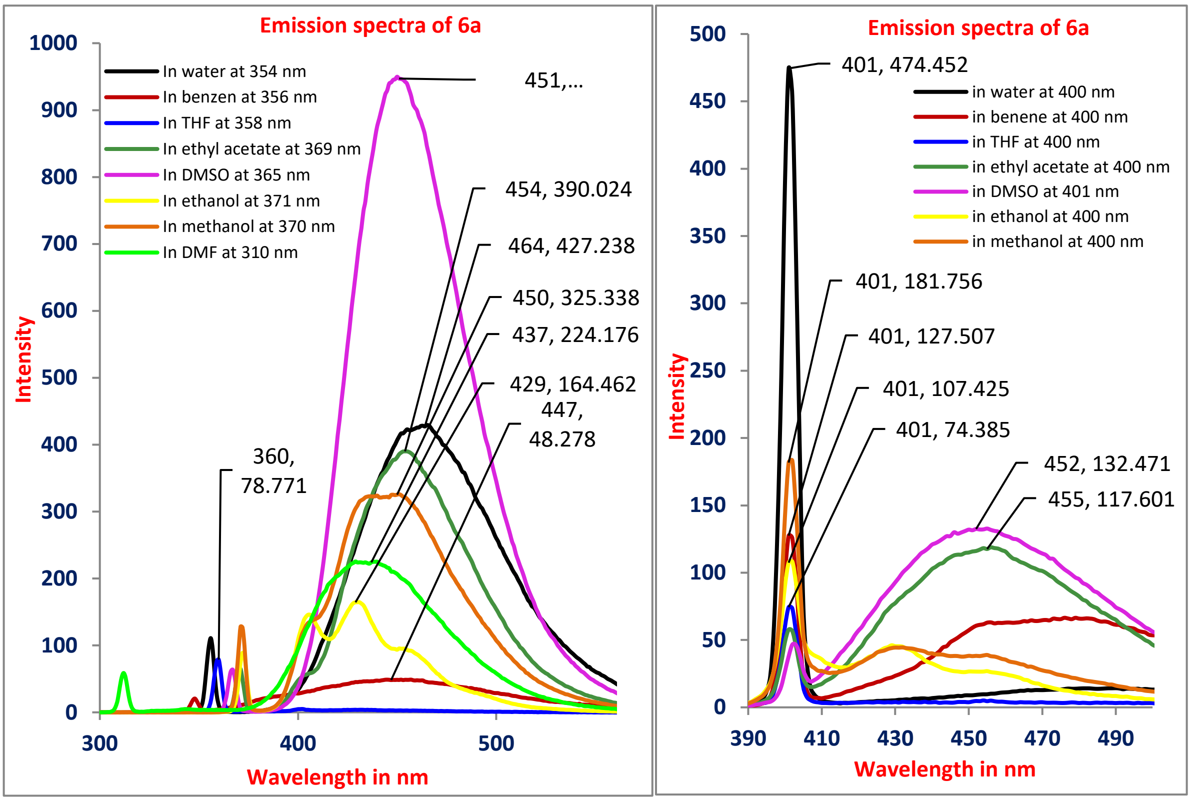


Fig. 6: Emission spectra of 6a

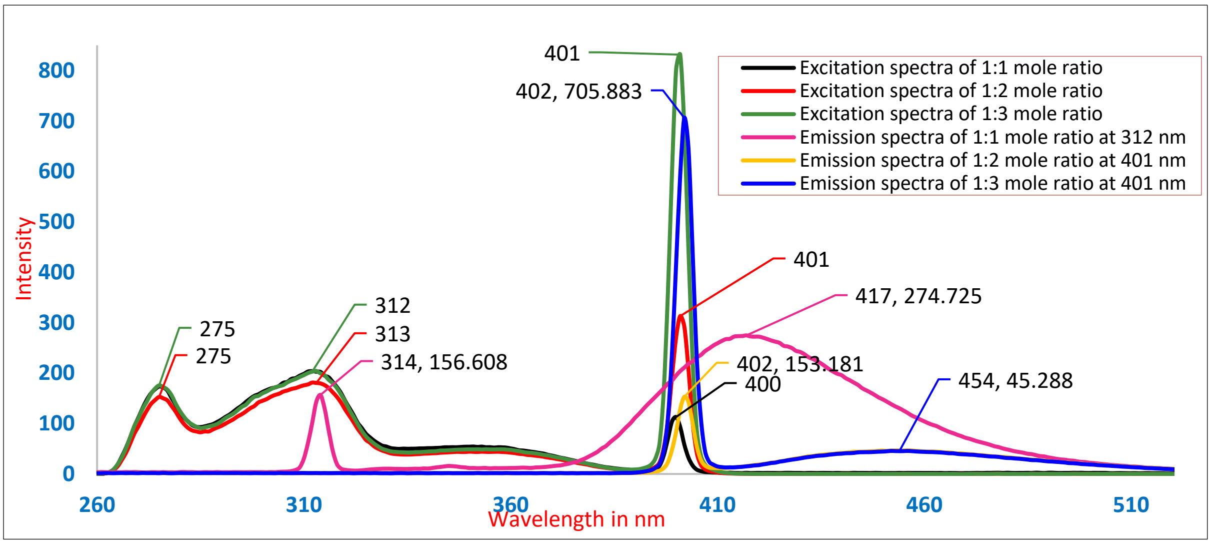


Fig. 7: Fluorescence Study of Zn(II)-complex (5a-c)

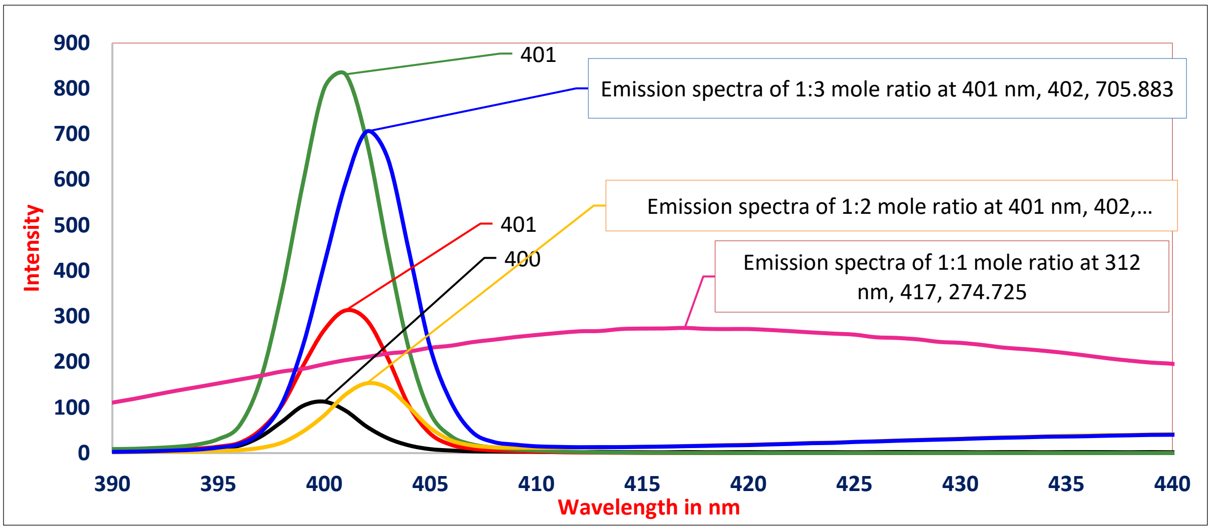


Fig. 8: Fluorescence Study of Zn(II)-complex (5a-c)

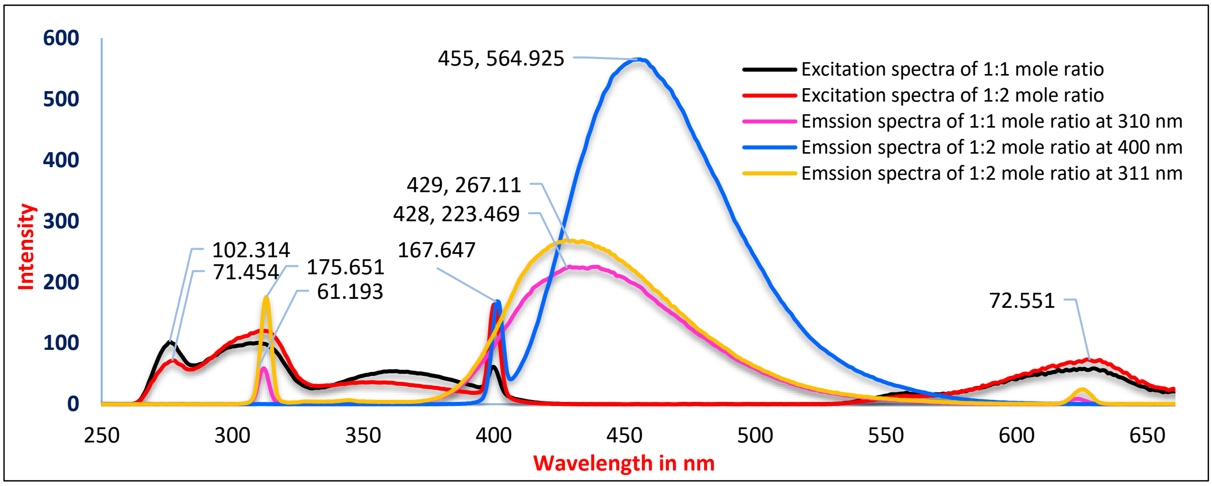
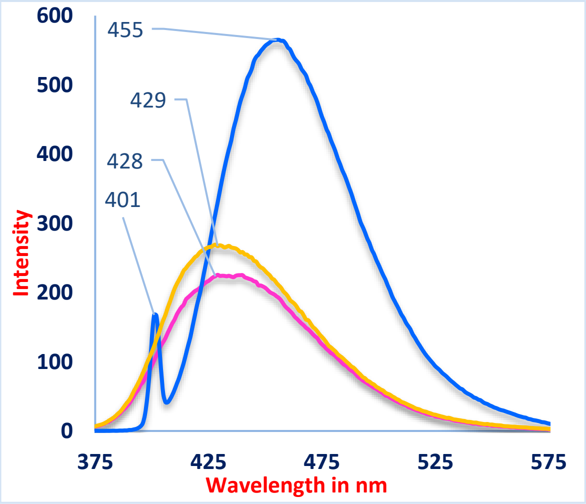


Fig. 9: Fluoroscence spectra of Zn(II)-complex (6a-b)



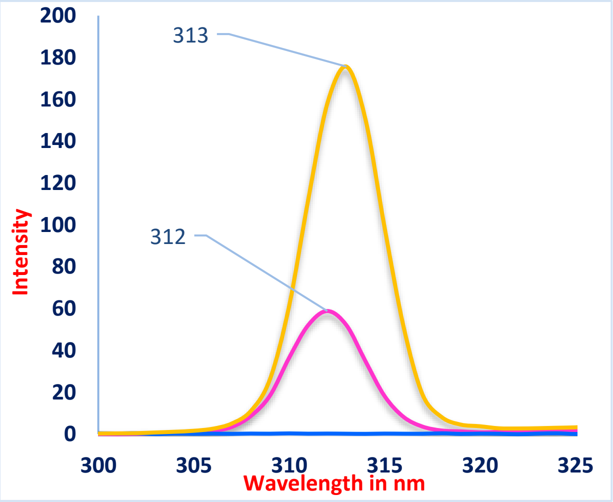


Fig. 10: Emission spectra of Zn(II)-complex (6a-b)

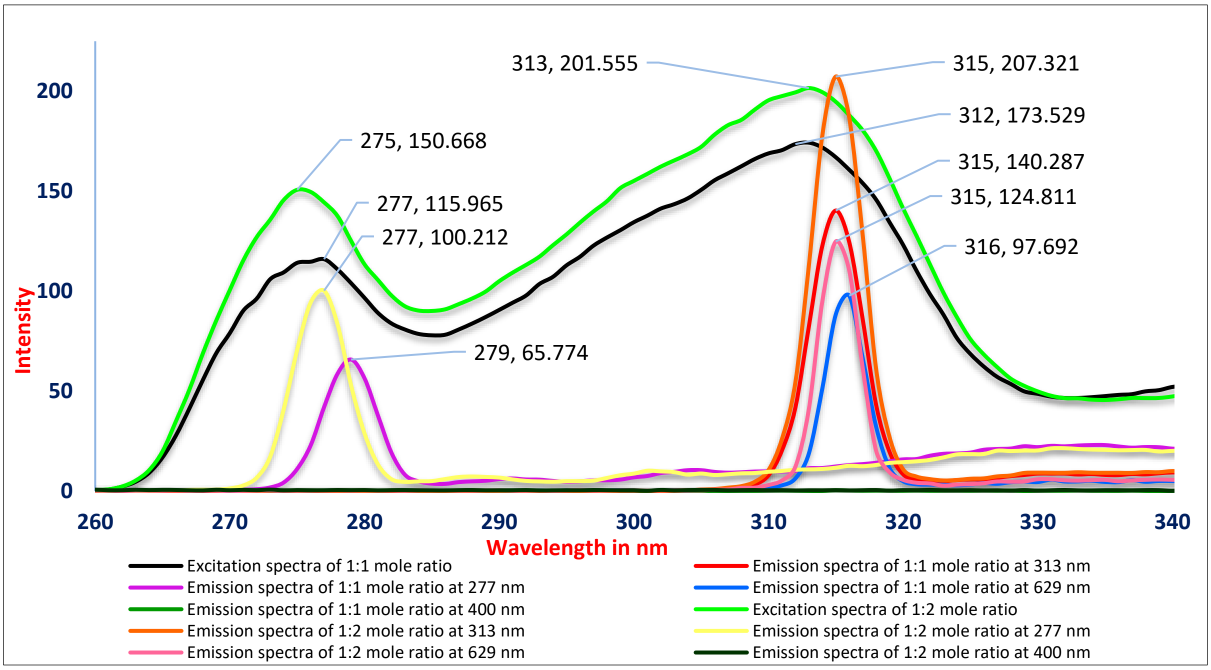


Fig. 11: Fluoroscence Spectra of Zn(II) complexes (7a-b)

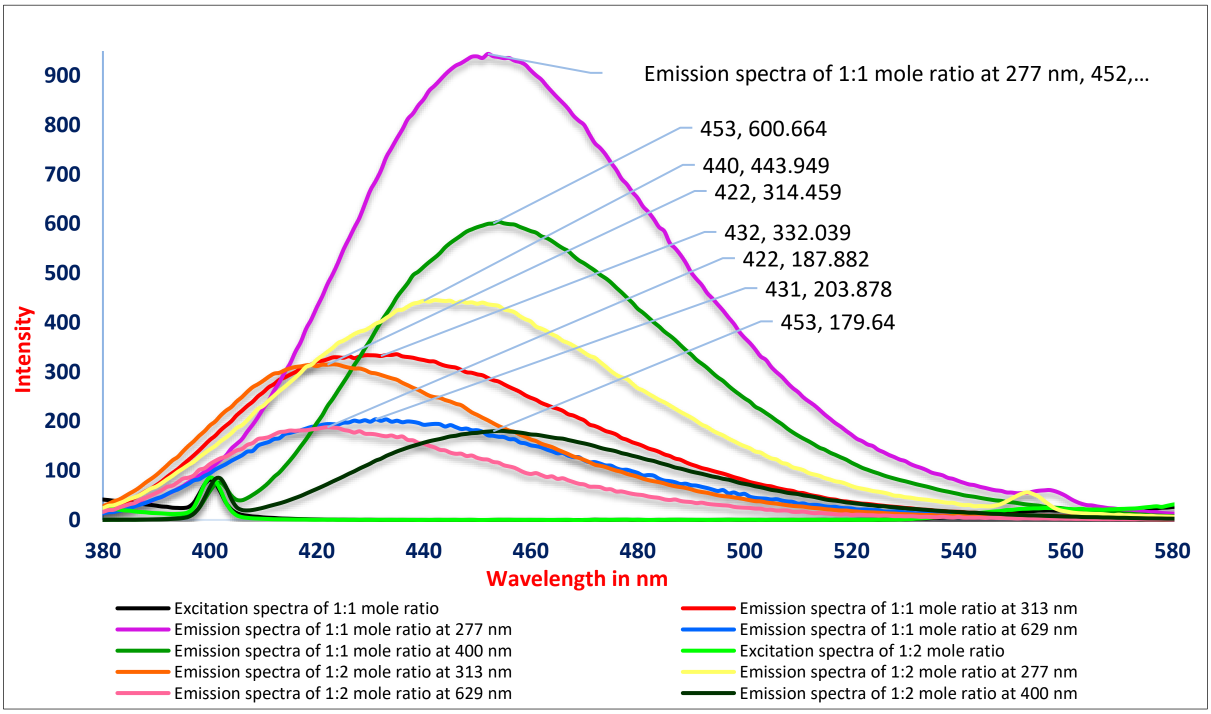


Fig. 12: Fluoroscence Spectra of Zn(II)-complexes (7a-b)

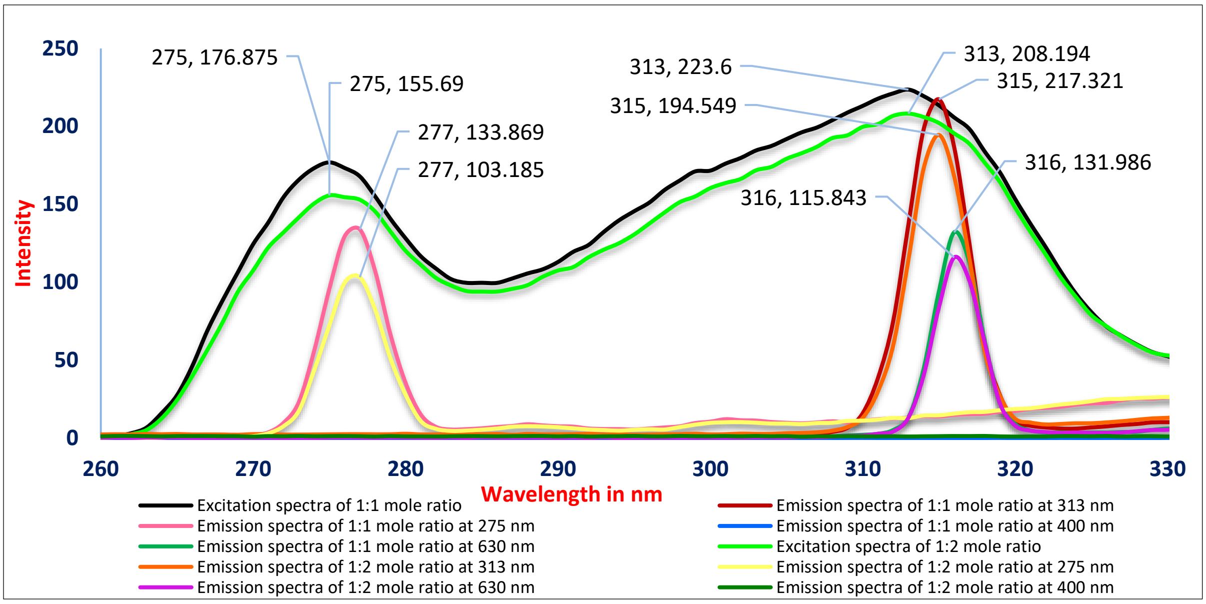


Fig. 13: Fluoroscence spectra of Zn(II)-complexes (9a-b)

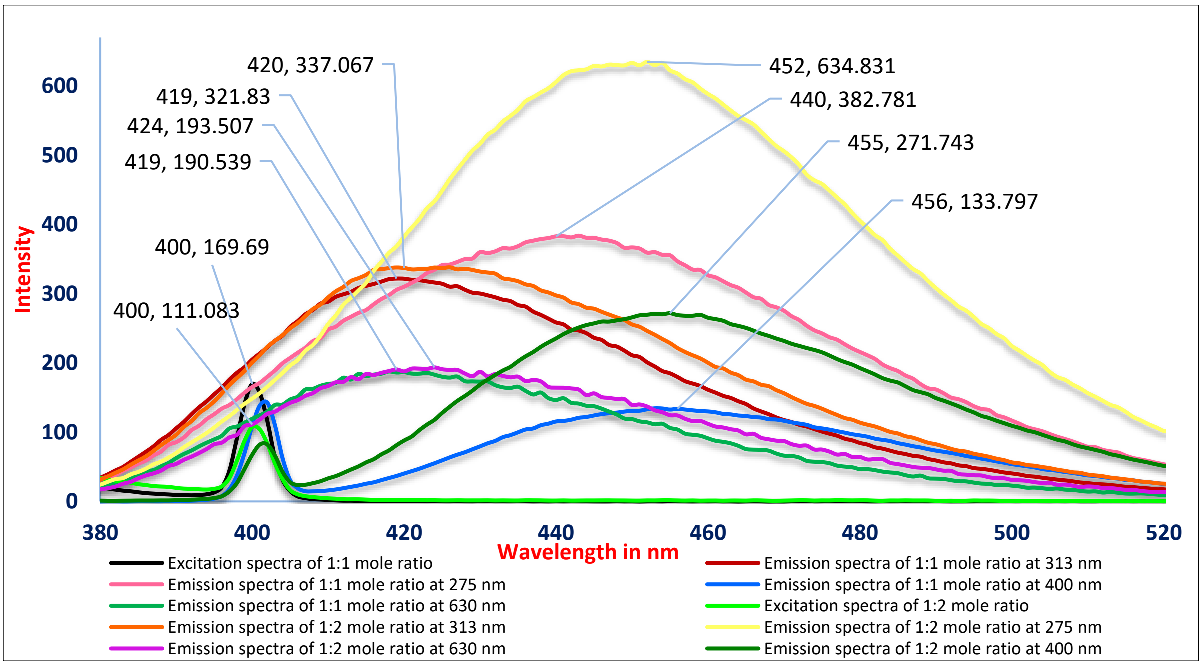


Fig. 14: Fluoroscence spectra of Zn(II)-complexes (9a-b)

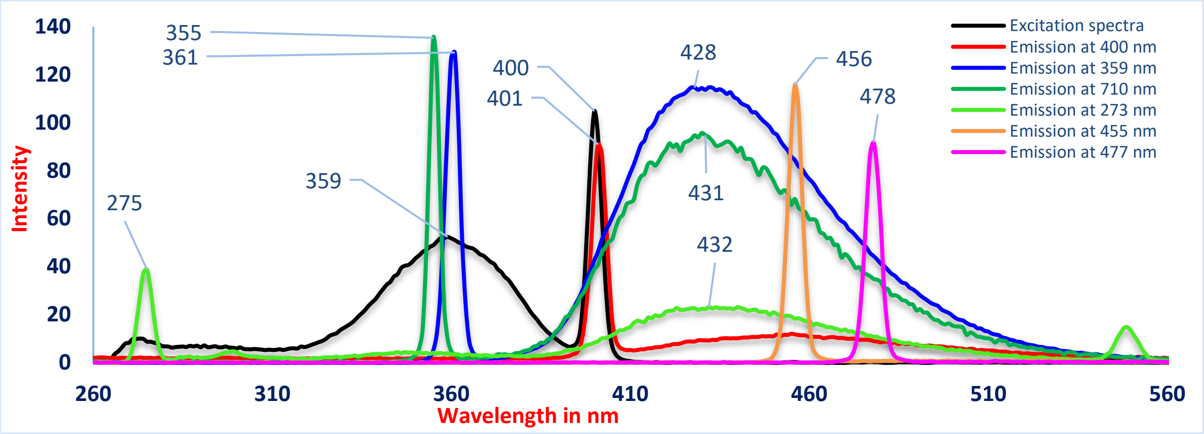


Fig. 15: Fluoroscence spectra of 4

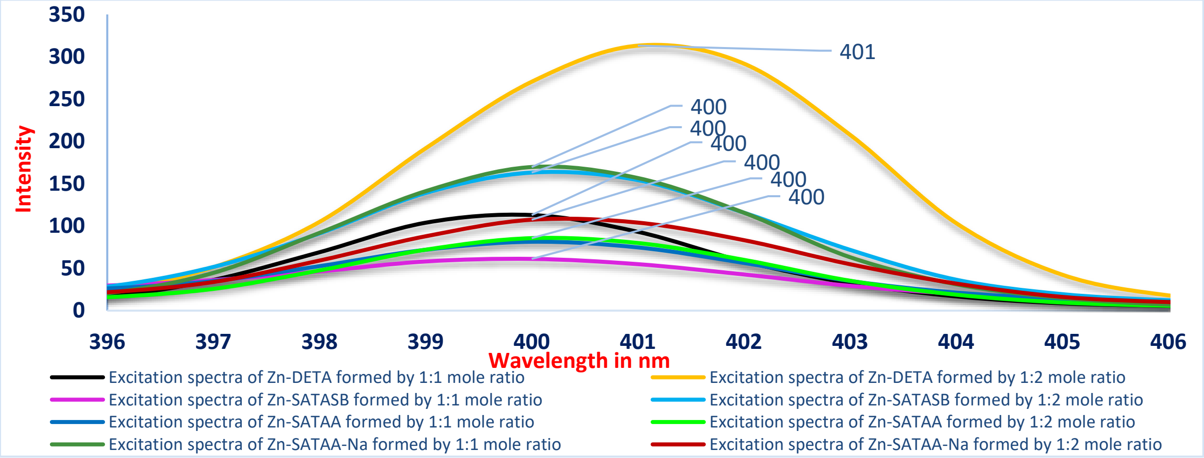


Fig. 16: Excitation spectra of different Zn(II) complexes

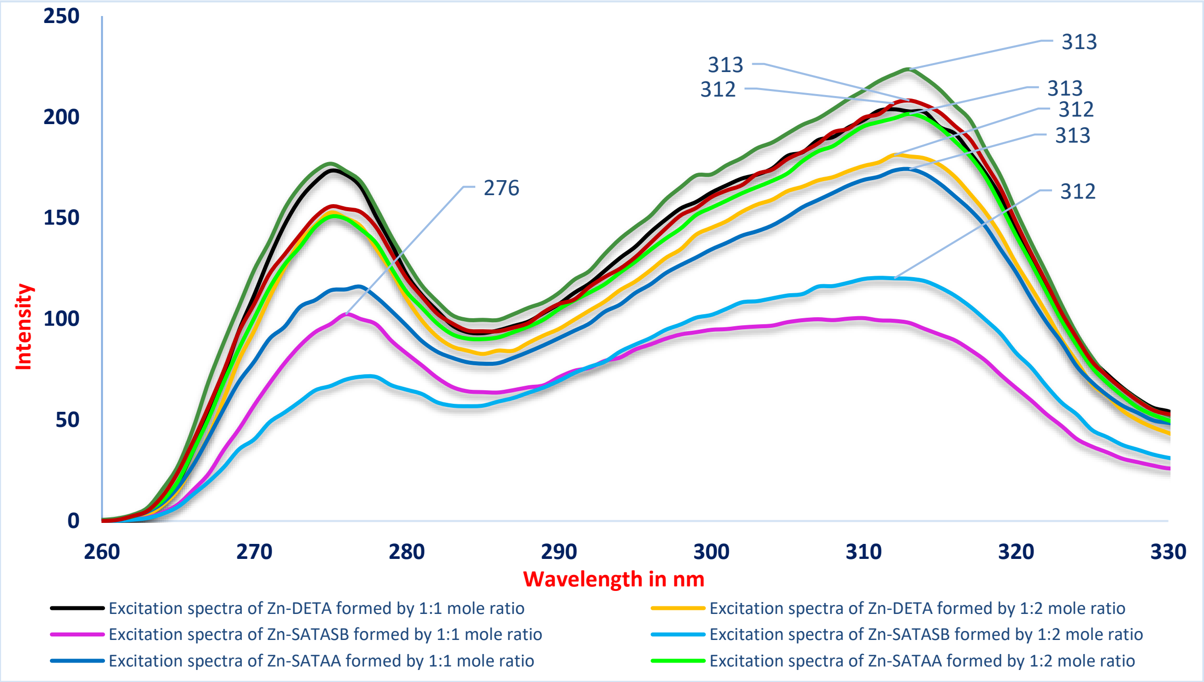


Fig. 17: Excitation spectra of different Cu(II) complexes

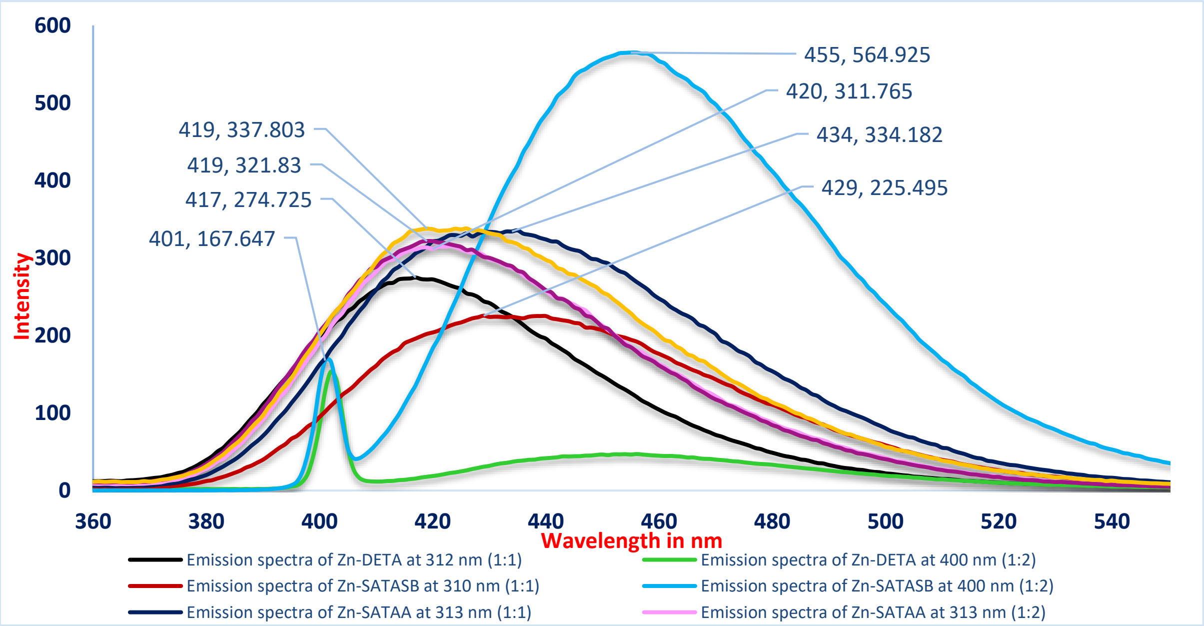


Fig. 18a: Emission spectra of different Zn(II) complexes

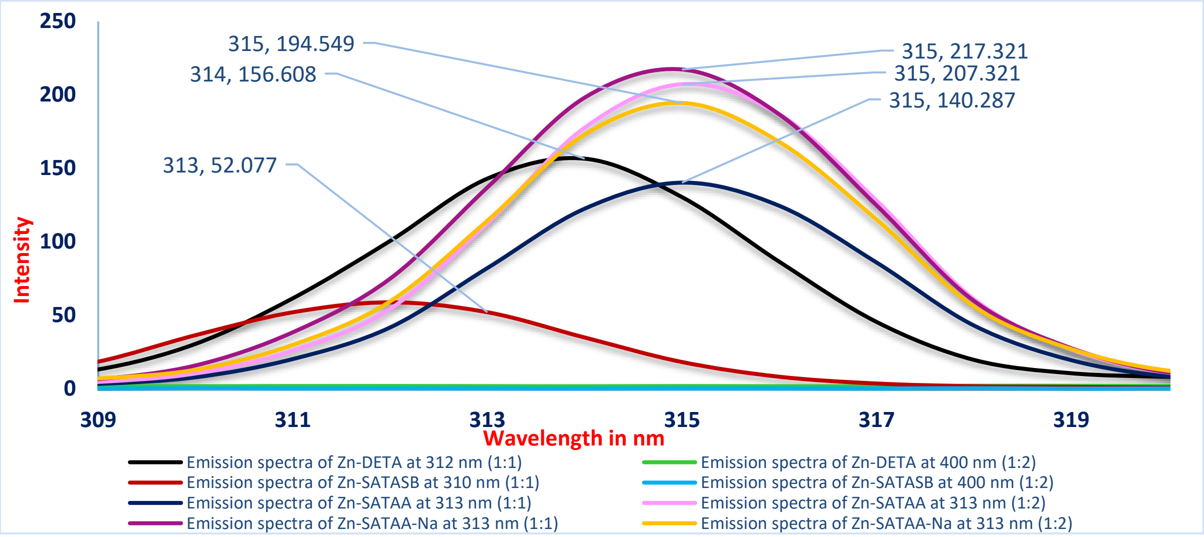


Fig. 18b: Emission spectra of different Zn(II) complexes