Impact Factor 3.025

ISSN 2349-638x

Refereed And Indexed Journal

AAYUSHI INTERNATIONAL INTERDISCIPLINARY RESEARCH JOURNAL (AIIRJ)

UGC Approved Monthly Journal

VOL-IV ISSUE-IX Sept. 2017

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CHIEF EDITOR – PRAMOD PRAKASHRAO TANDALE

Synthesis and fluorescence study of 5-Bromo-2-hydroxybenzaldehyde Schiff bases and their transition metal complexes.

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Abstract:

Series sequence of reduced Schiff bases were prepared from the reaction of two equivalents of salicylaldehyde with one equivalent ***5-bromo-2-hydroxybenzaldehyde*** *derivatives followed by reduction with* $NaBH_4$*. The complexes of these ligands were prepared by using Co (II), Ni (II), Cu (II) and Zn (II). Characterization of synthesized ligands and metal complexes were completed by FTIR,* ^1H *and MS, UV-Visible, Fluorescence and elemental study. The fluorescence study of the salophen Schiff bases 2a-2c and the tetrahydro type Schiff bases 3a-3c were also studied*

Keywords: *Salophen; Schiff base; Metal complex; Fluorescence.*

1. Introduction

Schiff bases of aliphatic aldehydes are comparatively unstable and willingly polymerizable [1], whereas those of aromatic aldehydes having active conjugation are more stable. The steric hinderous of active centre of aldehydes is less than that of ketone. Also, the additional carbon of ketone contributes electron density towards the azomethine carbon and therefore makes the ketone fewer electrophilic compared to aldehydes [2].

Schiff bases resulting from aromatic amines and aldehydes have a varied diversity of applications in many fields, such as analytical and bio-inorganic chemistry etc. [3, 4]. Transition metal complexes by Schiff bases have expanded extremely and comprised varied subjects comprising massive areas of organometallic compounds and also, numerous features of bio coordination chemistry [5]. The design and synthesis of regular Schiff bases have structural diversity and tunable electronic properties letting to carry out methodical reactivity studies based on auxiliary ligand alterations. [6,12,13].

Schiff base simply forms stable complexes with most of transition metal ions so, they show vital role in coordination chemistry. [7]. In the course of organic synthesis, Schiff base reactions are always beneficial in making carbon-nitrogen bonds. An important role was played by N, O and S atoms in the metal coordination by the active sites of many metallo-biomolecules [8]. Metal complexes of Schiff bases have been broadly studied as they have manufacturing, fungicidal, antiseptic, anticancer, antiviral applications [9-13]. They aid as models for biologically significant species and discover applications in bio-mimetic catalytic reactions.

2. Experimental:

2.1 General. The melting points of all compounds were determined by using open capillary tubes. UV–Visible spectra were found on Shimadzu UV-1800 spectrophotometer. By using Spectro fluorophotometer Shimadzu RF-5301pc and armed by quartz cuvette of 1.0 cm path length, the fluorescence bands were noted. On a FTIR-7600 Lambda Scientific Pty Ltd instrument, IR spectra were measured with KBr disk in the range 4000-400 cm^{-1}. Mass spectra were also completed using BRUKER ESQUIRE HCT spectrometer. Using tetramethyl silane (TMS) as an internal standard; ^1H-NMR spectra was studied using Varian-NMR-Mercury 300 MHz instruments in DMSO-d6 and the chemical shifts were reported as δ ppm units. The elemental examination was completed at the IIT Mumbai. TLC was achieved on pre-coated silica gel 60 F254 of TLC slips (Merck), envisioned by UV lamps.

2.2 Method for preparation of Schiff bases:

1,2-diamine derivative 1a-1c (2.0 mmol) in MeOH (8.0 mL) was stirred with a solution of *5-Bromo-2-hydroxybenzaldehyde* (4 mmol) for two hours. After completion of the reaction the product obtained was filtered and dried as shown in Fig. 1 and Table 1.

Figure 1: Preparation of hydrazones and metal complexes.

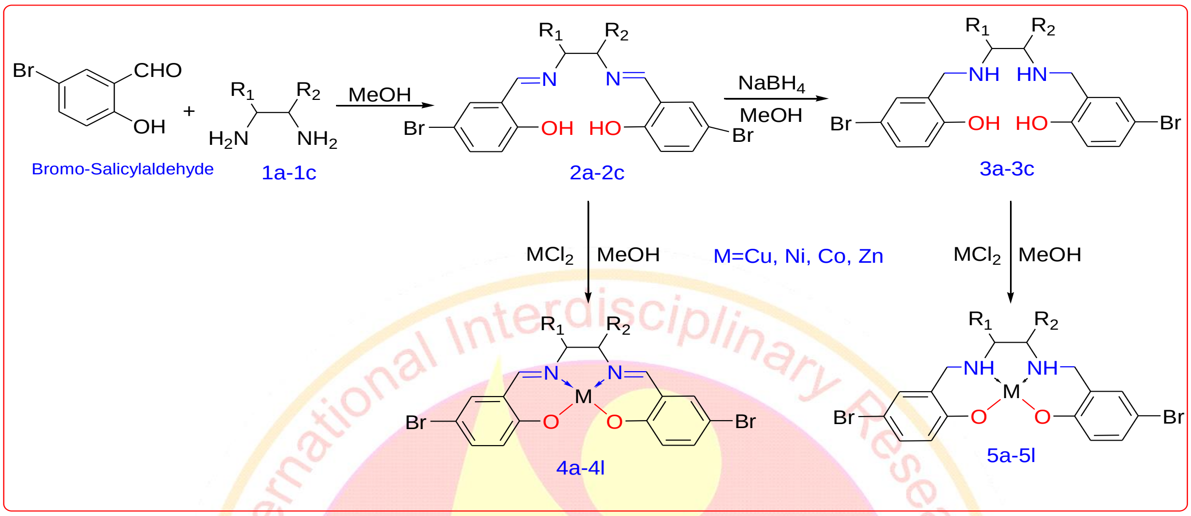
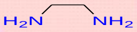
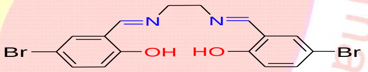
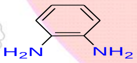
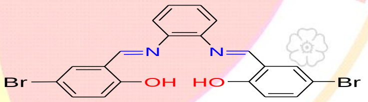
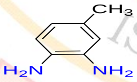
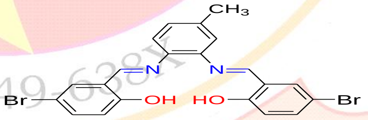
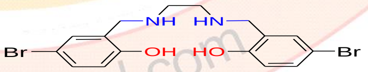
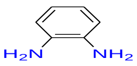
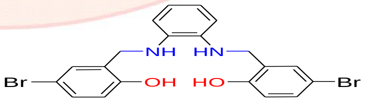
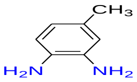
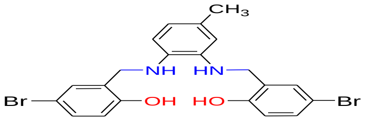


Table 1: Structure of Schiff bases [2a-2c] and reduced form [3a-3c]

Entry	Diamine	Product	Yield (%)
2a			95
2b			96
2c			93
3a			73
3b			80
3c			71

2.2.1 Preparation of 2-((E)-(2-((E)-5-bromo-2-hydroxybenzylideneamino) ethylimino) methyl)-4-bromophenol. [2a]

M.P.: 192-193^{0}C; Colour: Yellow; MS [M+2]: 427.6; FTIR (KBr cm^{-1}): 3026, 2940, 2906, 2873, 2738, 1636, 1567, 1477, 1392, 1361, 1276, 1218, 1186, 1079, 1033, 977, 914, 827, 777, 692, 628; ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ: 3.922(s, 2H), 6.823-6.853(m, 3H), 7.438-7.650(m, 3H), 8.57(m, 4H) 13.45(s, 2H); Elemental analysis [$C_{16}H_{14}Br_2N_2O_2$]: observed (calculated): C 45.14% (45.1%), H 3.38% (3.31%), N 6.60% (6.67%).

2.2.2 Preparation of 2-((E)-(2-((E)-5-bromo-2-hydroxybenzylideneamino) phenylimino) methyl)-4-bromophenol. [2b]

M.P.: 186-188^{0}C; Colour: Yellow; MS [M+2]: 475.42; FTIR(KBr cm^{-1}): 3057, 2733, 1614, 1585, 1562, 1481, 1450, 1362, 1277, 1192, 1151, 1045, 977, 910, 856, 831, 787, 759, 640, 580.; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 3.335 (s,2H), 7.222-7.899 (m, 3H), 8.116-8.145 (m, 3H), 8.925-8.953 (m, 4H), 10.805 (s, 2H); Elemental analysis [$C_{20}H_{14}$ $Br_2N_2O_2$]: observed (calculated): C 50.61% (50.66%), H 3.05% (2.98%), N 5.88% (5.91%).

2.2.3 Preparation of 2-((E)-(2-((E)-5-bromo-2-hydroxybenzylideneamino)-4-methyl phenyl imino) methyl)-4-bromophenol. [2c]

M.P.: 186-189^{0}C; Colour: Yellow; MS [M+H]: 487.53; FTIR (KBr cm^{-1}): 3055, 2984, 2918, 2712, 1616, 1564, 1487, 1365, 1279, 1190, 1151, 1115, 1032, 995, 908, 839, 767, 738, 638, 503; ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ: 2.389(s, 3H), 6.918-6.962(m, 3H), 7.228-7.898(m, 3H), 8.909-8.917(m, 3H), 12.910(s, 1H), 13.091(s, 1H); Elemental analysis [$C_{21}H_{16}Br_2N_2O_2$]: observed (calculated): C 51.61% (51.67%), H 3.33% (3.30%), N 5.68% (5.74%).

2.2.2 Preparation of 2-((E)-(2-((E)-5-bromo-2-hydroxybenzylideneamino) phenylimino) methyl)-4-bromophenol. [2b]

M.P.: 154-156 ^{0}C; Colour: Yellow; MS [M+2]: 475.41; FTIR(KBr cm^{-1}): 3056, 2734, 1614, 1585, 1562, 1481, 1450, 1363, 1276, 1192, 1151, 1045, 977, 910, 856, 831, 787, 759, 640, 580.; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 3.335(s,2H), 7.222-7.899(m, 3H), 8.116-8.145(m, 3H), 8.925-8.953(m, 4H), 10.805(s, 2H); Elemental analysis [$C_{20}H_{14}$ $Br_2N_2O_2$]: observed (calculated): C 50.61% (50.66%), H3.05% (2.98%) , Br 33.73% (33.7%), N5.88% (5.91%),O 6.73% (6.75%)

2.2.3 Preparation of 2-((E)-(2-((E)-5-bromo-2-hydroxybenzylideneamino)-4-methyl phenyl imino) methyl)-4-bromophenol. [2c]

Colour: Yellow; MS [M+H]: 487.54; FTIR(KBr cm^{-1}): 3055, 2985, 2918, 2713, 1616, 1564, 1487, 1365, 1279, 1190, 1151, 1115, 1032, 995, 908, 839, 767, 738, 638, 503; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 2.389(s, 3H), 6.918-6.962(m, 3H), 7.228-7.898(m, 3H), 8.909-8.917(m, 3H), 12.910(s, 1H), 13.091(s, 1H); Elemental analysis [$C_{21}H_{16}Br_2N_2O_2$]: observed (calculated): C 51.61% (51.67%), H 3.33% (3.30%) ,Br 33% (32.74%), N 5.68% (5.74%),O 6.60% (6.65%).

2.3 Method for preparation of reduced schiff bases:

To a solution of the Schiff base (2.27 mmol) in dichloromethane (10 mL) at 0°C was added a methanolic solution of $NaBH_4$ (2.0 mmol) comprising fewer drops of concentrated KOH solution. The pH was set to 6.0 and the solution stirred for several hours until the yellow colour had vanished. The solvent was evaporated to dryness and cold water (10 mL) was added to the residue. The pH was set to 4–5 by addition of 3M HCl. The white solid product was filtered, washed with cold water, ethanol and diethyl ether and dried under vacuum.

2.3.1 Preparation of 2-((2-(5-bromo-2-hydroxybenzylamino) ethylamino) methyl)-4- bromo phenol [3a]

Colour:; MS [M+2]: 273.99; FTIR(KBr cm^{-1}): 3492, 3463, 3363, 3052,2942, 2852, 2593, 1602, 1479, 1417, 1353, 1268, 1189, 1126, 1074, 960, 815, 757, 626; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 2.481 (m, 2H), 2.608(m,2H),3.332(s, 1H), 3.922(s, 1H), 5.031(s, 4H), 6.823-6.853(m, 3H), 7.438-7.656(m, 3H), 13.450(s, 2H); Elemental analysis [$C_{16}H_{18}Br_2N_2O_2$]: observed (calculated): C 44.70% (44.68%), H 4.25% (4.22%), Br 37.20% (37.15%), N 6.48% (6.51%), O 7.48% (7.44%).

2.3.2 Preparation of 2- ((2- (5-bromo-2-hydroxybenzylamino) phenylamino) methyl)-4-bromophenol [3b]

Colour: White; MS [M+]: 320.13; FTIR(KBr cm^{-1}): 3393, 3359, 3289, 3041, 2852, 1696, 1456, 1315, 1238, 1103, 1025, 929,750, 636; ^1H NMR (300 MHz, DMSO-d_6) δ: 4.236(s, 1H), 3.33 (s, 1H), 5.082(s, 4H), 6.39-6.769(m, 3H), 6.902-7.289(m, 3H), 7.489-7.902(m, 4H), 12.666(s, 2H); Elemental analysis [$C_{20}H_{18}Br_2N_2O_2$]: observed (calculated): C 50.28% (50.24%), H 3.84% (3.79%), Br 33.39% (33.42%), N 5.82% (5.86%), O 6.72% (6.69%).

2.3.3 Preparation of 2- ((2- (5-bromo-2-hydroxybenzylamino)-4-methylphenylamino) methyl)-4-bromophenol [3c]

Colour: White; MS [M+H]: 335.57; FTIR(KBr cm^{-1}): 3390, 3359, 3278, 2852, 1696, 1455, 1305, 1251, 1110, 935,844, 800, 752; ^1H NMR (300 MHz, DMSO-d_6) δ: 2.316(s, 3H), 4.146(s, 2H), 5.102(s, 4H), 7.056-7.282(m, 3H), 7.363-7.643(m, 3H), 7.813-8.146(m, 3H), 15.122(s, 1H), 15.649(s, 1H); Elemental analysis [$C_{21}H_{20}Br_2N_2O_2$]: observed (calculated): C 51.30% (51.24%), H 4.08% (4.10%), Br 32.50% (32.47%), N 5.63% (5.69%), O 6.45% (6.50%).

2.4 Method for preparation of metal complexes:

Dissolve Schiff base (0.050 mmol) in 10.0 ml of methanol in round bottom flask fitted with reflux condenser and $CaCl_2$ guard tube. Corresponding metal salt ($CuCl_2$, $NiCl_2$, $CoCl_2$, $ZnCl_2$) (0.050 mmol) was added and stirred the reaction mixture, lastly Potassium hydroxide (0.050 mmol) in methanol was added and reaction mixture was refluxed for 3-5 hours in water bath. Cooled properly and filter it. The solid separated and dried in oven.

Table 2: Structures of metal complexes of schiff bases [4a-4l]

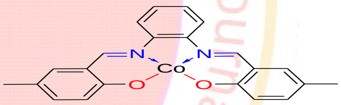
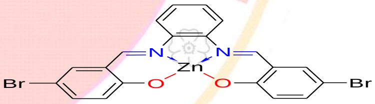
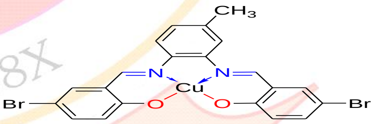
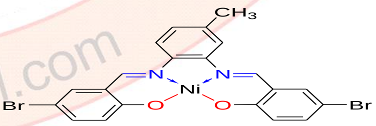
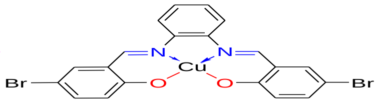
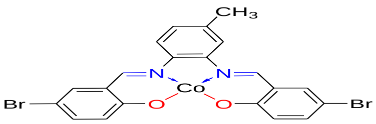
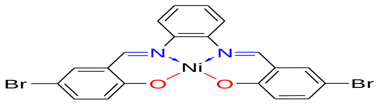
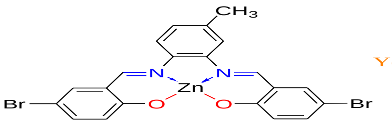
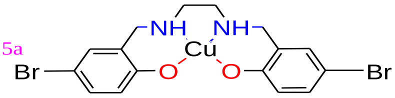
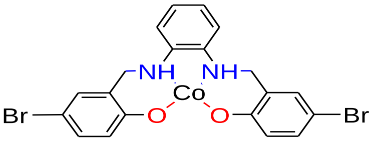
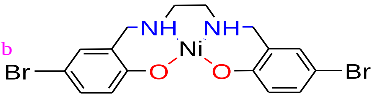
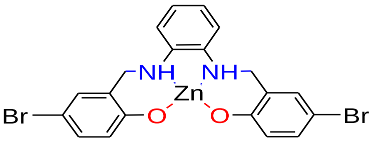
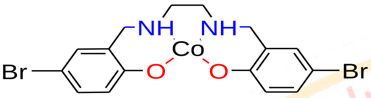
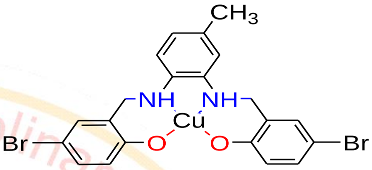
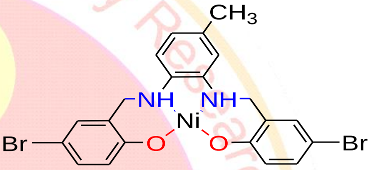
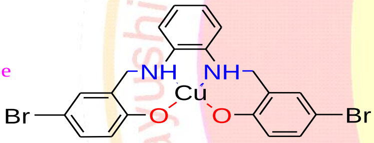
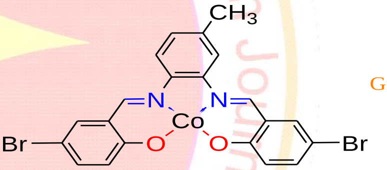
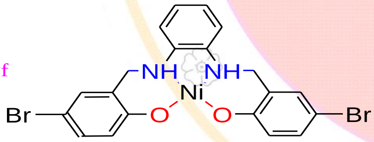
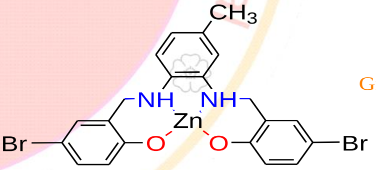
Entry	Complex	Colour	Entry	Complex	Colour
4a		Green	4g		Grey
4b		Shiny Red	4h		Yellow
4c		Grey	4i		Green
4d		Yellow	4j		Red
4e		Green	4k		Grey
4f		Shiny Red	4l		Yellow

Table 3: Structures of metal complexes of reduced schiff bases [5a-5l]

Entry	Complex	Colour	Entry	Complex	Colour
5a		Grey	5g		Grey
5b		Brown	5h		Grey
5c		Grey	5i		Grey
5d		Grey	5j		Brown
5e		Grey	5k		Grey
5f		Brown	5l		Grey

3. Results and Discussion

3.1 Chemistry

The target transition metal complexes (**4a-4l** and **5a-5l**) were synthesized as depicted in Fig.1. The primary step involves the synthesis of Schiff base derivatives by condensation of 5-bromo-2-hydroxybenzaldehyde with diamines **1a-1c** in warming ethanol at 70^0 C afforded schiff bases **2a-2c**. On treatment with sodium borohydride, imine bond undergo reduction yield reduced schiff base ligands **3a-3c**. Elemental analyses and spectral data (FT-IR, ^{1}H and MS, UV-Visible and Fluorescence) confirmed the structure of the synthesized products. The FTIR spectrum of Schiff bases **2a-2c** showed strong absorption bands at 1614-1635 cm^{-1} because of imine (-HC=N-) function, which disappears in the IR spectra of reduced schiff bases **3a-3c** confirms the reduction of schiff bases **2a-2c**. FTIR spectra of reduced schiff base ligands **3a-3c** showed broad peak within the region 3390-3394 cm^{-1} and 3359 cm^{-1} due to amino (-NH-) and hydroxyl group radical, respectively. The ^{1}H-NMR band of Schiff bases **2a-2c** shows expected aromatic signals, three singlets at δ 8.91 and 12.95 ppm are assignable to the azomethine proton (-CH=N-) and hydroxyl proton (-OH), respectively. The new singlets at δ 4.2 and 4.9 due to –CH_2- and –NH- group, respectively confirms the formation of reduced schiff bases **3a-3c**. Similarly, the mass spectrum of schiff bases exposed molecular ion peak confirming corresponding relative molecular mass of target compounds.

The Schiff bases **2a-2c** and reduced Schiff base ligands **3a-3c** were refluxed with appropriate transition metal chlorides in methanol with molar ratio 1:1 offer metal complexes **4a-4l** and **5a-5l** respectively. Due to water of crystallization, all metal complexes show broad peak in the region of 3330-3517 cm^{-1}. The coordination mode of hydrazones with central metal ion can be explained on the basis of FTIR spectral study. The region of the spectrum bands with low frequency showed the existence of two new medium intensity bands at about 443-485 cm^{-1} because of υM–O vibrations. The IR spectrums of metal complexes shows prominent band at nearby 501-620 cm^{-1} because of υM–N stretching. Elemental study of the metal complexes is in decent agreement with the theoretical values as shown in Table 4.

Table 4: Molar conductance (Λm) and % content of metal in complexes

Complex	Metal	% Metal Observed (Calculated)	Molar conductance Λm (Ω^{-1} mol^{-1} cm^2)
4a	Cu	17.80(17.76)	11.12
4b	Ni	12.13(12.16)	9.90
4c	Co	12.25(12.20)	8.73
4d	Zn	13.30(13.26)	7.30
4e	Cu	11.88(11.86)	11.32
4f	Ni	11.10(11.06)	10.01
4g	Co	14.73(14.68)	9.87
4h	Zn	12.20(12.17)	10.21
4i	Cu	11.60(11.56)	11.72
4j	Ni	10.84(10.77)	10.29
4k	Co	10.86(10.81)	9.83
4l	Zn	11.90(11.86)	6.40
5a	Cu	14.93(14.89)	11.33
5b	Ni	12.10(12.06)	10.40
5c	Co	12.14(12.10)	10.10
5d	Zn	13.30(13.25)	6.80
5e	Cu	11.81(11.77)	11.24
5f	Ni	11.04(10.97)	10.81
5g	Co	11.06(11.01)	9.10
5h	Zn	12.12(12.07)	7.30
5i	Cu	11.50(11.48)	10.96
5j	Ni	10.74(10.69)	11.40
5k	Co	10.88(10.81)	9.56
5l	Zn	11.83(11.77)	7.11

From the relation Λm= K/C the molar conductance of the metal complexes (Λm) can be calculated by dissolving in a proper solvent where C; molar concentration of the metal complex solutions. The metal complexes were dissolved in DMF to make 10^{-3} M of their solutions. The molar conductivities were measured at 25±2^{0}C. The study show negligible molar conductance values as shown in table 4, indicating that the complexes are non-electrolytes. The thermal behaviour of the metal complex **5d** was studied in temperature range of 25^0–1000^0 C. In the first stage, weight loss below 100^0 C corresponds to the presence of the lattice cell water in the complexes. Second step involves weight loss in the temperature range 110^0–200^0 C is due to elimination of coordinated water. A plateau was observed above 600^0 C corresponds to the formation of stable zinc oxide.

3.2 Fluorescence Study:

The UV-Visible spectra of the ligands **2a-2c** and **3a-3c** exhibit bands around 332-336 nm and 302-307 nm respectively as represented in Fig.2. The broad, intense band about 310 nm in the ligands **2a-2c** will be allocated to intra ligand $n–\pi^*$ transition related to azomethine which is not observed for ligands **3a-3c**. The bands at around 298-370 nm are attributed to the ligand to metal charge transfer transitions Fig. 2 and Fig. 3

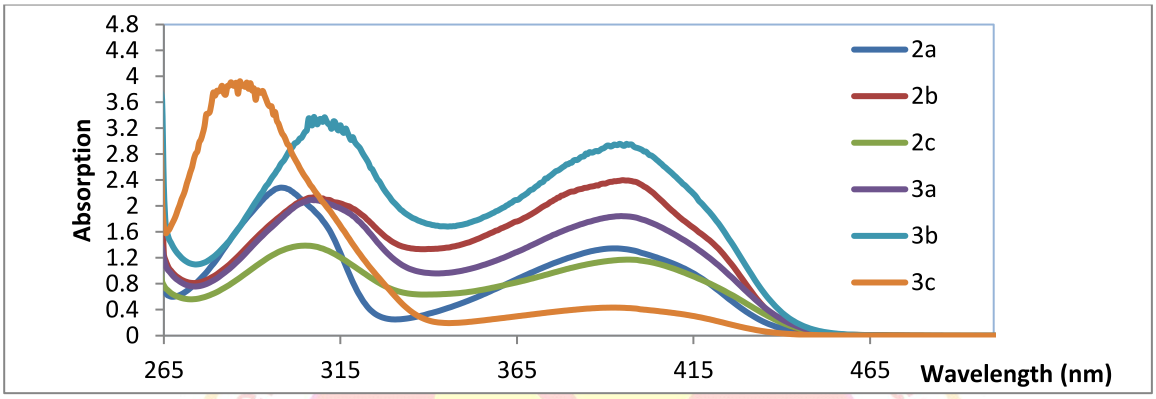


Figure 2.: Absorption spectra of [2a-3c]

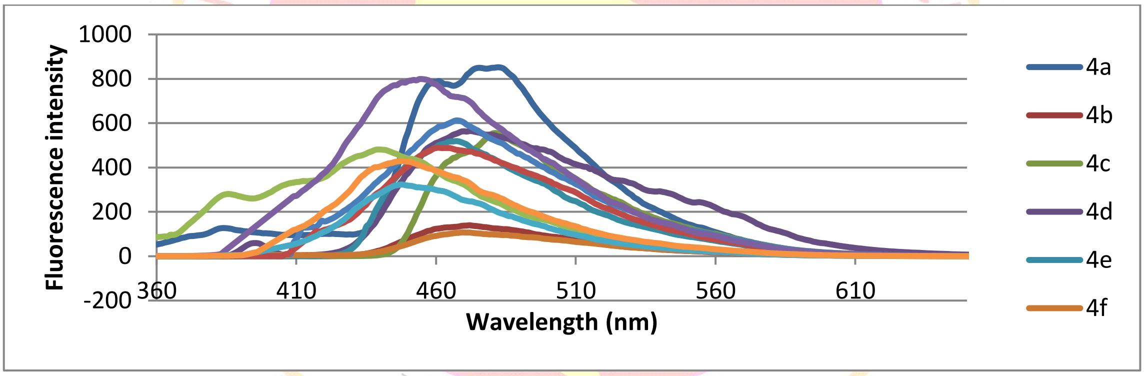


Figure 3: Fluorescence spectra of [4a-4j]

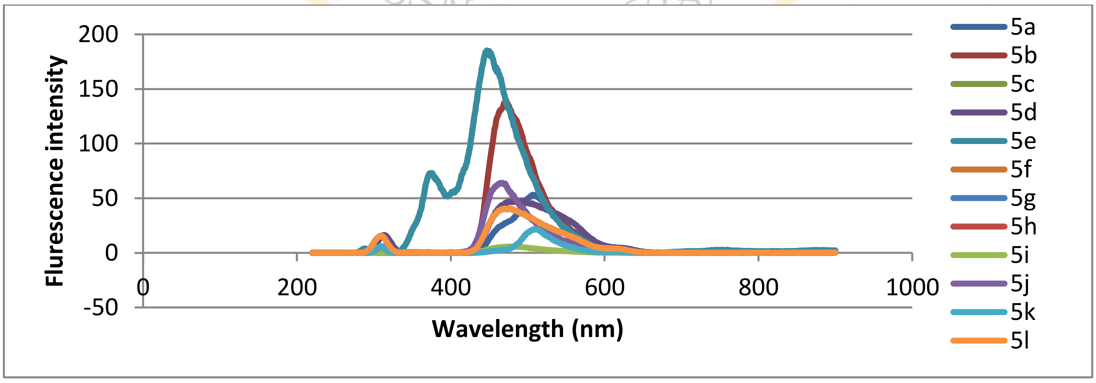


Figure 4: Fluorescence spectra of [5a-5j]

Table 5: The absorption and emission wavelength with intensity

Hydrazone	Absorption λ_{max} (Intensity)	Emission λ_{max} (Intensity)	Complex	Absorption λ_{max} (Intensity)	Emission λ_{max} (Intensity)
2a	298.5(2.283)	465(10.246)	**3a**	306.5(2.095)	474(0.707)
4a	374(0.612)	482(851.903)	**5a**	409(1.497)	507(53.099)
4b	385(0.816)	472(139.596)	**5b**	335(1.876)	472(139.596)
4c	385(0.568)	481(555.314)	**5c**	407(2.537)	376(72.878)
4d	405(0.876)	472(564.264)	**5d**	338(2.389)	491(47.356)
2b	395(2.399)	457(0.908)	**3b**	310.5(3.369)	464(3.099)
2c	305(1.389)	473(28.752)	**5e**	395(1.271)	447(185.159)
4e	386(1.289)	467(518.879)	**5f**	371(1.748)	508(21.638)
4f	335(0.734)	470(107.357)	**5g**	372(0.451)	471(40.571)
4g	393(0.755)	468(611.762)	**5h**	369(0.337)	467(64.001)
4h	395(1.157)	461(489.323)	**5i**	355(0.37)	472(5.671)
4i	328(0.616)	439(481.095)	**5j**	356(0.502)	467(64.001)
4j	322(1.434)	454(798.558)	**5k**	367(0.154)	508(21.638)
4k	332(1.346)	448(323.122)	**5l**	409(0.146)	471(40.571)
4l	333(1.078)	447(428.71)	**3c**	286.5(3.922)	455(67.21)

The emission spectra of ligands **2a-2c** Fig. 2 showed the emission band in the range of 461-463 nm while ligands **3a-3c** showed strong emission at 360 nm. The complexes 4a-4l Fig. 3 Table 5 showed emission band in the range of 378-516 nm. The complexes **5a-5l.** Fig. 3, Table 5.

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