

Synthesis, Characterization and Luminescence Studies of Metal-Diimine Complexes

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Abstract

Metal complexes have attracted great interest due to their potential application as luminescent materials in organic light emitting diodes (OLED) in the present technological displays. Through systematic study on the variation of ligands, structural and bonding modes of different metal centers, the structure-property relationships of the various classes of luminescent transition metal complexes can be obtained. The present research reports the synthesis and luminescence studies of some metal-diimine complexes. A diimine ligand namely N,N'-bis-(salicylidene)-4,4'-diaminodiphenylether (3a) was prepared through enamination reaction between diaminodiphenylether with salicylaldehyde in a 1:2 molar ratio. Subsequently, the corresponding Zn(II) (4a) and Cd(II) (4b) complexes were prepared in the presence of base according to a stoichiometric ratio of metal:ligand:NaOH=1:1:2. The synthesized ligand and all the complexes were characterized by CHN elemental analysis, ¹H and ¹³C NMR, UV-Vis and FTIR spectroscopic data and molar conductivity measurements. The spectroscopic data suggested that the ligands acted as N₂O₂-tetradentate, coordinating to the metal atom through both the azomethine N atoms and hydroxyl O atoms. The fluorescence properties of the synthesized metal complexes were investigated. The metal-diimine complexes displayed emission bands centered in the range of 465-490 nm with higher luminescence intensity due to ligand metal-metal charge transfer transitions (LMCT). The relatively large Stoke's shift observed probably indicates that the energy absorbed by the organic ligands was transferred efficiently to the metal ions and merits them to be used as promising emitters in OLED.

Keywords: Diimines; Electroluminescent materials; OLED's; Binuclear complexes

Introduction

Electroluminescent materials have attracted wide attention because of its superiority as emitting materials in latest flat panel displays. In general, there are three different types of electroluminescent materials depending on their structural designs as organic dyes, metal complexes and polymers. Chelated metal complexes which are characteristically heat resistant that resultantly enhance its utility in OLED design as well as their solubility has made them advantageous as it can be fabricated in the form of a layer after solvent evaporation [1,2].

It is well known that Schiff bases are important compounds not only because of their wide range of biological activities but also as being ligands in complexation with the transition metals. The chelate formation capability of the Schiff base ligands and their different coordination modes with different metal centers through nitrogen atoms of the imine group and other groups attached to the carbonyl compounds such as oxygen atoms have turned them vital in the field of coordination chemistry [3].

These transition metal Schiff base complexes display diverse structural features and, in some instances, exhibit interesting properties namely, anti-bacterial, anti-cancerous, anti-tumorous, analytical reagents, catalytic and luminescent materials [4-6]. Schiff base ligands namely, diimines are able to act as good chelating ligands because of the presence of multiple binding sites which may enhance

the luminescence behaviour upon coordinating to two metal ions forming binuclear complexes which exhibit high luminescence behaviour [7,8].

However, reports on the luminescent properties of binuclear Schiff base metal complexes are still rare and limited. The studies on binuclear metal complexes in which two metal centres are held in close proximity have attracted considerable interest in metal-metal interaction, spectroscopic properties and luminescence behaviour. These types of complexes still continue to play a very important role in our understanding of various aspects of coordination chemistry of metals.

In our attempt to evaluate the luminescence behaviour of binuclear metal complexes, diimine ligand containing a N₂O₂ donor sets and their transition metal complexes of Zn(II) and Cd(II) metal ions were chosen. The diimine ligand synthesized in this study contains a diaminodiphenylether backbone. Coordination of such type of conjugated Schiff base ligands with metals increases the rigidity of ligands, which subsequently will reduce the loss of energy via vibrational motions that will subsequently help in improved emission intensity. In addition, the unshared electron pair of nitrogen atoms in the diimines will eventually play a certain role in increasing the luminescence intensity due to the formation of covalent bonds between metal ions and oxygen atoms through π donation of lone pair of electrons on oxygen atoms to the metal ions thus reducing the energy gap between π^* to π orbitals.

Materials and Methods

Materials and physical measurements

All chemicals were purchased commercially either from Sigma-Aldrich, Merck or Fluka and were used as received without further purifications. Commercial grade solvents used in the preparation of the ligands and metal complexes were distilled according to standard procedures and dried over molecular sieves before used. All glasswares were thoroughly washed with deionised water and were dried overnight in an oven. All the reactions were carried out in an inert atmosphere of dry nitrogen using degassed solvents. All solid products formed were collected using vacuum filtration and were dried in a desiccator under vacuum before characterization.

All the products were characterised by melting point determination, CHN elemental analysis, Fourier Transform Infrared (FTIR) spectroscopy, ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy, Ultraviolet-Visible (Uv-Vis) spectroscopy and molar conductivity measurements. The melting point of all solid products were determined using an Electrothermal Digital Melting Point apparatus and are not corrected. The CHN elemental analysis for the synthesized samples was determined using Thermo Finnigan EA 1112 series CHN analyzer. FTIR spectra of the synthesized products were recorded as KBr disc using a Perkin Elmer Spectrum One spectrometer at spectral range of 4000 cm^{-1} to 400 cm^{-1} . Solution state Uv-Vis spectra of the samples were recorded on a Shimadzu 1601 spectrophotometer using a quartz cell of 10 mm path length in the wavelength range of 200-800 nm. ^1H and ^{13}C NMR spectra of the products were recorded on a Bruker Advance 400 MHz spectrometer using TMS as an internal standard. The NMR samples were dissolved in d_6 -acetone, CDCl_3 or d_6 -DMSO. All chemical shifts are reported in ppm relative to TMS. The molar conductivity for the complexes in DMF solution was recorded on a Mettler Toledo FG3/EL3.

Synthesis of ligand N,N'-bis-(salicylidene)-4,4'-diaminodiphenylether (3a)

N,N'-bis-(salicylidene)-4,4'-diaminodiphenylether (3a) was prepared by reacting diaminodiphenylether (3.2) with two moles equivalent of salicylaldehyde (3.1) (Figure 1). 1.043 mL of salicylaldehyde ($\rho=1.17$; 10 mmol) was added slowly to a solution of diaminodiphenylether (3.2) (1 g; 5 mmol) in ethanol (30 mL). The mixture was stirred and heated under reflux condition in nitrogen atmosphere for 2 hours. The microcrystalline golden yellow precipitates formed was filtered off, washed with cold ethanol and finally recrystallized from ethanol. Yield:92%. Melting point: 210-213°C. CHN elemental analysis (%): Experimental: C, 76.38; H, 4.89; N, 6.83. Calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3$ requires: C, 76.39; H, 4.89; N, 6.85.

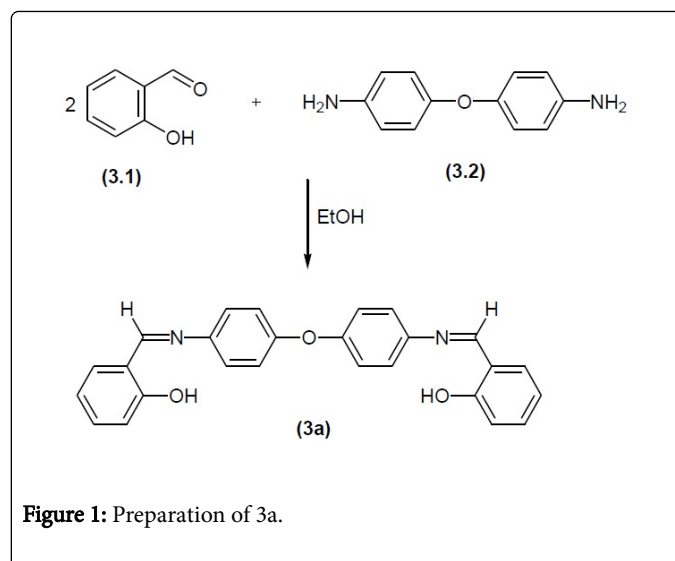


Figure 1: Preparation of 3a.

Synthesis of binuclear transition metal-diimine complexes

Synthesis of N,N'-bis-(salicylidene)-4,4'-diaminodiphenylether zinc(II) complex (4a): Complex (4a) was prepared by dissolving ligand (3a) (0.408 g; 1 mmol) in 10 mL of degassed ethanol on heating in the presence of 2 mmol ethanolic NaOH (4 mL, 0.5 M) in a three necked round bottomed flask. Zinc(II) chloride hydrate (0.136 g; 1 mmol) dissolved separately in ethanol (10 mL) was then added to the ligand solution. The Metal: Ligand: NaOH molar ratio was 1:1:2. The reaction mixture was subsequently stirred and refluxed under nitrogen for 3 hours after which a solid yellowish green solid which had formed was filtered, washed several times with cold ethanol and dried in an oven (Figure 2). Yield: 80%. Melting point: 260°C (decomposed).

Synthesis of N,N'-bis-(salicylidene)-4,4'-diaminodiphenylether cadmium(II) complex (4b): Complex (4b) was prepared by dissolving ligand (3a) (0.408 g; 1 mmol) in 10 mL of degassed ethanol on heating in the presence of 2 mmol ethanolic NaOH (4 mL, 0.5 M) in a three necked round bottomed flask. Cadmium(II) chloride hydrate (0.201 g; 1 mmol) dissolved separately in ethanol (10 mL) was then added to the ligand solution. The Metal: Ligand: NaOH molar ratio was 1:1:2. The reaction mixture was subsequently stirred and refluxed under nitrogen for 6 hours. The yellow coloured solid formed was filtered, washed several times with cold ethanol, recrystallized from chloroform and dried in an oven (Figure 2). Yield: 50%. Melting point: 280°C (decomposed).

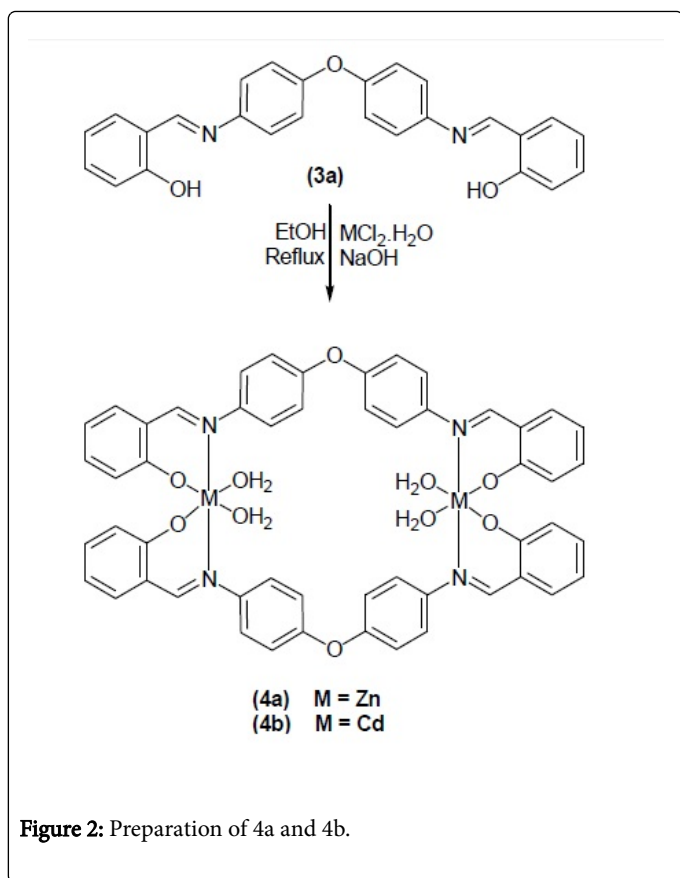


Figure 2: Preparation of 4a and 4b.

Results and Discussion

Uv-Vis spectroscopy

The Uv-Vis absorption spectra of the investigated ligand (3a) and their metal-diimine complexes were carried out in DCM solvent at room temperature. The numerical values of the maximum absorption wavelength (λ_{\max}) and the molar absorptivity (ϵ) for the ligand and their relevant metal-diimine complexes is shown in Table 1, respectively. The spectra are presented in Figure 3.

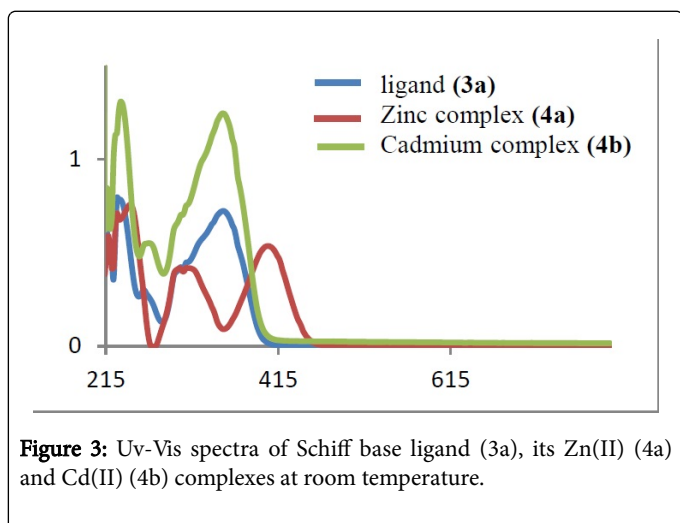


Figure 3: Uv-Vis spectra of Schiff base ligand (3a), its Zn(II) (4a) and Cd(II) (4b) complexes at room temperature.

Compounds	λ_{\max}	Band assignment	ϵ (M ⁻¹ cm ⁻¹)
3a	216 (s)	$\pi - \pi^*$	16000
	258 (w)	$\pi - \pi^*$	6000
	344 (s)	n - π^*	14000
4a	244	$\pi - \pi^*$	14000
	308	$\pi - \pi^*$	8000
	405	n - π^*	10700
4b	232	$\pi - \pi^*$	11960
	266	$\pi - \pi^*$	11000
	350	n - π^*	24860

Table 1: Uv-Vis spectral data of ligand (3a) and their corresponding Zn(II) (4a), Cd(II) (4b) complexes.

The absorption spectrum of the ligand shows three absorption bands appears at the range of λ_{\max} 216-344 nm. The band appearing at low energy side at 344 nm in the ligand (3a) is attributable to n- π^* transitions of conjugation between the lone pair of electrons of p orbital of N-atom in C=N group and a conjugated π bond of phenyl rings. The two bands appearing at higher energy 216 and 258 nm arise from $\pi-\pi^*$ transitions within the phenyl and $\pi-\pi^*$ transitions of the C=N group [9].

In case of complexes (4a) and (4b) these broad and strong n- π^* transitions of the azomethine group has shifted to a longer wavelength compared to the free ligand. This shifting towards a longer wavelength probably suggesting the coordination and the formation of a larger conjugated chelate ring in the complexes. These complexes (4a), (4b) showed a shift from 344 in the free ligand (3a) to 405, 350 nm. Similar observations have been documented by Yang et al. and Naemi and Moradian reporting that the main n- π^* absorption bands in the free ligands had shifted to lower energy upon complexation [7,10].

FTIR analysis

The main absorption bands of ligand (3a) and their corresponding Zn(II) (4a) and Cd(II) (4b) complexes are presented in Table 2.

Compounds	n(C=N) (s)	n(OH) (b)	n(H ₂ O) (b)	nM-O (m)	n(Ph-O) (m)
3a	1620	3446	-	-	1363
4a	1610	-	3441	523	1386
4b	1608	-	3458	644	1385

Table 2: Main infrared spectral data for ligand (3a) and their corresponding Zn(II) (4a) and Cd(II) (4b) complexes. s=strong, m=medium, b=broad.

The ligand and the complexes were characterized mainly by the appearance of azomethine (C=N) and Ar-OH vibrational bands as shown in Figure 4. The strong and sharp band at 1620 cm⁻¹ is a characteristic of azomethine C=N stretching frequency in free ligand [11]. The frequency lowering to 1608-1610 cm⁻¹ in their respective complexes probably suggest the coordination of C=N group through the involvement of nitrogen lone pair of electrons to the metal centre.

As a result, the contribution of C=N stretching has been reduced as the electron pairs on the nitrogen atoms are involved in bond formation with the metal ion. Such values are in agreement with other similar metal imine complexes [12-14]. The IR spectra of the ligand also exhibited certain bands at 3446 cm^{-1} which could be assigned to the hydroxyl -OH stretching. In the spectra of complexes, the broad bands between 3341-3458 cm^{-1} may be attributed to the presence of coordinated water molecules [15,16]. The presence of coordinated water may be further supported by the appearance of band in the range of 750-756 cm^{-1} that could be assigned to the O-H bending vibrations.

The observed values are consistent with literature values reported by [17]. In the spectra of the ligand, bands at 1363 cm^{-1} can be assigned to phenolic (C-O) vibrations. In metal complexes spectra, these bands are displaced to a higher frequency compared to ligand i.e., 1363 cm^{-1} (lower) in free ligand while 1385-1386 cm^{-1} (higher) in their respective complexes. In the complexes the appearance of vibrational bands in the range of 523-644 cm^{-1} can be attributed to the $\nu\text{M-O}$ stretching modes, which further supports that the oxygen atoms of the hydroxyl group are bonded to the metal.

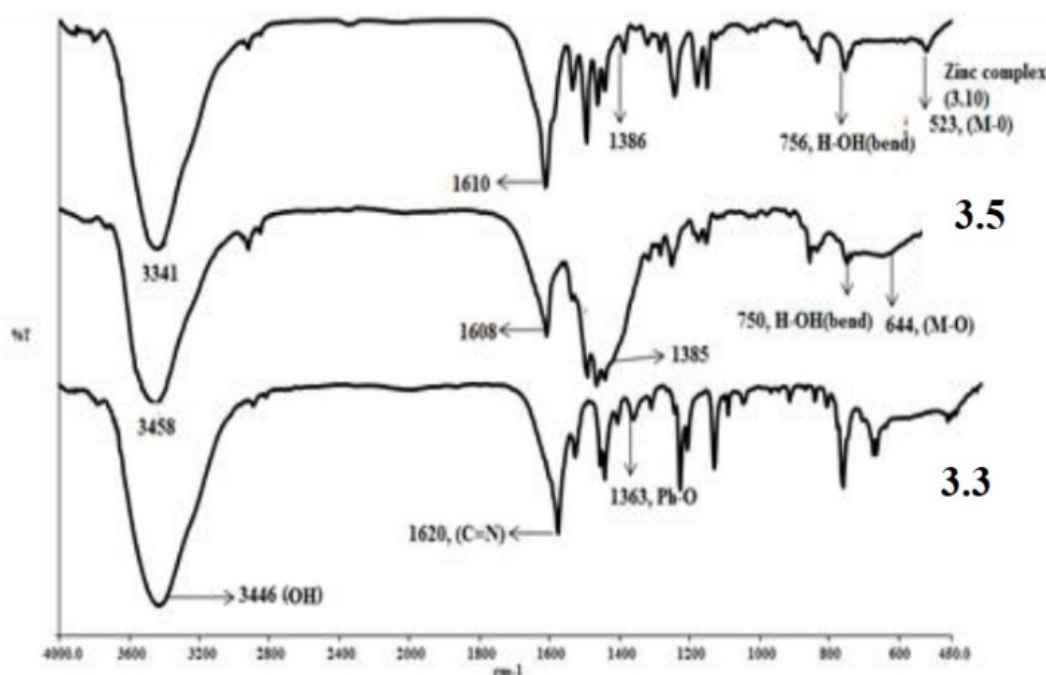


Figure 4: FTIR spectra of ligand (3a) and zinc (4a) and cadmium (4b) complexes.

Molar conductivity measurements

The molar conductivity measurements of Zn(II) and Cd(II) complexes in DMF solutions with Λ_m values for Zn(II) and Cd(II) complexes in the range of 38-40 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ reveals that the complexes are nonionic in nature as well as nonelectrolytes.

NMR spectroscopic studies

^1H NMR spectroscopy: Table 3 listed the ^1H NMR chemical shifts for diimine ligand (3a) and their corresponding Zn(II) (4a) and Cd(II) (4b) metal complexes. The NMR spectra of the ligand and the metal complexes are given in Figure 5. As observed in the ^1H NMR spectra of the ligand (3a) the resonance of the aromatic hydroxyl proton (Ar-OH) appeared as a singlet peak at downfield region in the range of δ 13.11 ppm. Meanwhile, the azomethine (HC=N) proton of the ligand also resonated as singlet and appeared in the range of 8.98 ppm, which is in agreement with other similar type of imine ligands [15,18]. Meanwhile, the ^1H NMR spectra of the Zn(II) and Cd(II) complexes showed upfield shift in the azomethine (HC=N) proton chemical shift as

compared to the free ligand. The shift may be attributed to the effect of the metal ion on the HC=N electron clouds upon its coordination with the nitrogen lone pair of electrons. In addition, the signal of hydroxyl proton (Ar-OH) is absent in the spectra of the metal complexes suggesting that deprotonation of the hydroxyl group had occurred and subsequently coordinated to the metal ion via the hydroxyl oxygen atoms.

Compounds	(2H, OH)	(2H, C=N)	Ar-CH ₃	C-CH ₃	Solvent
3a	13.28	8.98	-	-	d6-DMSO
3a	13.28	8.66	-	-	CDCl ₃
4a	-	8.29	-	-	CDCl ₃
4b	-	8.64	-	-	d6-DMSO

Table 3: ^1H NMR of ligand (3a) and their corresponding Zn(II) (4a) and Cd(II) (4b) complexes.

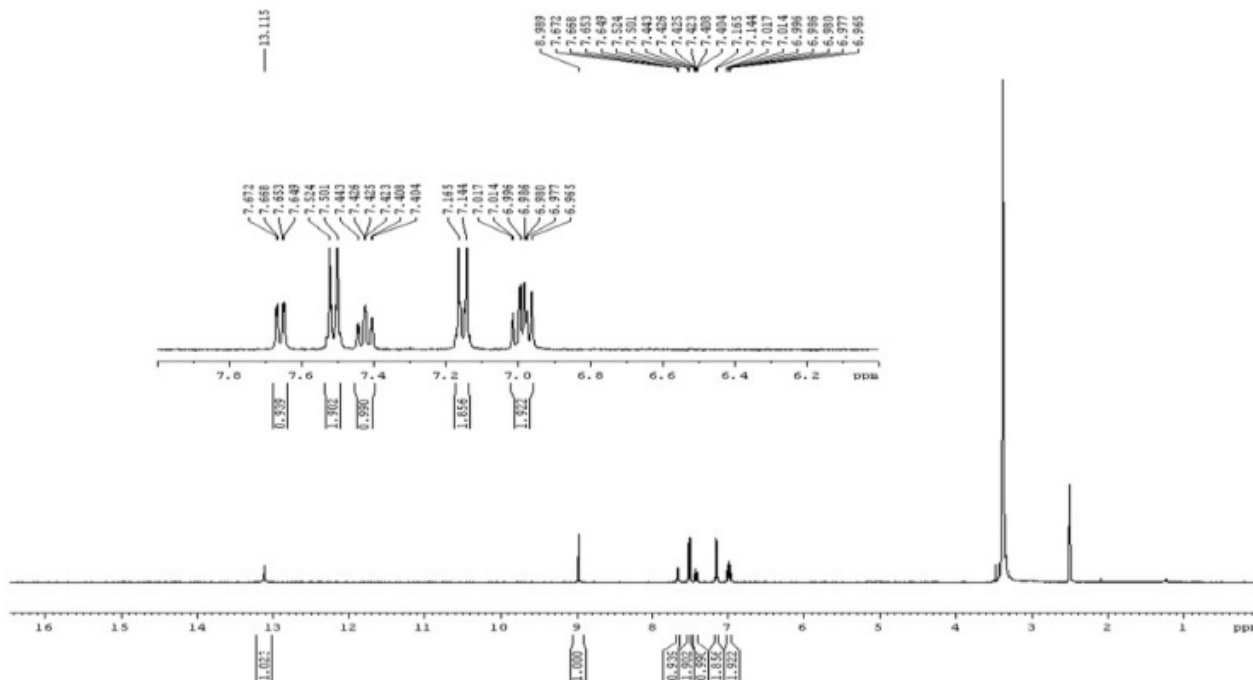


Figure 5: NMR spectra of the ligand and the metal complexes.

¹³C NMR spectroscopy: The main ¹³C chemical shifts as exhibited by the complexes spectra shows a displacement in the chemical shifts of the hydroxyl (-OH) carbon in the free ligand (3.3) appeared at towards downfield. Also, the displacement of azomethine (C=N) carbon to downfield in the complexes further affirms coordination of azomethine nitrogen and hydroxyl oxygen atoms to the metal ions [15].

Luminescence studies of diimine-transition metal complexes

The luminescent behavior of the binuclear Zinc(II) Cadmium(II) metal complexes were investigated in the solution state in dichloromethane (DCM). Figures 6 and 7 depicts the emission spectra of the Zinc(II) and Cadmium(II) complexes with ligand N,N'-bis-(salicylidene)-4,4'-diaminodiphenylether (3a). Upon excitation, Zinc complex (4a) at 405, 308 and 244 nm based on Uv-Vis absorbance, showed emission band centred at 490 nm with a Stoke's shift of 86-246 nm. Similarly, Cadmium(II) complex (4b) upon excitation at 350, 266 and 232 nm based on Uv-Vis absorbance, showed the emission band centred at 465 nm with a Stoke's shift of 113-237 nm, respectively. Both complexes showed higher luminescence intensity due to ligand metal-metal charge transfer transitions (LMMCT). The relatively large Stoke's shift probably indicates that the energy absorbed by the organic ligand was transferred efficiently to the Zinc (II) and Cadmium (II) ions.

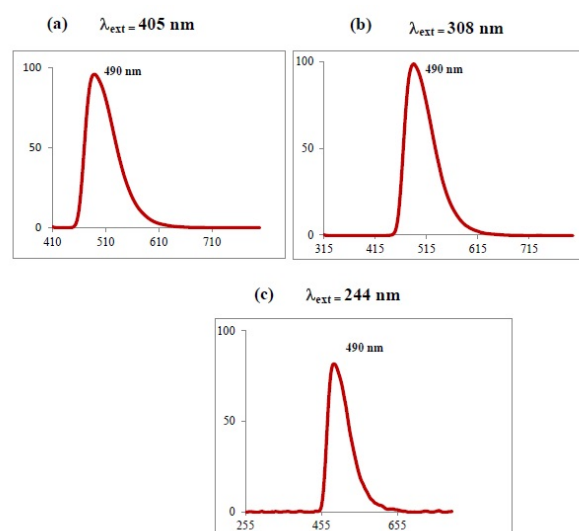


Figure 6: Solution-state emission spectrum of Zinc complex (4a) at (a) $\lambda_{\text{ext}}=405$, (b) $\lambda_{\text{ext}}=308$ and (c) $\lambda_{\text{ext}}=244$.

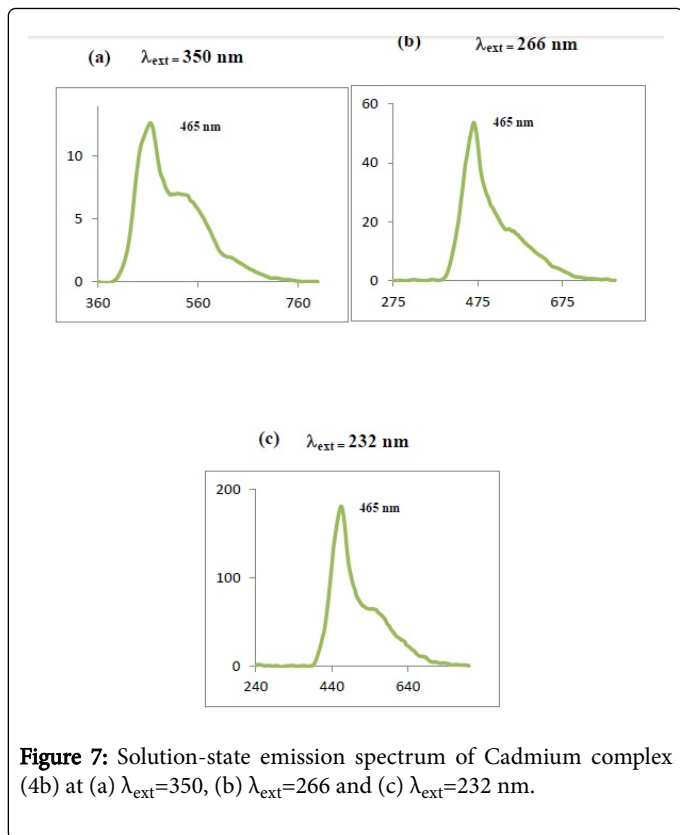


Figure 8 depicts the excitation spectra for Zinc and Cadmium complexes (4a) and (4b) at $\lambda_{\text{emi}}=490$ and 465 nm , respectively. Upon exciting the complex (4a) at 275 and 355 nm and (4b) at 411 nm , based on the λ_{ext} from the excitation spectra, depicts the emission bands centred at 490 and 486 nm for complex (4a) and 475 nm for complex (4b), respectively as shown in Figure 9.

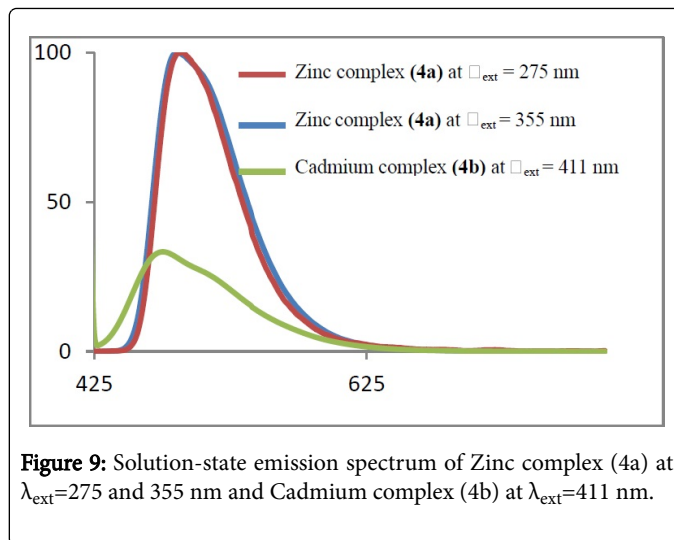
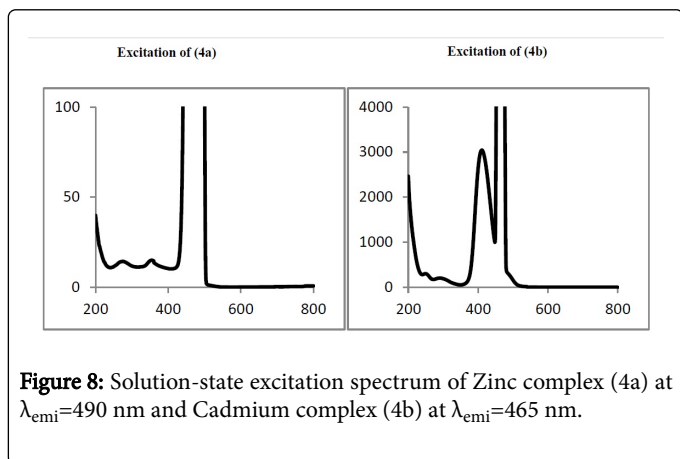
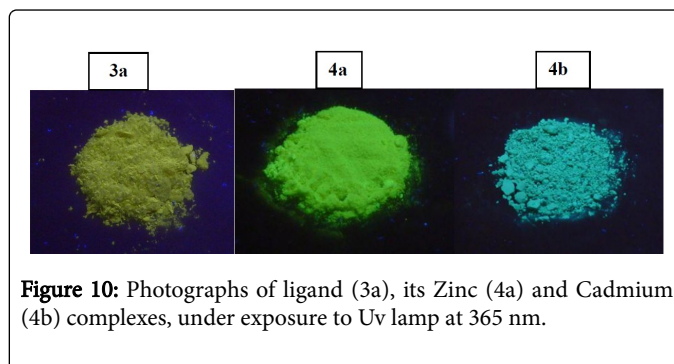


Figure 10 shows photographs of ligand (3a), its Zinc (4a) and Cadmium (4b) complexes, under exposure to Uv lamp at 365 nm whereas Figure 11 shows Photographs of ligand (3a), its Zinc (4a) and Cadmium (4b) complexes in dark under exposure to Uv lamp at 365 nm in a solution of DCM.



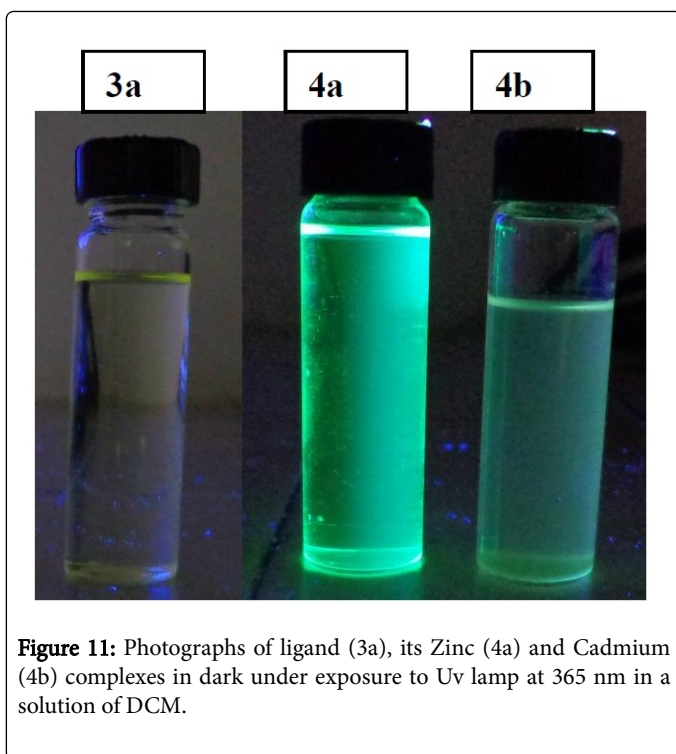


Figure 11: Photographs of ligand (3a), its Zinc (4a) and Cadmium (4b) complexes in dark under exposure to Uv lamp at 365 nm in a solution of DCM.

Conclusion

In this research we synthesized symmetrical N_2O_2 diimine (3a) and their Zn(II) and Cd(II) metal complexes displaying dinuclear structure forming the complexes through two nitrogen atoms of azomethine and two oxygen atoms of hydroxyl groups in the tetradentate manner. Metal to ligand stoichiometry in the presence of NaOH as base is 1:1:2. The luminescent analysis recommends that the large stoke's shift and enhanced luminescence intensity of the complexes enables them to be used as promising electroluminescent emitters in the OLEDs.

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