

Recent Trends in Luminescent Zn(II) and Ir(III) Complexes Bearing a Variety of Schiff Base Ligands

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Recently, there have been advancements in the field of metal complexes due to their vast utilisation in luminescence. Compared to other lower and higher transition metal complexes, there have been few studies on Zn(II) and Ir(III) azomethine complexes and their applications. However, complexes of both these metal ions manifest more potent properties and utilities than other metal ions. An overview of the recent developments in Zn(II) and Ir(III) azomethine complexes is presented, along with their applications such as luminescence. The correlation between structure, function and properties of Zn(II) and Ir(III) complexes and the prime factors that affect luminescence activities are discussed. Compared to the meticulous development of Zn(II) and Ir(III) mononuclear complexes, its dinuclear counterparts have been less researched. Finally, prospects for future studies are recommended, such as an investigation into dinuclear Zn(II) and Ir(III) azomethine metal complexes.

Key words: Zn(II); Ir(III); azomethine; luminescence

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Schiff base ligands are a dynamic group of compounds which have played a fundamental role in the arena of coordination chemistry, mostly to formulate proficient metal complexes with greater stability. The effects of various metals on the luminescence activity of such compounds and their fundamental chemical significance, such as ligands that possess multiple binding sites, have encouraged interest in the evaluation of their coordination studies [1, 2]. The evolution of new luminescent Schiff bases along with their metal complexes has captured the attention of researchers. This review is targeted at appraising the luminescent Zn(II) and Ir(III) metal complexes bearing various Schiff base ligands.

Schiff base ligands bearing azomethine groups were synthesised by the condensation reaction of primary amines and vigorous carbonyl compounds, such as aldehydes and ketones [3]. The synthesis of metal complexes with various Schiff base ligands has been promoted because of its importance as electro-luminescent materials [4].

Schiff base ligands are well known for their luminescent activities, as well as their conjugation with various transition and lanthanide metal ions. Schiff bases [5, 6] are also very special entities because of their simplicity of preparation, and their

structural diversity. The various binding sites of these ligands have made them a pivotal class of compounds in coordination chemistry [7, 8]. In addition, Schiff base complexes have the ability to form chelates, as well as various coordination types with diverse metal centres. Furthermore, Schiff base metal complexes exhibit miscellaneous structural types with interesting reactivity and photoluminescence [9]. Schiff base ligands have attracted interest due to their synthetic pliability, selectivity and sensitive nature towards various metal ions [10]. Furthermore, for various metal ions the luminescence intensity may be enhanced with conjugated structured ligands [11].

The basis for the selection of Zn(II) metal ions in this review was that Zn(II) salts were readily available, abundant and inexpensive [12, 13] modifiers of organic emitters, hence attractive to be explored along with nitrogen and oxygen donor functions [14, 15]. Owing to the stable d^{10} electronic configuration, the Zn(II) metal centre does not participate in metal to ligand charge transfer upon electronic excitation. Therefore, the complexation of an organic motif with the Zn(II) ion typically enhances intra-ligand fluorescence resulting from the consequent increased molecular rigidity [4, 16]. The binding of this metal further perturbs the intra-molecular charge transfer (ICT) that distinctly

changes the emission intensity of the complex compared to the free ligand [17].

The selection of Ir(III) metal ions was to further study and compare the luminescent properties of the lower transition metal Zn(II) ion with that of the higher transition metal Ir(III) ion. Currently, higher transition metal complexes such as iridium, ruthenium and rhodium have been noted for their dynamic role in luminescent materials due to their strong spin-orbit coupling properties [18–24]. Emission of various heavy metal complexes of Ru(II), Os(II), Eu(III), Re(I) and Ir(III) have been reported; Ir(III) metal complexes were comparatively superior to others because of their excellent emission, greater stability, tuneable emission colours (from blue to red) and higher luminescent lifetimes. The strong spin-orbit coupling property of heavy metals directly affects emission behaviour due to the effectual inter-system crossing between its corresponding singlet to triplet excited states [20].

This review will open new frontiers for the synthesis of binuclear Zn(II) and Ir(III) azomethine complexes with better and enhanced luminescence intensities, particularly in the near infrared (NIR) region.

1. Theory of Luminescence

Luminescence is the process of light emission from a substance in an electronically excited state; it is further divided into two main categories subject to the conditions of the excited state environment, namely fluorescence and phosphorescence. Luminescence can also be defined as the mechanism during which the whole or a fragment of energy is re-emitted in electromagnetic radiation from the visible or near visible region. Luminescence includes two essential steps. Firstly, electronic excitation of a material and secondly, a corresponding emission of photons. Various materials absorb different kinds of energy,

emitting some part of it as light. This is a two-stage process:

- a) The incidental energy causes electrons to be excited and move from the inner orbitals of atoms to the outer orbitals.
- b) A photon of light is emitted when the electrons in the excited state return to their original state.

The length of time between the two steps determines if fluorescence or phosphorescence occurs. The main difference is the time it takes to absorb and emit light, thus if it disappears immediately it is known as fluorescence, but if it lingers, it is considered as phosphorescence [28].

2. Fluorescence and Phosphorescence

Fluorescence is the absorption and re-emission of light with a duration of specifically 10^{-8} seconds. It fundamentally involves absorbed light emission at varying wavelengths. The process in which a fluorophore absorbs light from an external source i.e., ultraviolet light or visible light in the form of photons for excitation, in order to transfer from the ground state to an excited state is known as fluorescence. The concept is best verified by the Jablonski energy diagram as depicted in Figure 1.2 [29, 30].

The fluorophore from the excited state undergoes relaxation through several pathways, inducing fluorescence and phosphorescence. Principally, if photon emission takes place from the first excited state to the ground state (S_1-S_0), i.e., at the same spin state energy levels, it is considered as fluorescence. Whereas, if it occurs between various spin states, mainly from triplet to ground state T_1-S_0 , it is considered as phosphorescence. The consequent photon emission results when the fluorophore returns to its original state with a lower energy and extended wavelength compared to the photon of excitation [31].

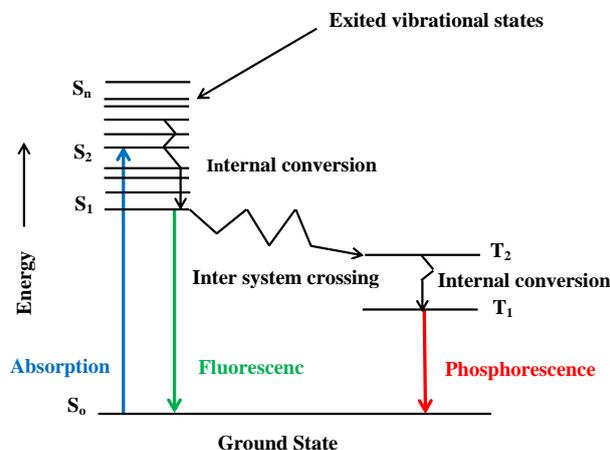


Figure 1. Jablonski energy diagram [29, 30].

Three nonradiative processes are discussed as follows:

- i. The nonradiative transition between energy levels having the same spins i.e.; internal conversion (IC).
- ii. The nonradiative transition between energy levels having different spins i.e.; intersystem crossing (ISC).
- iii. The most common nonradiative transition amongst all is vibrational relaxation. This happens faster and is stimulated by physical contact of the molecules in the excited state with other particles. Thus the energy, which is in two different forms such as vibration and rotation, can be transferred through collisions.

3. Metal Complexes as Luminescent Materials

Recently, there has been increasing research in the fields of coordination chemistry and the synthesis and design of luminescent metal complexes due to the rich demand for luminescent materials. Metal complexes display several structural and electronic features that allow their application in the field of luminescent materials. The search for new materials for organic light emitting diodes (OLEDs) is one of the major issues in current materials science. Despite the significant progress achieved in this field over the last decade, the production of thermally stable conducting materials that can be used as active layers in OLEDs remains important.

Highly specific metal complexes can be synthesised based on Schiff bases and applied as luminescent materials. Schiff base ligands are frequently used in coordination chemistry due to their significant ability to form stable complexes with metal ions. In addition, the luminescent properties of these compounds can be easily varied by changing the substituents in the ligands [40, 62, 72].

This has encouraged the authors to thoroughly study, investigate and present a review of numerous Zn and Ir complexes in order to open new frontiers in

the field of luminescence, and also to design new luminescent materials through a comparative study of optical properties of azomethine ligands with an understanding of substituent effects and the influence of structural features on emission behaviour.

4. Luminescent Zn(II) Schiff Base Metal Complexes

Lots of work and attention has been focused on the coordination compounds of Group 12 metal ions, i.e., Zn, Cd and Hg [32–35]. These metal ions with multiple binding site ligands have versatile applications [5, 16, 36], e.g., zinc (II) metal complexes can be used as promising luminescent materials and as efficient layers in OLEDs. Some of the studies discussed below have identified Zn(II) complexes as emitting materials in various electroluminescent devices. The emission of Zn(II) complexes is commonly initiated by intra-ligand transitions, unlike MLCT/LMCT excited states. This is because the zinc ion is in a stable oxidation state. The luminescence is from intra-ligand electronic transitions in the stable oxidation state [37–39]. In addition, the luminescence of Zn(II) complexes is tuneable by modifying the ligand structures.

The synthesis, characterisation and significant effects of numerous substituents as well as spacers, specifically ethylene and phenylene, on the luminescence behaviour of Zn(II) complexes as emitters, were summarised and reported [40] as shown in Figure 2. Conjugation extension using spacers caused a red shift in the emission spectra of the complexes. With the substitution of *p*-H with a *p*-tolyl group (ZnL1 vs ZnL2 or ZnL3 vs ZnL4), the emission and absorption spectra of the complex was red shifted by 20 nm. This was even more prominent with a spacer variation from ethylene to phenylene, where the emission maxima was red shifted by 60 nm (for ZnL3 vs ZnL1 as 480 nm to 540 nm; for ZnL4 vs ZnL2 as 500 nm to 565 nm). The consequent diatomic heteronuclear Zn(II)-lanthanide complexes ZnL1-ZnL4 manifested not only visible radiation but also emission relating to the Ln³⁺ ion in the NIR region.

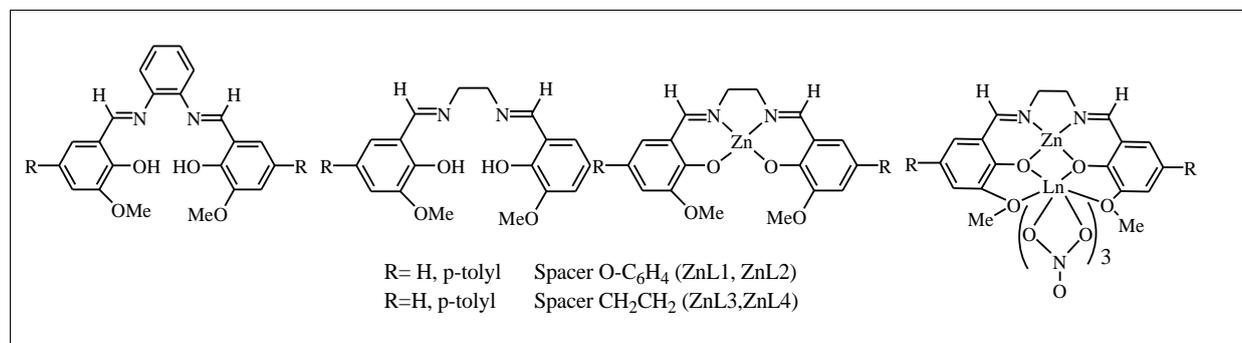


Figure 2. Schiff base Zn(II) complexes with ethylene and phenylene spacers.

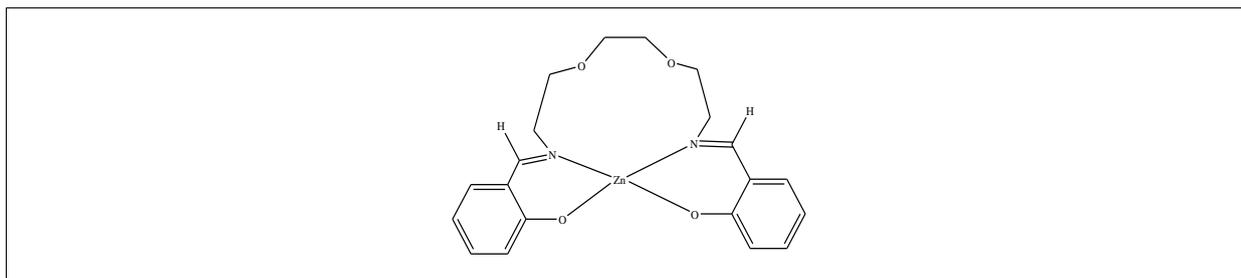


Figure 3. Mononuclear blue emissive Zn(II) complex with (N,N'-bis (salicylidene) -3,6-dioxa-1,8 diaminoctanemonehydrate).

The synthesis and characterisation of zinc complexes with Schiff base ligands namely (N,N'-bis(salicylidene)-3,6-dioxa-1,8-diaminoctanemone hydrate) was reported by another team of researchers [12], as depicted in Figure 3. A bright blue emission at 450 nm was exhibited by the complex both in the solution and solid states. This clearly demonstrated that the change of the spacer from diaminoacetonitrile to diaminoctane caused a shift in the emission from red at 620 nm to blue at 450 nm.

Chattopadhyay et al. [41] synthesised six Schiff base ligands [HL1 = 2, 6-bis[1-(2-aminoethyl) pyrrolidine-iminomethyl]- 4-methyl-phenol, HL2 = 2, 6-bis[1-(2-aminoethyl)piperidine-iminomethyl]-4-methyl-phenol, HL3 = N-{1-(2-aminoethyl)pyrrolidine}salicylideneimine, HL4 = N{1(aminoethyl)pipe ridin

salicylideneimine, HL5 = 2-benzoylpyridine-N-{1-(2-aminoethyl)pyrrolidine}, HL6 = 2-benzoylpyridine-N-{1-(2-aminoethyl)piperidine}] and their respective mononuclear and binuclear Zn(II) complexes as shown in Figure 4. A detailed analysis was carried out on the photoluminescence behaviour of the synthesised ligands and complexes. The findings established that binuclear complexes with HL1-HL2 Schiff base ligands manifested superior fluorescence activity with emissions at 450 nm and 452 nm compared to mononuclear complexes with HL3-HL4 ligands which produced emissions at 481 nm and 455 nm. Mononuclear complexes with HL5-HL6 Schiff base ligands manifested quenching upon coordination to the metal ion. The variance in luminescence behaviour may be due to differences in ligand design.

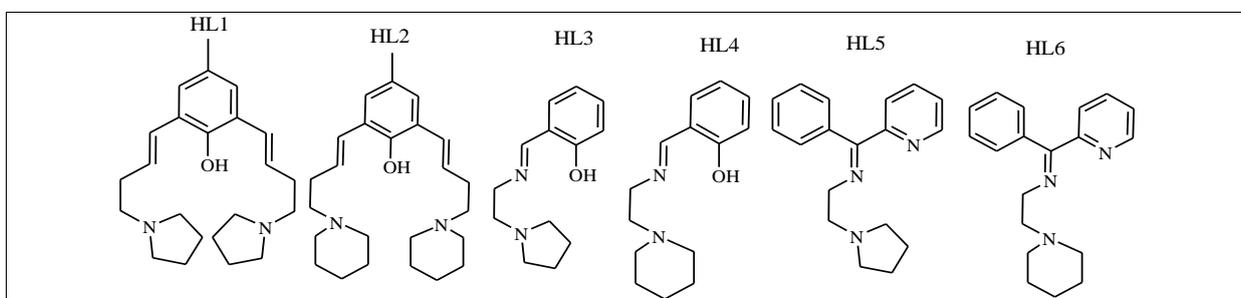


Figure 4. Mononuclear Zn(II) complexes HL3-HL6 and binuclear Zn(II) complexes HL1-HL2 with Schiff base ligands.

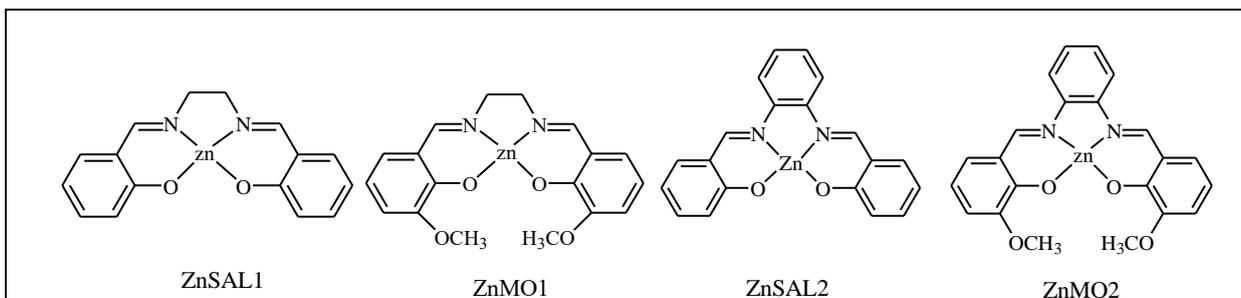


Figure 5. Mononuclear Zn(II) Schiff base complexes having ethylenediamine (ZnSAL1, ZnMO1), O-phenylenediamine spacers (ZnSAL2, ZnMO2) and derivatives of salicylaldehyde (ZnSAL1, ZnSAL2), O-vanillin (ZnMO1, ZnMO2).

The effects of various substituents in the structure of organic ligands were analysed and reported by another team of researchers [14], as shown in Figure 5. The respective Zn(II) complexes with tetradentate Schiff base ligands possessing spacers like ethylenediamine and *o*-phenylenediamine with different derivatives of salicylaldehyde (H2SAL1, H2SAL2) and *o*-vanillin (H2MO1, H2MO2) were examined thoroughly for photoluminescence spectra in bulk solids and thin films. The findings showed that the emission spectra of bulk solids of complexes (ZnSAL1 and ZnMO1) possessed a different long wavelength band relative to the corresponding thin films. Similarly, the emission spectra for complexes ZnSAL2 and ZnMO2 with *O*-phenylenediamine spacers were analogous in both the bulk solids and thin films. An analysis of the electroluminescent properties of OLEDs with ITO/NPD/ZnL/Ca:A1 was also carried out.

Synthesis of novel complexes namely, bis-(*N*-(2-hydroxybenzidene)-*p*-aminodimethyl aniline) zinc (II) (complex 3) and bis-(*N*-(2-hydroxy-1-naphthidene)-*p*-amino dimethylaniline) zinc (II) (complex 4) were reported as depicted in Figure 6. Fabrication of complexes in OLEDs was conducted. Complex 4 demonstrated a luminescence proficiency of 0.28 cd/A that exhibited red LED, whereas complex 3 showed a yellow emission [42].

Synthesis and characterisation of two metal complexes with bis tetradentate Schiff base ligands, namely 2,4-dibromo-6-((*E*)(mesitylimino)methyl phenol) and 2-((*E*)-(2,6-dipropylphenylimino) methyl) -4,6-dibromophenol) were reported [9] as shown in Figure 7. The metal complexes [Pd(L1)₂] (1) and [Zn(L2)₂] (2) possessed mononuclear cyclometallated structures bearing square and tetrahedral geometry. Both synthesised complexes exhibited solid-state photoluminescence at 508 nm and 506 nm.

Synthesis of further attractive type tetradentate Schiff base ligands L1 = *N*-(4-fluorobenzylidene)-2,6-diisopropylbenzamine and L2 = 2,4-dibromo-6-((*E*) (mesityl imino)methyl phenol) and their respective complexes [Pd₂(L1)₂Cl₂] (1) and [Zn(L2)₂] (2) were presented by Ma and his group [43] as depicted in Figure 8. Complex (1) [Pd₂(L1)₂Cl₂] possessed a meta-chloro-bridged dinuclear cyclometallated Pd(II), while in complex (2) [Zn(L2)₂], Zn(II) is tetrahedrally coordinated to two ligands L2 possessing a mono-nuclear structure. Analysis of the synthesised complexes showed luminescence in the solid-state with a high fluorescence lifetime, whereas the emission wavelength of zinc complex (2) [Zn(L2)₂] was 490 nm. These findings indicate its suitability as an electroluminescent material.

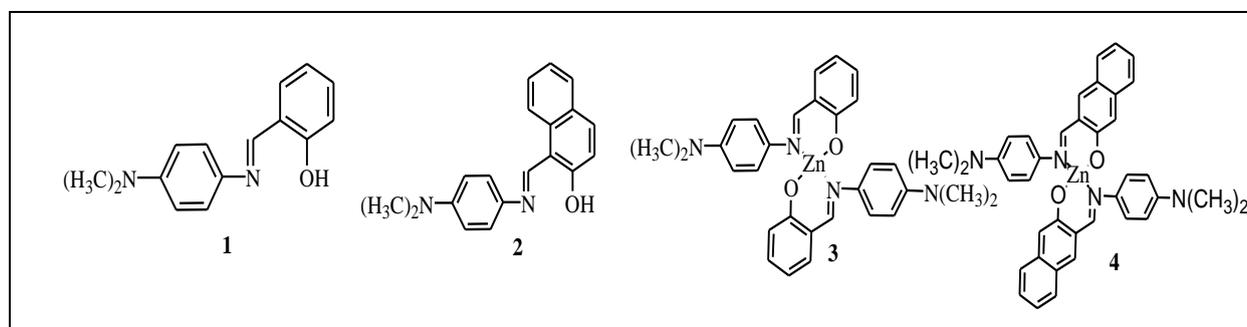


Figure 6. Mononuclear yellow emissive bis-(*N*-(2-hydroxybenzidene)-*p*-aminodimethylaniline)zinc(II) (3) and red emissive bis-(*N*-(2-hydroxy-1-naphthidene)-*p*-aminodimethylaniline)zinc(II) (4) Schiff base complexes.

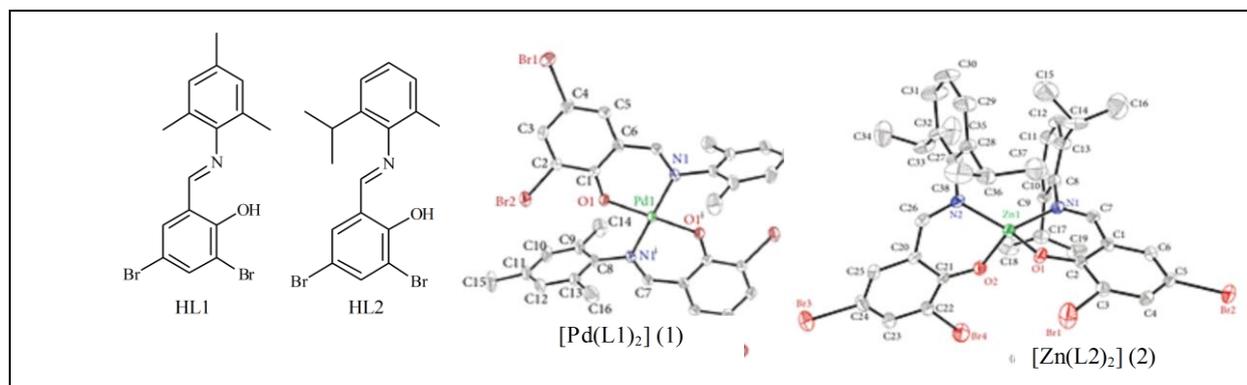


Figure 7. [Pd(L1)₂] (1) and [Zn(L2)₂] (2) mononuclear Schiff base complexes [9].

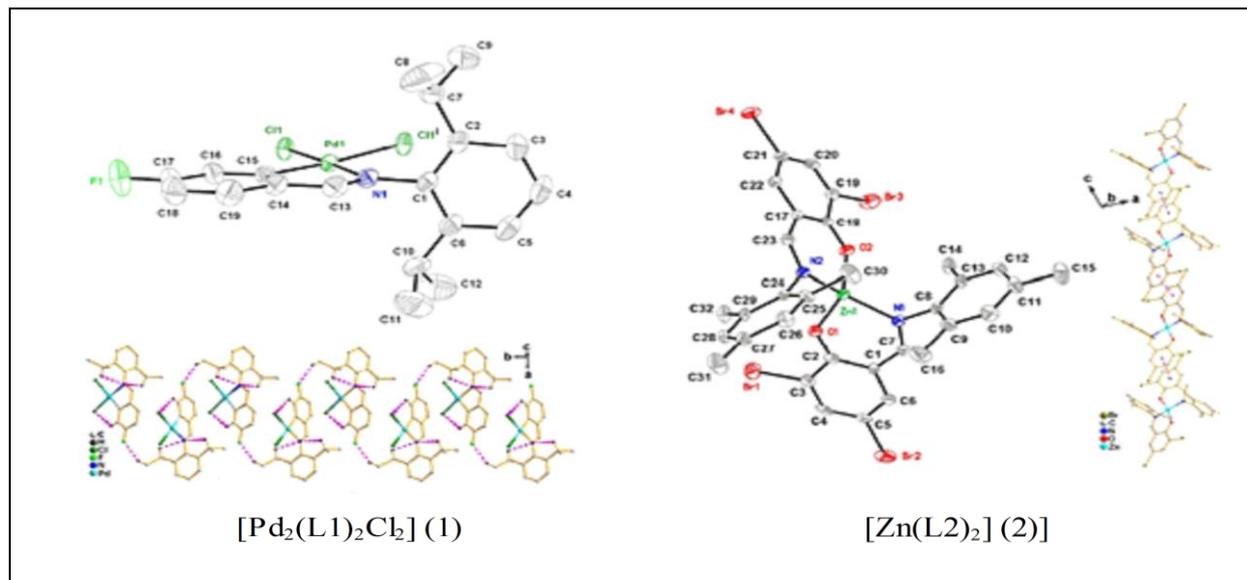


Figure 8. Dinuclear [Pd₂(L₁)₂Cl₂] (1) and mononuclear [Zn(L₂)₂] (2) Schiff base complexes [43].

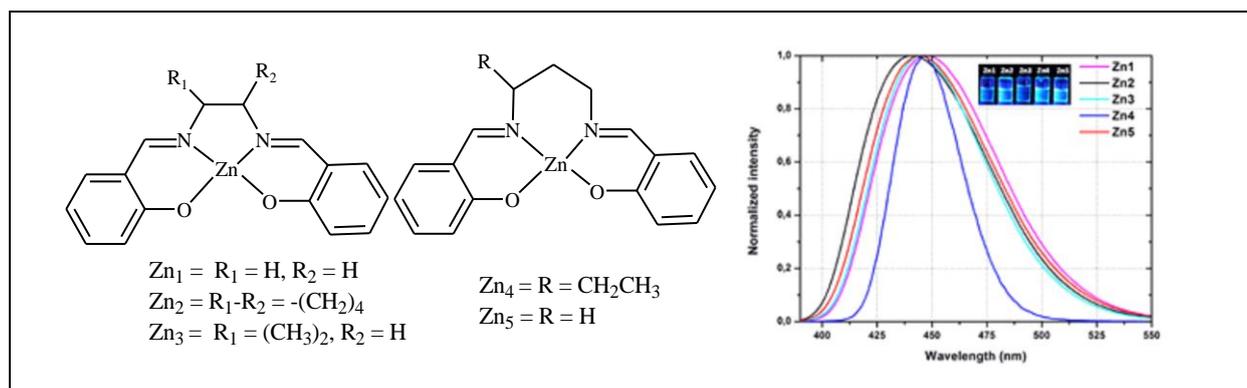


Figure 9. Structures and emission spectra of mononuclear blue emissive Zn(II) Schiff base complexes [13].

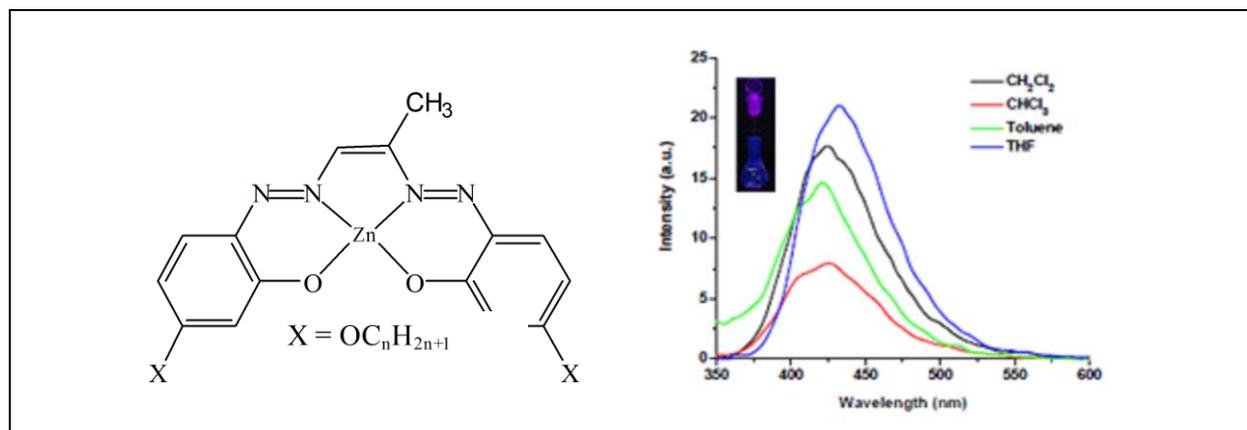


Figure 10. Blue photoluminescent [N,N'-bis-(4-n-alkoxysalicylidene)-1,2-diaminopropane] Zn(II) Schiff base complex and emission spectra of (Zn-16dap) (2×10^{-5} M) in different non-coordinating and coordinating solvents) [44].

Synthesis of five Zn(II) metal complexes (Zn_1 – Zn_5) with corresponding Schiff base ligands were reported by Dumur and his team [13] as presented in Figure 9. Additionally, the complexes were analysed for utilisation in white organic light emitting diodes (WOLED). Significantly, Zn_1 exhibited yellow OLED, a remarkable behaviour, while the rest manifested deep blue and sky-blue OLEDs. The Zn_4 complex emitting a deep blue was primarily attributed to the diamino spacer. Thermal stability of the complexes was confirmed as well. In this study the extremely promising luminescent complexes for WOLED were reported. The results revealed that colour tuneability is fundamentally subject to the design of the ligands and spacers employed.

Synthesis of a series of novel photoluminescent Zn(II)-Salen type asymmetric Schiff base complexes [ZnL], $H_2L=[N,N'$ -bis-(4-n-alkoxysalicylidene)- 1,2-diaminopropane] ($n = 12, 14$ and 16), were carried out

and reported as presented in Figure 10 [44]. An exceptionally strong blue emission was manifested by the synthesised complexes at ambient temperatures in both solid and solution states. Aggregation behaviour was observed in dilute solutions of various coordinating and non-coordinating solvents, indicating the Lewis acidity of metal ions in the synthesised complexes. More photophysical behaviour variation in the complexes was caused by asymmetric methyl substitution at the aliphatic spacer in relation to symmetric molecules possessing ethylenediamine spacers.

The synthesis and characterisation of luminescent zinc-Schiff base complexes employing organic ligands processed with various diamine spacers and salicylaldehyde were reported by Nishal and his co-workers [15], as shown in Figure 11. Strong thermal stability was demonstrated by all the synthesised metal complexes. Schiff base complexes with zinc

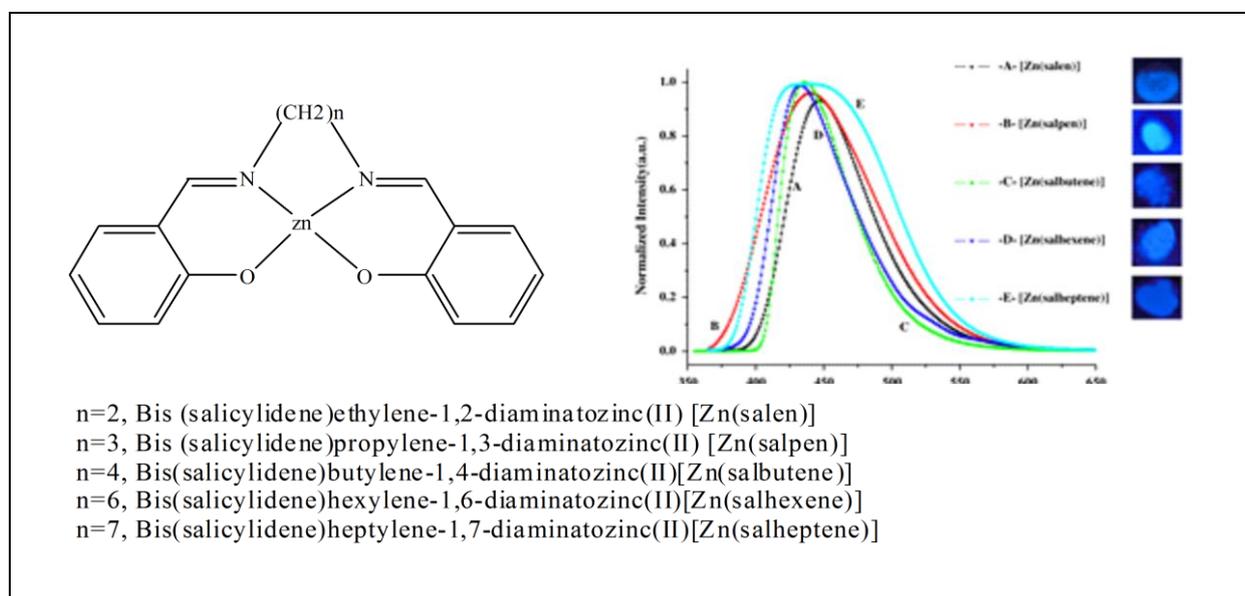


Figure 11. Structures and emission spectra of mononuclear blue luminescent Zinc-Schiff base complexes bearing various spacers [15].

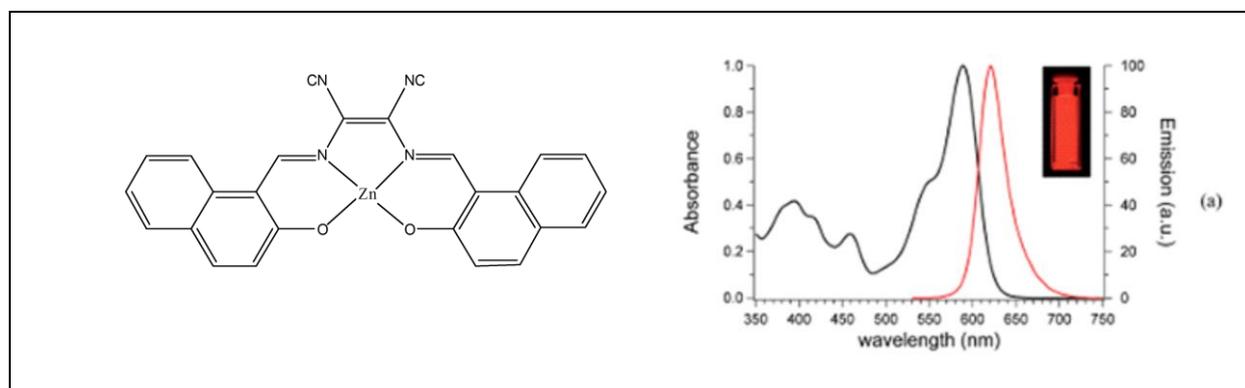


Figure 12. Structure and emission spectrum of mononuclear red emissive Zn(II) complex when doped with PMMA [45].

manifested blue luminescence at 430 – 450 nm when excited by an ultraviolet source; this is usually effectively employed for white light generation in display applications. The study remained focused on enhancing the number of alkyl groups in bridging, but a slight decline in the conjugation chain and a decrease in the emission wavelength blue shift was noticed, resulting in the colour tuning of displays and meriting the utilisation of metal complexes as emissive materials in OLEDs. As no d-d transitions exist in zinc complexes, the emission of light from higher to lower levels is attributable to intra-ligand transitions.

The synthesis and analysis of luminescent solar concentrators conforming to poly (methyl methacrylate) (PMMA) doped with a Zn(II) complex of ligand type N,N'-bis(2-hydroxy-1-naphthylidene-diaminoacetonitrile) were reported by Minei and his group [45] as depicted in Figure 12. The simplicity and low-cost synthesis of ZnL is its most appealing aspect. In addition to the prevalent benefits, ZnL produced a significant red emission in the Zn(II) complex; when doped with PMMA, it instantly amplified thin film optical ability, consequently warranting it profoundly eligible for LSC's configuration and development.

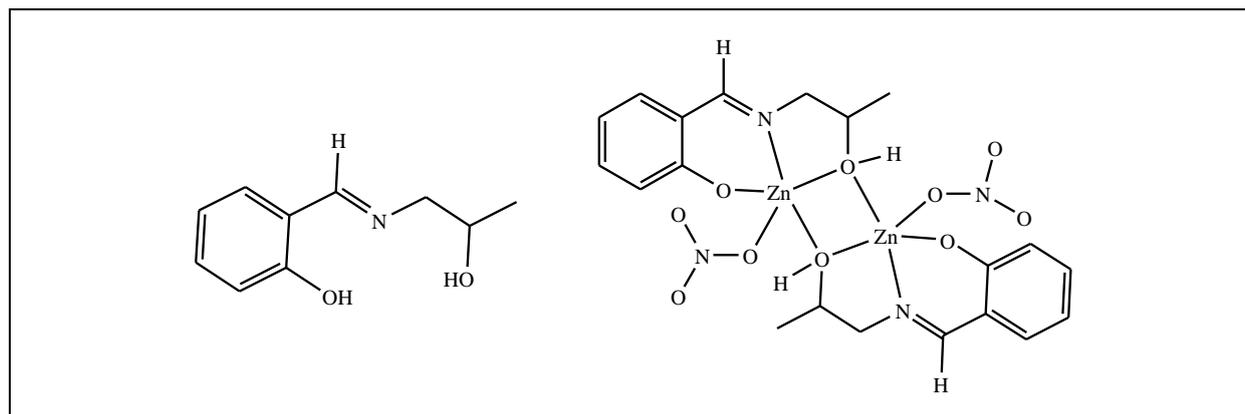


Figure 13. Binuclear luminescent [Zn(HL)NO₃, HL=2-[[2-(2-hydroxypropyl)imino]phenyl]phenol] Schiff base complex.

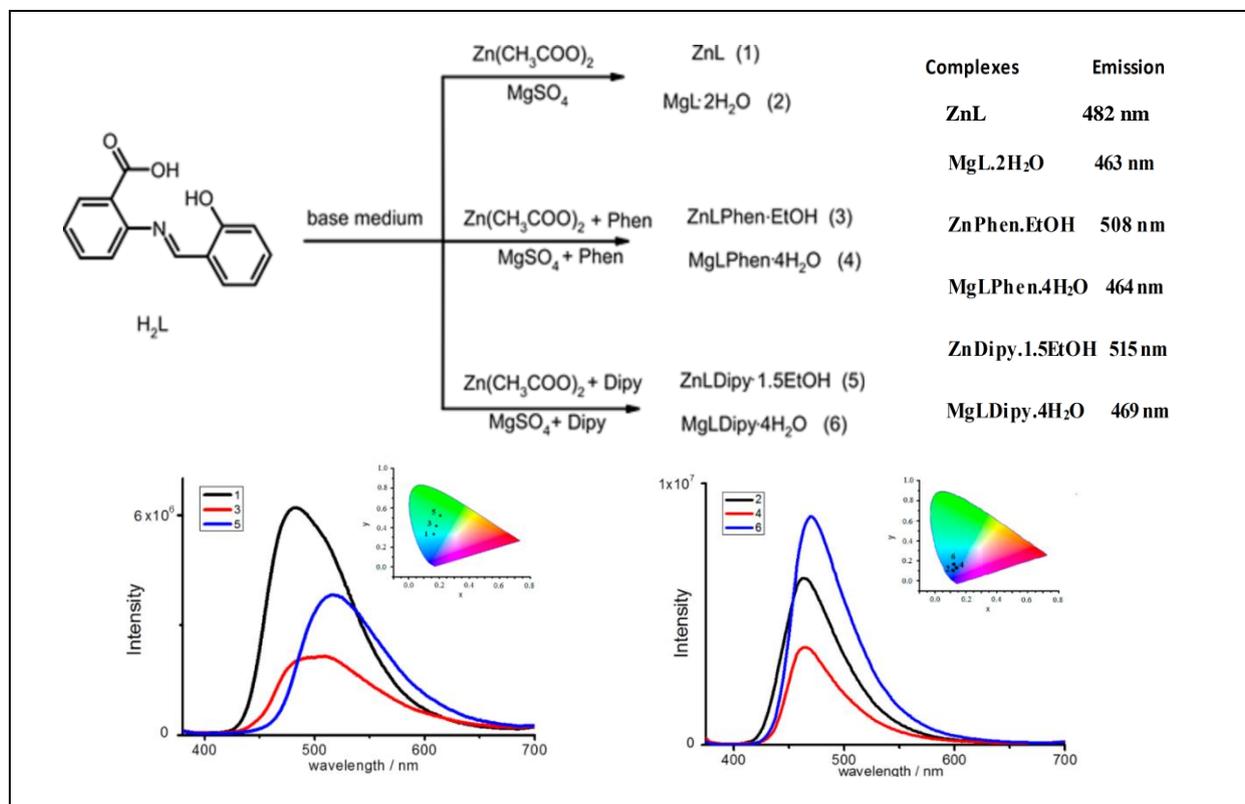


Figure 14. Structures and emission spectra of mononuclear blue to green emissive Zn(II) and Mg(II) N-(2-carboxyphenyl)salicylideneimine Schiff base complexes [47].

ZnL exhibited an emission wavelength exceeding 620 nm, a Stokes shift at 30 nm in the solution state, as well as PMMA with 23% of QY values.

Synthesis of a Zn(II) Schiff base complex, namely [Zn(HL)NO₃, HL=2-[2-hydroxy-propylimino] 2methyl]phenol] was reported by Saeednia and his group [46] as depicted in Figure 13. The stable d¹⁰ electronic configuration characteristic of the Zn(II) metal ion impedes oxidation or reduction, consequently the complex exhibited no emissions from the metal-centred excited state (MLCT/LMCT), whereas it showed amplified emission against the parent ligand from an intra-ligand $\pi-\pi^*$ transition. The results revealed that upon coordination, the enhanced overlap of the Zn-N bond was achieved due to either better chelate ring size formation or conformational improvement in the rigidness of the Schiff base ligand. Thus the Zn(II) metal ion was accommodated, which lessened non-radiative decay or energy loss due to thermal vibrational intra-ligand decay.

The synthesis and characterisation of the Schiff base ligand N-(2-Carboxyphenyl) salicylideneimine and its six new Zn(II) and Mg(II) complexes were reported by Gusev and his co-workers [47] as shown in Figure 14. Both sets of complexes exhibited tuneable luminescence from blue to green in the solid

state and quantum yield values ranging between 0.11 and 0.44 with a lifetime of nanoseconds. The stronger thermal stability of the compounds confirmed their proficient nature as favourable electroluminescent materials in comparison with the parent Schiff base ligands.

Synthesis of blue light emitting Zn(II) complexes with their respective Schiff base ligands, namely bis(salicylidene)cyclohexyl-1,2-diamino, were reported by Srinivas and his team [4] as shown in Figure 15. The analysis demonstrated that Zn(II) complexes with the preferred ligands manifested blue emission and photoluminescence peaks ranging from 395 nm – 600 nm, in both solid and solution states. Therefore, Zn(II) complexes may be utilised as excellent blue light emitters in flat-panel displays. The synthesised compounds were analysed further for forensic applications, and found to be active.

A fascinating Zn(II) Schiff base metal complex was designed from its respective ligand 4-methyl-N-[2-[(E)-pyridinylmethyl]phenyl]benzoesulfimide as depicted in Figure 16 and accordingly characterised by single-crystal X-ray diffraction analysis [48]. The synthesised complex was further fabricated in an OLED device as a light emitting layer and consequently exhibited yellow light at 525 nm and

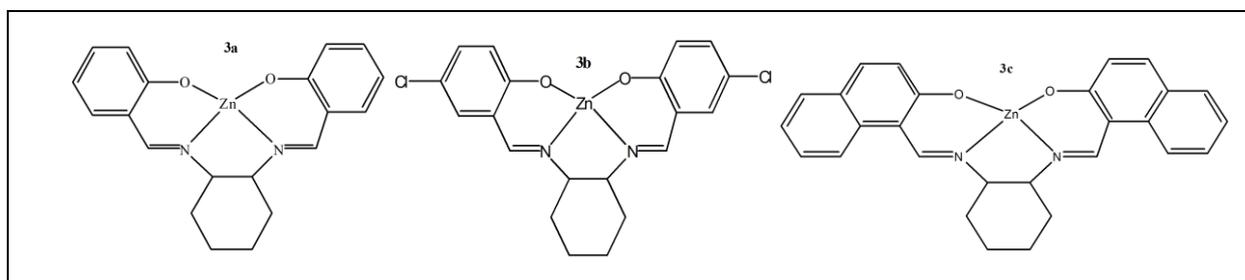


Figure 15. Mononuclear blue emissive Zn(II) bis(salicylidene)cyclohexyl-1,2-diamino Schiff base complexes.

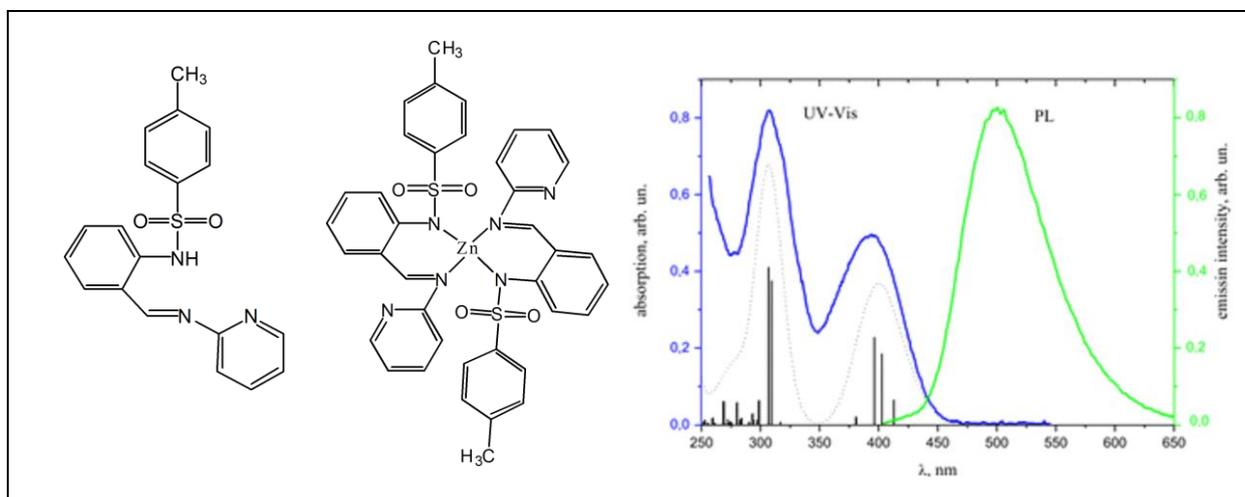


Figure 16. Structure and emission spectra of mononuclear yellow emissive Zn(II) 4-methyl-N-[2-[(E)pyridinylmethyl]phenyl]benzoesulfimide Schiff base complex [48].

another peak at 650 nm, along with luminescence generation of more than 1000 cd/m² at 16V. The colour tuneable characteristic was induced by the organic fluorophore substituents.

Salen-type Schiff base ligands synthesised by condensation of salicylaldehydes, as well as different diamines chiefly in alcoholic solution, possess prominent properties and thus were the most favourable compounds in the development of luminescent complexes. The phenyl ring changeover tuned electronic behaviour, thus metal complexes involving salen-type ligands have various applications in different fields. The luminescence proficiency of these complexes transformed them into a principally established class of materials in OLEDs upon coordination to various metal ions, such as Be²⁺, Mg²⁺, Al³⁺, Ga³⁺, In³⁺, and Zn²⁺ [49, 50]. Various Zn(II) and Ni(II) complexes of the said ligands are utilised as building blocks in the structure of fluorescent polymers in OLEDs [51, 52] as shown in Figure 17. Not only do mononuclear complexes of these ligands act as luminescent materials in OLEDs, but binuclear

Zn(II) Salen-type complexes also play a potent role as luminescent materials in aggregation induced enhanced emission (AIEE), as depicted in Figure 18.

Bearing in mind the excellent emissive properties of Zn(II) complexes with bis-Schiff base ligands, Zhao and his co-workers synthesised Zn(II) Salphen complexes with pyridyl bearing ligands [53] as depicted in Figure 19. The complexes were further investigated for their photophysical, electrochemical and electroluminescent behaviour. The complexes were found to be highly stable at up to 417 °C and exhibited an emission peak at 565 nm in solution, as well as in the form of a thin film.

The corresponding dinuclear Zn(II) complexes had a peak luminance of 3589 cd m⁻², a maximal external quantum efficiency of 1.46%, a maximum current efficiency of 4.1 cd A⁻¹ and a maximal power efficiency of 3.8 lm W⁻¹. These results provided support for the synthesis of various Salphen based dinuclear Zn(II) complexes which were efficient emitters.

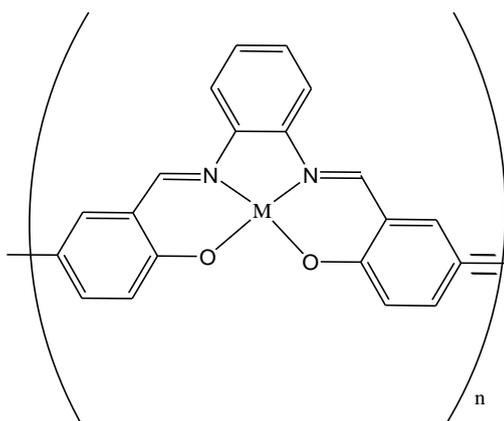


Figure 17. Mononuclear Zn(II) and Ni(II) Schiff base polymer as luminescent material.

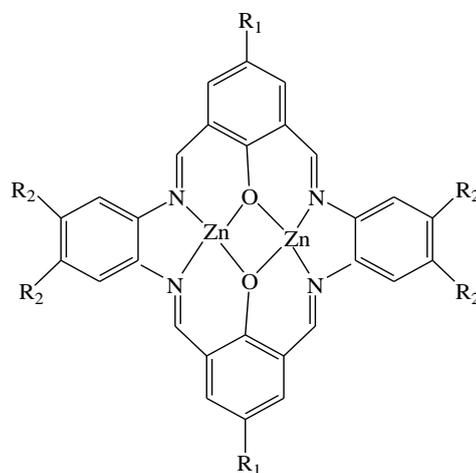


Figure 18. Binuclear Zn(II) macrocyclic Schiff base complexes with aggregation induced enhanced emission (AIEE).

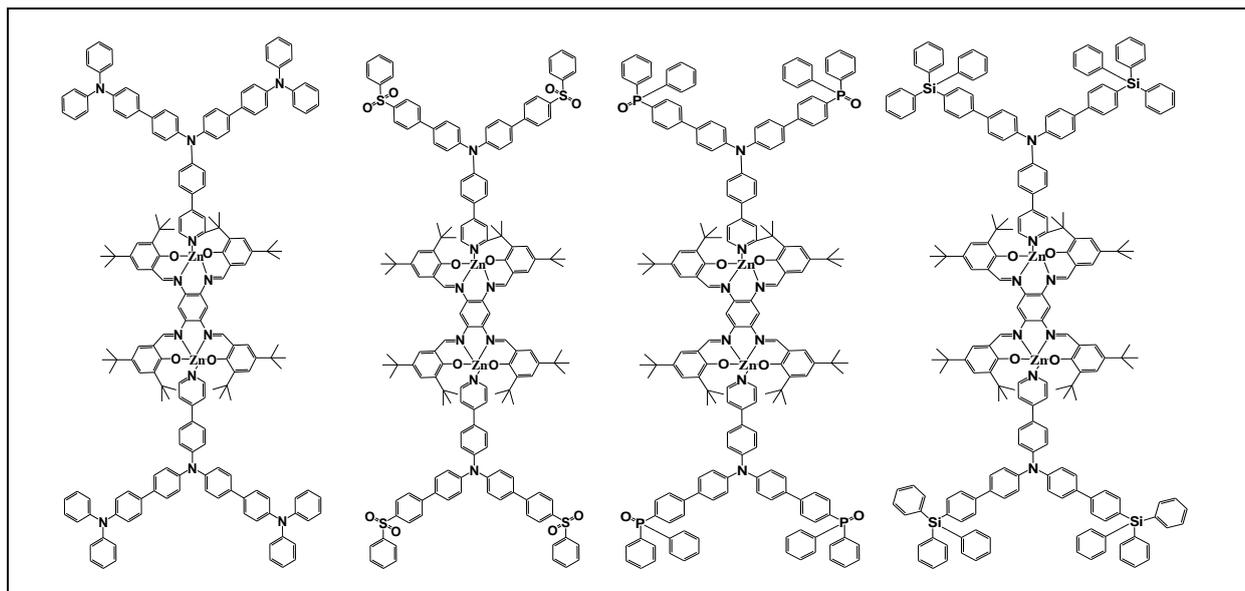


Figure 19. Dinuclear Zn(II) Salphen complexes with pyridyl ligands.

The synthesis of a set of eight novel Zn(II) and Cd(II) complexes with its respective tetradentate Schiff base ligand 2,4-dichloro-2-[(2-piperazine-4-yl-ethylimino)-methyl]-phenol (HL) having the structural formulae: [Zn(LH)(SCN)₂](1), [Zn(LH)(N₃)₂](2), [Zn(LH)(NO₂)₂](3), [Zn(LH)(dca)(Oac)](4), [Cd₂(LH)₂(SCN)₄](5), [Cd(LH)(N₃)₂](6), [Cd(LH)(NO₂)₂](7), and [Cd(LH)(dca)-(Oac)](8) [54] was reported as shown in Figure 20. Quantum yield values of the synthesized complexes appeared anion dependent in the order: LH < Cd-SCN(5) < Cd-dca(8) < Cd-N₃(6) < Cd-NO₂(7) < Zn-dca(4) < Zn-N₃(2) < ZnNO₂(3) < ZnSCN(1). The amplified photoluminescence proficiency and elevated quantum yield values of the complexes with reference to the parent ligand is attributed to their rigidity upon coordination. This study testifies that ligand structure modification, anion alterations and changes in metal ions caused improved potency.

The synthesis of a series of Zn(II) complexes

with their corresponding ligands 4-formylpyrazolone containing several substituents, is depicted in Figure 21[55]. The results revealed that particularly active blue range photoluminescence activity was exhibited in solid state at ambient temperatures demonstrating that these complexes were proficient electroluminescent materials. A detailed analysis showed that a change of solvents and excitation permitted tuneable colours from blue to orange. Solid state photoluminescence measurements at room temperature indicate their ability to serve as photoactive materials. The complexes produced a solid-state bright blue emission of up to 55% of quantum yield values. The wavelengths of emission could be tuned over a large range of 436 nm – 485 nm due to the electron donating capability of the ligands. In chloroform solution the complexes revealed a very rare excitation-dependent emission. This exclusive characteristic of the synthesised compounds indicates that they may be employed as electroluminescent materials.

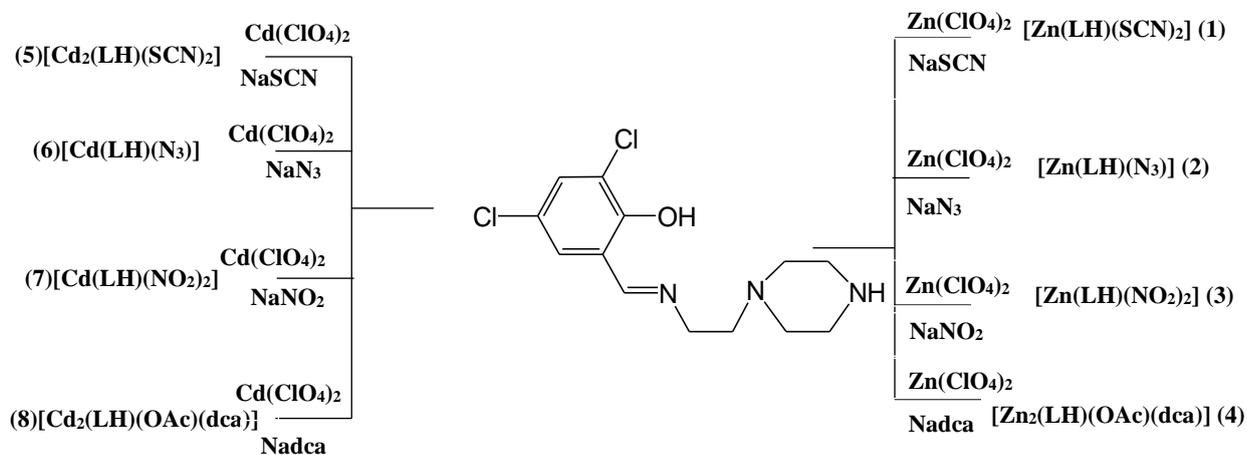


Figure 20. Mononuclear Zn(II) and Cd(II) complexes with a tetradentate 2,4-dichloro-2-[(2-piperazine-4-yl-ethylimino)-methyl]-phenol Schiff base ligand.

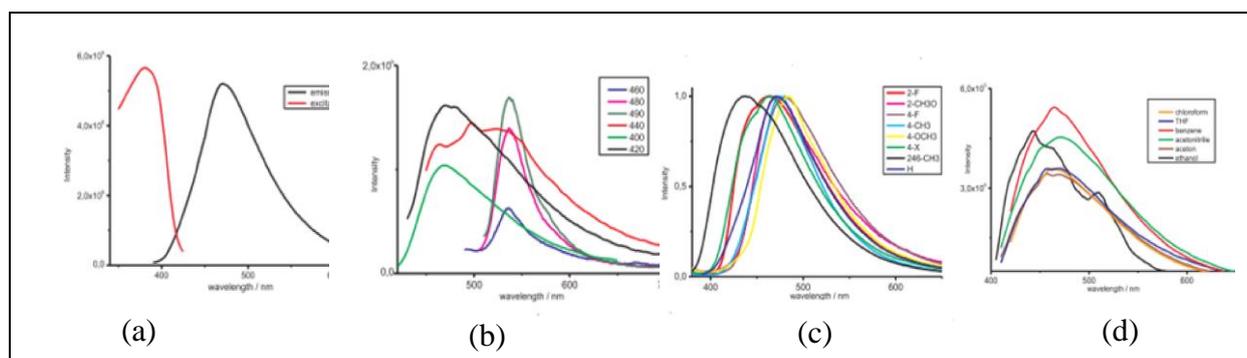
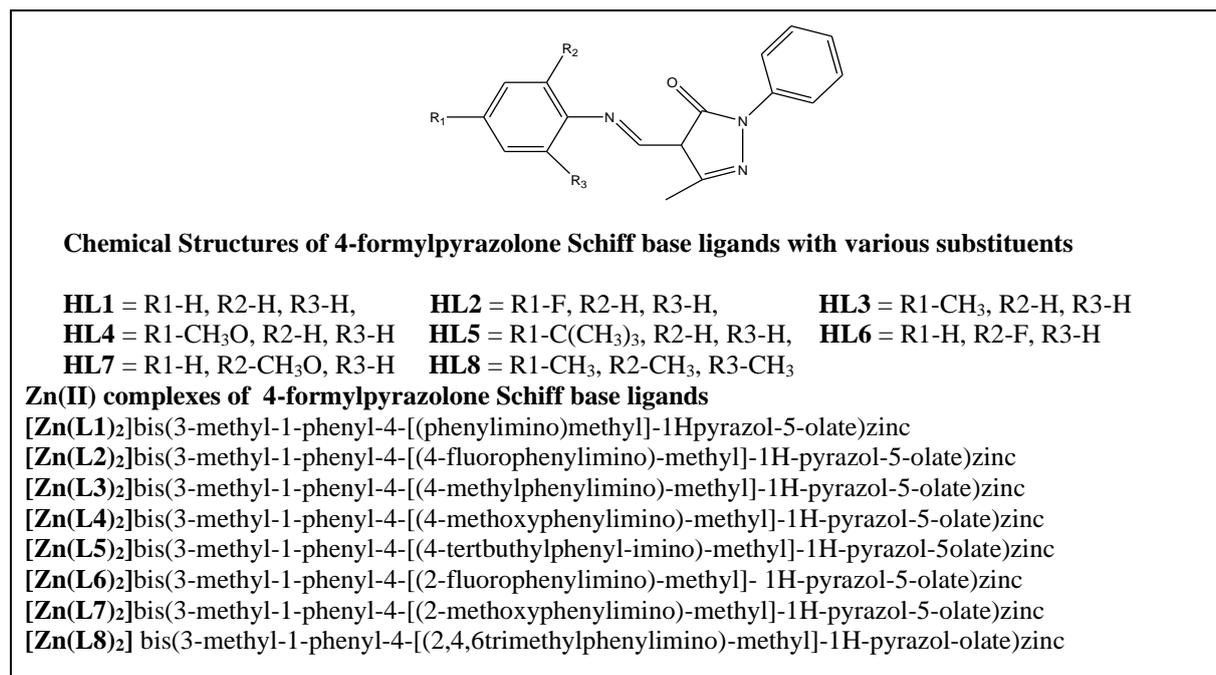


Figure 21. Structures (a) Excitation and emission spectra of complex 1 in solid state (b) Emission spectra of complex 1 in chloroform solution at different excitations (c) Emission spectra of complexes 1-8 in solid state at room temperature (d) Emission spectra of complex 1 in different solvents [55].

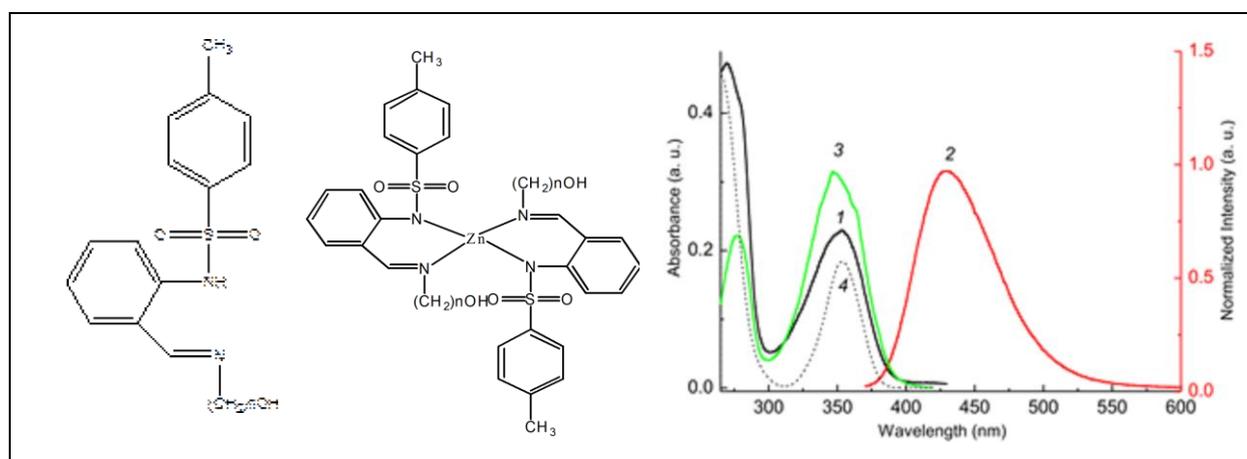


Figure 22. Structures and emission spectra of mononuclear blue emissive Zn(II) complexes derived from 2-tosylammonobenzaldehyde and aminoalcohol Schiff base ligands [56].

The design and synthesis of another series of Zn(II) complexes with its corresponding Schiff base ligands derived from the condensation of 2-tosylammonobenzaldehyde with different aminoalcohols possessing aliphatic spacers $(\text{CH}_2)_n$ ($n = 2-6$) were reported by Burlov and his team [56] as depicted in Figure 22. A thorough analysis was performed to determine their photoluminescence and biological properties. Emission wavelengths were obtained ranging from 428 - 430 nm along with quantum yield values in the range of 0.32–0.35. The results also revealed that the optical characteristics of the synthesised complexes were fundamentally subjected to coordination spheres while unaffected by the length of the $(\text{CH}_2)_n$ spacers. Hence, these exciting zinc complexes may perhaps be utilised as proficient luminescent materials owing to their PL properties in the blue region.

The synthesis and characterisation of a series of different novel Zn(II) complexes: $[\text{Zn}_2(\text{L1})(\text{CH}_3\text{OH})_2(\text{SCN})(\text{OAc})]$ (1), $[\text{Zn}_2(\text{L1})(\text{CH}_3\text{OH})_2(\text{N}_3)_2]$ (2) and $[\text{Zn}_2(\text{L1})(\text{Cl})_2(\text{CH}_3\text{OH})]\text{CH}_3\text{OH}$ (3) derived from

the $[\text{N},\text{N}'\text{-Bis}(3\text{-ethoxy salicylideneimino})\text{-}1,3\text{-diaminopropane}]$ Schiff base were reported as shown in Figure 23 [16]. The results revealed that Zn(II) metal complexes demonstrated an improved luminescence efficiency in relation to the synthesised Schiff base ligand, which was fundamentally due to LMCT. The chosen parent Schiff base ligand exhibited an emission wavelength of 423 nm, while its corresponding complexes exhibited emission at 468 nm – 471 nm. A strong chelating effect may be the cause of this improved fluorescence behaviour [57–59].

Synthesis of Schiff base ligand HL ((2-[(3,5-dibromo-2-hydroxy-benzylidene)-amino]-2-hydroxy methyl-propane-1,3-diol)) and its corresponding $[\text{Zn}(\text{L}_2)]$ (1), $[\text{Cd}(\text{L}_2)]$ (2) and $[\text{Hg}(\text{L}_2)]$ (3) complexes, were reported and thoroughly analysed for their fluorescent properties, as depicted in Figure 24 [60]. The results revealed that remarkable fluorescent properties were manifested not only by the synthesised ligand but also by the mononuclear complexes MX₂. Fluorescence efficiency of the compounds was enhanced upon coordination with metal ions,

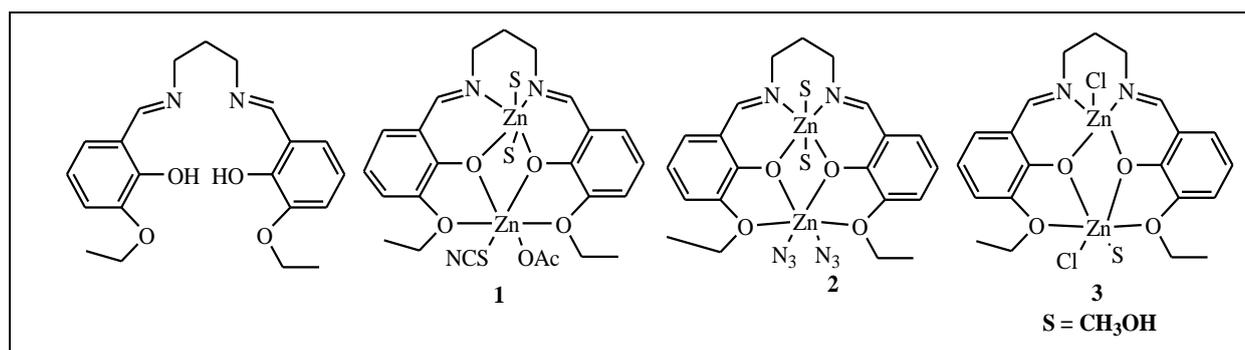


Figure 23. Dinuclear blue emissive $[\text{Zn}_2(\text{L1})(\text{CH}_3\text{OH})_2(\text{SCN})(\text{OAc})]$ (1), $[\text{Zn}_2(\text{L1})(\text{CH}_3\text{OH})_2(\text{N}_3)_2]$ (2) and $[\text{Zn}_2(\text{L1})(\text{Cl})_2(\text{CH}_3\text{OH})]\text{CH}_3\text{OH}$ (3), $[\text{N},\text{N}'\text{-Bis}(3\text{-ethoxysalicylideneimino})\text{-}1,3\text{-diaminopropane}]$ Schiff base complexes.

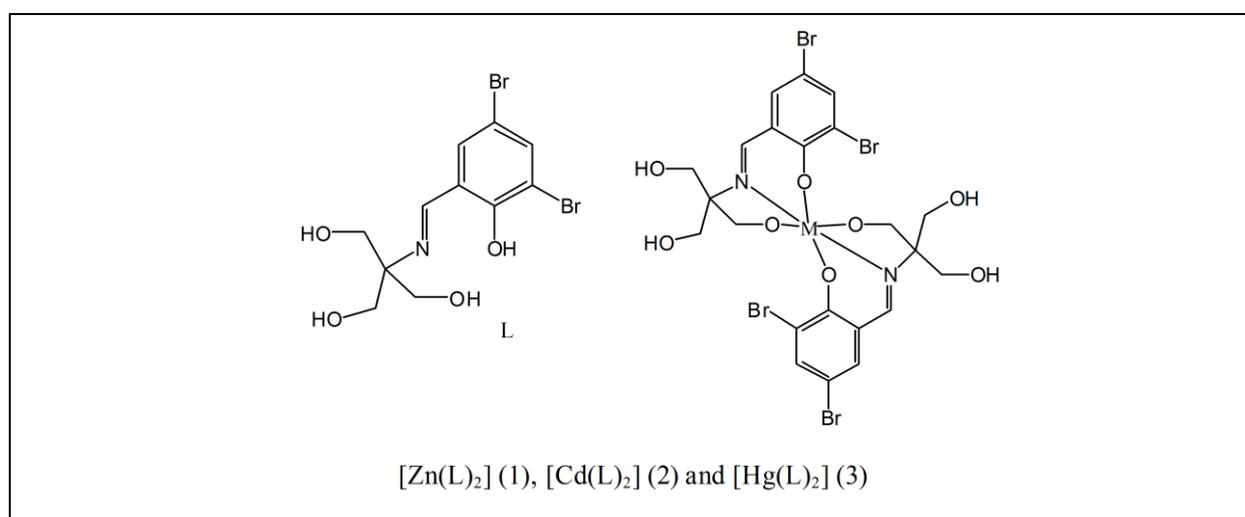


Figure 24. Luminescent Zn(II), Cd(II) and Hg(II) ((2-[(3,5-dibromo-2-hydroxy-benzylidene)-amino]-2-hydroxymethyl-propane-1,3-diol)) Schiff base

attributable to the rigidity of the complexes. The emission band in the ligand may perhaps be ascribed to the $\pi-\pi^*$ transition, whereas LMCT was responsible for emission in the complexes.

Synthesis of two novel luminescent Zn(II) complexes ZnH_2L^1 and ZnH_2L^2 was reported by Ozlem [61], as presented in Figure 25. The synthesised complexes exhibited a green emission in DMSO solution upon photoexcitation at 350 nm. The results revealed that complex 1 (ZnH_2L^1) manifested a weak green emission at 537 nm, while complex 2 (ZnH_2L^2) exhibited an intense green luminescence with intra-ligand and charge transfer bands ranging from 506 – 523 nm and 653 – 680 nm, respectively.

The existence of two extra nitro groups in the structure of complex 2 may be the cause of this enhanced luminescence intensity compared to complex 1. This led to the enhanced resonance energy of the whole structure, consequently providing a higher stabilisation. These groups also reduced non-radiative processes.

A group of researchers [62] synthesised binuclear azomethine-Zn(II) complexes from 4,4-diaminodiphenylsulphide derived Schiff bases, *N,N*-bis-(3,4-dihydroxybenzaldehyde)-4,4-diaminodiphenyl sulphide (L1), *N,N*-bis-(5-nitrosalicylidene)-4,4-diaminodiphenylsulphide (L2), *N,N*-bis-(5-chlorosalicylidene)-4,4-diaminodiphenylsulphide(L3). In this work,

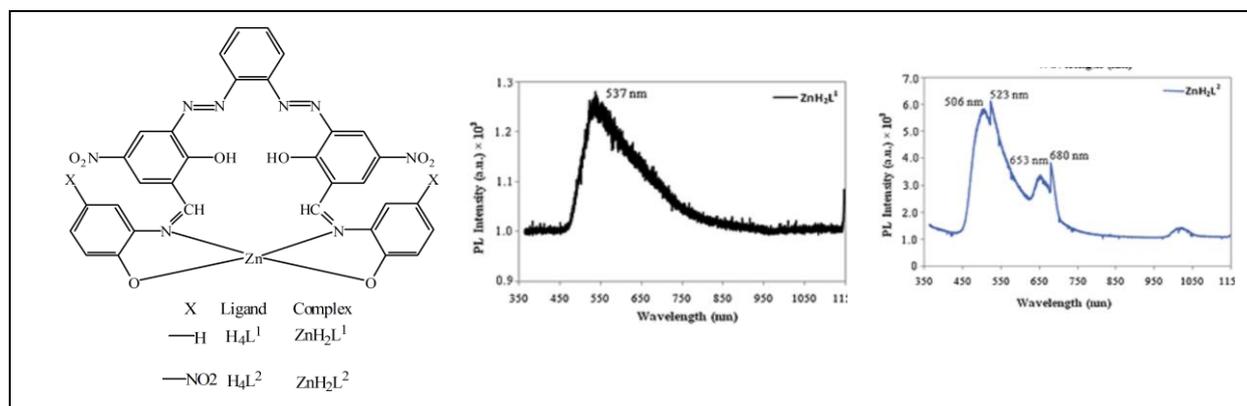


Figure 25. Structures and emission spectra of mononuclear green emissive Zn(II) complexes (ZnH_2L_1 and ZnH_2L_2) [61].

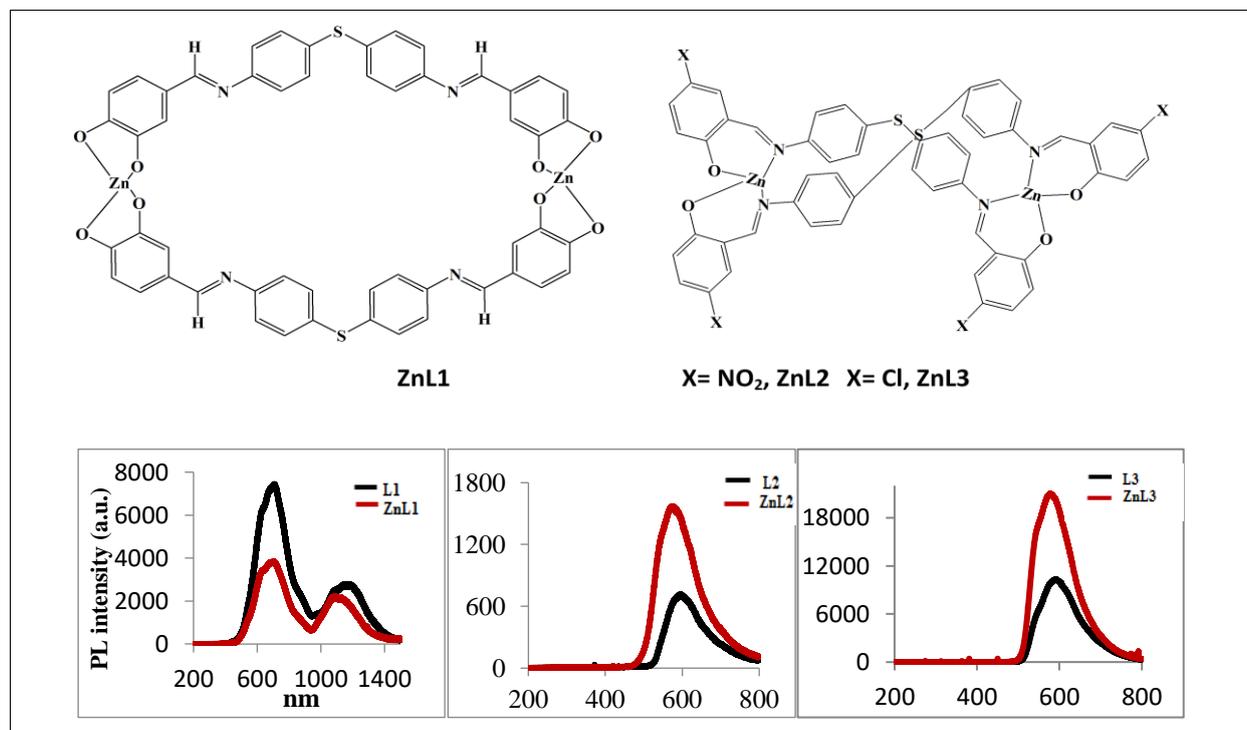


Figure 26. Structures and emission spectra of binuclear Zn(II) complexes (ZnL_1 - ZnL_3) with diaminodiphenyl sulphide bridged ligand [62].

the designed ligands proved to be superior organic chromophores for energy transfer to the Zn(II) ion, that led to improved solid-state emissive complexes. Amongst the synthesised complexes, ZnL3 with a Cl substituent manifested a remarkable emission intensity, followed by the ZnL2 complex in the solid state with an NO₂ substituent producing an emission at 585 nm in the visible region. ZnL1 in the solid state with two OH substituents displayed dual emissive peaks at 710 nm and 1199 nm in the near infrared region (NIR). The most striking feature of this study was that the complexes possessed enhanced luminescence intensity together with a high Stokes shift ($\Delta\lambda$) of 260 – 385 nm in the solid state, as depicted in Figure 26. This enables the further development of cost-efficient photoluminescent solid-state materials.

From the above review of Schiff base Zn(II) metal complexes, it may be concluded that binuclear Zn(II) Schiff base metal complexes, tetradentate in nature with $[N,N,O,O]$ and $[O,O,O,O]$, have scarcely been investigated for their luminescence studies, especially in the solid state. In addition, the luminescence results of zinc (II) complexes reviewed could boost the synthesis of low-cost light emitting materials as previously reported [13, 62].

5. Luminescent Ir(III) Schiff Base Metal Complexes

Currently, higher transition metal complexes of mainly iridium, ruthenium and rhodium have played a prominent role in the development of luminescent materials due to their strong spin-orbit coupling properties [18–24]. Metal complexes have been synthesised with various heavy metals such as Ru(II), Os(II), Eu(III), Re(I), Ir(III), however Ir(III) metal complexes have superiority over others due to their excellent emission, greater stability, tuneable emission colours (from blue to red) and higher luminescent lifetimes [20, 21, 25–27]. The strong spin-orbit coupling properties of heavy metals directly affect

emission behaviour due to the effectual inter-system crossing between its corresponding singlet to triplet excited states [20].

The synthesis of luminescent heavy transition metal complexes has attracted interest due to its various uses, predominantly as phosphors. Among the heavy transition metals, Ir(III) is considered as a triplet emitter and has recently gained a lot of attention as an isoelectronic material [27, 63, 64].

Unfortunately, there has been little research on luminescent Ir(III) azomethine metal complexes compared to the d⁸ transition metal complexes. Therefore, there have been few reports in the literature of Schiff base Ir(III) complexes as emitting materials.

Luo and his co-workers [65] synthesised a variety of compounds possessing aggregation induced emission (AIE), with inadequate emission in the solution state but showing excellent emission in the aggregated form or in the solid state. Similar to Luo, another group in 2002 [66] reported AIE emission in a similar type of compound. There has been increasing interest in synthesising compounds with AIE due to its promising application in optoelectronics, such as OLEDs. The design of the ligand has a key role in the luminescence behaviour of the complexes. Due to its structural diversity, Schiff base ligands can behave as dominant chelating agents with multiple binding positions as they have a flexible nature. The flexibility of the diimines in the Schiff base ligands causes bending and rotation in the metal ion coordination, which in turn forms stable geometries with the metal ions [18]. Various Schiff base heavy metal Ir(III) complexes are promising emitters.

Imidazole Schiff base ligands and their respective four iridium and rhodium complexes were designed and synthesised by Mandal and his co-workers in 2014 [67]. Upon excitation at 330 nm,

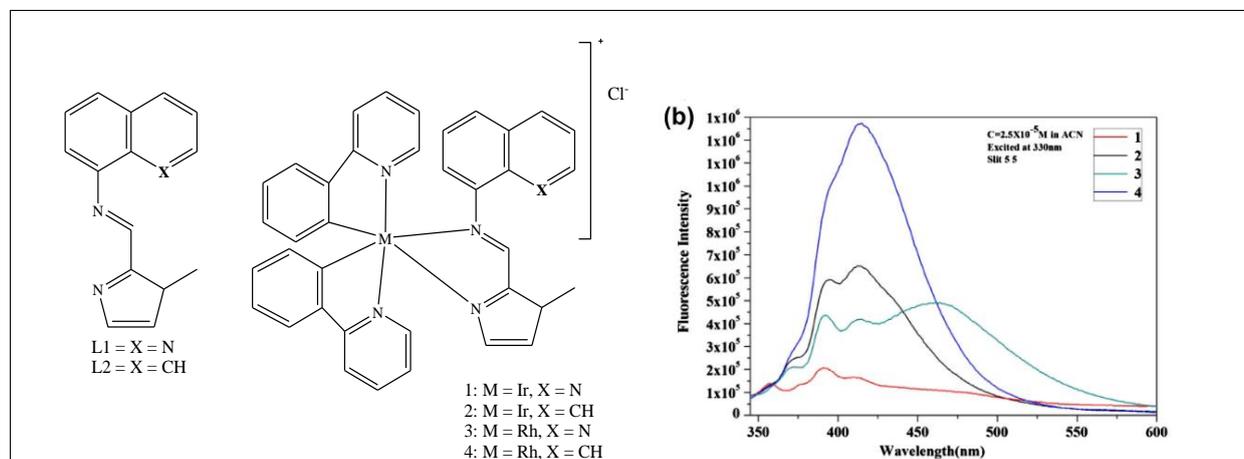


Figure 27. Structures and emission spectra of mononuclear iridium and rhodium complexes 1-4 upon excitation at 330 nm [67].

the synthesised complexes manifested emissions ranging from 390 nm to 476 nm as depicted in Figure 27. When excited at 405 nm, emission was observed between 445 nm and 514 nm. The photophysical analysis results confirmed that the fluorescence displayed by all the complexes at ambient temperatures had quantum yield values of about 3×10^{-2} to 5×10^{-2} . Synthesised complexes were utilised for cellular imaging.

Dinuclear ionic Ir(III) Schiff base complexes were reported by Li and his group [18] as shown in Figure 28. AIEP was exhibited by both the synthesised complexes (in the form of films), having a quantum yield of 37.3% and 26.4 %, respectively. Complex 2 with a bridging biphenyl unit had an

escalated emission wavelength of about 48 nm and was regarded as the absolute red luminescent material relative to complex 1, which had a single bridging phenyl unit. This characteristic was attributed to the higher conjugation of the ligand in complex 2 compared to complex 1.

Both complexes were inactive with no emission in the CH₃CN solution, whereas they showed a greater emission in neat films at 644 nm and 692 nm, which confirmed the active nature of both complexes towards AIE. This AIE behaviour was further studied in dissimilar proportions of water and acetonitrile. Insolubility of the complexes in water showed a greater AIE as shown in Figure 29.

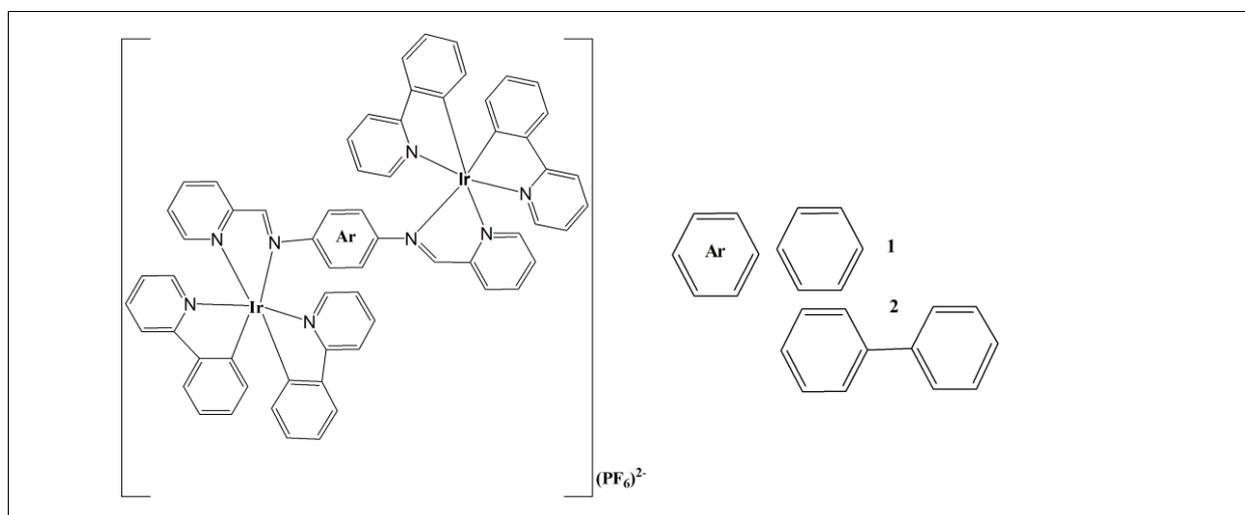


Figure 28. Dinuclear ionic Ir(III) Schiff base metal complexes with bridging phenyl (1) and biphenyl (2) units.

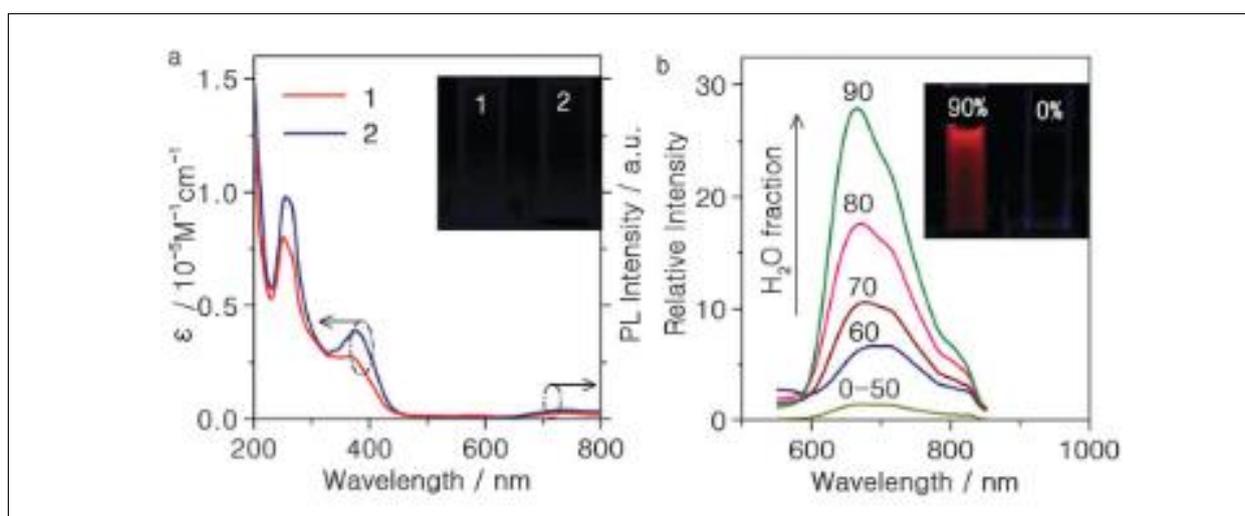


Figure 29. (a) UV-Vis absorption and emission spectra of dinuclear ionic Ir(III) Schiff base complexes 1 with (phenyl bridge) and 2 (biphenyl bridge) in acetonitrile solution (b) Emission spectra of complex 1 in CH₃CN-water mixtures with different water fractions (0-90% v/v) at room temperature [18].

The synthesis and design of four novel mono-nuclear Ir(III) complexes having a general formula $[\text{IrHCl}(\text{C}^{\wedge}\text{N})(\text{PPh}_3)_2]$ comprising various conjugated Schiff base ligands ($\text{C}^{\wedge}\text{N}$) were performed by Climent and his team [68] as presented in Figure 30. Three Schiff base ligands were synthesised by condensation of benzaldehyde with pyridine-2-amine/ pyrimidine-2-amine/5methyl pyridine-2-amine, whereas the fourth was derived by the condensation of 4-(diphenylamino) benzaldehyde with pyridimine 2-amine.

The positions as well as the relative intensities of the vibronic peaks in the thin film emission spectra almost matched their analogues in solution. This resemblance was demonstrated yet again when a comparable assessment was made during colour emission in the thin film alongside colour emission in DCM solution as depicted in a chromaticity diagram, whereby a similar green to yellow transition was noticed, as exhibited in Figure 31 and Figure 32.

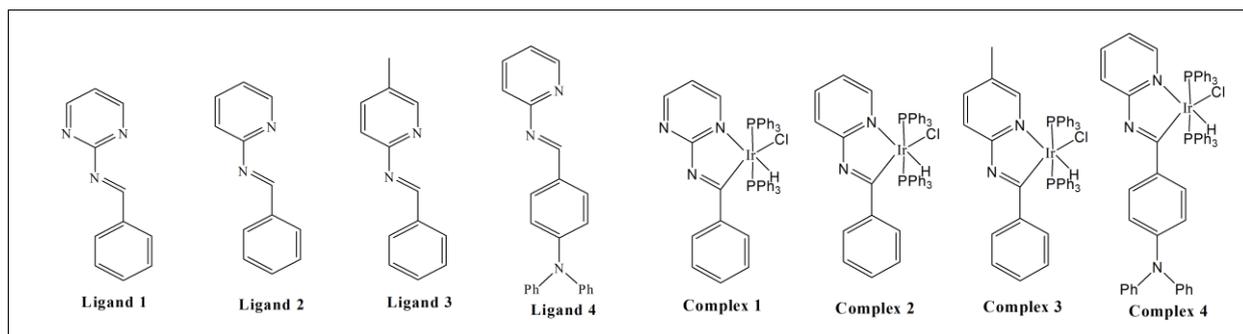


Figure 30. Schiff base ligands and their relative mononuclear Ir(III), $[\text{IrHCl}(\text{C}^{\wedge}\text{N})(\text{PPh}_3)_2]$ complexes.

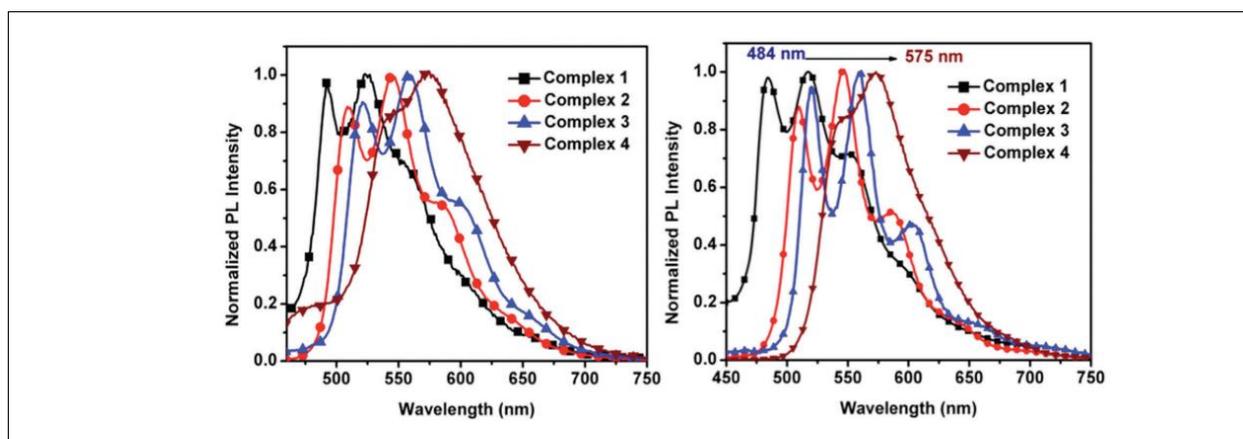


Figure 31. Emission of 1-4 in DCM (left) and thin film (right) at room temperature [68].

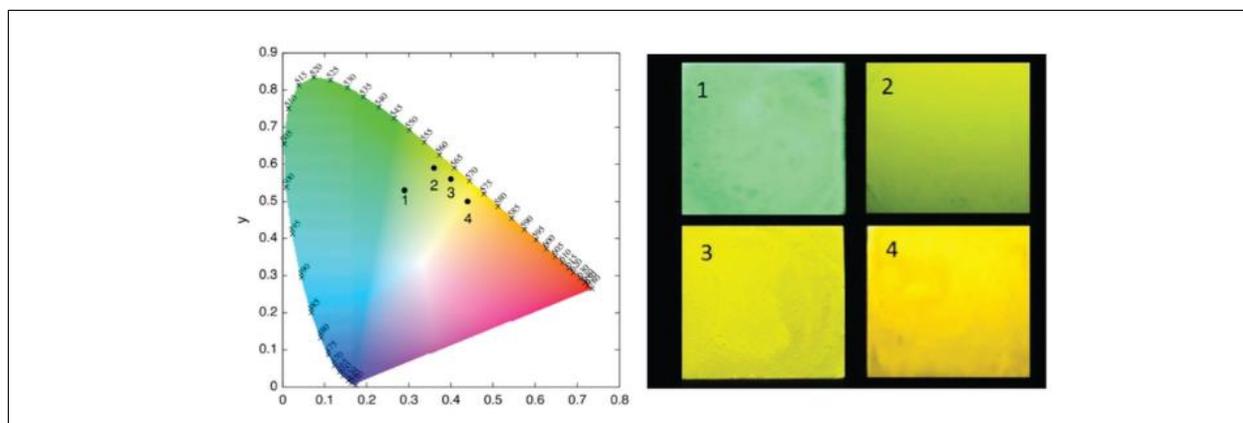


Figure 32. Chromaticity diagram for the emission of 1-4 in DCM (left) and thin film (right) under 365 nm UV lamp [68].

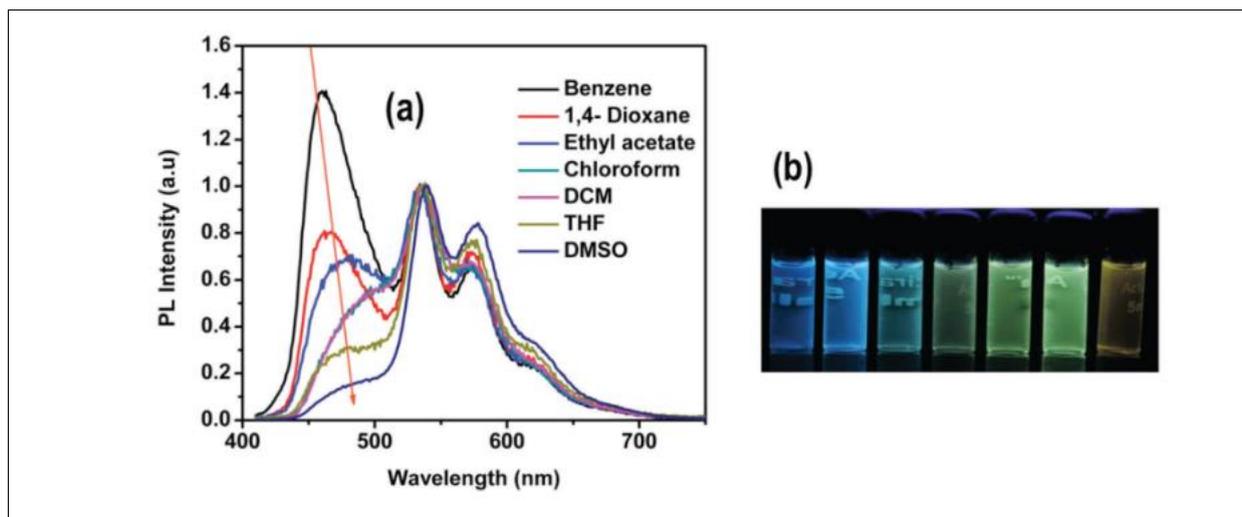


Figure 33. (a) Emission spectra of 4 in different solvents. (b) Photographs showing the emission colors of 4 under UV light in different solvents (from left to right): benzene, 1,4-dioxane, ethyl acetate, CHCl₃, DCM, THF and DMSO [68].

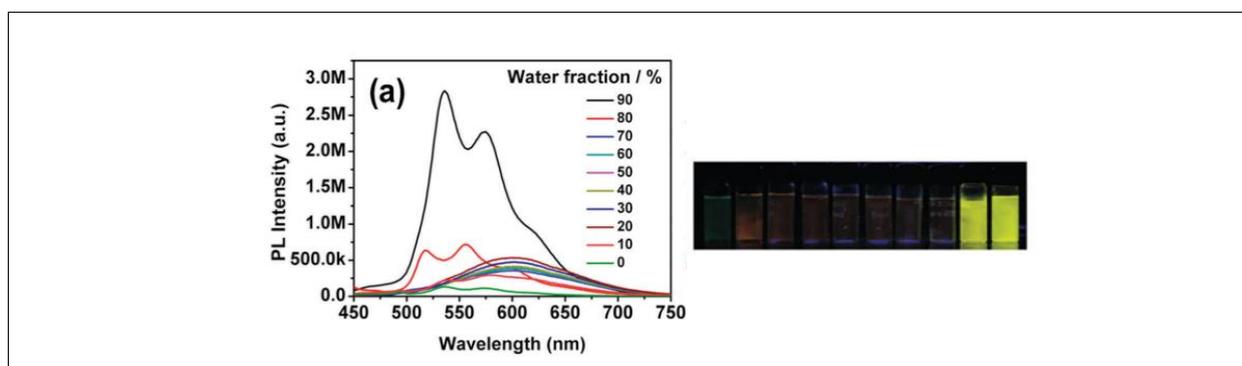


Figure 34. (a) Emission spectra of 4 in THF/water mixtures (0–90%) and photographs of 4 in THF/water mixtures taken under UV lamp [68].

In almost all organic solvents, the complexes exhibited weak emissions in the solution state. However, they showed stronger emissions in the solid state as shown in Figure 33.

This motivated researchers to thoroughly analyse the AIEE of the complexes. The THF solubility and relative water insolubility of the three complexes added a new dimension, hence widening the prospects for the PL properties of metal complexes in THF-water solutions of different ratios as shown in Figure 34. Nano-sized aggregates ranging from 124 – 674 nm in diameter developed in water. Emission was poor in pure THF but improved with the increase in water content in the THF-water ratio. Complex 4 exhibited almost equivalent AIEE tendencies and effects.

The synthesis, structures and luminescence behaviour of dinuclear iridium complexes [Ir₂(ppy)₄(L)] (1) and [Ir₂(F₂-ppy)₄(L)] (2) (ppy = 2-phenyl pyridine, F₂-ppy = 2-(2,4-difluorophenyl)

pyridine, H₂L = N,N'-bis(2-hydroxynaphthylmethylidene)-2-hydroxy-1,3-propanediamine were thoroughly analysed and reported by Sun and his team [69] as depicted in Figure 35. Coordination of the ligand to the metal ion in a tetradentate manner was endorsed by the results of X-ray crystal diffraction studies.

It was clearly demonstrated in this study that structural modification of ligands tuned luminescence behaviour. Emission spectra of both the synthesised complexes were examined in CH₂Cl₂, with emission wavelengths detected at 604 nm and 595 nm as shown in Figure 36. Complex 2 [Ir₂(ppy)₄(L)], unlike complex 1 [Ir₂(F₂-ppy)₄(L)], exhibited a blue shift which was primarily attributable to the fluorine substituent attached to the aromatic ring, in agreement with previous studies by Zhou and his team on cyclometallated β-diketone iridium complexes [Ir(ppy)₂(avo)] and [Ir(F₂-ppy)₂(avo)] (λ_{max} 629 and 664 nm, avo = avobenzene), which exhibited a 35 nm blue shift [70].

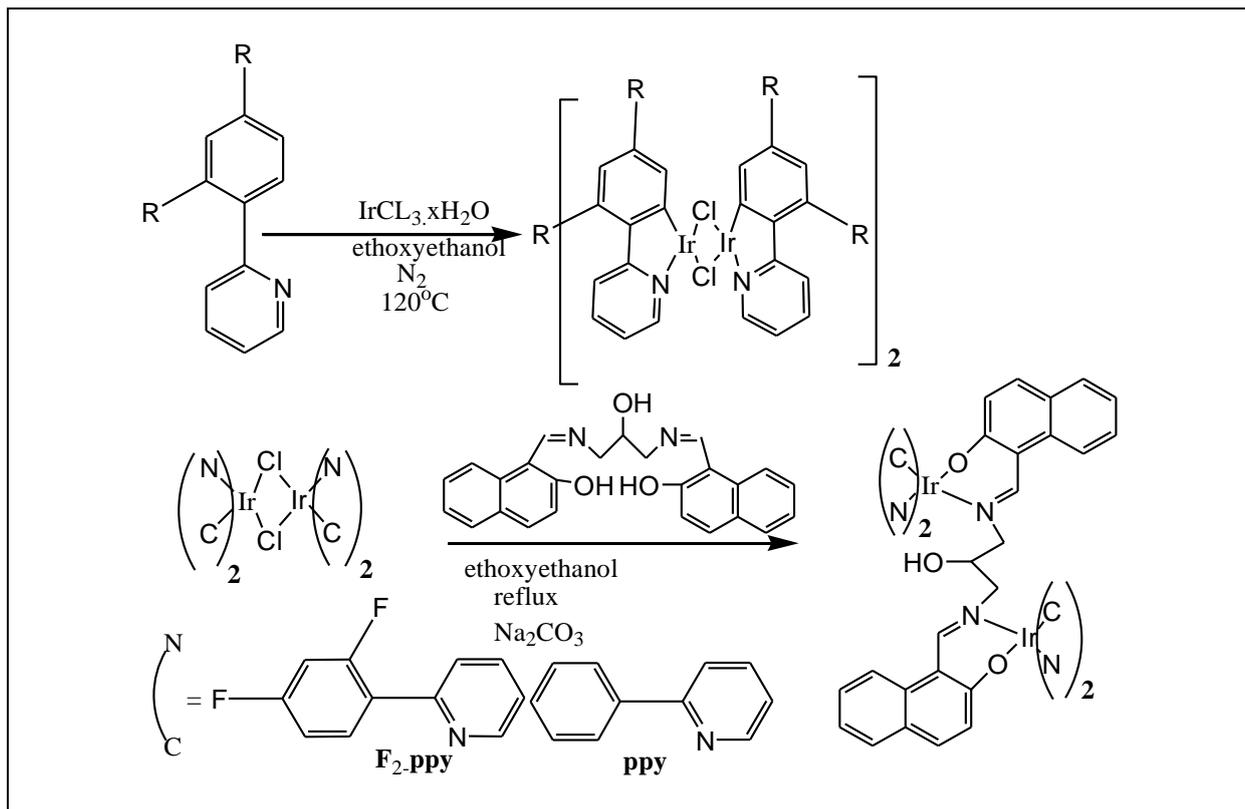


Figure 35. Schiff base N,N' -bis(2-hydroxynaphthylmethylidene)-2-hydroxy-1,3-propanediamine dinuclear $[\text{Ir}_2(\text{ppy})_4(\text{L})]$ (1) and $[\text{Ir}_2(\text{F}_2\text{-ppy})_4(\text{L})]$ (2) complexes.

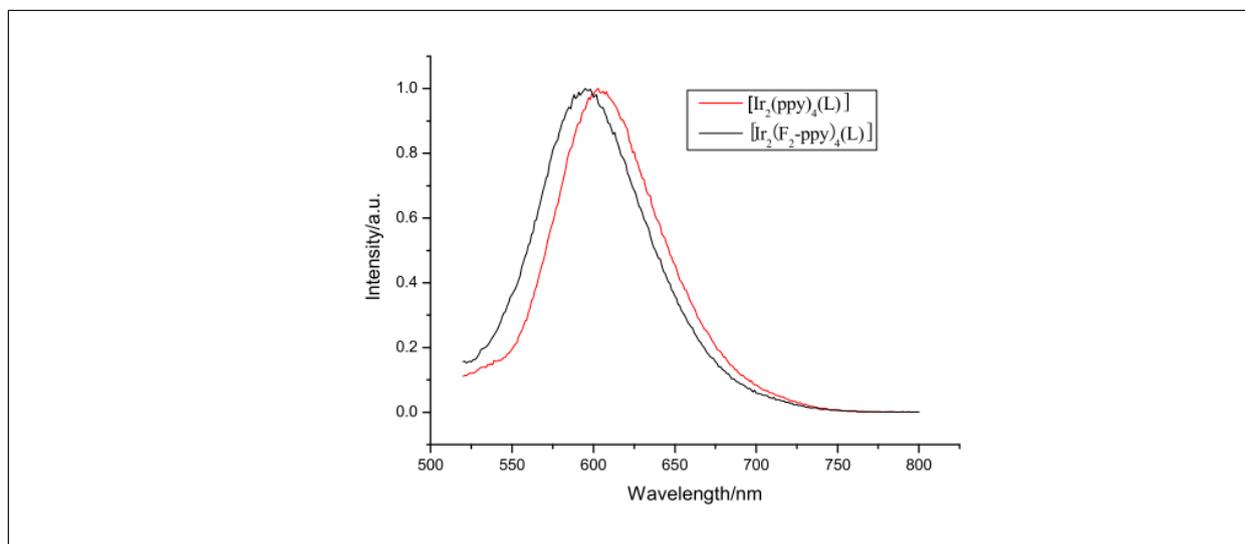


Figure 36. Emission for complexes $[\text{Ir}_2(\text{ppy})_4(\text{L})]$ (1) and $[\text{Ir}_2(\text{F}_2\text{-ppy})_4(\text{L})]$ (2) in CH_2Cl_2 [70].

The synthesis of a series of Ir(III) complexes of general formula $[\text{Ir}(\text{ppy})_2(\text{L})]^{0/+}$ ($\text{ppy} = 2\text{-phenyl pyridine}$, $\text{L} = \text{Schiff base}$) derived from dichloro-bridged dimeric starting material, $[(\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{ppy})_2]$ [71] is shown in Figure 37. The synthesised complexes were analysed for photoluminescence behaviour in both solid and

solution states. All the complexes proved to be non-luminescent. This inexistence of luminescence behaviour may perhaps be assigned to their dominant ligand centred transitions over MLCT transitions. Strong MLCT bands were crucial for Ir(III) emissive complexes. Ligand centred transitions did not ensure luminescence.

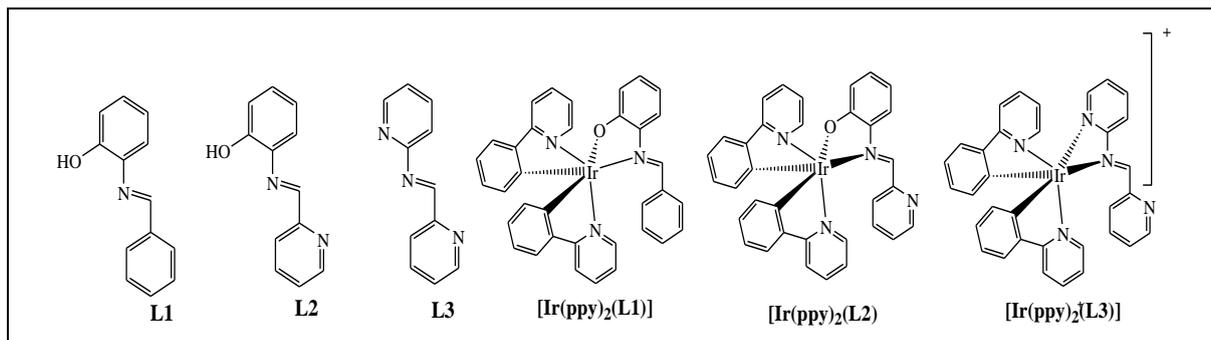


Figure 37. Ir(III) complexes of general formula $[\text{Ir}(\text{ppy})_2(\text{L})]$ (ppy = 2-phenyl pyridine, L = Schiff base).

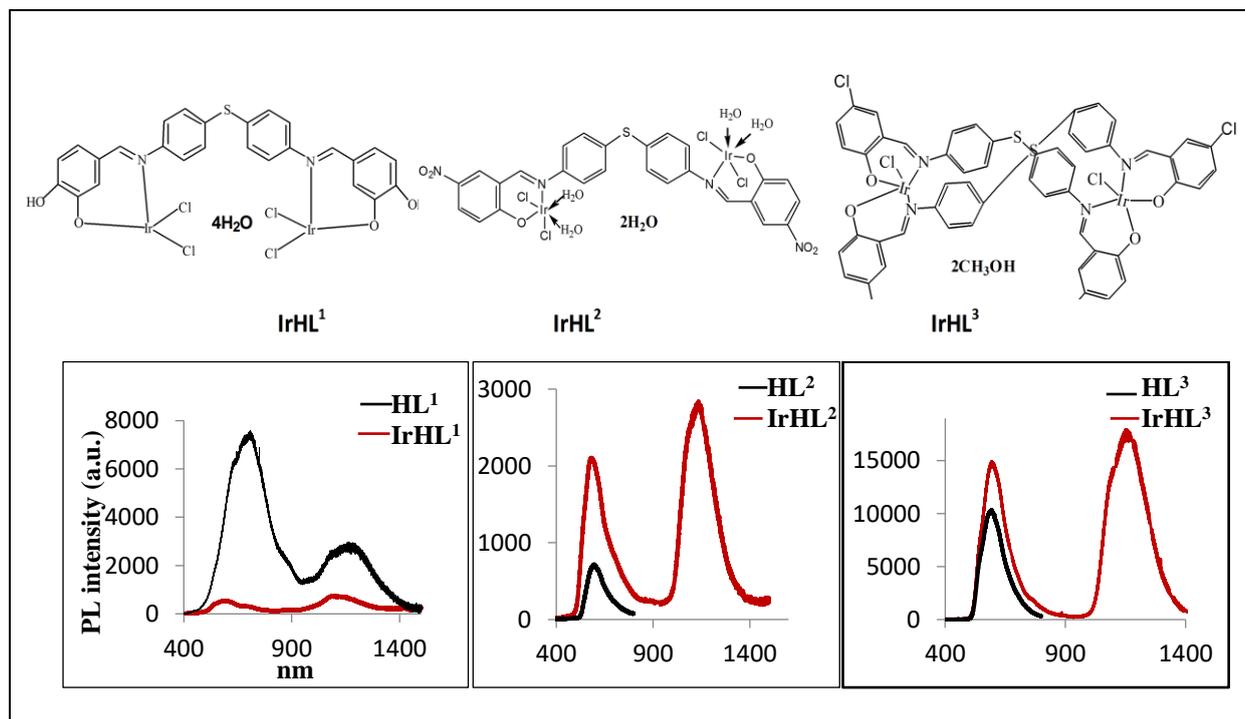


Figure 38. Dinuclear Ir(III) azomethine complexes with dual emissive peaks [72].

Another group [72] synthesised three new dinuclear Ir(III) azomethine complexes from Schiff bases, specifically *N,N*-bis-(3,4-dihydroxybenzaldehyde)-4,4-diaminodiphenylsulphide (HL^1), *N,N*-bis-(2-hydroxy-5-nitrobenzaldehyde)-4,4-diamino diphenyl sulphide (HL^2) and *N,N*-bis-(2-hydroxy-5-chloro benzaldehyde)-4,4-diaminodiphenylsulphide (HL^3), as depicted in Figure 38. Complexes in the solid state exhibited two strong emissions in the near infra-red (NIR) and visible regions. Initially, an emission peak in the visible region of 610 – 615 nm was ascribed to ligand-centred photoluminescence. The second emission peak was found at 1119 – 1177 nm, in the NIR region, and attributed to the triplet excited state emission of the iridium centre. All the synthesised complexes manifested thermal stability beyond 230 °C until decomposition. IrHL^3 and IrHL^2 showed significant solid-state photoluminescence

activities through Stokes Shift ($\Delta\lambda$) values of 285 nm and 289 nm, respectively, thus opening new avenues with dual emissive complexes in the solid state.

It can be concluded that azomethines are a specific class of chelating ligands extensively utilised to formulate metal-organic complexes, but not so much with Ir(III) centres. Azomethine ligands are considered better ancillary ligands to accelerate the synthesis of Ir(III) complexes due to their numerous intrinsic properties, particularly as tetradentate chelates, facilitating Ir(III) coordination with two nitrogen atoms and two hydroxyl groups. Their aromatic rings form a conjugated system, suitable for enhanced luminescence. Moreover, the

luminescence may be finetuned by structural modification of the azomethine ligands.

CONCLUSION

Analysis of the literature has revealed that a huge amount of work has been done on the mononuclear Zn(II) and Ir(III) luminescent Schiff base metal complexes with emissions in the green, blue and red regions, i.e., the visible region. In comparison to the thorough research on Zn(II) or Ir(III) mononuclear metal complexes, there have been few comparative studies of their binuclear counterparts and their dual emissive metal complexes, particularly in the near infrared region. Binuclear complexes whose ligands allow for two metal centres to be attached to the same molecule constitute a vital criterion in transition metal system analysis compared to mononuclear species, a consequence of tuning the bridging ligands or the two metal centres. In addition, binuclear-azomethine complexes with two metal centres held in close proximity may allow a significant metal-metal interaction that could give rise to unusual spectroscopic properties and enhanced luminescence behaviour unattainable by their mononuclear analogues. A fundamental understanding of such binuclear complexes permits their electronic absorption and luminescent properties to be fine-tuned.

Azomethine ligands with hard donor atoms, such as [N,O,O,N] can stabilise relatively hard Lewis acids, such as Zn(II) and Ir(III), causing reduced energy gaps for $\pi-\pi^*$ and $n-\pi^*$ electronic transitions and possible reduced energy loss caused by vibrational motions, inducing improved emission intensity.

FUTURE PROSPECTS

Despite the speedy progress achieved in the synthesis and design of Schiff base metal complexes, designing efficient red and near infrared luminophores as active materials remains a challenge. Compared to the visible light emitting metal complexes with Schiff base ligands which are widely used in various fields, there is a lack of research on the synthesis as well as application of NIR emitters. Most studies investigate the spectrum of NIR complexes with various ligands without material applications.

It is hoped that this review illustrating the different types of Schiff bases and their complexes that have been explored to develop luminescent materials with improved properties in the visible region highlights the need for further work which will open new frontiers for the material application and design of novel complexes with red and near infrared (NIR) emissive behaviour.

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DECLARATION OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the paper.

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