8-hydroxyquinoline was used extensively in fluorimetric determination of metals such as aluminum in a variety of substances since 1950’s [1-2]. The 8-hydroxyquinoline ligand was found to form complexes with many metals such as copper, lead, nickel, zinc and iron, as well as with group thirteen metals like aluminum, gallium and indium. These complexes were called as metalloquinolates and it was found that the metalloquinolates of group 13 metals and zinc were fluorescent [3]. However, it was in 1987, when Tang and Van Slyke fabricated the first bilayered organic thin film device and showed that the compound aluminum tris (8-hydroxyquinoline) Alq$_3$ played a major role in the development of OLEDs. The organic thin film device emitted green light under forward bias [2]. The two layers were comprised of Alq$_3$ and an aromatic diamine, where Alq$_3$ layer transported electrons and diamine layer conducted holes and light was emitted. Since this report extensive research and development has exploded for the development of Alq$_3$ as electron transport and emitting layer in OLEDs [4-19]. Today, the electrochemistry, the charge transport, the molecular packing of Alq$_3$ has all been reported in the literature [6, 10, 20-25].

Since 1987, various efforts have been made in various laboratories for tuning the emission color as well as efficiency of the device. Now Alq$_3$ has been widely used in organic light emitting devices as both electron transport layer and emissive layer [4-7, 9-19]. This is due to its high thermal stability up to 350°C, bright emission of green color, high photoluminescence efficiency (30%) and good electron mobility. The emitting color and the efficiency of the device of Alq$_3$ and other complexes can be tuned [9-13] either by changing the 8-hydroxyquinoline ligand or the central metal ion.

Metal chelates are considered to be ideal materials for OLEDs because of their high fluorescence in the solid state and their ability to transport electrons. Other metals that form fluorescent materials with quinolate ligands include gallium, indium, zinc, magnesium and beryllium. However all the metals could not be coordinated to the 8-hydroxyquinoline ligands and be used as fluorescent materials. Chelates with paramagnetic metal ions such as chromium and nickel are non fluorescent due to the high rate of intersystem crossing. Fluorescence is also reduced with increase in atomic number of metal ion due to increase rate
of intersystem crossing, so that Gaq$_3$ shows more fluorescence than Inq$_3$ and Alq$_3$ be the most fluorescent among these [7]. The emission wavelength can be tuned through metal centre. If the metal ligand bond is more covalent then it will be red shifted as compared to the ionic one.

The emission wavelength is red shifted if the metal ligand bond is more covalent than ionic one, for example, Mgq$_2$ emits at 540 nm while Znq$_2$ emits at 557 nm. The emission wavelength of metal chelates with 8-hydroxyquinoline can be shifted by adding different substituents to the quinoline ligand as mentioned earlier the filled orbitals (HOMO) are on the phenoxide side of the quinoline ligand while the unfilled orbitals LUMO are on the pyridyl side of the quinoline ligand. Addition of electron withdrawing group on the phenoxide side of the ligand will lower the energy of the filled state resulting in a blue shift in emission [20].

The most common and important factor is the thermal vibration of the chromophore, which provides a path for the loss of energy via a radiation less pathway. One can reduce the loss of energy via thermal vibration by increasing the rigidity of the chromophore. For coordination compounds, this reduction can be achieved by chelating the appropriate chromophore to a suitable metal ion, which reduces the degree of freedom of the thermal vibrations of the chromophore, thus increasing its emission efficiency. Compared with polymers, one advantage of metal chelates is that they can be prepared very pure. Therefore, they may have high luminescence quantum yields and high stabilities at high operating voltages.

Luminescent organic/organometallic compounds have been attracting much attention in recent years because of their potential applications in flat panel displays based on organic light emitting diodes (OLEDs). These materials have been especially important because of their high stability and efficiency [4, 19]. Among these materials, zinc complexes have been especially important because of their simplicity in synthesis procedures wide spectral response. Extensive research work is going on in various laboratories to synthesize new zinc complexes with new ligands to produce a number of novel luminescent zinc complexes having better efficiency [26-34]. The coordination number and bonding of zinc metal with different ligands are variable making it possible to synthesize new emitter material for varying opto-electronic applications.

The choice of metal ions for EL chelates is limited to those metals which do not exhibit d-d transitions that may interfere with the luminescence of the ligand. Therefore, aluminum (III), boron (III), beryllium (II) and zinc (II) are ideal, since beryllium (II), boron (III) and aluminum (III) has no d electron and zinc (II) has a closed shell of d electrons. Here
the metal ions only serve a structural purpose by stabilizing a luminescent ligand. In many cases it is observed that zinc metal complexes can be used both as an electron transport layer, hole transport layer or as an emissive layer, as these complexes have a wide range of spectrum in the visible region [19, 27]. Mixed ligand complexes are those which are composed of two or more different ligands. Luminescent materials based on metal complexes with two different ligands have been reported in literature for their use as emissive material as well as electron transport material [31, 35].

Mixed ligand aluminum complex BAlq (bis (2-methyl-8-quinolinate) 4- phenylphenolato) aluminum as a blue emitter [36-38] was first introduced by Kodak group [39], and are mostly used as hole blocking layer [40]. Xu et al. reported [41] a mixed-ligand bis (8-hydroxyquinoline) acetylacetone aluminum complex (Alq2A) with higher electron mobility and electroluminescent efficiency compared with Alq3. Blue emitting mixed-ligand Al complex with electron donating NH2 groups (at 2nd position) of 8-hydroxyquinoline ligand was reported by Nayak et al. [42]. Petrova et al. [43, 44] presented mixed ligand aluminum complex bis (8-hydroxyquinoline) acetylacetonate aluminum (Alq2Acac) and successfully used as electroluminescent and electron transporting layer for OLEDs. Mixed ligand zinc complex were successively used for fabrication of white OLEDs [45].

Taking into consideration the importance of Alq3 and the tuning of colors through mixed ligand complexes as electroluminescent materials, it was thought worthwhile to explore the possibility of metal complexes of derivatives of 8-hydroxyquinoline with benzothiazole or benzimidazole derivatives to be electroluminescent materials. Conventional methods for synthesis were used for this purpose.

In this chapter the synthesis and characterization of luminescent mixed ligand complexes so called ternary complexes of zinc, beryllium and magnesium with different derivatives of 8-hydroxyquinoline and (2-(2-hydroxyphenyl)benzothiazole), (2-(pyridyl) benzimidazole), (2-(2-hydroxyphenyl)benzoxazole) are presented. Structural and photo-physical properties of these metal complexes are presented in this chapter.

4.1 Synthesis of Zinc metal complexes:

The zinc complexes were synthesized by reacting zinc metal salt in water with ligands in ethanol as under:

4.1.1 (2-(2-Hydroxyphenyl)benzothiazolato)(5-chloro-8-hydroxyquinolinato)zinc(II) [ZnBTZ(Clq)]
The metal complex was obtained by the reaction of the two ligands 2-(2-hydroxyphenyl)benzothiazole (BTZ) and 5-chloro-8-hydroxyquinoline (Clq) with zinc acetate (ligands and metal) in 1:1:1 molar ratio in ethanol. A solution of BTZ (1.5 mmol) was prepared in 20 ml pure ethanol and then a solution of Clq (1.5 mmol) in 20 ml of pure ethanol was added to the reaction mixture and stirred at 60 °C for 2 h. A solution of zinc acetate (1.5 mmol) in 5 ml of deionized water was then added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered, washed with ethanol, deionised water and dried at 100 °C. The synthetic scheme is given below (scheme 4.1):

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\text{N} & \quad \text{S} \\
\text{HO} & \quad \text{Znacetate} \\
\text{60 °C, 2h} & \\
\end{align*}
\]

Scheme 4.1 Synthetic route of [ZnBTZ(Clq)]

4.1.2 (2-(2-hydroxyphenyl)benzothiazolato)(5, 7-dichloro-8-hydroxyquinolinato)zinc(II) [ZnBTZ(Cl₂q)]

The metal complex was prepared by the reaction of the two ligands 2-(2-hydroxyphenyl)benzothiazole (BTZ) and 5, 7-dichloro-8-hydroxyquinoline (Cl₂q) with zinc acetate (ligands and metal) in a molar ratio of 1:1:1 in ethanol following the method as described above. The reaction scheme is given below (Scheme 4.2):

\[
\begin{align*}
\text{Cl} & \quad \text{OH} \\
\text{N} & \quad \text{S} \\
\text{HO} & \quad \text{Znacetate} \\
\text{60 °C, 2h} & \\
\end{align*}
\]

Scheme 4.2 Synthetic route of [ZnBTZ(Cl₂q)]
4.1.3 (2-(2-Hydroxyphenyl)benzothiazolato)(5,7-dimethyl-8-hydroxyquinolinato)zinc(II) 
[ZnBTZ(Me₂q)]

In similar way as discussed above a solution of 2-(2-hydroxyphenyl)benzothiazole (BTZ) (1.5 mmol) was prepared in 20 ml pure ethanol and then a solution of 5, 7-dimethyl-8-hydroxyquinoline (Me₂q) (1.5 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. A solution of zinc acetate (1.5 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and washed with distilled water, ethanol and dried in oven.

\[
\text{Scheme 4.3 Synthetic route of [ZnBTZ(Me₂q)]}
\]

4.1.4 (2-(2-hydroxyphenyl)benzothiazolato)(2-methyl-8-hydroxyquinolinato)zinc(II) 
[ZnBTZ(Meq)]

[ZnBTZ(Meq)] was prepared by reacting a solution of 2-(2-hydroxyphenyl) benzothiazole (BTZ) (1.5 mmol) and 2-methyl-8-hydroxyquinoline (Meq) (1.5 mmol) in 20 ml pure ethanol and a solution of zinc acetate (1.5 mmol) in 5 ml of deionized water at 1:1:1 molar ratio. The procedure was followed as discussed above. A yellowish precipitate of the complex was filtered, washed and dried in oven. The synthetic scheme is given in scheme 4.4.

4.1.5 (2-(2-hydroxyphenyl) benzothiazolato)(8-hydroxyquinolinato)zinc(II) 
[ZnBTZ(q)]

The material ZnBTZ(q) was obtained by the reaction of 2-(2-hydroxyphenyl) benzothiazole (BTZ) and 8-hydroxyquinoline (q) with zinc acetate (ligands and metal) in
1:1:1 molar ratio in ethanol. The ZnBTZ(q) was synthesized according to the procedure reported above by taking (1.5 mmol) BTZ, (1.5 mmol) q and (1.5 mmol) zinc acetate. The synthetic scheme is given below (Scheme 4.5):

![Scheme 4.4 Synthetic route of [ZnBTZ(Meq)]]

![Scheme 4.5 Synthetic route of [ZnBTZ(q)]]

4.1.6 (2-(2-Hydroxyphenyl)benzothiazolato)(2-carbonitril-8-hydroxyquinolinato)zinc (II) [ZnBTZ(CNq)]

In similar way as above a solution of BTZ (1.5 mmol) prepared in 20 ml pure ethanol, a solution of 2-carbonitril-8-hydroxyquinoline (CNq) (1.5 mmol) in 20 ml of pure ethanol and a solution of zinc acetate (1.5 mmol) in 5 ml of deionized water with stirring at 60 °C for 2 h to get a yellowish precipitate of the complex which was filtered, washed with distilled water, ethanol and dried in oven. The reaction scheme is given below in scheme 4.6.
Characterization of zinc metal complexes

The synthesized zinc metal complexes were characterized with various techniques like CHN, FTIR, NMR, UV-visible absorption, Photoluminescent emission characterizations.

4.2 Structural characterization

4.2.1 ZnBTZ(Clq)

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzothiazolato)(5-chloro-8-hydroxyquinolinato)zinc(II) (C_{22}H_{13}N_{5}SO_{2}ZnCl) (found: C, 59.6; H, 3.06; N, 9.18; calc.: C, 59.8; H, 3.03; N, 9.10%)

FTIR Analysis:

5-Chloro-8-hydroxyquinoline showed a broad peak at 3340 cm⁻¹ due to the stretching vibration \(\nu\) (O-H) while 2-(2-hydroxyphenyl)benzothiazole showed its \(\nu\) (O-H) at 3145 cm⁻¹. On complexation with Zn (II) the broad characteristic peaks at 3340 cm⁻¹ and 3145 cm⁻¹ in 5-chloro-8-hydroxyquinoline and 2-(2-hydroxyphenyl)benzothiazole were vanished in the IR spectrum which confirmed the formation of the Zn-O bond. Other peaks, viz. the peak centred at 2990 cm⁻¹ was attributed to the stretching vibration of C-H bond in aromatic ring. Other vibrational modes at 1662 cm⁻¹ and 1574 cm⁻¹ were assigned to the skeleton stretching vibration of C=C bond in aromatic ring. The peak at 1606 cm⁻¹ was attributed to the stretching vibration of C=N bond. The vibrational absorption peaks of C–S at 949 cm⁻¹ was weak and narrow. The characteristic peaks of quinolinic rings from 600 to 800 cm⁻¹ showed the existence of quinolinic rings. Hence the complex formation occurred successfully and confirmed finally the structure to be a (2-(2-hydroxyphenyl)benzothiazolato)(5-chloro-8-hydroxyquinolinato)zinc (II).
For further confirmation of the complex formation, $^1$HNMR spectrum was taken in CDCl$_3$ and following observations were made. The $^1$HNMR spectral studies of the ZnBTZ (Clq) showed that the peaks for aromatic hydrogens were present at 6.79(m 1H), 7.14(m 1H), 7.34-7.92(m 9H), 8.4(m 1H) and 8.72(m 1H). The peak due to hydroxyl proton at 8.3 (which was present in 5-chloro-8-hydroxyquinoline) and at 8.7 which was present in 2-(2-hydroxyphenyl) benzothiazole) were absent in the $^1$HNMR spectra of the complex and confirmed the formation of the complex. The results also showed that the peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself taken from literature, indicated the formation of the reported complex.

4.2.2 ZnBTZ(Cl$_2$q)

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzothiazolato)(5,7-dichloro-8-hydroxyquinolinato)zinc(II)
(C$_{22}$H$_{12}$N$_2$SO$_2$ZnCl$_2$)
(found: C, 53.871; H, 2.62; N, 5.81; calc.: C, 54.06; H, 2.46; N, 5.73%)

FTIR Analysis:

The FTIR spectra of the (2-(2-hydroxyphenyl)benzothiazolato)-5,7-dichloro-8-hydroxyquinolinatozinc (II) showed different vibration peaks at:
2904 cm$^{-1}$ due to stretching vibration of C-H bond,
1661 cm$^{-1}$ and 1579 cm$^{-1}$ due to skeleton stretching vibration of C=C bond in aromatic ring,
1608 cm$^{-1}$ due to stretching vibration of C=N bond,
950 cm$^{-1}$ due to stretching vibration of C-S bond,
600 to 800 cm$^{-1}$ due to stretching vibration of quinolinic rings,
the broad characteristics peaks due to $\nu$ (O-H) were almost vanished in the complex which confirmed the formation of Zn-O bond.

$^1$HNMR

The $^1$HNMR spectral studies of the ZnBTZ(Cl$_2$q) showed peaks at 6.91(m 1 H), 7.09(m 1H), 7.35-7.91(m 8H), 8.35(m 1H) and 8.82(m 1H). The peaks shifted significantly downfield against the $^1$HNMR peak values of the ligand itself, taken from literature indicated the formation of the reported complex.
4.2.3 ZnBTZ(Me₂q)

**CHN Analysis:**

The C, H, N analysis of the complex indicated the formula of the complex to be \((2-(2\text{-hydroxyphenyl})\text{benzothiazolato})(5,7\text{-dimethyl-8-hydroxyquinolinato})\text{zinc(II)}\) 
\((C_{24}H_{18}N_2SO_2Zn)\)

(found: C, 61.87; H, 3.94; N, 6.09; calc.: C, 62.15; H, 3.88; N, 6.04%)

**FTIR Analysis:**

The FT-IR analysis of the complex \((2-(2\text{-hydroxyphenyl})\text{benzothiazolato})\text{-5,7-dimethyl-8-hydroxyquinolinatozinc (II)}\) showed vibration peaks at:
- \(2900 \text{ cm}^{-1}\) due to stretching vibration of C-H bond in aromatic ring,
- \(1660 \text{ cm}^{-1}\) and \(1575 \text{ cm}^{-1}\) due to skeleton stretching vibration of C=C bond in aromatic ring,
- \(1604 \text{ cm}^{-1}\) due to stretching vibration of C=N bond,
- \(940 \text{ cm}^{-1}\) due to vibrational absorption peaks of C–S bond,
- 600 to 800 \(\text{cm}^{-1}\) due to stretching vibrations of quinolinic rings,

the broad characteristics peaks due to \(\nu (O-H)\) were almost vanished in the complex which confirmed the formation of Zn-O bond.

**¹H NMR**

The \(¹\text{H NMR}\) spectral studies of the ZnBTZ(Me₂q) showed peaks at \(2.50 (s \text{ 3 H}), 3.62 (s \text{ 3H}), 6.95 (m \text{ 2H}), 7.10 (m \text{ 2H}), 7.26-7.92 (m \text{ 7H}), \text{ and 8.04 (m 1H)}\). The peaks shifted significantly downfield against the \(¹\text{H NMR}\) peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

4.2.4 ZnBTZ(Meq)

**CHN Analysis:**

The C, H, N analysis of the complex indicated the formula of the complex to be \((2-(2\text{-hydroxyphenyl})\text{benzothiazolato})(2\text{-methyl-8-hydroxyquinolinato})\text{zinc (II)}\) (C23H16N2SO2Zn)

(found: C, 61.37; H, 3.58; N, 6.26; calc.: C, 61.42; H, 3.56; N, 6.23%)

**FTIR Analysis:**

The FTIR analysis of the complex \((2-(2\text{-hydroxyphenyl})\text{benzothiazolato})(2\text{-methyl-8-hydroxyquinolinato})\text{zinc (II)}\) showed vibration peaks at:
- \(2990 \text{ cm}^{-1}\) due to stretching vibration of C-H bond in aromatic ring,
- \(1662 \text{ cm}^{-1}\) and \(1574 \text{ cm}^{-1}\) due to skeleton stretching vibration of C=C bond in aromatic ring,
1606 cm$^{-1}$ due to stretching vibration of C=N bond, 
949 cm$^{-1}$ vibrational absorption peaks of C–S bond, 
600 to 800 cm$^{-1}$ due to quinolinic rings, 
the broad characteristics peaks due to $\nu$(O-H) were almost vanished in the complex which confirmed the formation of Zn-O bond.

$^1$HNMR

The $^1$HNMR spectral studies of the ZnBTZ(Meq) showed peaks at 2.55(m 3H), 6.53(m 1H), 7.08-7.92(m 11H), and 8.22(m 1H). The peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

4.2.5 ZnBTZ(q)

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzothiazolato)(8-hydroxyquinolinato)zinc (II) (C$_{22}$H$_{14}$N$_2$SO$_2$Zn) 
(found: C, 60.61; H, 3.23; N, 6.47; calc.: C, 60.63; H, 3.21; N, 6.43%)

FTIR Analysis:

The FT-IR analysis of the complex (2-(2-hydroxyphenyl)benzothiazolato)-8-hydroxyquinolinato zinc (II) showed vibration peaks at: 
2990 cm$^{-1}$ due to stretching vibration of C-H bond in aromatic ring, 
1662 cm$^{-1}$ and 1574 cm$^{-1}$ due to skeleton stretching vibration of C=C bond in aromatic ring, 
1606 cm$^{-1}$ due to stretching vibration of C=N bond, 
949 cm$^{-1}$ vibrational absorption peaks of C–S bond, 
600 to 800 cm$^{-1}$ due to quinolinic rings, 
the broad characteristics peaks due to $\nu$(O-H) were almost vanished in the complex which confirmed the formation of Zn-O bond.

$^1$HNMR

The $^1$HNMR spectral studies of the ZnBTZ(q) showed peaks at 6.9-7.19 (m 3H), 7.29-7.99 (m 9H), 8.10(m 1H) and 8.7(m 1H). The peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.
4.2.6 ZnBTZ(CNq)

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzothiazolato)(2-carbonitril-8-hydroxyquinolinato)zinc(II)
(C$_{23}$H$_{13}$N$_{3}$SO$_{2}$Zn)
(found: C, 59.6; H, 3.06; N, 9.18; calc.: C, 59.8; H, 3.03; N, 9.10%)

FTIR Analysis:

The FTIR analysis of the complex (2-(2-hydroxyphenyl)benzothiazolato)(2-carbonitril-8-hydroxyquinolinato)zinc (II) showed vibration peaks at:
- 2990 cm$^{-1}$ due to stretching vibration of C-H bond in aromatic ring,
- 1660 cm$^{-1}$ and 1576 cm$^{-1}$ due to stretching vibration of C=C bond in aromatic ring,
- 1608 cm$^{-1}$ due to stretching vibration of C=N bond,
- 947 cm$^{-1}$ vibrational absorption peaks of C–S bond,
- 600 to 800 cm$^{-1}$ due to quinolinic rings,

the broad characteristics peaks due to $\nu$ (O-H) were almost vanished in the complex which confirmed the formation of Zn-O bond.

$^1$HNMR

The $^1$HNMR spectral studies of the ZnBTZ(CNq) showed peaks at 6.54(m 1H), 7.10-7.91(m 10H), and 8.21(m 1H). The peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

4.3 UV-Visible absorption and photo-luminescence (PL) characterization

The electronic spectra of zinc-quinolates complexes show multiple absorption bands, which are appearing in UV-visible part of the electromagnetic spectrum. The electronic spectra of these complexes are quite similar to the ligand precursors; indicate that the nature of excitations as ligand centred. Shifting of electron density from ligand to metal centre or reverse can be seen by shifting in peak positions. Jacobson et. al [46] explained the absorption spectra of similar type of metal complexes. They assigned the moderate electronic transitions ranging from 250-340 nm as $\pi–\pi^*$ ligand centred transitions. Kim et. al. [47] had observed similar transition in the coordination of zinc with organic ligands. They also
explained the electronic transitions ranging from 350-450 nm are not due to metal to ligand charge transfer but this behaviour should arise from an intra ligand charge transfer (ILCT) states [48-52].

4.3.1 ZnBTZ(Clq)

The UV-vis absorption and photo-luminescent emission spectrum of the complex ZnBTZ(Clq) were taken in ethanol. The complex had absorption band around 337 nm, which could be assigned to ligand centred (LC) \( \pi-\pi^* \) electronic transition. The complex had another low energy absorption band at 407 nm may be because of ligand centered n-\( \pi^* \) electronic transition as explained above. The PL spectrum of ZnBTZ(Clq) is shown in fig. 4.1. The complex exhibited bright yellowish-green photoluminescence with peak at 549 nm upon excitation at these wavelengths. The emitted color of PL yellowish-green had CIE color coordinates at \( x = 0.42, y = 0.52 \).

4.3.2 ZnBTZ(Cl_{2}q)

The UV-vis absorption and PL emission spectra of ZnBTZ (Cl_{2}q) were recorded in ethanol. The complex had absorption band around 344 nm as shown in fig. 4.2, which could be assigned to ligand centred (LC) \( \pi-\pi^* \) electronic transition. The complex had another low energy absorption band at 390 nm due to ligand centered n-\( \pi^* \) electronic transition. The complex exhibited bright green photoluminescence with peak at 532 nm upon excitation at these wavelengths as shown in PL spectrum of the complex. The emitted color of PL green had CIE color coordinates at \( x = 0.35, y = 0.56 \).
4.3.3 ZnBTZ(Me$_2$q)

Figure 4.3 shows the UV-vis absorption curve and PL spectra of ZnBTZ(Me$_2$q). The spectra were recorded in ethanol. The complex had absorption band around 341 nm, which could be assigned to ligand centred (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 401 nm due to ligand centered $n-\pi^*$ electronic transition. The PL spectrum of ZnBTZ(Me$_2$q) complex exhibited bright yellowish photoluminescence with peak at 572 nm upon excitation at these wavelengths. The emitted color of PL yellowish had CIE color coordinates at $x = 0.49$, $y = 0.47$.

4.3.4 ZnBTZ(Meq)
In figure 4.4 UV-vis absorption curve and PL spectra of ZnBTZ(Meq) are shown. The UV-vis absorption spectra were taken in ethanol. The complex had absorption band around 336 nm, which could be assigned to ligand centred (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 364 nm due to ligand centered $n-\pi^*$ electronic transition as explained above. The PL spectrum of ZnBTZ(Meq) was taken in solid state and is shown in fig. 4.4. The complex exhibited bright green photoluminescence with peak at 523 nm upon excitation at these wavelengths. The emitted color of PL green had CIE color coordinates at $x = 0.33$, $y = 0.45$.

4.3.5 ZnBTZ(q)

Figure 4.5 shows the UV-vis absorption and photo-luminescent emission spectra of ZnBTZ(q). The complex had absorption band around 334 nm, which could be assigned to ligand centred (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 386 nm due to ligand centered $n-\pi^*$ electronic transition. The PL spectrum of ZnBTZ(q) was taken in solid state and is shown in fig. 4.5. The complex exhibited bright yellowish-green photoluminescence with peak at 558 nm upon excitation at these wavelengths. The emitted color of PL yellowish-green had CIE color coordinates at $x = 0.36$, $y = 0.41$. 
4.3.6 ZnBTZ(CNq)

The UV-vis absorption curve and PL spectra of ZnBTZ(CNq) recorded in ethanol. The complex had absorption band around 336 nm, which could be assigned to ligand centered (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 485 nm because of ligand centered $n-\pi^*$ electronic transition. The PL spectrum of ZnBTZ(CNq) in ethanol is shown in fig. 4.6. The complex emitted bright orange photoluminescence with peak at 591 nm upon excitation at these wavelengths. The emitted color of PL orange had CIE color coordinates at $x = 0.48$, $y = 0.40$.

---

**Figure 4.5 UV-visible absorption and PL of [ZnBTZ(q)]**

**Figure 4.6 UV-visible absorption and PL of [ZnBTZ(CNq)]**
**Figure 4.7 Combined UV-visible absorption spectra of zinc complexes**

**Figure 4.8 Combined Photo-luminescent Spectra of zinc complexes**

**Table: 4.1 Photo-physical properties of zinc metal complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-vis absorption, $\lambda_{\text{max}}$(nm)</th>
<th>PL $\lambda_{\text{max}}$(nm)</th>
<th>CIE X/Y</th>
<th>Color of Emitted Light</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBTZ(Clq)</td>
<td>337, 407</td>
<td>549</td>
<td>x=0.42, y=0.52</td>
<td>Yellowish Green</td>
</tr>
<tr>
<td>ZnBTZ(Cl$_2$q)</td>
<td>344, 390</td>
<td>532</td>
<td>x=0.35, y=0.56</td>
<td>Green</td>
</tr>
<tr>
<td>ZnBTZ(Me$_2$q)</td>
<td>341, 401</td>
<td>572</td>
<td>x=0.48, y=0.47</td>
<td>Yellow</td>
</tr>
<tr>
<td>ZnBTZ(Meq)</td>
<td>336, 364</td>
<td>523</td>
<td>x=0.33, y=0.45</td>
<td>Green</td>
</tr>
<tr>
<td>ZnBTZ(q)</td>
<td>334, 386</td>
<td>558</td>
<td>x=0.36, y=0.41</td>
<td>Yellow</td>
</tr>
<tr>
<td>ZnBTZ(CNq)</td>
<td>336, 356</td>
<td>591</td>
<td>x=0.48, y=0.40</td>
<td>Orange</td>
</tr>
</tbody>
</table>
4.3.7 Discussion-

2-(2-hydroxyphenyl)benzothiazole and 8-hydroxyquinoline are known for formation of metal complexes with various metal ions, for their use as light emitting materials in organic light emitting diodes. Due to their chelating ability mixed ligand complexes of zinc with 2-(2-hydroxyphenyl)benzothiazole and 8-hydroxyquinoline derivatives had synthesized. It has been known that in 8-hydroxyquinoline HOMOs are located on the phenol ring and LUMOs are located on the pyridyl ring. Addition of electron donating group to phenol ring decreases the energy gap and addition of electron withdrawing group increases the energy gap resulting in red shift and blue shift in the emission wavelength, respectively. In our work we had taken two different ligands for complexation in order to form ternary metal complex. A series of complexes had been prepared by changing one ligand with its different derivatives. This was done to tune the color for the fabrication of full color displays and use of these metal complexes as emissive layer in OLEDs. ZnBTZ(Clq) emit at 551 nm, ZnBTZ(Cl$_2$q) at 532 nm, ZnBTZ(Me$_2$q) at 570 nm, ZnBTZ(CNq) at 591 nm, ZnBTZ(Meq) at 523 nm, ZnBTZ(q) at 558 nm, here electron withdrawing groups at phenoxide ring hypsochromically shifted the emission wavelength and electron donating group at phenoxide ring caused bathochromic shift in emission wavelength. It was concluded that attaching of electron withdrawing groups on phenol ring resulted in blue shift and addition of electron donating group phenol ring resulted in red shift.

4.4 Synthesis of zinc metal complexes

4.4.1 [2-(2-pyridyl)benzimidazolato](5-chloro-8-hydroxyquinolinato)zinc(II) [ZnPBI(Clq)]

The metal complex was obtained by the reaction of the two ligands 2-(2-pyridyl) benzimidazole (PBI) and 5-chloro-8-hydroxyquinoline with zinc acetate (ligands and metal) at 1:1:1 molar ratio in ethanol. A solution of PBI (1.5 mmol) was prepared in 20 ml pure ethanol and then a solution of 5-chloro-8-hydroxyquinoline (1.5 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of zinc acetate (1.5 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 100 °C.
4.4.2 [2-(2-pyridyl) benzimidazolato](2-methyl, 8-hydroxyquinolinato) zinc (II) [ZnPBI(Meq)]

The metal complex was synthesized by the reaction of the two ligands 2-(2-pyridyl) benzimidazole (PBI) and 2-methyl-8-hydroxyquinoline with zinc acetate (ligands and metal) at 1:1:1 molar ratio in ethanol and following the method as described above. The reaction is given below in scheme 4.8.

4.4.3 (2-(2-pyridyl)benzimidazolato)(8-hydroxyquinolinato)zinc(II) [ZnPBI(q)]

A solution of PBI (1.5 mmol) was prepared in 20 ml pure ethanol and stirred on a magnetic stirrer at 60 °C for 30 min and then a solution of 8-hydroxyquinoline (1.5 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of zinc acetate (1.5 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 100 °C.
Characterization

The ternary zinc metal complexes were characterized with various techniques like CHN, FTIR, NMR, UV-visible absorption, Photo-luminescent emissions characterizations.

4.5 Structural characterization

4.5.1 ZnPBI(Clq)

CHN Analysis

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-pyridyl)benzimidazolato)(5-chloro-8-hydroxyquinolinato)zinc(II) \( (C_{21}H_{14}N_{4}O_{2}Zn) \)

(found: C, 57.61, H, 2.98, N, 12.81, cal: C, 57.54, H, 2.96, N, 12.78 %)

FTIR Analysis

The broad characteristic peak at 3350 cm\(^{-1}\) corresponding to OH stretching vibration \( v_{(O-H)} \) in 5-chloro-8-hydroxyquinoline were almost vanished in the spectra which confirmed the formation of Zn-O bond. The peak centred at 2925 cm\(^{-1}\) was attributed to the stretching vibration of the C-H bond in aromatic ring. Other vibrational modes at 1597 cm\(^{-1}\) was assigned to the skeleton stretching vibration of C=C bond in aromatic ring. The peak at 1573 cm\(^{-1}\) was attributed to the stretching vibration of C=N bond. The vibrational absorption peaks of C-O at 1242 cm\(^{-1}\) was weak and narrow. The characteristic peaks of quinolinic rings from 600 to 800 cm\(^{-1}\) showed the presence of quinolinic rings. Hence the complex formation occurred successfully and confirmed finally the structure to be a (2-(2-pyridyl) benzimidazolato)5-chloro-8-hydroxyquinolinatozinc(II).

\(^1\)HNMR

The \(^1\)HNMR spectral studies of the ZnPBI(Clq) showed that the peaks for aromatic hydrogens were present at 7.10-7.75 (m 8H), 8.1-8.9(m 4H). The singlet peak due to
hydroxyl proton at 8.2 (which was present in 5-chloro-8-hydroxyquinoline) and also the N-H proton peak (which is present in 2-(2-pyridyl)benzimidazole) were absent in the $^1$HNMR spectra of the complex and confirmed the formation of the complex. The results showed that the peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

4.5.2 ZnPBI(Meq)

CHN Analysis

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-pyridyl)benzimidazolato)(2-methyl-8-hydroxyquinolinato)zinc (II) (C$_{22}$H$_{16}$N$_4$OZn)
(found: C, 63.28, H, 3.85, N, 13.45, cal: C, 63.25, H, 3.83, N, 13.41 % )

FTIR Analysis

The FT-IR analysis of the complex (2-(2-pyridyl)benzimidazolato)-2-methyl-8-hydroxyquinolinatozinc(II) showed vibration peaks at:
2940 cm$^{-1}$ due to stretching vibration of the C-H bond in aromatic ring,
1604 cm$^{-1}$ and 1592 cm$^{-1}$ due to skeleton stretching vibration of C=C bond in aromatic ring,
1566 cm$^{-1}$ due to stretching vibration of C=N bond,
1240 cm$^{-1}$ vibrational absorption peaks of C-O bond,
600 to 800 cm$^{-1}$ due to quinolinic rings,
the broad characteristics peaks due to $\nu$ (O-H) were almost vanished in the complex which confirmed the formation of Zn-O bond.

$^1$HNMR Analysis

The $^1$HNMR spectral studies of the ZnPBI(Meq) showed peaks at 2.55(m 3H), 6.11(m 1H), 6.32-6.9(m 5H), 7.15(m 1H), 7.24(m 1H), 7.35(m 2H), 7.75(m 1H), 8.00(m 2H) and 8.65(m 1H). The peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

4.5.3 ZnPBI(q)

CHN Analysis

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-pyridyl)benzimidazolato)(8-hydroxyquinolinato)zinc(II) (C$_{21}$H$_{14}$N$_4$OZn)
FTIR Analysis

The FTIR analysis of the complex (2-(2-pyridyl)benzimidazolato)(8-
hydroxyquinolinato)zinc(II) showed vibration peaks at:
2950 cm\(^{-1}\) due to stretching vibration of the C-H bond in aromatic ring,
1601 cm\(^{-1}\) due to skeleton stretching vibration of C=C bond in aromatic ring,
1574 cm\(^{-1}\) due to stretching vibration of C=N bond,
1233 cm\(^{-1}\) vibrational absorption peaks of C-O bond,
600 to 800 cm\(^{-1}\) due to quinolinic rings,
the broad characteristics peaks due to \(\nu\) (O-H) were almost vanished in the complex which
confirmed the formation of Zn-O bond.

\(^1\)HNMR

The \(^1\)HNMR spectral studies of the ZnPBI(q) showed
peaks at 7.19-7.77(m 8H),
8.11(m 2H), 8.4(m 2H) and 8.77(m 2H). The peaks shifted significantly downfield against the
\(^1\)HNMR peaks values of the ligand itself, taken from literature indicated the formation of the
reported complex.

4.6 UV-Visible absorption and photoluminescence (PL) characterization

As explained earlier, the electronic spectra of zinc-quinolate complexes show multiple
absorption bands, which are appearing in UV-visible part of the electromagnetic spectrum.
The electronic spectra of these complexes are quite similar to the ligand precursors; indicate
that the nature of excitations as ligand centred. Shifting of electron density from ligand to
metal centre or reverse can be seen by shifting in peak positions.

4.6.1 [ZnPBI(Clq)]

Figure 4.9 shows the UV-vis absorption spectrum of ZnPBI(Clq) which was recorded
in ethanol. The complex had absorption band around 341 nm, which could be assigned to
ligand centred (LC) \(\pi-\pi^*\) electronic transition. The complex had another low energy
absorption band at 400 nm due to ligand centered n-\(\pi^*\) electronic transition. The PL spectrum
of ZnPBI(Clq) in solid state is shown in fig. 4.9. The complex exhibited bright yellowish
photoluminescence with peak at 556 nm upon excitation at these wavelengths. The emitted
color of PL yellowish had CIE color coordinates at \(x = 0.37, y = 0.39\).
4.6.2 [ZnPBI(Meq)]

The UV-vis absorption spectrum of the complex was taken in ethanol. The complex had absorption band around 253 nm, which could be assigned to ligand centred (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 355 nm due to ligand centered n- $\pi^*$ electronic transition. The PL spectrum of ZnPBI(Meq) was taken in solid state and is shown as curve B fig. 4.10. The complex exhibited bright green photoluminescence with peak at 534 nm upon excitation at these wavelengths. The emitted color of PL green had CIE color coordinates at $x = 0.34$, $y = 0.40$. 

4.6.3 [ZnPBI(q)]
The UV-vis absorption spectrum of ZnPBI(q) was taken in ethanol. This complex had absorption band around 335 nm as shown in fig. 4.11, which could be assigned as ligand centred (LC) π-π* electronic transition. The complex had another low energy absorption band at 383 nm may be because of ligand centered n-π* electronic transition as explained above. The PL spectrum of ZnPBI(q) in solid state is shown as curve B in fig. 4.11. The complex exhibited bright yellow photoluminescence with peak at 564 nm upon excitation at these wavelengths. The emitted color of PL yellow had CIE color coordinates at x = 0.38, y = 0.44.

**Table: 4.2 Photo-physical properties of zinc metal complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-vis absorption, ( \lambda_{\text{max}} ) (nm)</th>
<th>PL ( \lambda_{\text{max}} ) (nm)</th>
<th>CIE X/Y</th>
<th>Color of Emitted Light</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{ZnPBI(Clq)}])</td>
<td>341, 400</td>
<td>556</td>
<td>x = 0.37, y = 0.39</td>
<td>Yellow</td>
</tr>
<tr>
<td>([\text{ZnPBI(Meq)}])</td>
<td>253, 355</td>
<td>534</td>
<td>x = 0.34, y = 0.40</td>
<td>Green</td>
</tr>
<tr>
<td>([\text{ZnPBI(q)}])</td>
<td>335, 383</td>
<td>564</td>
<td>x = 0.38, y = 0.44</td>
<td>Yellow</td>
</tr>
</tbody>
</table>
4.6.4 Discussion-

Color tuning is very important for the fabrication of full color displays. Keeping this in view, mixed ligand complexes of zinc metal with 2-(2-pyridyl)benzimidazole and 8-hydroxyquinoline were prepared. Different derivatives of 8-hydroxyquinoline were taken for this purpose. It was observed that addition of electron donating group to phenol ring decreases the energy gap and addition of electron withdrawing group increases the energy gap resulted in red sift and blue shift in the emission wavelength, respectively in these complexes.
4.7 Synthesis of Beryllium metal complexes:

4.7.1 (2-(2-hydroxyphenyl)benzoxazolato)(5-chloro,8-hydroxyquinolinato)beryllium(II) [BeHPB(Clq)]

The metal complex was obtained by the reaction of the two ligands 2-(2-hydroxyphenyl)benzoxazole (HPB) and 5-chloro-8-hydroxyquinoline (Clq) with beryllium sulphate (ligands and metal) at 1:1:1 molar ratio in ethanol. A solution of HPB 0.5 g (1 mmol) was prepared in 20 ml pure ethanol and stirred on a magnetic stirrer at 60 °C for 30 min and then a solution of 5-chloro-8-hydroxyquinoline 0.36 g (1 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of beryllium sulphate (1 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 100 °C. The synthetic scheme is shown in scheme 4.10.

\[
\text{Scheme 4.10 Synthetic route of } [\text{BeHPB(Clq)}]
\]

4.7.2 (2-(2-hydroxyphenyl)benzoxazolato)(5,7-dichloro-8-hydroxyquinolinato)beryllium (II) [BeHPB(Cl₂q)]

The metal complex was obtained by the reaction of the two ligands 2-(2-hydroxyphenyl)benzoxazole (HPB) and 5,7-dichloro-8-hydroxyquinoline (Cl₂q) with beryllium sulphate (ligands and metal) at 1:1:1 molar ratio in ethanol. A solution of HPB 0.5 g (1 mmol) was prepared in 20 ml pure ethanol and stirred on a magnetic stirrer at 60 °C for 30 min and then a solution of 5,7-dichloro-8-hydroxyquinoline 0.36 g (1 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of beryllium sulphate 0.52 g (1 mmol) in 5 ml of deionized
water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 100 °C.

![Scheme 4.11 Synthetic route of [BeHPB(Cl₂q)]](image)

**Scheme 4.11 Synthetic route of [BeHPB(Cl₂q)]**

### 4.7.3 (2-(2-hydroxyphenyl)benzoxazolato)(2-methyl-8-hydroxyquinolinato)beryllium(II) [BeHPB(Meq)]

In similar way a solution of HPB 0.5 g (1 mmol) was prepared in 20 ml pure ethanol and stirred on a magnetic stirrer at 60 °C for 30 min and then a solution of 2-methyl, 8-hydroxyquinoline 0.36 g (1 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of beryllium sulphate 0.52 g (1 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and washed with deionised water and ethanol then dried in oven.

![Scheme 4.12 Synthetic route of [BeHPB(Meq)]](image)

**Scheme 4.12 Synthetic route of [BeHPB(Meq)]**

### 4.7.4 (2-(2-hydroxyphenyl) benzoxazolato)(8-hydroxyquinolinato)beryllium(II) [BeHPB(q)]
[BeHPB(q)] was obtained by the reaction of HPB 0.5 g (1 mmol) 8-hydroxyquinoline (q) 0.36 g (1 mmol) in 20 ml of pure ethanol and a solution of beryllium sulphate 0.52 g (1 mmol) in 5 ml of deionized water at 1:1:1 molar ratio. The method was followed as discussed above. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered and dried at 100 °C. The synthetics scheme is given below (Scheme 4.11):

![Scheme 4.13 Synthetic route of [BeHPB(q)]](image)

**Characterization**

The beryllium metal complexes were characterized using various techniques as CHN, FTIR, $^1$HNMR, UV-visible excitation spectroscopy and emission spectroscopy.

**4.8 Structural characterization**

**4.8.1 [BeHPB(Clq)]**

**CHN Analysis:**

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzoxazolato)(5-chloro-8-hydroxyquinolinato)beryllium(II)

(C$_{22}$H$_{13}$N$_2$O$_3$BeCl)

(found: C, 66.32; H, 3.29; N, 7.06; calc.: C, 66.41; H, 3.27; N, 7.04%)

$^1$HNMR

The $^1$HNMR spectral studies of the BeHPB(Clq) showed that the peaks for aromatic hydrogens were present at 6.77(m 1H), 7.10(m 1H), 7.34-7.92 (m 8H), 8.4(m 1H) and 8.72(m 1H). The singlet peak due to hydroxyl proton at 8.2 (which was present in 5-chloro-8-hydroxyquinoline) and at 8.7 (which was present in 2-(2-hydroxyphenyl)benzoxazole) were absent in the $^1$HNMR spectra of the complex and confirmed the formation of the complex. The results also showed that the peaks shifted significantly downfield against the $^1$HNMR
peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

FTIR Analysis:

The broad characteristic peaks at 3340 cm\(^{-1}\) corresponding to OH stretching vibration ν(O-H) in 5-chloro-8-hydroxyquinoline were absent in the spectra which confirmed the formation of Be-O bond. The peak centred at 2990 cm\(^{-1}\) was attributed to the stretching vibration of C-H bond in aromatic ring. Other vibrational modes at 1662 cm\(^{-1}\) and 1574 cm\(^{-1}\) was assigned to the skeleton stretching vibration of C=C bond in aromatic ring. The peak at 1606 cm\(^{-1}\) was attributed to the stretching vibration of C=N bond. The vibrational absorption peaks of C–O at 1256 cm\(^{-1}\) is weak and narrow. The characteristic peaks of quinolinic rings from 600 to 800 cm\(^{-1}\) showed the existence of quinolinic rings. Hence the complex formation occurred successfully and confirmed finally the structure to be (2-(2-hydroxyphenyl)benzoazolato)(5-chloro-8-hydroxyquinolinato)beryllium (II).

4.8.2 [BeHPB(Cl\(_2\)q)]

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzoazolato)(5,7-dichloro-8-hydroxyquinolinato)beryllium(II) (C\(_{22}\)H\(_{12}\)N\(_2\)O\(_3\)BeCl\(_2\))

(found: C, 61.06; H, 2.79; N, 6.51; calc.: C, 61.11; H, 2.77; N, 6.48%)

\(^1\)HNMR

The \(^1\)HNMR spectral studies of the BeHPB(Cl\(_2\)q) showed peaks at 6.91(m 1H), 7.09(m 1H), 7.35-7.91(m 8H), 8.35(m 1H) and 8.82(m 1H). The peaks shifted significantly downfield against the \(^1\)HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

FTIR Analysis:

The FTIR analysis of the complex (2-(2-hydroxyphenyl)benzoazolato)(5, 7-dichloro-8-hydroxyquinolinato)beryllium(II) showed vibration peaks at:

- 2904 cm\(^{-1}\) due to stretching vibration of 2904 cm\(^{-1}\) in aromatic ring,
- 1661 cm\(^{-1}\) and 1579 cm\(^{-1}\) due to skeleton stretching vibration of C=C bond in aromatic ring,
- 1608 cm\(^{-1}\) due to stretching vibration of C=N bond,
- 1251 cm\(^{-1}\) vibrational absorption peaks of C–O bond,
600 to 800 cm\(^{-1}\) due to quinolinic rings,
the broad characteristics peaks due to \(\nu\) (O-H) were almost vanished in the complex which confirmed the formation of Be-O bond.

### 4.8.3 [BeHPB(Meq)]

**CHN Analysis:**

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzoxazolato)(2-methyl-8-hydroxyquinolinato)beryllium(II)  
\(\text{C}_{23}\text{H}_{16}\text{N}_{2}\text{O}_{3}\text{Be}\)  
(found: C, 73.16; H, 4.26; N, 7.45; calc.: C, 73.20; H, 4.24; N, 7.42%)

**\(^1\)HNMR**

The \(^1\)HNMR spectral studies of the BeHPB(Meq) showed peaks at 2.50(s 3H), 6.95(m 1H), 7.10-7.92(m 11H), and 8.04(m 1H). The peaks shifted significantly downfield against the \(^1\)HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

**FTIR Analysis:**

The FTIR analysis of the complex (2-(2-hydroxyphenyl)benzoxazolato)-2-methyl-8-hydroxyquinolinatoberyllium(II) showed vibration peaks at:
- 2905 cm\(^{-1}\) due to stretching vibration of C-H bond in aromatic ring,
- 1661 cm\(^{-1}\) and 1579 cm\(^{-1}\) due to skeleton stretching vibration of C=C bond in aromatic ring,
- 1608 cm\(^{-1}\) due to stretching vibration of C=N bond,
- 1245 cm\(^{-1}\) vibrational absorption peaks of C–O bond,
- 600 to 800 cm\(^{-1}\) due to quinolinic rings,
the broad characteristics peaks due to \(\nu\) (O-H) were almost vanished in the complex which confirmed the formation of Be-O bond.

### 4.8.4 [BeHPB(q)]

**CHN Analysis:**

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzoxazolato)(8-hydroxyquinolinato)beryllium(II)  
\(\text{C}_{22}\text{H}_{14}\text{N}_{2}\text{O}_{3}\text{Be}\)  
(found: C, 72.75; H, 3.87; N, 7.74; calc.: C, 72.72; H, 3.85; N, 7.71%)

**\(^1\)HNMR**
The $^1$HNMR spectral studies of the BeHPB(q) showed peaks at 6.93(m 1H), 7.15(m 2H), 7.26-7.92(m 9H), and 8.06(m 1H). The peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

FTIR Analysis:

The FTIR analysis of the complex (2-(2-hydroxyphenyl)benzoxazolato)-8-hydroxyquinolinatoberyllium(II) showed vibration peaks at:
- 2993 cm$^{-1}$ due to stretching vibration of C-H bond in aromatic ring,
- 1662 cm$^{-1}$ and 1570 cm$^{-1}$ due to skeleton stretching vibration of C=C bond in aromatic ring,
- 1607 cm$^{-1}$ due to stretching vibration of C=N bond,
- 1250 cm$^{-1}$ vibrational absorption peaks of C–O bond,
- 600 to 800 cm$^{-1}$ due to quinolinic ring,
- the broad characteristics peaks due to $\nu$(O-H) were almost vanished in the complex which confirmed the formation of Be-O bond.

4.9 Optical characterization

The beryllium metal complexes were optically characterized using excitation and emission spectroscopy.

4.9.1 [BeHPB(Clq)]

The excitation spectrum of the complex was taken in methanol. The complex had absorption band at 287 nm as shown in fig. 4.14, which could be assigned to ligand centred (LC) $\pi$-$\pi^*$ electronic transition. The complex had another low energy absorption band at 338 nm due to ligand centered n-$\pi^*$ electronic transition. The emission spectrum of complex upon excitation at 338 nm is shown in fig. 4.14. In emission spectrum broad peak at 496 nm resulting in a bright blue green emission had a considerable intensity as shown in fig. 4.14. The emitted color of PL had CIE (1931) color coordinates at x = 0.15, y = 0.43.
4.9.2 [BeHPB(Cl₂q)]

The excitation spectrum of the complex BeHPB(Cl₂q) was taken in methanol solution. The excitation spectrum was evidenced by the metal perturbed ligand centred $\pi-\pi^*$ transition. The complex had absorption band at 278 nm as shown in fig. 4.15, which could be assigned to ligand centred (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 378 nm due to ligand centered n- $\pi^*$ electronic transition. The emission spectrum of complex upon excitation at 378 nm is shown in fig. 4.15. The emission spectrum in solid state had a broad peak at 510 nm resulting in a bright blue green emission and had a considerable intensity as shown in fig. 4.15. The emitted color of PL blue-green had CIE (1931) color coordinates at $x = 0.21$, $y = 0.56$. 

Figure 4.14 UV-visible and emission spectra of [BeHPB(Clq)]

Figure 4.15 UV-visible and emission spectra of [BeHPB(Cl₂q)]
4.9.3 [BeHPB(Meq)]

The excitation spectrum of the complex BeHPB(Meq) was taken in methanol solution. The excitation spectrum was evidenced by the metal perturbed ligand centred $\pi \rightarrow \pi^*$ transition. The complex had absorption band at 246 nm as shown in fig. 4.16, which could be assigned to ligand centred (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 365 nm due to ligand centered n- $\pi^*$ electronic transition. The emission spectrum of complex upon excitation at 365 nm is shown in fig. 4.16. The emission spectrum in solid state had a broad peak at 487 nm resulting in a bright blue emission and had a considerable intensity as shown in fig. 4.16. The emitted color of PL blue had CIE (1931) color coordinates at $x = 0.14$, $y = 0.38$.

4.9.4 [BeHPB(q)]

The excitation spectrum of the complex BeHPB(q) was taken in methanol solution. The excitation spectrum was evidenced by the metal perturbed ligand centred $\pi-\pi^*$ transition. The complex had absorption band at 282 nm as shown in fig. 4.17, which could be assigned to ligand centred (LC) $\pi-\pi^*$ electronic transition. The complex had another low energy absorption band at 332 nm because of ligand centered n- $\pi^*$ electronic transition. The luminescence spectrum of complex upon excitation at 332 nm is shown in fig. 4.17. The emission spectrum in solid state had a broad peak at 497 nm resulting in a bright blue emission and had a considerable intensity as shown in fig. 4.17. The emitted color of PL blue had CIE (1931) color coordinates at $x = 0.17$, $y = 0.41$. 
**Figure 4.17 UV-visible and emission spectra of [BeHPB(q)]**

**Table: 4.3 Photo-physical properties of Beryllium metal complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-vis absorption, $\lambda_{\text{max}}$(nm)</th>
<th>Emission Peak</th>
<th>Color of emitted light</th>
<th>Color Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\pi-\pi^*$</td>
<td>$n-\pi^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BeHPB(Clq)</td>
<td>287</td>
<td>338</td>
<td>496</td>
<td>Blue Green</td>
</tr>
<tr>
<td>BeHPB(Cl₂q)</td>
<td>278</td>
<td>378</td>
<td>510</td>
<td>Greenish Blue</td>
</tr>
<tr>
<td>BeHPB(Meq)</td>
<td>246</td>
<td>365</td>
<td>490</td>
<td>Blue Green</td>
</tr>
<tr>
<td>BeHPB(q)</td>
<td>282</td>
<td>332</td>
<td>505</td>
<td>Bluish Green</td>
</tr>
</tbody>
</table>

**Figure 4.18 Combined excitation spectra of beryllium metal complexes**
4.9.5 Discussion-

A series of beryllium metal complexes with 2-(2-hydroxyphenyl)benzoxazole and 8-hydroxyquinoline derivatives had been prepared. The metal complexes emitted blue-green light on excitation with ultraviolet visible light. This was done for color tuning purposes for full color displays fabrication and use of these metal complexes as emissive layer in OLEDs. There was a shift in emission wavelength on attaching substituents, an electron withdrawing group on phenol ring resulted in blue shift and addition of electron donating group phenol ring resulted in red shift. The emission wavelength of BeHPB(Clq) i.e. 496 nm was hypsochromically shifted as compared to BeHPB(q) PL i.e. 505 nm. Similarly BeHPB(Meq) emit at 490 nm, at lower wavelength than BeHPB(q) emission wavelength. Beryllium metal complexes emit at lower wavelength than Zinc metal complexes as Be is lighter metal than Zn. Beryllium complexes emit in blue and blue-green region while the zinc complexes emit in blue-green to yellow to orange region. This shows that there is increase in covalent character in metal ligand bond with increase in size of metal that shift the wavelength to red region.

4.10 Synthesis of magnesium metal complexes

4.10.1 2-(2-hydroxyphenyl)benzoxazolato)(5-chloro,8-hydroxyquinolinato)magnesium (II)

[MgHPB(Clq)]
The metal complex was obtained by the reaction of the two ligands 2-(2-hydroxyphenyl)benzoxazole (HPB) and 5-chloro-8-hydroxyquinoline (Clq) with magnesium sulphate (ligands and metal) at 1:1:1 molar ratio in ethanol. A solution of HPB 0.5 g (1.5 mmol) was prepared in 20 ml pure ethanol and stirred on a magnetic stirrer at 60 °C for 30 min and then a solution of 5-chloro-8-hydroxyquinoline 0.36 g (1.5 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of magnesium sulphate 0.52 g (1.5 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered, washed with deionized water, ethanol and dried at 100 °C.

Scheme 4.14 Synthetic route of [MgHPB(Clq)]

4.10.2 2-(2-hydroxyphenyl)benzothiazolato)(5-chloro, 8-hydroxyquinolinato)magnesium (II)

[MgBTZ(Clq)]

A solution of BTZ 0.5 g (1.5 mmol) was prepared in 20 ml pure ethanol and stirred on a magnetic stirrer at 60 °C for 30 min and then a solution of 5-chloro,8-hydroxyquinoline (Clq) 0.36 g (1.5 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of magnesium sulphate 0.52 g (1.5 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered, washed and dried at 100 °C.
4.10.3 (2-(2-hydroxyphenyl)benzothiazolato)(5,7-dichloro,8-hydroxyquinolinato) magnesium(II)
[MgBTZ(Cl₂q)]

In similar way a solution of BTZ 0.5 g (1.5 mmol) was prepared in 20 ml pure ethanol and stirred on a magnetic stirrer at 60 °C for 30 min and then a solution of 5, 7-dichloro,8-hydroxyquinoline (Cl₂q) 0.43 g (1.5 mmol) in 20 ml of pure ethanol was added to the reaction mixture, and stirred at 60 °C for 2 h. This was allowed to cool to 50 °C and a solution of magnesium sulphate 0.52 g (1.5 mmol) in 5 ml of deionized water was added drop wise to the reaction mixture. After 2 h of stirring a yellowish precipitate of the complex was separated from the reaction mixture which was filtered, washed and dried at 100 °C. The synthetic route is given below (Scheme 4.16):

**Scheme 4.15 Synthetic route of [MgBTZ(Clq)]**

**Scheme 4.16 Synthetic route of [MgBTZ(Cl₂q)]**

**Characterization**

The magnesium metal complexes were characterized using various techniques as CHN, ¹HNMR, FTIR, UV-visible absorption spectroscopy and photo-luminescence spectroscopy.

4.11 Structural Characterization
4.11.1 [MgHPB(Clq)]

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzoxazolato)(5-chloro-8-hydroxyquinolinato)magnesium(II)

\( (C_{22}H_{13}N_2O_3MgCl) \)

(found: C, 63.96 ; H, 3.18 ; N, 6.81 ; calc.: C, 64.00 ; H, 3.15 ; N, 6.78 %)

\(^1\)HNMR

The \(^1\)HNMR spectral studies of the MgHPB(Clq) showed that the peaks for aromatic hydrogens were present at 6.78(m 1H), 7.10(m 1H), 7.32-7.89(m 8H), 7.83(m 1H) and 8.73(m 1H). The singlet peak due to hydroxyl proton at 8.2 (which was present in 5-chloro, 8-hydroxyquinoline) and at 8.6 (which was present in 2-(2-hydroxyphenyl)benzoxazole) were absent in the \(^1\)HNMR spectra of the complex and confirmed the formation of the complex. The results also showed that the peaks shifted significantly downfield against the \(^1\)HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

FTIR Analysis:

The broad characteristic peaks at 3350 cm\(^{-1}\) corresponding to OH stretching vibration \( \nu (O-H) \) in 5-chloro-8-hydroxyquinoline were vanished in the spectra which confirmed the formation of the Mg-O bond. The peak centred at 2950 cm\(^{-1}\) was attributed to the stretching vibration of C-H bond in aromatic ring. Other vibrational modes at 1650 cm\(^{-1}\) and 1579 cm\(^{-1}\) was assigned to the skeleton stretching vibration of C=C bond in aromatic ring. The peak at 1608 cm\(^{-1}\) was attributed to the stretching vibration of C=N bond. The vibrational absorption peaks of C–O at 1230 cm\(^{-1}\) was weak and narrow. The characteristic peaks of quinolinic rings from 600 to 800 cm\(^{-1}\) showed the existence of quinolinic rings. Hence the complex formation occurred successfully and confirmed finally the structure to be a (2-(2-hydroxyphenyl) benzoxazolato)(5-chloro-8-hydroxyquinolinato)magnesium (II).

4.11.2 [MgBTZ(Clq)]

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzothiazolato)(5-chloro-8-hydroxyquinolinato)magnesium(II)

\( (C_{22}H_{13}N_2O_2SCLMg) \)

(found: C, 61.4 ; H, 3.06 ; N, 6.57 ; calc.: C, 61.6 ; H, 3.03 ; N, 6.53 %)
The $^1$H NMR spectral studies of the MgBTZ(Cl$_2$q) showed that the peaks for aromatic hydrogens were present at 6.79(m 1H), 7.13(m 1H), 7.33-7.92(m 9H), 8.4(m 1H) and 8.72(m 1H). The singlet peak due to hydroxyl proton at 8.2 (which is present in 5-chloro, 8-hydroxyquinoline) and at 8.7 (which was present in 2-(2-hydroxyphenyl)benzothiazole) were absent in the $^1$HNMR spectra of the complex and confirmed the formation of the complex. The results also showed that the peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

FTIR Analysis:

The broad characteristic peaks at 3335 cm$^{-1}$ corresponding to OH stretching vibration $\nu$(O-H) in 5-chloro,8-hydroxyquinoline came were vanished in the spectra which confirmed the formation of the Mg-O bond. The peak centred at 2975 cm$^{-1}$ is attributed to the stretching vibration of C-H bond in aromatic ring. Other vibrational modes at 1646 cm$^{-1}$ and 1587 cm$^{-1}$ was assigned to the skeleton stretching vibration of C=C bond in aromatic ring. The peak at 1612 cm$^{-1}$ is attributed to the stretching vibration of C=N bond. The vibrational absorption peaks of C–S at 939 cm$^{-1}$ was weak and narrow. The characteristic peaks of quinolinic rings from 600 to 800 cm$^{-1}$ showed the existence of quinolinic rings. Hence the complex formation occurred successfully and confirmed finally the structure to be a (2-(2-hydroxyphenyl)benzothiazolato)(5-chloro-8-hydroxyquinolinato)magnesium(II).

4.11.3 [MgBTZ(Cl$_2$q)]

CHN Analysis:

The C, H, N analysis of the complex indicated the formula of the complex to be (2-(2-hydroxyphenyl)benzothiazolato)(5,7-dichloro,8-hydroxyquinolinato)magnesium(II)

(C$_{22}$H$_{12}$N$_2$O$_2$SCl$_2$Mg)

(found: C, 56.94; H, 2.61; N, 6.06; calc.: C, 57.02; H, 2.59; N, 6.04%)

$^1$HNMR

The $^1$HNMR spectral studies of the MgBTZ(Cl$_2$q) showed peaks at 6.90(m 1H), 7.10(m 1H), 7.34-7.89(m 8H), 8.37(m 1H) and 8.83(m 1H). The peaks shifted significantly downfield against the $^1$HNMR peaks values of the ligand itself, taken from literature indicated the formation of the reported complex.

FTIR Analysis:
The FTIR analysis of the complex (2-(2-hydroxyphenyl)benzothiazolato)(5,7-dichloro-8-hydroxyquinolinato)magnesium(II) showed peaks at:

- 2904 cm\(^{-1}\) due to stretching vibration of C-H bond in aromatic ring,
- 1661 cm\(^{-1}\) and 1579 cm\(^{-1}\) due to skeleton stretching vibration of C=C bond in aromatic ring,
- 1608 cm\(^{-1}\) due to stretching vibration of C=N bond,
- 956 cm\(^{-1}\) vibrational absorption peaks of C–S bond,
- 600 to 800 cm\(^{-1}\) due to quinolinic rings,

the broad characteristics peaks due to \(\nu\) (O-H) were almost vanished in the complex which confirmed the formation of Mg-O bond.

4.12 Optical characterization

The optical properties of the magnesium metal complexes were studied by taking their ultraviolet-visible absorption and photo-luminescent emission spectra in ethanol solvent. The magnesium complexes showed absorption peaks due to ligand centred \(\pi-\pi^*\) and \(n-\pi^*\) transitions.

4.12.1 [MgHPB(Clq)]

The UV-vis absorption and PL spectra of MgHPB(Clq) was recorded in ethanol. This complex have absorption band around 283 nm, which could be assigned to ligand centred (LC) \(\pi-\pi^*\) electronic transition. The complex had another low energy absorption band at 323 nm may be because of ligand centered n- \(\pi^*\) electronic transition as explained above. The PL spectrum of MgHPB(Clq) is shown in fig. 4.20. The complex exhibited bright bluish-green photoluminescence with peak at 500 nm upon excitation at these wavelengths. The emitted color of PL bluish-green was having CIE color coordinates at \(x=0.22, y=0.43\).

![Figure 4.20 UV-visible absorption and photo-luminescent emission spectra of [MgHPB(Clq)]](image-url)
4.12.2 [MgBTZ(Clq)]

The UV-vis absorption and PL spectra of MgBTZ(Clq) was taken in ethanol. The complex had absorption band around 286 nm, which could be assigned to ligand centred (LC) \( \pi-\pi^* \) electronic transition. The complex had another low energy absorption band at 337 nm may be because of ligand centered \( n-\pi^* \) electronic transition as explained above. The complex exhibited bright bluish-green photoluminescence with peak at 494 nm upon excitation at these wavelengths. The emitted color of PL bluish-green had CIE color coordinates at \( x = 0.42, y = 0.52 \).

4.12.3 [MgBTZ(Cl_2q)]

Figure 4.22 shows the UV-vis absorption and PL spectra of MgBTZ(Cl_2q) in ethanol. This complex have absorption band around 235 nm, which could be assigned to ligand centred (LC) \( \pi-\pi^* \) electronic transition. The complex has another low energy absorption band at 328 nm due to ligand centered \( n-\pi^* \) electronic transition. The PL spectrum of MgBTZ(Cl_2q) was recorded on excitation at 328 nm. The complex exhibited bright green photoluminescence with peak at 532 nm. The emitted color of PL green had CIE color coordinates at \( x=0.23, y=0.35 \).

![Figure 4.21 UV-visible absorption and PL of [MgBTZ(Clq)]](image)
Figure 4.22 UV-visible absorption and photo-luminescent emission spectra of [MgBTZ(Cl₂q)]

Table: 4.4 Photo-physical properties of Magnesium metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-vis absorption, $\lambda_{\text{max}}$(nm)</th>
<th>PL Emission Peak</th>
<th>Color of emitted light</th>
<th>Color Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\pi$-$\pi^*$</td>
<td>$n$-$\pi^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgHPB(Clq)</td>
<td>283</td>
<td>323</td>
<td>500</td>
<td>Blue Green</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x=0.22, y=0.43</td>
</tr>
<tr>
<td>MgBTZ(Clq)</td>
<td>286</td>
<td>337</td>
<td>494</td>
<td>Blue Green</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x=0.42, y=0.52</td>
</tr>
<tr>
<td>MgBTZ(Cl₂q)</td>
<td>235</td>
<td>328</td>
<td>532</td>
<td>Green</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x=0.23, y=0.35</td>
</tr>
</tbody>
</table>

Figure 4.23 Combined UV-visible spectra of magnesium complexes
4.12.4 Discussion -

A series of magnesium metal complexes with 2-(2-hydroxyphenyl)benzothiazole and 8-hydroxyquinoline derivatives had prepared. The metal complexes emitted light in bluish green region with high photo-luminescence intensity. The emission wavelength of magnesium complexes was at longer wavelength than the beryllium complexes.

4.13 Conclusion -

In conclusion, we synthesized some ternary metal complexes using N, O and N, N chelating agents as primary ligands and 8-hydroxyquinoline and its derivatives as secondary ligand. The metal complexes showed high luminescence intensity under ultraviolet-visible radiations excitation. Zinc, beryllium and magnesium metal complexes had synthesized. These complexes can be suitable emission source for fabrication of organic light emitting devices. Color tuning can be obtained by using these metal complexes for full color display applications.

Addition of different substituent on ligands had either increased or decreased the energy difference between the HOMO and LUMO of ligand moiety which promoted the energy transfer from ligand to metal thereby enhancing the photoluminescence. This trend could also be seen in the electroluminescence properties of the complexes. It was also noticed that emitted color could also be tuned by selecting either a suitable substituent in substituted 8-hydroxyquinoline or a metal ion for the synthesis of metal quinolates. It has happened due to changes in band gap between HOMO and LUMO of the metal quinolates. Based on these
facts, we synthesized metal chelates using metals zinc, beryllium, magnesium etc. and suitably substituted 8-hydroxyquinoline and other ligands as discussed earlier. It is pertinent to mention here that increase in covalent character of metal ligand bond had also resulted in red shift of emission wavelength. Beryllium complexes emit at shorter wavelength as compared to the magnesium complexes and magnesium complexes emit at shorter wavelength as compared to the zinc complexes. Furthermore, emitted color was tuned by choosing the metal centre and suitably substituted 8-hydroxyquinolines. It is also noteworthy that excitation wavelength of the complex was red shifted when electron donating group is introduced in phenoxide moiety particularly at 5 and 7 positions of quinoline ring and vice versa. It is due to increase in electron density in HOMO of the phenoxide ring. As a result, HOMO is destabilized which in turn decrease the band gap between HOMO and LUMO hence excitation wavelength is red shifted. This was in accordance with the reports available in the literature. A series of metal chelates so synthesized showed excellent luminescent properties as reported here.
References:


