Research Article

Synthesis and Optical Characterization of Mixed Ligands Beryllium Complexes for Display Device Applications

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Synthesis and photoluminescent behaviour of mixed ligand based beryllium complexes with 2-(2-hydroxyphenyl)benzoxazole (HPB) and 5-chloro-8-hydroxyquinoline (Clq) or 5,7-dichloro-8-hydroxyquinoline (Cl₂q) or 2-methyl-8-hydroxyquinoline (Meq) or 8-hydroxyquinoline (q) are reported in this work. These complexes, that is, [BeHPB(Clq)], [BeHPB(Cl₂q)], [BeHPB(Meq)], and [BeHPB(q)], were prepared and their structures were confirmed by elemental analysis, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and thermal analysis. The beryllium complexes exhibited good thermal stability up to ~300°C temperature. The photophysical properties of beryllium complexes were studied using ultraviolet-visible absorption and photoluminescence emission spectroscopy. The complexes showed absorption peaks due to $\pi-\pi^*$ and $n-\pi^*$ electronic transitions. The complexes emitted greenish blue light with peak wavelength at 496 nm, 510 nm, 490 nm, and 505 nm, respectively, consisting of high intensity. Color tuning was observed with changing the substituents in quinoline ring ligand in metal complexes. The emitted light had Commission Internationale d'Eclairage color coordinates values at $x = 0.15$ and $y = 0.43$ for [BeHPB(Clq)], $x = 0.21$ and $y = 0.56$ for [BeHPB(Cl₂q)], $x = 0.14$ and $y = 0.38$ for [BeHPB(Meq)], $x = 0.17$ and $y = 0.41$ for [BeHPB(q)]. Theoretical calculations using DFT/B3LYP/6-31G(d,p) method were performed to reveal the three-dimensional geometries and the frontier molecular orbital energy levels of these synthesized metal complexes.

1. Introduction

Small molecular metal complexes [1, 2] and polymeric materials [3, 4] have been extensively used for the fabrication of organic light emitting devices (OLEDs) which have been widely exploited due to their potential applications in future generation flat panel displays and solid state light sources [5, 6]. OLEDs offer several advantages over inorganic counterparts such as low cost, self-emission, broad tunability, and high luminous efficiency [7, 8]. For the commercial application of active matrix full color displays with OLEDs much effort has been directed towards improving their characteristics especially color tuning [9, 10]. There is a wide selection of emission colors in electroluminescent (EL) displays attainable through structural design of organic materials. The photophysical properties such as light emission, charge transport, and degradation at high temperature have been modified by

organic ligands used in metal complexes [11]. Numerous derivatives of 8-hydroxyquinolines have been synthesized and used for metal complex formation [12, 13].

For color tuning tris(8-hydroxyquinolinato)aluminium (Alq₃) [1] and bis(10-hydroxybenzo[h]quinolinato)beryllium (Bebq₂) [14] which emit green light are considered as the most excellent emitting materials for organic EL devices. The emissions of Alq₃ and Beq₂ originate from the electronic $\pi-\pi^*$ transitions within q or bq ligands. The two molecules are typical ligand-centered luminescent complexes. Beryllium complexes with N,O ligands have also been developed as efficient electron transport host materials for electroluminescent devices [15, 16]. Beryllium(II) complexes of aromatic N,O-chelate ligands, as blue EL materials, have been reported by Tong et al. [17] who have shown that the absorption and luminescent properties of these complexes are ligand based. The work has demonstrated that the ligand-tuning approach

FIGURE 1: Synthetic route of the beryllium complexes.

might be useful for the preparation of potential luminescent metal-organic materials with different emitting colors.

Here we have tried quinolate and N,O donor ligand for tuning the color of the emissive metal chelates and therefore synthesized mixed ligand beryllium complexes with 2-(2-hydroxyphenyl)benzoxazole and 8-hydroxyquinoline as well as its substituted derivatives. The photophysical properties of these materials have also been investigated.

2. Experimental Details

2.1. Synthesis of Metal Complexes. All the chemicals used to synthesize metal complexes were of analytical grade and purchased from Fluka. Solvents were of high purity and used as supplied.

Beryllium complexes were prepared by reacting two ligands, first as 2-(2-hydroxyphenyl)benzoxazole (HPB) and second as 5-chloro-8-hydroxyquinoline (Clq)/5,7-dichloro-8-hydroxyquinoline (Cl₂q)/2-methyl-8-hydroxyquinoline (Meq)/8-hydroxyquinoline (q) separately 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 Clq 0.36 g (1 mmol)/Cl₂q 0.43 g (1 mmol)/Meq 0.32 g (1 mmol)/q 0.29 g (1 mmol) in 20 mL of pure ethanol was added to the reaction mixture. The reaction mixture was stirred at 60°C for 2 h; then a solution of beryllium sulphate (1 mmol) in 5 mL of deionized water was added dropwise. The yellowish precipitate of the complexes was formed, filtered, and dried at 100°C. The synthetic scheme is shown in Figure 1.

2.2. Instrumentation. The elemental contents of carbon, hydrogen, and nitrogen were detected by Elemental Analyzer PerkinElmer 2400 CHN using combustion technique. PerkinElmer 2000 FTIR spectrometer using dry KBr was used to run IR spectral data in the range 4000–400 cm⁻¹. ¹H NMR analysis was performed by Bruker Avance 300 Proton NMR Spectrometer in CDCl₃. Thermal gravimetric analysis

(TGA) and differential thermal analysis (DTA) were carried out using Mettler Toledo TGA/SDTA851e instrument. Absorbances of these complexes (in methanol) and photoluminescence spectra (in solid and thin film) were recorded using spectrophotometer Horiba Jobin YVON Fluorolog Model FL-3-11 equipped with 450 W Xenon lamp as the excitation source. Optimized three-dimensional stable structures of metal complexes and their selected frontier molecular orbitals were obtained by density functional theory using Gaussian 03 package.

2.3. Structural Characterization of Synthesized Complexes

2.3.1. (2-(2-Hydroxyphenyl)benzoxazolato)(5-chloro-8-hydroxyquinolinato)beryllium(II). Yield: 65.2%; Anal. Calc. (C₂₂H₁₃N₂O₃BeCl) (found: C, 66.32; H, 3.29; N, 7.06; calc.: C, 66.41; H, 3.27; N, 7.04%); IR(KBr): ν (cm⁻¹) 2990, 1662, 1574, 1606, 1256, 600–800; ¹H NMR(CDCl₃): δ (ppm) 6.77 (m 1H), 7.10 (m 1H), 7.34–7.92 (m 8H), 8.4 (m 1H), 8.72 (m 1H).

2.3.2. (2-(2-Hydroxyphenyl)benzoxazolato)(5,7-dichloro-8-hydroxyquinolinato)beryllium(II). Yield: 63.8%; Anal. Calc. (C₂₂H₁₂N₂O₃BeCl₂) (found: C, 61.06; H, 2.79; N, 6.51; calc.: C, 61.11; H, 2.77; N, 6.48%); IR(KBr): ν (cm⁻¹) 2904, 1661, 1608, 1579, 1251, 600–800; ¹H NMR(CDCl₃): δ (ppm) 6.91 (m 1H), 7.09 (m 1H), 7.35–7.91 (m 8H), 8.35 (m 1H), 8.82 (m 1H).

2.3.3. (2-(2-Hydroxyphenyl)benzoxazolato)(2-methyl-8-hydroxyquinolinato)beryllium(II). Yield: 66.8%; Anal. Calc. (C₂₃H₁₆N₂O₃Be) (found: C, 73.16; H, 4.26; N, 7.45; calc.: C, 73.20; H, 4.24; N, 7.42%); IR(KBr): ν (cm⁻¹) 2905, 1661, 1608, 1579, 1251, 600–800; ¹H NMR (CDCl₃): δ (ppm) 2.50 (s 3H), 6.95 (m 1H), 7.10–7.92 (m 11H), 8.04 (m 1H).

2.3.4. (2-(2-Hydroxyphenyl)benzoxazolato)(8-hydroxyquinolinato)beryllium(II). Yield: 62.8%; Anal. Calc. (C₂₂H₁₄N₂O₃Be) (found: C, 72.75; H, 3.87; N, 7.74; calc.: C, 72.72; H, 3.85; N, 7.71%); IR(KBr): ν (cm⁻¹) 2993, 1662, 1607, 1570, 1250, 600–800; ¹H NMR (CDCl₃): δ (ppm) 6.93 (m 1H), 7.15 (m 2H), 7.26–7.92 (m 9H), 8.06 (m 1H).

TABLE 1: Photophysical properties of beryllium complexes.

Compound	Absorption (nm)	Emission $\lambda_{\max}$ (nm)	Optical band gap (eV)	Thin film PL (nm)	Emitted light	Color coordinates
BeHPB(Clq)	287, 338	493	3.02	497	Greenish blue	$x = 0.15, y = 0.43$
BeHPB(Cl ₂ q)	278, 378	496	2.93	499	Green	$x = 0.21, y = 0.56$
BeHPB(Meq)	246, 365	486	3.07	487	Greenish blue	$x = 0.14, y = 0.38$
BeHPB(q)	282, 332	507	2.98	511	Greenish blue	$x = 0.17, y = 0.41$

FIGURE 2: Curve (A): TGA, and curve (B): DTA plots of [BeHPB(Clq)] complex.

FIGURE 3: UV-visible absorption spectra of beryllium complexes at 10^{-4} M concentration in methanol.

3. Results and Discussion

3.1. Thermal Characterization. The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) of beryllium complexes were carried out in nitrogen atmosphere with a heating rate of $10^{\circ}\text{C}/\text{min}$ in temperature range of 0 – 500°C . The metal complexes exhibited high thermal stability and analogous thermal pattern of weight loss was observed at decomposition temperature for all complexes. The onset temperature of weight loss was 300°C , and temperature for nearly 10% weight loss was 350°C as shown in TGA plot of [BeHPB(Clq)] in Figure 2. Above 400°C temperature the complex lost all of its weight continuously and decomposed completely. TGA data of the complex shows that this complex exhibited excellent thermal stability. Curve B of Figure 2 corresponds to DTA of [BeHPB(Clq)] in nitrogen atmosphere.

3.2. Optical Absorption and Photoluminescent Spectra. The photophysical properties as absorption and emission characteristics of beryllium complexes were studied using spectroscopy techniques. Figure 3 shows the room temperature UV-visible absorption spectra of beryllium complexes in methanol. The beryllium complexes [BeHPB(Clq)], [BeHPB(Cl₂q)], [BeHPB(Meq)], and [BeHPB(q)] exhibited similar absorption bands from 200 to 400 nm with maximum absorption at 287, 278, 246, and 282 nm due to π - π^* transition

and at 338, 378, 365, and 332 nm due to n - π^* electronic transitions, respectively. The molar absorptivity of beryllium complexes [BeHPB(Clq)], [BeHPB(Cl₂q)], [BeHPB(Meq)], and [BeHPB(q)] was 1398, 1412, 2191, and 1175 cm^{-1} , respectively, at maximum absorption wavelength.

The optical band gap was calculated from absorption spectra; Figure 4 shows band gap graph for [BeHPB(Clq)] and [BeHPB(Cl₂q)] with values 3.03 and 2.98 (eV), respectively.

Upon excitation at absorption wavelengths the materials [BeHPB(Clq)], [BeHPB(Cl₂q)], [BeHPB(Meq)], and [BeHPB(q)] fluoresced at 493, 496, 486, and 507 nm, respectively, in the visible spectra as shown in Figure 5. The photoluminescence intensities of beryllium complexes were found in order as [BeHPB(Cl₂q)] < [BeHPB(q)] < [BeHPB(Clq)] < [BeHPB(Meq)] as observed from the graph in Figure 5. The complexes emitted bright greenish blue colored light. The values of electronic transitions and emission wavelengths are presented in Table 1. Beryllium complex with 2-(2-hydroxyphenyl)benzoxazole ligand emits light at 440 nm [17] and with 8-hydroxyquinoline ligand emits light at 520 nm [18]. Beryllium metal complexes emit at lower wavelength than Zinc metal complexes as Be is lighter metal than Zn. Beryllium complexes emit in greenish blue region while zinc complexes with similar ligands emit in blue-green region. The electroluminescent devices based on Be(II) complexes have

FIGURE 4: Energy versus absorption² plot of beryllium complexes.

FIGURE 5: Photoluminescence spectra of beryllium(II) complexes in solid state.

brighter luminance than devices fabricated with other similar metal complexes [14]. There was shift in emission wavelength on attaching electron withdrawing groups on phenol ring as in quinolate complexes [19, 20]. Blue shift in emission wavelength of [BeHPB(Clq)] and [BeHPB(Meq)] was observed as compared to that of [BeHPB(q)]. This was due to attaching of electron withdrawing groups, that is, chloro at phenolic ring, and electron donating groups, that is, methyl at pyridyl ring. The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) in 8-hydroxyquinoline were present on phenoxide ring and pyridyl ring, respectively [21]. The central metal atom provided stability to the ligands and modification of ligands lead to change in emission wavelength as well as energy. The thin film PL of the beryllium complexes was recorded at absorption wavelength by deposition of a thin film of thickness 200 Å on the glass substrate by thermal deposition technique.

FIGURE 6: Photoluminescence spectra of beryllium(II) complexes in thin film form on glass substrate.

FIGURE 7: CIE chromaticity diagram.

The photoluminescent spectra of beryllium metal complexes in thin film form have been shown in Figure 6 and the peak values are mentioned in Table 1. The PL peaks values were slightly red shifted and having high intensity as compared to that in solid powdered form. The synthesized complexes exhibited film forming behaviour and here it is also observed that ligand alteration and improvement approach can be useful for synthesis of desired potential fluorescent materials especially beryllium complexes, with different emitting colors and required energy gap between HOMOs and LUMOs.

The Commission Internationale d'Eclairage (CIE) 1931 chromaticity color coordinates for emitted color of PL in solid powdered form were $x = 0.15$ and $y = 0.43$ for [BeHPB(Clq)], $x = 0.21$ and $y = 0.56$ for [BeHPB(Cl₂q)], $x = 0.14$ and $y = 0.38$ for [BeHPB(Meq)], and $x = 0.17$ and $y = 0.41$ for [BeHPB(q)], also represented in Figure 7.

FIGURE 8: Optimized 3D molecular geometry, molecular orbital surfaces (0.05 e au^{-3}), and energies (in parenthesis, eV) of the selected frontier molecular orbitals of beryllium(II) complexes.

3.3. Density Functional Theory (DFT) Calculations. The minimal energy three-dimensional geometries and frontier molecular orbitals of prepared beryllium(II) complexes were computed with DFT/B3LYP/6-31G(d,p) method [22]. The FMOs are principally dominated by the orbitals originating from those of the ligand in the complex and contribution from the beryllium(II) ion appears to be small.

The optimized 3D structures and selected FMOs such as HOMO – 1, HOMO, LUMO, and LUMO + 1 are shown in Figure 8. The electron withdrawing nature of chloro (-Cl) substituents fixed to the 5-position and 7-position of ligand and electron donating nature of methyl (-CH₃) substituents fixed to 2-position of ligand are used to tune the energy of HOMO and LUMO levels to achieve blue shift emission as optical transition responsible for photoluminescence may be attributed due to the transition between HOMO and LUMO [23]. The numerical values of all selected FMOs in eV are also shown in Figure 8. The findings of optical band gap were supported by the DFT calculation of the FMOs and the HOMO-LUMO gap at DFT/B3LYP/6-31G(d,p) studies.

4. Conclusions

Beryllium complexes were synthesized and characterized by elemental analysis, ¹HNMR, and FTIR techniques. The metal complexes had high thermal and chemical stability which were confirmed by TGA and DTA. The photophysical properties were investigated by absorption and emission spectroscopy. The emission maxima of the complexes were found in the greenish blue region having high intensity. The emission wavelength was 493 nm for [BeHPB(Clq)], 496 nm for [BeHPB(Cl₂q)], 486 nm for [BeHPB(Meq)], and 507 nm for [BeHPB(q)] material. Ligand tuning can be useful for desirable light emission. The photoluminescent characterization confirmed the better luminescence properties of these complexes that could be efficiently used as emissive materials for display device applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this work.

Authors' Contribution

Vandna Nishal and Devender Singh contributed equally to this work.

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