

## Zn-quinoline Metal Organic Phosphor for PLLCD and OLED Applications

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### ABSTRACT

The main prerequisite for Photoluminescent Liquid Crystal Display (PLLCD) is ultraviolet (UV) excited phosphor for backlight illumination and hence we propose the synthesis and characterization of Zinc bis(8-hydroxyquinoline) organo-metallic complex Znq<sub>2</sub>. Znq<sub>2</sub> complex was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Photoluminescence (PL) spectroscopy. XRD confirms crystalline nature of the complex and FTIR portrays the IR peaks that confirms the molecular structure of the complex. Intense green narrow photoluminescence (PL) emission band with maxima at 503 nm was obtained when Znq<sub>2</sub> complex was excited by UV radiation. These investigations reveal that Znq<sub>2</sub> complex has the potential as green light emission phosphor for PLLCD and Organic Light Emitting Diode (OLED) application.

**Keywords :** PLLCD, OLED, quinoline complex, precipitation method, Znq<sub>2</sub>

### I. INTRODUCTION

Over the past few decades, Organic Light Emitting Diode (OLED) has made great strides in the field of lighting. Over the years, the efficiency of OLED devices has seen considerable improvement. Internal quantum efficiency of up to 100% has been reported for red, green and blue colours [1–5]. However, some lifetime issues have been reported in those devices [5–7]. Efforts are being made to identify the causes of these vulnerabilities and rectify them. As per the literature, deterioration of the excretory layer (EML) is an important cause. To address this problem, the density of the extrusion created in the EML needs to be adjusted, which should not cause too much and too little charge transport. In particular, it is necessary to

match the dynamics of the two charge carriers so that holes and electrons flow properly and effectively transfer to the dopants [8–10]. Organic and inorganic luminescent phosphors are at present the main working materials for upcoming modern optoelectronic industry. Light weight, good resolution, thin and slim structure and low driving voltage are the key imperative parameters of optoelectronic flat panel display device, namely Photoluminescent Liquid Crystal Display (PLLCD) and Organic Light Emitting Diodes (OLEDs) [11–14]. In such display devices, optical transmission is modified by the application of voltage to the display element. In order to convert this modified optical transmission into visible display, back light source is highly prerequisite. Full colour LCD display can be obtained by using colour filter in

addition to the back light source in its architecture. Important features of LCD display such as contrast, brightness and colour considerably vary with viewing angle and even their viewing angle is restricted. Contrarily, Photoluminescent Liquid Crystal Display architecture offer same contrast, brightness and no variation in colour at all viewing angle as described by W. A. Crossland et al in 1997 [15] and A. Vecht et al in 1998 [16], thereby eliminates all above cited drawbacks. This is possible with the selection of right metal complex that dictates the performance and the life time of the fabricated display device. PLLCD applications are wide and varied as portrayed in Fig.1.

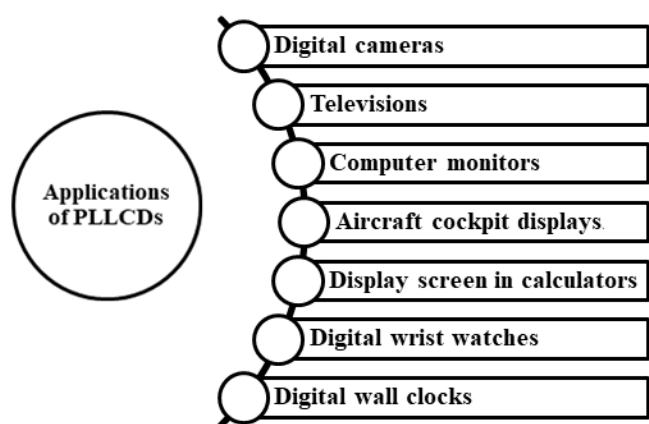


Fig.1: Wide and varied applications of PLLCD

Till now, green emitting material for use in organic EL devices have been tris 8- hydroxyquinoline –Al complex ( $Alq_3$ ). Although  $Alq_3$  has low fluorescence efficiency, it has been more frequently used as emissive material due to its excellent carrier (electron) transportation ability, stable film formation capability and good heat resistance [17–19]. In this perspective, 8-Hydroxyquinoline metal complexes with general molecular formula ( $Mq_x$ ) [where x indicates oxidation state of metal M] have been studied by many researchers [20–23]. Poly (quinoline) as an electroluminescent material remains a subject of intense research in the field of OLED. The main reason for which is the extraordinary ability of poly (quinoline) which has attracted the attention of the research society. Poly (quinoline) is known for its excellent physical properties such as high electron

mobility, photoluminescence efficiency and stability. Electro active and blue light-emitting diphnylquinoline (DPQ) was synthesized in almost quantitative yield by a simple modification of polystyrene. It emits blue light in neutral solutions and thin solid films. Hence, we propose the investigations on the suitability of  $Znq_2$  as a green emitting organic material for PLLCD.

## II. Experimental

### 2.1 Synthesis

$Znq_2$  complex has been synthesized by simple precipitation method [24] at room temperature by adopting the following procedure- 8-Hydroxyquinoline (Merck, 2gram) was dissolved in a mixture of 25 mL double distilled water and 25 mL of acidic acid, stirred it well till orange transparent solution was obtained.  $ZnCl_2$  (LOBA chem., 0.5602 gram) was dissolved in double distilled water, and stirred till clear solution was obtained.

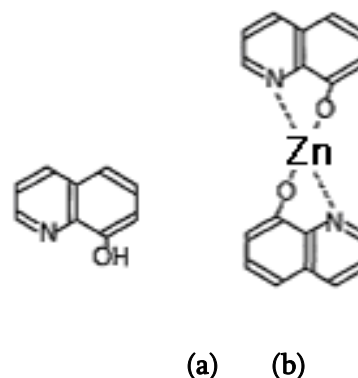


Fig.2: Molecular structure of (a) 8-hydroxy quinoline and (b) its derivative – $Znq_2$

These two solutions were mixed and resulting suspension was stirred for 10 min. Solution of ( $NH_4OH$ ) Ammonium Hydroxide (precipitating agent) was added into this mixture drop by drop with continuous stirring. Yellow-green precipitate was filtered out. The obtained precipitate was washed with double distilled water for 8-10 times and dried. The molecular structure of the initial precursor 8-hydroxyquinoline and the so formed  $Znq_2$  complex are portrayed in Fig. 2(a) and (b), respectively.

## 2.2 Characterization:

The synthesized complex is characterized for its structural and optical properties by employing X-ray diffraction, Fourier Transform Infrared Spectra and Photoluminescence techniques. The XRD pattern of synthesized samples were measured by using X-ray Diffractometer System XPERT-PRO (PAN analytical). The XPERT-PRO (PAN analytical) is a multipurpose x-ray diffractometer equipped with a Cu K $\alpha$  source. Fourier Transformed Infra Red spectra (FT-IR) spectra of the synthesized material gives the information of vibrational bonds and stretching. FT-IR of the synthesized Znq<sub>2</sub> complex were measured by using Bruker Alpha FT-IR Spectrometer. The photoluminescence properties were measured using Hamamatsu F-4500 spectrofluorometer with a Xenon flash lamp (150 W) and R3788 Photomultiplier tube. The Emission and excitation spectra were recorded using a spectral band pass of 2.5 nm. All the experimental activities performed at room temperature.

## III. RESULTS AND DISCUSSION

### 1.1. X-Ray Diffraction (XRD)

The phase purity and crystalline nature of the synthesized Znq<sub>2</sub> were investigated by using XRD pattern. The figure 3 shows the powder x-ray diffraction (PXRD) pattern of synthesized Znq<sub>2</sub>. The main diffraction peaks of ZnQ<sub>2</sub> occur at  $2\theta=16.76^\circ$ ,  $18.17^\circ$ ,  $21.17^\circ$ ,  $23.43^\circ$ , and  $28.49^\circ$  [25,26]. The XRD pattern of the synthesized ZnQ<sub>2</sub> were matched with previous reported research paper related to ZnQ<sub>2</sub> by Zahra Shahedi et al [27]. The XRD pattern clearly revealed strong diffraction peaks in the diffractogram, which confirmed crystalline nature of the complex. The average crystallite size of the synthesized sample was calculated by Debye Scherrer's formula [28].

$$d = \frac{k\lambda}{\beta \cos\theta} \dots\dots\dots (1)$$

Where,  $\lambda$  is wavelength of X-Ray ( $\lambda=0.154\text{nm}$ ),  $k$  is constant ( $k=0.94$ ),  $\beta$  is size of particle,  $\theta$  is bragg's angle and  $d$  is half width full maxima (FWHM). The calculated crystallite size of the Znq<sub>2</sub> was found to be about 46-48nm.

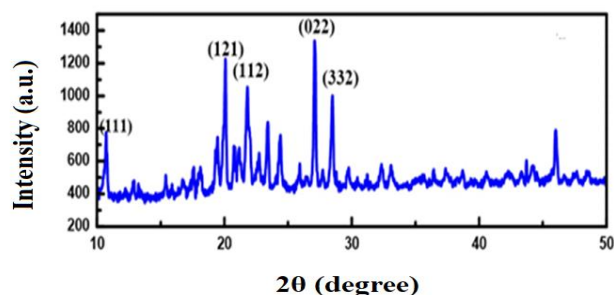


Fig.3: X-ray diffractogram of synthesized Znq<sub>2</sub>

### 3.2 FT-IR Spectra

Fourier Transform-Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. Infrared spectroscopy (IR) relies on the fact that most molecules absorb light in the infrared region of the electromagnetic spectrum, converting it to molecular vibration. This absorption is characteristic of the nature of the chemical bonds present in a sample. FT-IR spectra of Znq<sub>2</sub> complex was carried out over the range of 4000 – 400 cm<sup>-1</sup> by averaging 64 scans at a maximum resolution of 4 cm<sup>-1</sup>. The peaks approximately at 1600, 1550, 1300 cm<sup>-1</sup> of FT-IR were associated with quinoline group. FT-IR pattern of Znq<sub>2</sub> Peaks at 400-600cm<sup>-1</sup> can be attributed to Zn-O and Zn-N stretching vibration. C=N vibrations (1570 cm<sup>-1</sup>), C-O stretching vibrations (1450, 1300 cm<sup>-1</sup>), aromatic stretching C=C (1600 cm<sup>-1</sup>), C-C (1450, 1580 cm<sup>-1</sup>), C-N vibrations (1580 cm<sup>-1</sup>), and C-C-H bending vibrations (1170 cm<sup>-1</sup>) clearly depicted in Fig.4, were found to be concurrent with the prior state of art [26,29-31].

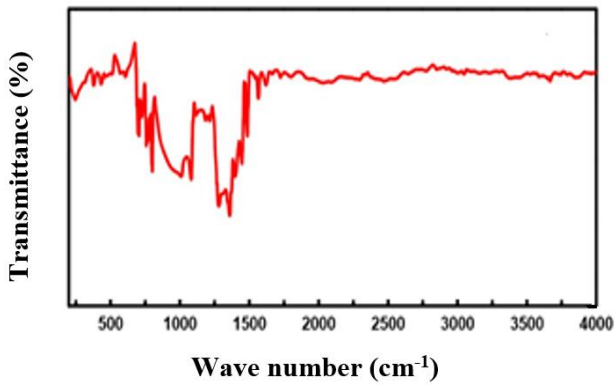


Fig.4: FTIR Spectra of Znq<sub>2</sub>

### 3.3 Photoluminescence spectra

Photoluminescence is a common technique used to characterize the optoelectronic properties of semiconductors and other materials. **Photoluminescence** is a property of a material to absorb, store and convert photons to light. Photoluminescent materials have important applications in lighting. Photoluminescence (PL) spectra of the synthesized Znq<sub>2</sub> metal complex was studied using a Hamamatsu F-4500 spectrofluorometer, at room temperature, using 2.5 nm spectral slit width in the range of 200–700 nm. Fig.5 shows PL excitation and emission spectra of Znq<sub>2</sub>. The PL excitation and emission spectrum shows strong and broad bands. The center of the excitation band found around 380 nm with long tail in the lower wavelength region. Under 380 nm excitation, PL emission spectra were measured. The emission spectra shows strong broad band centered around 503 nm. The visible emission in the PL-spectrum of Znq<sub>2</sub>, shown in Fig.5 is due to the ligand and is largely dominated by the emission from triplet state as explained by Jablonski diagram shown below in Fig.6. Photophysical properties such as maximum emission wavelength, Full width at half maxima (FWHM) and Stokes shift of the synthesized complex are summarized in Table 1 for divalent metal quinoline Znq<sub>2</sub> complex.

The Stokes Shift is the spectral shift to lower energy between the incident light and the scattered or

emitted light after interaction with a sample. In fluorescence spectroscopy, the Stokes shift is the difference between the spectral position of the maximum of the first absorption band and the maximum of the fluorescence emission and can be expressed in either wavelength or wavenumber units.

$$\begin{aligned} \text{Stock shift (Wavelength)} \Delta\lambda &= \lambda_{\text{emission(max)}} \\ &- \lambda_{\text{excitation(max)}} \dots \dots \dots (2) \end{aligned}$$

Where,  $\lambda_{\text{emission(max)}}$  is the wavelength at the highest emission intensity and  $\lambda_{\text{excitation(max)}}$  is the wavelength at the highest excitation intensity.

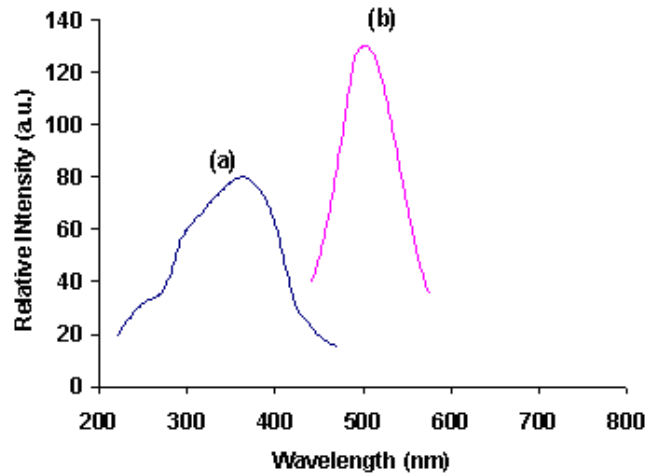


Fig. 5: PL spectra of Znq<sub>2</sub> (a) Excitation and (b) emission spectrum of Znq<sub>2</sub>

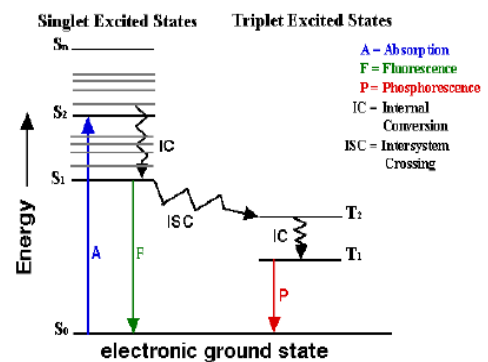


Fig. 6: Jablonski diagram showing pathway of absorption, fluorescence, and phosphorescence

Table 1: Photophysical properties of divalent metal quinoline Znq<sub>2</sub> metal complex

Complex	Excitation Wavelength (nm)	Emission wavelength (nm)	FWHM (nm)	Stokes Shift (nm)	Relative Intensity (a.u.)
Znq <sub>2</sub>	385	503	72	118	2080

#### IV. Conclusion

Many researchers are fascinated towards organic metal complexes due to the fact that they have high thermal stability and amazing luminescent property. In concurrent lines, we synthesized organic metal complex Znq<sub>2</sub> by cost effective precipitation method and characterization techniques that are associated with physical, chemical and optical properties are studied in detail. The crystalline nature of Znq<sub>2</sub> complex was revealed from the XRD, while FT-IR confirms the formation of the desired Znq<sub>2</sub> complex. The intense emission peak at 503 nm under 385 nm excitation revealed intense green light emission from Zn-quinoline complex, proving its potential as one of the most suitable phosphors for PLLCD and OLED applications.

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