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Electroluminescent characteristics of bis(5-chloro-8-hydroxyquinolino)-zinc(II) complex

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A zinc(II) complex with 5-chloro-8-hydroxyquinoline has been used as emitting material to produce yellow light. On excitation by UV light at 385 nm, thin film of the complex fluoresced at 550 nm. Multilayer organic electroluminescence devices fabricated using this fluorescent material produce emission with good chromaticity (CIE coordinates $x = 0.313$ and $y = 0.576$). Maximum luminance of 466 cd/m^2 is achieved when 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane is used as dopant in 4,4-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl at 12 V. The devices show typical non-linear diode current-voltage characteristics under forward bias with the threshold voltage of 6V. The CIE coordinates are found to be independent of the operating voltage.

Keywords: Luminescence, Electroluminescence, Light emitting devices, Hydroxyquinoline, Zinc(II)

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Organic electroluminescence finds extensive applications in devices such as backlights of liquid-crystal displays, ultra-thin flat-displays, solid-state lighting devices, efficient illuminators, etc.¹⁻⁴ The process responsible for electroluminescence requires the injection of electrons from one electrode and holes from the other electrode, followed by electron-hole recombination to form excitons, and light generation through the radiative decay of the excitons⁵.

Color tuning is very important for the preparation of full color displays. The desired tuning can be made by choosing appropriate substituents that help to shift the emission wavelength, i.e., color of emitted light. While several fluorescent dyes and charge transport materials have been developed for this purpose⁶⁻⁸,

efforts are still being made in terms of color tuning. The use of metal complexes as efficient electroluminescent materials has received considerable attention as the emission properties of organometallic species are controlled by a number of factors, including electronic properties of the ligand and metal ion, coordination number, etc. Keeping this in view, 5-chloro substitution in 8-hydroxyquinoline was chosen and its zinc complex $(5\text{-Clq})_2\text{Zn}$ was synthesized using conventional method. The electroluminescent devices with this complex have been fabricated by depositing thin layers of the $(5\text{-Clq})_2\text{Zn}$ complex by thermal evaporation in vacuum. These devices have been studied for their optical and luminescence spectroscopic properties.

Experimental

High purity 5-chloro-8-hydroxyquinoline, zinc sulphate and the solvents were purchased from Aldrich Co. The zinc(II) complex was prepared by adding a solution of zinc sulphate (1 mmol) in water to a solution of the ligand (2 mmol) in ethanol and pH was adjusted to neutral. After stirring the mixture for 2 h at 60°C on a magnetic stirrer, a crude product precipitated from the solution. The cream colored precipitate was washed with deionised water to remove excess metal ions and then recrystallized with absolute alcohol, to give the pure bis(5-chloro-8-hydroxyquinolino)zinc(II) complex. The chelate exhibited yellow fluorescence under UV light.

Elemental analysis of the sample was carried out on an Perkin Elmer elemental analyzer (400 CHN). The CHN analysis of complex indicates the formula to be $\text{Zn}(\text{Clq})_2$ (Found: C, 47.90; H, 2.15; N, 6.96; Calc.: C, 48.75; H, 2.48; N, 6.90; %). ¹HNMR spectrum was recorded on a Bruker Avance 300 spectrometer (300 MHz) in deuterated chloroform (CDCl_3).

The FTIR spectrum of the complex was recorded in KBr using Perkin Elmer 2000 FTIR spectrometer. Excitation and emission spectra were recorded on Horiba Jobin YVON Fluolog (model FL 3-11) spectrofluorometer in thin solid film. The luminance-current density-voltage (L-I-V) characteristics were recorded using a luminance meter (model no LMT RS 232) and a digital voltmeter.

The organic light emitting diode (OLED) devices containing zinc complex were fabricated by vacuum deposition. The substrate was an indium tin oxide (ITO)-coated glass with a sheet resistance of $20 \Omega/\text{cm}^2$. The ITO-coated glass was pretreated according to a regular chemical cleaning process using detergent, deionized water and alcohol in sequence, followed by ozone cleaning. The thermal evaporation of organic materials was carried out at a chamber pressure of 10^{-6} torr. The organic layers were deposited at a rate $1\text{--}2 \text{ \AA s}^{-1}$, followed by a 0.3 nm LiF used as a buffer layer. Finally, a shadow mask was used to define the cathode which was formed of a 100 nm thick layer of Al. The thickness of the deposited films was monitored *in situ* by quartz crystal. Further confirmation of the deposited film thickness was done by ellipsometric studies.

The devices were fabricated in the following configuration: (i) ITO/TPD(30 nm)/(5-Clq)₂Zn (35 nm)/LiF(0.3 nm)/Al(100 nm), (ii) ITO/ α -NPD (30 nm)/(5-Clq)₂Zn (35 nm)/BCP (60 nm)/Alq₃ (25 nm)/LiF(0.3 nm)/Al(100 nm), (iii) ITO/0.8% F₄TCNQ doped α -NPD(37 nm)/(5-Clq)₂Zn (35 nm)/BCP (60 nm)/Alq₃ (30 nm)/LiF(0.3 nm)/Al(100 nm), where BCP = bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), Alq₃ = aluminium-tris-(8-hydroxy-quinolate), TPD = 4,4'-bis(3-methyl phenyl phenyl amino)-biphenyl, F₄TCNQ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, α -NPD = 4,4'-bis(N-(1-naphthyl)-N-phenyl-amino)-biphenyl.

Results and discussion

The IR spectrum of the Zn(II) complex shows a broad characteristic peak at 3300 cm^{-1} corresponding to OH stretching vibration, which confirms that the Zn-O bond is coordinate in nature and not ionic. The peaks centered at 2855 cm^{-1} is attributed to the stretching vibration of C—H bond in the aromatic ring. The sharp peak at 1376 cm^{-1} is due to C—N vibrational absorption. The peaks at 1458 cm^{-1} and 1577 cm^{-1} are assigned to C—C skeletal vibrational stretching of the aromatic ring. The vibrational absorption peak of C—O at 1116 cm^{-1} is weak and narrow. The characteristic peaks of quinolinic rings from 600 to 800 cm^{-1} show the presence of quinolinic rings.

The ¹H NMR chemical shifts were found to be as follows: 7.00–7.04 (s, 2H); 7.60–7.72 (m, 6H); 8.61–8.65 (m, 2H).

The excitation spectrum of the Zn(5-Clq)₂ complex shows a peak at 385 nm (Fig. 1, curve A). The

excitation spectrum gives evidence of an efficient ligand-to-metal charge transfer; since the most intense feature is a broad band corresponding to transitions populating ligand centered excited states. The luminescence spectrum of the complex upon ligand excitation (385 nm) emits a broad peak at 550 nm resulting in a bright yellow emission (Fig. 1, curve B). The CIE coordinates of the complex are $x = 0.313$, $y = 0.596.35$

The effect of ligand structure on emission wavelength of the electroluminescent complex was investigated. It is reported that the electron-donating groups and electron-withdrawing groups when introduced to the 8-hydroxyquinoline ligand moieties of organometallic electrolumophore such as Alq₃, cause change in electronic properties of the ligand involved in the emission of light⁹. An electroluminescence spectrum of the fabricated device was measured as a function of the operating voltage (Fig. 2). The (5-Clq)₂Zn complex shows bright yellow photoluminescence when illuminated by a 365 nm UV lamp as light source. The optical transition responsible for the photoluminescence is due to a transition from the electron rich phenoxide ring (location of the highest occupied molecular orbital, HOMO) to the electron deficient pyridyl ring (location of the lowest unoccupied molecular orbital, LUMO)¹⁰. It is reported that the introduction of electron withdrawing groups in phenoxide and pyridyl ring causes the blue shift and red shift in the emission spectrum of the complex respectively. This effect is reverse in the case of introduction of the electron

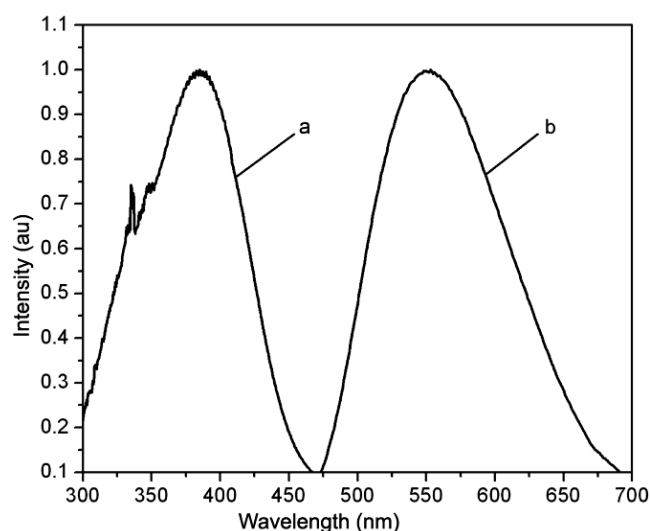


Fig. 1—Excitation (a) and emission (b) spectra of complex in THF solvent.

donating group⁹. Hopkins *et al.*¹¹ have reported the electroluminescent spectra of the zinc quinolate at 554 nm. When an electron withdrawing group like chlorine was introduced in the phenoxide ring, the HOMO of the material was stabilized, and hence, emission from the complex shifted towards shorter wavelength. It is well known that the electroluminescence peak wavelength of Alq₃ is always located at about 528 nm, and emits a bright green light. In the present case, the electron-hole recombination in the emitting layer leads to the emission of yellow light with a peak at $\lambda_{\text{max}} = 550$ nm. This indicates that the emission is from the zinc complex. When the operating voltage is increased, the intensity of emission peak at 550 nm increases sharply. BCP and Alq₃ act as hole blocking layer and electron transport layer respectively. BCP acts as a good hole blocking layer since the HOMO of BCP (6.5 eV) lies below that of the emissive layer. Hence, holes coming from ITO (anode) encounter a barrier and accumulate in the emissive layer. The LUMO of Alq₃ (3.2 eV) is almost the same as that of BCP (3.2 eV) and the emissive layer, and hence, there is no barrier for the electrons coming from the metal electrode (cathode).

Figure 3 shows the voltage–current–luminance characteristics of the fabricated electroluminescence devices. The forward bias current was obtained when the ITO was a positive electrode and the Al a negative one. The current and light output increased with

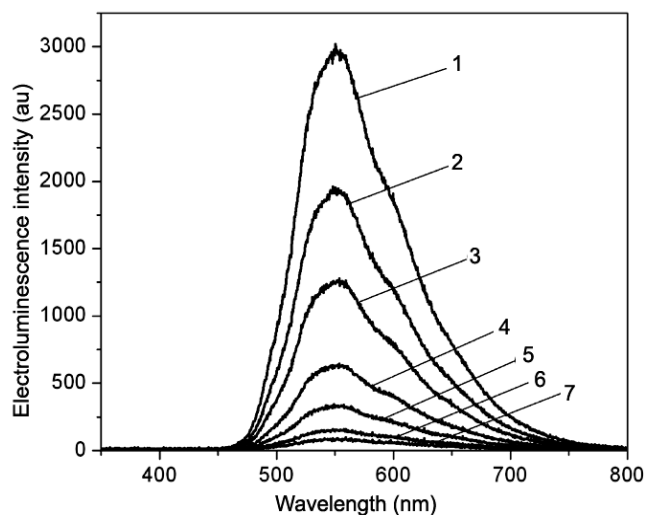


Fig. 2—Electroluminescence characteristics of ITO/0.8% F₄TCNQ doped-NPD (25 nm)/5-Clq₂Zn (35 nm)/LiF (3 nm)/Al (150 nm) device at varying voltage. [1, 14 V; 2, 13 V; 3, 12 V; 4, 11 V; 5, 10 V; 6, 9 V; 7, 8 V].

increase in the forward bias voltage and the turn-on voltage of the devices was about 6 V. A luminance of 100 cd/m² was achieved at the applied voltage of 10 V, which corresponds to the operating voltage of the electroluminescent devices. The devices exhibited good stability at the operating voltage. The maximum luminance that could be achieved was 466 cd/m² in the yellow region when the voltage reached 12 V. It is a significant observation that the electroluminescence peak position and the CIE coordinates of the device are independent of the operating voltage. The electroluminescence emission remained at 550 nm (Fig. 2) with the CIE chromaticity coordinates at $x = 0.313$, $y = 0.596$.

The bright yellow light emitted from electroluminescent devices fabricated using TPD as hole transport layer had a maximum brightness of 206 cd/m², while the electroluminescent devices fabricated using α -NPD as hole transport layer had a maximum brightness of 342 cd/m² and the electroluminescent devices fabricated using F₄TCNQ doped α -NPD as hole transport layer had a maximum brightness of 466 cd/m² at 12V (Fig. 3.). From this figure it is clear that maximum brightness is found in the case of doped α -NPD devices due to smooth charge transportation which causes the increase in luminance.

The zinc complex synthesized herein with 5-chloro-8-hydroxyquinoline shows high photoluminescence intensity. Based on this material, organic light emitting devices were fabricated using

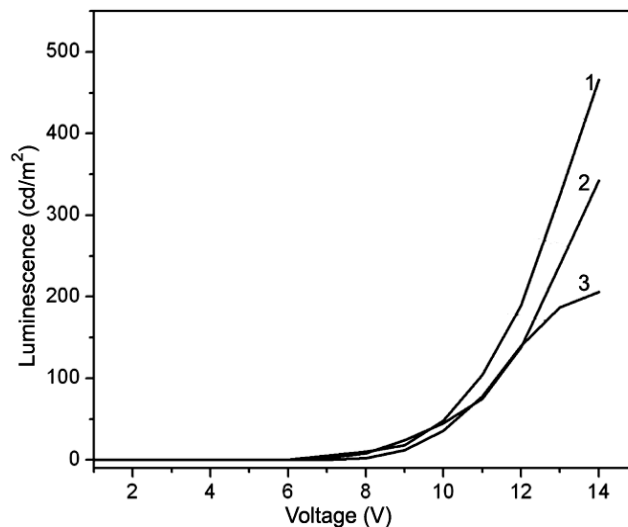


Fig. 3—Luminance-voltage curve for the different fabricated EL devices using different hole transport layers. [1, F₄TCNQ doped α -NPD; 2, α -NPD; 3, TPD].

different hole transport layers. The exciton formation occurred at the zinc complex during the operation of the electroluminescent device with yellow emission peaking at 550 nm. The chromaticity of the device was found to be independent of the operating voltage and showed typical diode characteristics in forward bias. The luminance of the device increased further when the F₄TCNQ doped α -NPD was used as hole transport layer. The turn-on voltage of the device was as low as 6V. This zinc complex can be used as a good emission source for electroluminescent devices.

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