Blue-green emission from organic light emitting diodes based on aluminum complex

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Bluish-green emission from double layer organic light emitting diode (OLED), based on an aluminium complex, bis-(2-methyl 8-hydroxyquinoline) aluminium hydroxide (Almq\textsubscript{2}OH), as an emissive material and \(N,N',N''\)-bis(3-methylphenyl)-\(N,N''\)-bis(phenyl)benzidine (TPD), as hole transport material with an electro-luminescence maximum at 506 nm, has been reported. The good thermal stability, good performance for the OLED applications, and a noticeable blue shift in the electroluminescence, in comparison to Alq\textsubscript{3}, make this Al complex a good contender for OLED applications for light emission in the blue-green region. It was also found that the devices based on this material have a slightly higher turn-on voltage than similar Alq\textsubscript{3} devices. This can be attributed to the higher energy-gap of the material. The photoluminescence and electroluminescence spectra are reported and a shift of 9 nm in peaks is observed. The current-voltage characteristics of the device have also been studied.

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Since the first report on electroluminescence from small molecule Alq\textsubscript{3}, it has become one of the most studied materials\textsuperscript{1} used for organic light emitting diodes (OLEDs). It has a fluorescent emission maximum at about 525 nm, which falls in the green spectral region. A large variety of derivatives of Alq\textsubscript{3} have been synthesized with the aim of colour tuning\textsuperscript{2,3} and for better device performance.

Colour tuning in Alq\textsubscript{3} type quinoline derivatives can be achieved by changing the central metal atom\textsuperscript{4,6}, i.e., using beryllium, boron, magnesium or zinc in place of aluminium in the organic complexes or by attaching various substituents to the different positions on the 8-hydroxyquinoline molecule\textsuperscript{3,7-10}. Light emission from these complexes originates from the electronic \(\pi \rightarrow \pi^*\) transitions located on the quinolinolate ligands. The HOMOs (highest occupied molecular orbital) are located on the phenoxide side of the ligand, while the LUMOs (lowest unoccupied molecular orbital) are located on the pyridine ring\textsuperscript{11}. Thus, the attachment of electron-donating substituents to the phenolate ring results in a red shift in emission, while the attachment of electron-donating substituents to the pyridine ring results in a blue shift in emission.

The performance of OLED device fabricated with bis(2-methyl 8-hydroxyquinoline) aluminum hydroxide (Almq\textsubscript{2}OH) as the emissive material has been reported. The device was fabricated in a standard double layer configuration ITO/TPD/Almq\textsubscript{2}OH/Al, and a considerable blue shift in EL, compared to similar Alq\textsubscript{3} based devices has been observed. The material was found to have better PL efficiency compared to Alq\textsubscript{3}.

**Experimental Procedure**

**Synthesis of Almq\textsubscript{2}OH**

Almq\textsubscript{2}OH was synthesized by dropwise mixing of Al(OH)\textsubscript{3} solution in deionized water to a solution of 2-methyl-8-hydroxyquinoline in pure ethanol, in 1:2 equivalent ratio, with continuous stirring\textsuperscript{12}. The pH of the solution was adjusted to 5 and stirring was continued for 6 h. At the end of the reaction, a yellowish precipitate was obtained in high yield. The crude material obtained, was purified by microsoxhlet extraction for 12 h with diethyl ether, followed by vacuum sublimation to yield yellowish-white powder, which was highly luminescent when irradiated by UV. The synthetic route of Almq\textsubscript{2}OH is shown in Fig. 1.

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Fabrication of the OLED

The devices were fabricated on precleaned indium tin oxide (ITO) coated glass substrates having the sheet resistance ~20 Ω/□, which acts as anode. The substrates were cleaned sequentially in detergent, deionized water, boiled in toluene, washed with acetone and isopropanol and finally dried in vacuum oven at about 100°C at 1 mm of Hg for 4 h. The bilayer light-emitting diodes were fabricated in a diffusion pumped vacuum chamber at the pressure of about 2×10⁻⁵ torr and the thickness of the films were measured using a HINDHIVAC quartz crystal thickness monitor model DTM-101. All the thin films were grown by the thermal evaporation of the materials. On cleaned ITO substrates TPD (250 Å) was evaporated at about 1~2 Å/s, to facilitate better hole injection into the electron-hole recombination zone. Subsequently, Almq₂OH (350 Å) was evaporated at the rate of about 1~2 Å/s onto the TPD layer. Finally, aluminum was evaporated to get a thick film of about 1500 Å for cathode contact. The device configuration and the molecular structure of TPD are as shown in Fig. 2. On the application of a bias potential across the device (anode is given a positive bias with respect to the cathode), injection of the holes from anode into the highest occupied molecular orbital (HOMO) of the hole-transport layer (HTL), and that of the electrons from cathode into the lowest unoccupied molecular orbital (LUMO) of emitting layer, take place. The carriers are drifted under the influence of external electric field and form excitons (electron-hole pairs), which decay radiatively at the organic/organic interface to emit light. The emitted light is extracted out of the device from the transparent ITO side. The basic operating mechanism of an OLED device is shown in Fig. 3.

Results and Discussion

Thermal stability

The thermal stability of the complex was determined by its’ Thermo Gravimetric Analysis (TGA). Fig. 4 shows the TGA and its first derivative curves for Almq₂OH. It was recorded on a Mettler TA 3000 System at a scan rate of 10°C/min under nitrogen atmosphere. It is clear from the curve that the complex is thermally stable with a degradation onset temperature of about 405°C and the maximum weight loss occurs at about 482°C.

Absorption, luminescence and device performance

The optical absorption spectrum of Almq₂OH thin film is shown in Fig. 5. Thin films of Almq₂OH were prepared by thermal evaporation of the material on the cleaned quartz substrates at a vacuum of ~ 2×10⁻⁵ torr. The absorption maximum was found at 363 nm, which is consistent with that previously reported. The absorption spectrum was recorded on a Shimadzu 2401 PC spectrophotometer in the range 250-525 nm. Figure 6 represents the electroluminescence (EL) and photoluminescence (PL) spectra of the Almq₂OH
and Alq₃. The photoluminescence emission maximum of Almq₂OH and Alq₃ occurs at 497 nm and 525 nm respectively, and it is attributed to the radiative recombination of excitons formed due to photoexcitation. The electroluminescence emission maximum of the Almq₂OH based device occurs at 506 nm, which is 9 nm red shifted in compared to PL. For a similar device based on Alq₃, the EL occurs at 530 nm. Alq₃ was purchased from Aldrich and was resublimed at about 2×10⁻⁵ torr before use. We studied the EL spectra of the material at different voltages and found that it was independent of the operating voltage and stayed fixed at 506 nm as the voltage was varied. In comparison with Alq₃, the blue shift obtained in the PL is about 28 nm, with a higher percentage of blue emission (430-499.2 nm). Very high luminance efficiency from similar derivative has been reported¹³, supporting it as a good candidate for OLED devices with blue-green emission.

The reason for the red shift in the emission spectrum of the material synthesized by us, in comparison to that reported by Leung et al.¹², is not clearly understood, but may be attributed to the formation of bridged oxo-complexes and/or isomerization that may occur on heating. Such colour change on isomerization has been observed in Alq₃¹⁴. A small and inseparable quantity of green emitting Alq₃ type complex may also be responsible for such a shift.

Figure 7 represents the current-voltage (I-V) characteristic of the device in the forward bias. The I-V measurements were taken at room temperature, using a Keithley picomammeter-480. A reasonable Schottky model for the heterojunction can be used to explain this characteristic. The electroluminescence from the device can be observed at a turn on voltage ~ 6 V and onwards. A higher turn-on voltage in comparison to the similar device based on Alq₃ has been observed, and this can be attributed to the higher energy band-gap of the material, leading to the higher potential barriers for charge injection, at the interfaces of the multilayers. The brightness of the light emitted,
increases as the driving voltage is increased. After a certain voltage it begins to fall rapidly and at a higher voltage (~20V) breakdown of the organic layers takes place and it fails.

We have compared the PL intensities of \( \text{Alq}_3 \), \( \text{Mg(mq)}_2 \) and \( \text{Almq}_2\text{OH} \) under identical conditions. The \( \text{Alq}_3 \) has been obtained from Aldrich and it was resublimed before use and \( \text{Mg(mq)}_2 \) was synthesized in the laboratory. The PL intensities were studied at different photoluminescence excitation wavelengths. Fig. 8 shows the comparative fluorescence intensities of \( \text{Almq}_2\text{OH} \), \( \text{Alq}_3 \) and that of \( \text{Mg(mq)}_2 \) at excitation light wavelength of 400 nm at constant intensity. As the PL efficiency can be correlated with the area under the curve of the spectrum, it is the evidence that \( \text{Almq}_2\text{OH} \) has much better efficiency than commercially available \( \text{Alq}_3 \) and synthesized \( \text{Mg(mq)}_2 \) complexes.

**Conclusions**

The aluminum complex \( \text{Almq}_2\text{OH} \) has been synthesized and used as a greenish-blue emitter for organic LEDs. The electroluminescence (EL) and photoluminescence (PL) of the material were blue shifted into the blue-green spectral region in comparison to that of \( \text{Alq}_3 \). The shifts for EL and PL were 24 nm and 28 nm respectively. The devices based on \( \text{Almq}_2\text{OH} \) were stable in atmosphere, but such devices are known to have a higher turn-on voltage, in comparison to \( \text{Alq}_3 \). It has been found that \( \text{Almq}_2\text{OH} \) has much far better PL efficiency in comparison to \( \text{Alq}_3 \) and \( \text{Mg(mq)}_2 \) complexes and it is thermally stable up to 405°C. It makes the material good choice for OLED applications for emission in the blue-green spectral region.

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