Synthesis and characterization of greenish-blue light emitting lithium-boron complex for organic light emitting diode applications

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A lithium-boron complex, lithium tetra (2-methyl 8-hydroxy quinolinato) boron (LiBqm₄), which emits greenish-blue light has been synthesized by the reaction of LiBH₄ with 2-methyl 8-hydroxyquinoline in a molecular weight ratio of 1:4, and used for organic light emitting diodes (OLEDs) fabrication. The complex has been characterized by optical absorption, Fourier Transform Infrared (FTIR), photoluminescence (PL) and electroluminescence (EL) spectroscopic methods. The thermo-gravimetric analysis (TGA) suggests that the material is quite thermally stable up to 380°C. An optical band gap of 3.15 eV using the well-known Tauc relation and an exciton binding energy of 0.69 eV has been evaluated. OLEDs have been fabricated in ITO/ N,N′-di-(3-methyl-phenyl)-N,N′diphenyl-4,4′diaminobiphenyl(TPD)/LiBqm₄/Al configuration. PL and EL peaks exist at 503 nm. I-V characteristic of device reveals that at higher voltages the current follows I ∝ Vᵐ law, where m > 1.

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In the recent years there has been a lot of interest among researchers towards organic electroluminescence (EL) because of its potential applications in thin and full colour flat panel display systems. Organic electroluminescence involves various operations like carrier injection at the electrodes, transport of carriers through the materials, excitons formation and their radiative decay 1-4. Since the first report on a highly efficient light emitting diode based on a small molecule by Tang et al 5 in 1987 and that based on a conjugated polymeric material in 1990 by Burroughes et al 6, a dramatic improvement has been achieved in the efficiency and lifetime of organic electroluminescent devices 7. This fast improvement has recently led to the commercialization of OLED based full colour flat panel displays. OLEDs are two electrode systems containing anode and cathode and organic materials are sandwiched between them. Generally, OLEDs based on small molecules consists of vacuum deposited emitter layers 8-14, while those based on polymers, consists of either spin coated or dip coated layers 15-19. In both types of the devices the emitter layers are casted over a high work function optically transparent and electrically conducting indium tin oxide (ITO) coated glass or plastic substrate, which serves as the hole-injecting anode. The electron-injecting cathode is usually a low work function metal such as aluminum, magnesium, calcium or their alloys. On the application of a bias voltage, holes and electrons are injected from the anode and cathode respectively into emitter layer, where they recombine to form the singlet and triplet excitons of which singlet excitons decay radiatively to give light at a wavelength corresponding to the emitter band gap.

We report the synthesis and characterization of LiBqm₄ boron complex and its suitability for OLEDs applications. It has been recognized that the charge transport mechanism is an important phenomenon in the organic light emitting diodes (OLEDs) and it is being studied extensively 20-22. To improve the performance of OLEDs a good understanding of basic device physics is very necessary. OLEDs have been fabricated in a triphenyl diamine derivative (TPD)/LiBqm₄ bilayer configuration. The complex emits a quite bright greenish-blue light with a peak wavelength at 503 nm. The Commission Internationale l’Eclairage (CIE) co-ordinates at different voltages have been studied and have been found to be independent of the applied voltage. This independence of CIE co-ordinates on the applied voltage makes LiBqm₄ a good candidate for full colour display applications. The current-voltage characteristic of the OLEDs shows that the charge transport through

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LiBqm₄ is space charge limited with a combined effect of diffusion, trapping and recombination of the charge carriers.

**Experimental Procedure**

**Synthesis of the complex**

The complex has been synthesized by the reaction of lithium borohydride (2 mmol) with four times of 2-methyl 8-hydroxyquinoline (8 mmol) in ethanol solution at room temperature. Lithium borohydride and 2-methyl 8-hydroxyquinoline were purchased from MERCK India Limited. Route of the material synthesis is shown in Scheme 1. The product was purified with a micro-soxhlet extractor for 8 h using diethyl ether as a solvent, followed by vacuum sublimation at a pressure of 5×10⁻⁵ Torr. For all the spectroscopic studies of the complex in thin films, the films were prepared by the vacuum evaporation of the complex on different substrates.

**OLEDs fabrication**

OLEDs have been fabricated on the pre-patterned, pre-cleaned ITO coated glass substrates. The substrates were patterned using standard photolithography technique and then cleaned with soap solution followed by boiling in trichloroethylene and isopropyl alcohol and finally dried under vacuum at about 140°C. Prior to any material deposition cleaned ITO substrates were exposed to oxygen plasma for 5 min. The devices were fabricated in the configuration ITO/TPD/LiBqm₄/Al. TPD (25 nm) was evaporated onto the ITO substrate to facilitate better transport of holes into the electron-hole recombination zone (emissive layer). Subsequently, the emissive material LiBqm₄ (35 nm) was evaporated onto the TPD layer. Finally, a 150 nm thick aluminium (cathode) was evaporated on LiBqm₄ in the same vacuum conditions. All the evaporation were carried out in a diffusion pumped vacuum chamber at a base pressure of 1×10⁻⁵ Torr. TPD and LiBqm₄ were evaporated at the rate of 1~2 Å/s, while Al was evaporated at about 10 Å/s. The thickness of the thin films was measured using a HINDHIVAC quartz crystal thickness monitor DTM-101. The active area of the devices fabricated was 2×2 mm². After fabrication the devices were transferred to a glove box, which resulted in a brief exposure of the devices to air. The devices were sealed in a glove box under dry nitrogen atmosphere and then were taken out. Now, all the electrical measurements were done in the ambient atmosphere. The device configuration is shown in Fig. 1. Keithley Source measure unit 2400 interfaced with a computer was used to measure the current versus voltage (I-V) characteristics of the device.

**Results and Discussion**

Optical absorption studies were carried out on the vacuum deposited LiBqm₄ thin film (300 nm) on a quartz substrate in the range 200-800 nm. A Shimadzu UV 2401 PC spectrophotometer was used to study the optical absorption of the complex at room temperature. Fig. 2 shows the absorption maximum at 275 nm with another peak at 348 nm and the cutoff wavelength at 410 nm, which is same as that reported earlier. The optical band gap was calculated from the optical absorption and using the Tauc relation,

![Scheme 1—Synthesis of LiBqm₄.](image1)

![Fig. 1—Schematic diagram of the organic light emitting diode fabricated.](image2)

![Fig. 2—Absorbance, photoluminescence and electroluminescence spectra of LiBqm₄.](image3)
which relates the absorbance $A$, with the band gap\textsuperscript{24, 25} as,$$
abla h v = (h v - E_g )^n$$... (1)

where $n$ is $1/2$ for direct band gap material and 2 for indirect band gap materials, $A$ is the absorbance, $E_g$ is the band gap corresponding to a particular absorption occurring in the film and $h v$ is the photon energy. The value of the direct optical band gap was obtained from extrapolation of the straight-line portion of the $A^2$ versus $h v$ plot, to $A = 0$. Fig. 3 shows the linearity of $A^2$ with the photon energy $h v$. Using the above relation the band gap of the complex has been estimated to be 3.15 eV.

The PL and EL spectra of thin films (Fig. 2) were recorded using HR 2000 Ocean Optics spectrometer with an optical fiber array. The emission peak lies at 503 nm, which is 30 nm shorter than that of Alq\textsubscript{3}.\textsuperscript{26} This blue shift is attributed due to different co-ordination structure of boron complexes compared to Alq\textsubscript{3}.\textsuperscript{27} EL spectrum is similar to PL spectrum, which shows that both emissions are due to the singlet excitons decay only. It has been reported that in the Mq\textsubscript{3} complexes (M = Al, Ga, In), the 8-hydroxyquinoline works as a bidentate ligand and form chelate complexes with central metals.\textsuperscript{28} But in case of LiBqm\textsubscript{4}, the central boron atom has small size, therefore only four oxygen atoms are co-ordinated to it and 2-methyl 8-hydroxyquinoline works as a monodentate ligand. It is well known fact that as the covalent nature of the metal-nitrogen bonding in Mq\textsubscript{3} complexes is decreased, emission shifts to shorter wavelength.\textsuperscript{29-30} LiBqm\textsubscript{4} emission spectrum is blue shifted in comparison to Mq\textsubscript{3} complexes, because of the absence of co-ordination bonds between boron and nitrogen atoms.

With the help of EL peak the exciton energy $E_{ex}$ was calculated to be 2.46 eV using the relation $E_{ex} = 1240/\lambda_{max}$ (nm), where $\lambda_{max}$ is the EL peak position. The band gap $E_g = 3.15$ eV determined from the absorbance measurements allows us to calculate the excitons binding energy $E_{bind} = E_g - E_{ex} \sim 0.69$ eV.

The thermogravimetric analysis (TGA) has been carried out to determine the thermal stability of the complex. The TGA curve of LiBqm\textsubscript{4} is shown in

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**Fig. 4**—Electroluminescence spectra of ITO/TPD/LiBqm\textsubscript{4}/Al device at different voltages.

**Fig. 5**—TGA curve (solid) and its first derivative (dotted) at the rate of 10\textdegree C/min under N\textsubscript{2} purging.

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Fig. 3—Selected environmental carcinogens along with estrogen (usually, these chemicals have a structural similarity with estrogen).
Fig. 5. It has been 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 up to 380°C under ambient conditions and the maximum weight loss occurs at about 515°C. Fig. 6 shows the FTIR spectrum of the vacuum deposited complex on freshly cleaved KBr single crystal. It suggests the molecular contents of the material. The strong peaks below 900 cm\(^{-1}\) are because of out-of-plane bending of ring C-H bonds and indicate the presence of aromatic ring. The strong peak at 665 cm\(^{-1}\) is because of the out-of-plane bending of C=C bonding. The peaks at 1099 cm\(^{-1}\) are because of C-O stretching. The peaks at 1277-1365 cm\(^{-1}\) suggest aromatic amine resonance (C–N–C stretching in pyridine ring). The bands at 1458-1560 cm\(^{-1}\) are because of carbon to carbon (C=C) stretching within the ring. The peaks at 2857 and 2916 cm\(^{-1}\) are because of the presence of aliphatic C-H stretching indicating the presence of a methyl group. The peak at 3033 cm\(^{-1}\) is because of aromatic C-H stretching. The C-H out-of-plane bending and aliphatic C-H stretching decide the presence of the methyl-substituted quinolines.

The room-temperature \(I-V\) characteristic of ITO/TPD (25 nm)/LiBqm\(_4\) (35 nm)/Al (150 nm) diode in the forward bias is shown in Fig. 7. We considered the applied voltage as the operating voltage when emitted light is firstly detected. The operating voltage of the above diode was observed to be 6 V. The current rises steeply above 6 V, and it results sudden rise in the brightness. The emission was uniform over the entire active area of the device. Inset in Fig. 7 represents the \(I-V\) characteristic on log-log scale. It is clear from the inset that initially at low voltages the slope of \(I-V\) characteristic is nearly 1 and current is ohmic up to about 1 V. This ohmic behaviour of \(I-V\) characteristic may be due to background doping carriers or thermally generated carriers. As the voltage increases further, slope of \(I-V\) curve increases and current follow the \(V^m\) law where \(m > 1\). This \(I \propto V^m\) behaviour of current is space charge limited with a combined effect of diffusion, trapping and recombination of charge carriers.

Conclusions
An organic fluorescent lithium-boron complex has been synthesized and used as active layer in bilayer OLED devices. The complex is thermally stable up to 380°C. The position of the PL and EL peaks at the same wavelength (503 nm) show their origin due to singlet excitons decay only. The complex has an exciton binding energy of 0.69 eV. The CIE co-ordinates have been observed independent of the applied voltage. Results show that synthesized fluorescent boron complexes have great potential as greenish-blue emitters for OLED full color display applications.

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