

Communications to the Editor

Highly Efficient Blue Electroluminescence of Lithium Tetra-(2-methyl-8-hydroxy-quinolinato) Boron

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Blue electroluminescent emitter is essential for the development of a full-color display based either on the "color changing medium" technology or the RGB filtered white emission. However, in general, blue emitting organic light emitting diodes (OLEDs) have lower efficiencies than those of green or red devices due to the larger band-gap energy of the emission material, which inhibits the injection of electrons at cathode, and efficient organic or organometallic blue emitters are still very rare.¹⁻⁵ Since the first report of high-efficiency electroluminescence (EL) of a bilayer device using tris-(8-hydroxyquinoline) aluminum (Alq₃) as electron transfer and luminance material by Tang et al.,⁶ this material has become one of the most widely used and thoroughly studied molecular emitter materials because of its good stability and luminescence properties. Alq₃ is a green emitter with peak wavelength around 530 nm. To shift the luminance of Alq₃ to blue region, a lot of research has been done, such as, introducing donors at the positions 2 or 4 or acceptors at position 5 of the quinoline ligand.⁷⁻⁹ Meanwhile all other group 13 element complexes of hydroxyquinolines have also been reported for EL applications.¹⁰ In these complexes, the quinolines all function as chelating ligands and bind to the central atom through both nitrogen and oxygen donor atoms, and the coordination numbers are 6. The emission wavelengths of the Mq₃ (M = Al, Ga, In) complexes are primarily determined by the covalent nature of the metal–nitrogen bond: the weaker the metal–nitrogen bonding, the shorter the emission wavelength.⁷

Boron also belongs to group 13, but it is a metalloid element and has both nonmetallic and metallic characters. Moreover, boron has small size, and the coordination numbers of boron complexes

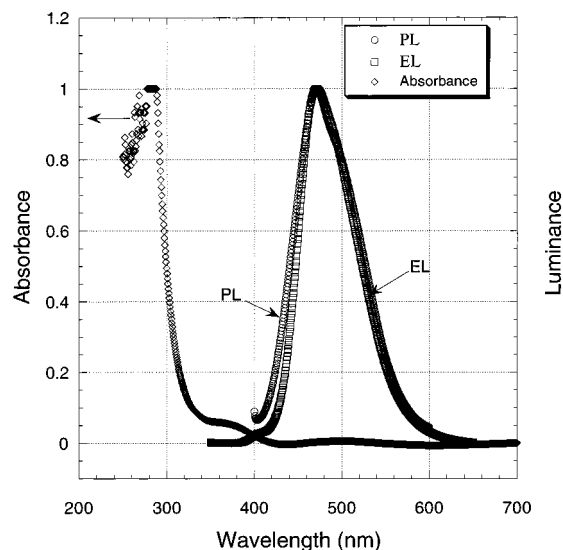
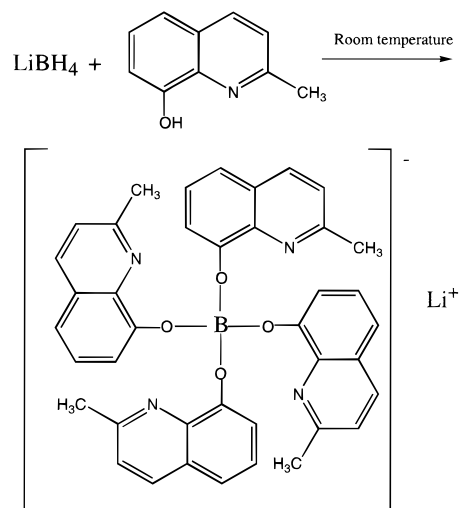


Figure 1. Normalized absorption and photoluminescence spectra of LiB-(q_m)₄ and electroluminescence spectrum of a bilayer device: ITO/PVK:TPD (50 nm)/LiB(q_m)₄ (60 nm)/Mg:Ag.

Scheme 1



are generally 4 or 3. We sought to synthesize some novel complexes using hydroxyquinolines as ligands, and only oxygen atoms coordinated to the central metals. Such kinds of complexes should have apparently more blue-shifted emission wavelengths than that of Alq₃. In this communication, we report the first example of hydroxyquinoline complexes without metal–nitrogen bonding for bright blue emission applications.

Lithium tetra-(2-methyl-8-hydroxy-quinolinato) boron [LiB-(q_m)₄] was prepared in near quantitative yields by reaction of lithium borohydride (LiBH₄) with four times of 2-methyl-8-hydroxy-quinoline in ethanol at room temperature as shown in Scheme 1. The product precipitated from solution as a white powder. The products were further purified by sublimation method at a pressure of 10⁻⁴ Torr or lower. The composition of this complex was verified by elemental and NMR analysis.

Figure 1 shows the absorption, photoluminescence (PL) spectra of the LiB(q_m)₄ as well as the electroluminescence spectrum of a

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bilayer device: ITO/PVK:TPD(50 nm)/LiB(q_m)₄ (60 nm)/Mg:Ag. The absorption cutoff wavelength of LiB(q_m)₄ is 410 nm, which is 60 nm shorter than that of Alq₃. The blue emission peak at 470 nm for LiB(q_m)₄ is about 60 nm blue shifted with respect to that of Alq₃. Such large blue shift is attributable to the different coordination structures of boron complexes to Alq₃. In Alq₃, the 8-hydroxyquinoline is functionalized as a bidentate ligand. However, in LiB(q_m)₄, due to the small size of boron atom, there are only four oxygen atoms coordinated to the central boron atom and the 2-methyl-8-hydroxy-quinoline is functionalized as a monodentate ligand. It was known that, as the covalent nature of the metal–nitrogen bonding is decreased, the emission shifts to shorter wavelength in the complexes of Mq₃, due to the ligand-to-metal charge transfers.⁷

The devices were grown on glass slides precoated with ITO (Indium Tin Oxide) with a sheet resistance of ~20 W/square. The hole transfer layer (HTL) was formed by spin coating a *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl) 1,1'-biphenyl-4,4'-diamine (TPD) doped poly(*N*-vinylcarbazole) (PVK) (1:1 weight) in 1,2-dichloroethane. On the HTL, the LiB(q_m)₄ was deposited by thermal evaporation from a graphite crucible loaded with prepurified LiB(q_m)₄ at a nominal deposition rate of ~0.3 Å/s, followed by deposition of metallic cathodes (Mg:Ag) in a vacuum at pressures below 2×10^{-6} Torr.

The current–voltage and luminance–voltage curves of the bilayer devices ITO/PVK:TPD (50 nm)/LiB(q_m)₄(60 nm)/Mg:Ag are presented in Figure 2. The LEDs show turn-on voltage of about 5 V for current and luminance. The luminance efficiency of the device is in the range of 1.3 lm/W and the maximum luminance is 6900 cd/cm². This is one of the highest blue emissions for a bilayer device.

The EL spectrum of the bilayer device is similar to that of the single layer PL spectrum of LiB(q_m)₄, as shown in Figure 1. The emission from the bilayer device is blue with peak wavelength at 470 nm and a full width at half-maximum of 75 nm. Since there is no additional electron transfer layer such as Alq₃ into which the recombination zone can extend, all emissions originate from LiB(q_m)₄. This results in excellent color purity and a relatively narrow spectrum.

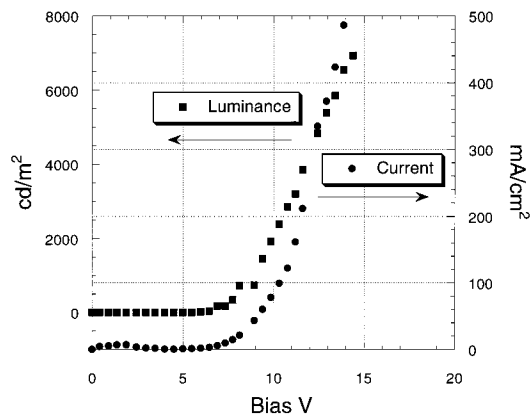


Figure 2. The forward-biased current–voltage and luminance–voltage characteristics of a bilayer LED device ITO/PVK:TPD(50 nm)/LiB(q_m)₄ (60 nm)/Mg:Ag.

In conclusion, a new blue emitting boron complex LiB(q_m)₄ has been synthesized and used as an active layer in bilayer LED devices. The luminance efficiency is in the range of 1.3 lm/W and with a maximum luminance of 6900 cd/m². Till now, this is one of the best results for a bilayer blue emission device. Work is currently in progress to further increase the efficiency by modifying the interface structures between the emission layer and cathode.

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Supporting Information Available: The details on the synthesis and purification and the elemental and ¹H NMR analysis of LiB(q_m)₄. This material is available free of charge via Internet at <http://pubs.acs.org>.

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