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A High-Efficiency Blue Emitter for Small Molecule-Based Organic Light-Emitting Diode

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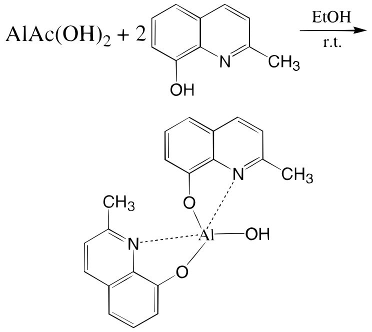
Since the 1987 report by Tang et al. for a high efficiency small molecule-based hetero-junction organic light-emitting diodes (OLED), substantial progress has been made so that the state-of-the-art device is becoming a viable commercially product.[1] The typical cell structure for a multilayer OLED device is: an anode (indium tin oxide (ITO) on glass substrate)/a hole-transporting layer/a light-emitting layer/an electron transporting layer/a cathode (a low work function metal). For most designs, the electron transporting compound is also the emitter. One of the better known emitters with high emission efficiency is aluminum(III) complex of 8-hydroxyquinoline (Alq_3). It is a green emitter with emission maximum in the range of 530 nm. For the design of a full color RGB display, high efficiency dyes with emission in red and blue are also desired. Other than the desired hue and color purity, there are other criteria for the materials design. They are: (i) an appropriate molecular mass so that the vapor phase deposition method can be used, (ii) the compound is thermally stable, yet (iii) it has high carrier mobility, and (iv) high emission efficiency.

Traditionally, a blue emitter has a lower efficiency due to its larger band-gap energy which may deter injection of electrons from the cathode. One method to achieve blue emission is through the use of a dopant. Tang reported doping BAlq (an aluminum(III) complex with a 2:1 mix ligand ratio of 2-methyl-8-hydroxyquinaldine and 4-phenyl-phenol) with perylene to achieve a blue OLED with luminance of 355 cd/m^2 at 20 mA/cm^2.[2] The device has a current efficiency of 1.8 cd/A and a luminescence efficiency of 0.56 lm/W. The doped OLED, however, has multiple maxima in the emission spectrum. Inserting an electron donating group at the 2- and 4-positions of the quinoline ligand can also achieve blue-shift in the emission spectrum. Kido reported one of the highest efficiencies (external quantum efficiency of 2.5% photons/electron) small molecule OLED based on tris(4-methyl-8-quinolinolato) Al(III) complex.[3] The bluish green emitter has a single emission peak at 506 nm. Hamada et al. reported a gallium complex ($GaMq_2Cl$) consists of two 8-hydroxyquinaldines and one chlorine atom. The compound has a greenish blue emission with maxima at 492 and 530 nm, and its performance (maximum intensity 10,490 cd/m^2) is similar to Alq_3.[4] A recent study proposed that a weaker metal-nitrogen in Alq_3 type complexes can also result in a shorter emission wavelength.[5] One such blue emitter without the metal−nitrogen bond reported was lithium tetra(2-methyl-8-hydroxy-quinolinato) boron ($LiBq_{m4}$).[6] The electroluminescence (EL) spectrum for the OLED has a single emission maximum at 470 nm. The luminescene efficiency of the device is in the range of 1.3 lm/W and a maximum luminance of 6900 cd/m^2, which represents one of the highest efficiency blue emitter reported yet with good color purity. Parallel to this latest development, we would like to report in this contribution that a bis(2-methyl-8-quinolinolato) aluminum(III) hydroxide complex ($AlMq_2OH$) is also a high-efficiency blue dye with a single emission maximum at 485 nm. The compound has excellent thermal stability and can be processed similar to Alq_3. The synthesis procedures are simple, using chemicals that are readily available from commercial sources. The blue-shift is suggested to be a result of two conditions. (i) The aluminum complex is trivalent in nature, and (ii) steric hindrance provided by the 2-methyl groups on the 8-hydroxyquinaldine ligands weakened or prohibited the formation of Al−N bondings.

Scheme 1



The $AlMq_2OH$ complex was prepared by mixing a 1:2.2 equivalent ratio of aluminum acetate($AlAc(OH)_2$) in DI water to 8-hydroxyquinaldine in absolute alcohol (EtOH) at room temperature and stirred for hours.[7] The pH of the solution was than adjusted using a NaOH buffer solution. A white precipitant resulted with over 80% yield. The reaction is shown in Scheme 1. Similar complexes can be prepared by using other polar solvents and various aluminum salts. The product was than washed by Soxhlet and then purified using the train-sublimation method at 10^{-6} Torr. The structure of the final product was confirmed by ^{1}H NMR and FTIR. The molar mass and composition of the sublimed product was determined with elemental analysis, MS, and AAS.[8]

Two multilayer small molecule OLEDs using either $AlMq_2OH$ or Alq_3 as the emission layer were built and their characteristics compared. The Alq_3 device was used as a benchmark for comparison purposes only and does not necessary imply that the device configuration has been optimized. The OLED cell has a general structure of ITO (72 ohm/sq)/copper(II) phthalocyanine, (10 nm)/*N*,*N*′-bis-(1-naphthy)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine, (NPB, 50 nm)/emitter, $AlMq_2OH$ or Alq_3 (80 nm)/LiF (0.7 nm)/Al(80 nm). The $AlMq_2OH$ or Alq_3 was evaporated from a “homemade” Mo boat at a deposition rate of 1 Å/sec. The properties of the two OLEDs are listed in Table 1. It was found that at similar current density (80 mA/cm^2), both the brightness and current efficiency of the $AlMq_2OH$ device was 3 times that of Alq_3. The maximum brightness of the $AlMq_2OH$-based device is 14,000 cd/m^2 at 480 mA/cm^2, which is one of the highest-intensity blue emitter reported. The slightly higher turn-on voltage for the $AlMq_2OH$ device indicates that it has a higher energy barrier for charge injection. Figure 1 shows the UV−vis absorption, photoluminescence (PL) spectra of $AlMq_2OH$ solid thin film on quartz, and the electroluminescence (EL) spectrum of the

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(8) Results from elemental analysis (C, H, N) and AAS (Al). Calculated $AlO_{2.45}N_{1.96}C_{19.6}H_{15.5}$; theoretical $AlO_3N_2C_{20}H_{17}$.

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Table 1. Comparison of I−L-V Characteristics of Two Similar OLEDs (see text for cell structure) with either $AlMq_2OH$ or Alq_3 as the Emitting Layer

emitting layer	turn-on voltage (V)	luminance at 80 mA/cm^2 (cd/m^2)	current efficiency at 80 mA/cm^2 (cd/m^2)	maximum luminance (cd/m^2)
$AlMeq_2OH$	9	4025	5.03	14070
Alq_3	7	1500	1.88	3190

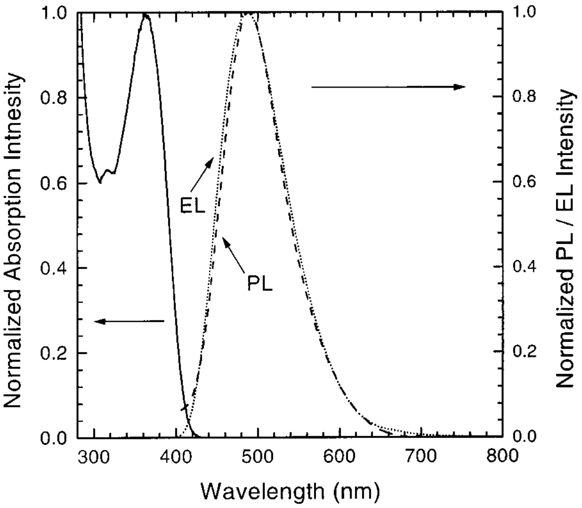

Figure 1. Normalized UV−vis absorption and fluorescence spectra of $AlMeq_2OH$ solid thin film. Electroluminescene spectrum is from a heterojunction OLED device with structure described in text.

$AlMq_2OH$-based OLED. Both the EL and PL spectrum of $AlMq_2OH$ have a similar shape, a single emission maximum at 485 nm, and a fwhm of 80 nm. The 50 nm blue-shift for the 8-hydroxyquinaldine-based complex is consistent with similar dyes without the Al−N bonding.[6]

In a patent disclosed by Van Slyke et al., the properties for a series of 8-hydroxy-quinaldine-based aluminum(III) complexes were described.[9] Their compounds have the general structure (R′-Q)$_2$−Al−O−L, in which R′-Q can be a 2-methyl-8-quinolinolato ligand and L represents a series of phenolato ligands with 6−24 carbon atoms. The presence of the phenolato ligand was suggested to cause a blue-shift of the complex to below 500 nm. The stability of the various OLEDs was also found to be related to the chemical structure of the phenolato groups. Results from this work, however, indicated that the steric hindrance was required to reduce the metal−N bonding, and therefore the required blue-shift was provided by the two 2-methyl-8-hydroxyquinolinato ligands, irrespective of the size of the third phenolato group. We have also studied a series of other Mq-based complexes using metals from groups IIIB to IVA. In general, the blue-shift is related to the size of the metal atom, its coordination number, and the acidity of the metal group. In general, divalent complexes have none or minimum blue-shift, and the stability of the complexes decreased with an increase in the size of the metal atom.

Table 2. Results from Thermogravimetric Analysis. the Heating Rate Was 10 °C/min and under a Nitrogen Purge

sample	onset degradation temp (°C)	DGA (derivative) maximum wt loss temp (°C)	wt loss (%)
$AlMeq_2OH$	424	467	72
Alq_3	428	470	94

The $AlMq_2OH$ complex described here is among one of the highest-efficiency blue emitter reported, yet it can be processed using methods similar to that for Alq_3. The complex itself is stable both under air and high temperatures. Table 2 shows the TGA results of $AlMq_2OH$ compared to those for Alq_3 under nitrogen atmosphere. A yellowish side-product with EL and PL similar to that for Alq_3, however, was collected during the train sublimation process. It has a lower molecular mass compared to that of $AlMq_2OH$ as observed from the lower temperatures required for sublimation. Results from MS and elemental analysis indicated its chemical composition was $AlMq_2$,[10] which maybe a degradation product of the less stable $AlMq_2Ac$. The re-establishment of the Al−N bondings after losing the third ligand reconfirmed that steric hindrance prohibiting the formation of metal−N bonding was the cause for the blue-shift. Additional chemical and physical methods are being attempted for further improvement of the long-term stability of the $AlMq_2OH$-based EL devices.

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(9) Van Slyke, S. A.; Bryan, P. S.; Lovecchio, F. V. U.S. Patent No. 5,150,006.

(10) Results from elemental analysis (C, H, N). Calculated $AlO_2N_{1.94}C_{19.7}H_{15.73}$, theoretical $AlO_2N_2C_{20}H_{16}$.