Efficient Electroluminescence from Tris(4-methyl-8-quinolinolato)aluminum(III)

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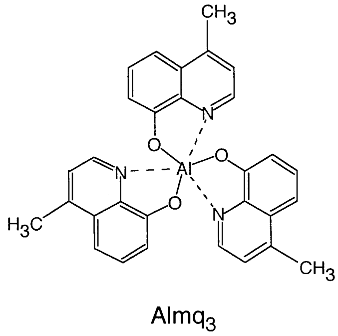
A green-light-emitting aluminum complex, tris(4-methyl-8-quinolinolato)Al (III) ($Almq_3$), was synthesized and used as an emitter material in organic electroluminescent (EL) devices. The device structure of glass substrate / indium-tin oxide / tetraphenyldiamine derivative / $Almq_3$ / Mg:Ag was employed. The EL device exhibited efficient green light originating from $Almq_3$ with a maximum luminance of 26000 cd/m^2 at 14 volt. The maximum external quantum efficiency was 2.5% photons/electron.

Organic electroluminescent (EL) devices are now expected to be the flat panel displays of the next generation.[1] In these devices, organic emitter layers are sandwiched between two electrodes and the organic emitting centers are excited by the recombination of holes and electrons injected from the electrodes. In order to maximize carrier recombination efficiency, EL devices usually consist of a multilayer structure with a hole-transporting layer and an electron-transporting layer to confine injected carriers as well as generated excitons in the organic layers.[2] One of the electron-transporting materials is tris(8-quinolinolato)Al(III) (Alq_3) complex which was introduced by Tang and VanSlyke in 1987.[2] Since then, this metal complex has been widely used, and various types of EL devices have been developed using Alq_3, which include a high luminance device[3] and white-light-emitting devices.[4,5] A similar metal complex, bis(10-benzo[h] quinolinolato) Be(II), was reported later to be a good electron-transporting emitter material by Hamada et al.[6] These two metal complexes are still the best electron-transporting emitters in terms of device efficiency as well as durability.

In this study, we synthesized an aluminum complex having 4-methyl-8-quinolinolato as ligands, tris(4-methyl-8-quinolinolato)Al (III) ($Almq_3$), and investigated the EL properties of the complex.



$Almq_3$

4-Methyl-8-quinolinol having a m.p. of 139.9–141.2 °C[7] was received from Chemipro Kasei Kaisha, Ltd. and used without further purification. $Almq_3$ was synthesized from aluminum chloride hexahydrate and 4-methyl-8-quinolinol. To a solution of aluminum chloride hexahydrate in tetrahydrofurane (THF) / deionized water, a solution of 4-methyl-8-quinolinol in THF containing an equivalent of piperidine was slowly added. After stirring for 1 h, solvent was removed on a rotary evaporator. The yellow powder obtained was dried in a vacuum oven, and was finally purified by the train sublimation method (yield 65%). Found: C, 71.94; H, 4.87; N 8.29. Calcd for $C_{30}H_{24}N_3O_3Al_1$: C, 71.85; H, 4.82; N, 8.38.

$Almq_3$ was evaluated as an emitter layer in a bilayer-type device having a hole transport layer inserted between the anode and the emitter $Almq_3$ layer. The device structure is a glass substrate / indium-tin oxide (ITO) / *N,N'*-diphenyl-*N,N'*-(3-methyl phenyl)-1,1'-biphenyl-4,4'-diamine (TPD) (300 Å) / $Almq_3$ (700 Å) / Mg:Ag (10:1). The organic layers were successively deposited onto an ITO-coated glass substrate at 1.0 x 10^{-5} Torr. The Mg:Ag top electrode was finally codeposited at 7.0 x 10^{-6} Torr. The emitting area was 0.5x0.5 cm^2. ITO (1000 Å)-coated glasses, having a sheet resistance of ca. 17 Ω/square, were received from Sanyo Vacuum Industries Co., Ltd. Luminescence measurements including electroluminescence and photoluminescence (PL) were carried out on an optical multichannel analyzer PMA 10 (Hamamatsu Photonics K. K.). Luminance was measured with a Topcon BM-8 luminance meter at room temperature and ionization potential (Ip) was measured by atmosphere ultraviolet photoelectron analysis using a Riken Keiki AC-1 under ambient atmosphere.

From the bilayer device, bright green light peaking at around 506 nm was observed when operated in a continuous dc mode with Mg:Ag negative. The EL spectrum in Figure 1 (a) is identical with the PL spectrum of the vacuum deposited film of $Almq_3$, Figure 1 (b), which indicates that electron-hole

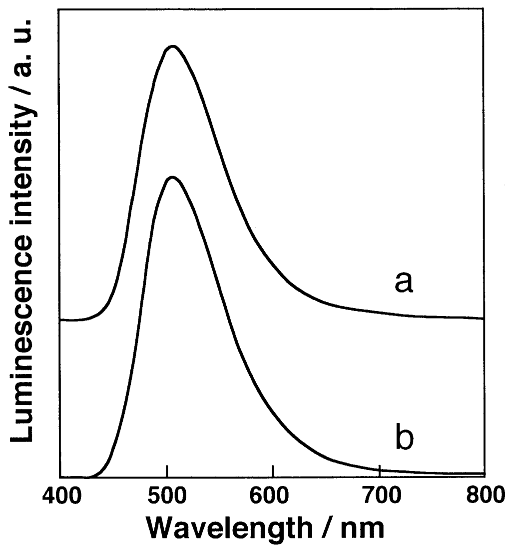


Figure 1. (a) EL spectrum of an ITO/TPD(300 Å)/$Almq_3$ (700 Å)/Mg:Ag device, and (b) PL spectrum of a vacuum deposited film of $Almq_3$ (λem = 390 nm). Spectra are offset for clarity.

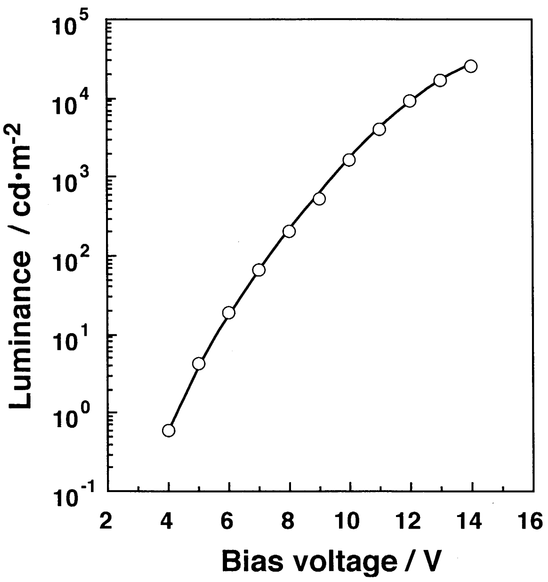


Figure 2. Luminance-voltage characteristics of an ITO/TPD (300 Å)/$Almq_3$(700 Å)/Mg:Ag device.

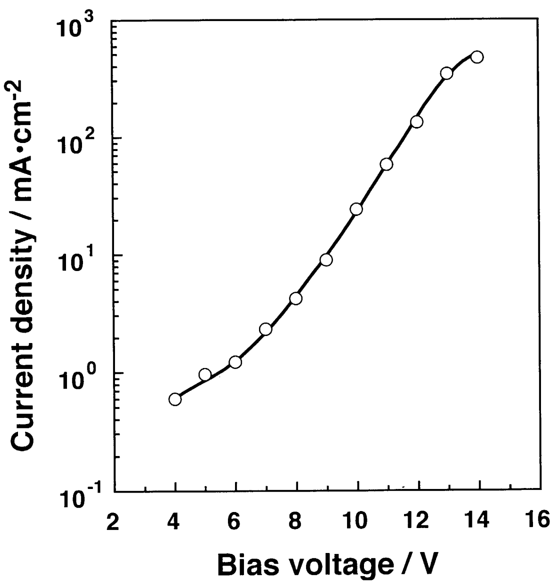


Figure 3. Current density-voltage characteristics of an ITO/TPD(300 Å)/$Almq_3$(700 Å)/Mg:Ag device.

recombination occurs in the $Almq_3$ layer. Compared with the PL spectrum of Alq_3, peaking at around 520-530 nm, the PL spectrum of $Almq_3$ is blue shifted due to the electron-donating methyl group at the 4 position. Similar tendency was observed for tris(2-methyl-8-quinolinolato)Al(III) complex[8].

The luminance (L)-voltage (V) curve for the ITO / TPD / $Almq_3$ / Mg:Ag device is displayed in Figure 2. Luminance increases with increasing injection current as well as bias voltage. The maximum luminance and the external quantum efficiency (QE) of the device are 26000 cd/m^2 at 14 V and 2.5% photons/electron at 12V, respectively, which are higher than those of Alq_3-based devices (QE=1.3%).[2]

The current (I)-voltage (V) curve of the device is plotted in Figure 3. High current densities such as 480 mA/cm^2 at 14 V are observed, which may indicate that $Almq_3$ has high electron affinity. From the Ip value of the complex (5.9 eV) and the optical energy gap (2.7 eV), the pseudo electron affinity (Ea) value is estimated to be 3.2 eV, which is larger than that of Alq_3 (3.0 eV). This suggests that the high QE of the $Almq_3$-based device is attributed to the larger Ip and Ea values of $Almq_3$ that improve electron-hole recombination efficiency by confining holes and electrons to the organic layers.

In conclusion, we demonstrated that $Almq_3$ is an excellent electron-transporting green light emitter. The device lifetime will be measured and dye-doped $Almq_3$-based devices will be fabricated to improve device efficiency.

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