A Novel Electroluminescent Metal Complex: Tris(4-phenanthridinolato)aluminum(III)

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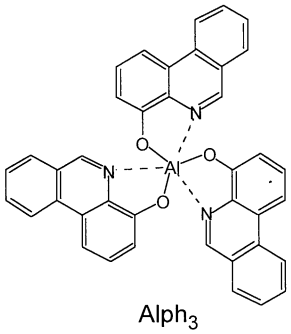
A yellow fluorescent aluminum complex ($Alph_3$) having 4-phenanthridinolato ligands was synthesized and used as an emitter material in organic electroluminescent (EL) devices. The device structure of glass substrate / indium-tin oxide / tetraphenyldiamine derivative / $Alph_3$ / Mg:Ag was employed. The EL device exhibited bright yellow light originating from $Alph_3$ with a maximum luminance of 13000 cd/m^2 at 11 volt.

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 ($Alph_3$) having 4-phenanthridinolato as ligands and investigated the EL properties of the complex.



$Alph_3$

4-Phenanthridinol was received from Chemipro Kasei Kaisha, Ltd. and used without further purification. $Alph_3$ was synthesized from aluminum chloride hexahydrate and 4-phenanthridinol. To an aqueous solution of aluminum chloride hexahydrate, an ethanol solution of 4-phenanthridinol was slowly added. Then, the pH value of the solution was brought to about 7 by the addition of an aqueous solution of sodium hydroxide. Precipitated $Alph_3$ was collected by filtration and dried in a vacuum oven, and it was finally purified by the train sublimation method (yield 30%). [Elemental analysis: H 3.90 (3.97), C 76.98 (76.83), N 6.88 (6.90), ( ) Calcd]

$Alph_3$ was evaluated as an emitter layer in a bilayer-type device having a hole transport layer inserted between the anode and the emitter $Alph_3$ 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) (400 Å) / $Alph_3$ (600 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-coated glasses, having a sheet resistance of 15 Ω/square, were purchased from Asahi Glass Co., Ltd. Luminance was measured with a Topcon BM-8 luminance meter at room temperature and ionization potential was measured by atmosphere ultraviolet photoelectron analysis using a Riken Keiki AC-1 under ambient atmosphere.

From the bilayer device, bright yellow light peaking at 560 nm was observed when operated in a continuous dc mode with Mg:Ag negative. The EL spectrum in Figure 1 (a) is nearly identical with the photoluminescence (PL) spectrum of the vacuum deposited film of $Alph_3$, Figure 1 (b), indicating that electron-hole recombination occurs in the $Alph_3$ layer. Compared with the PL spectrum of Alq, the luminescence spectrum of $Alph_3$ is red shifted. This is due to the extended π-conjugation of the ligands, which causes narrower energy gap between the HOMO and the LUMO of $Alph_3$ compared with that of 8-quinolinol.

The luminance (L)-voltage (V) curve for the ITO / TPD / $Alph_3$ / Mg:Ag device is displayed in Figure 2. Luminance

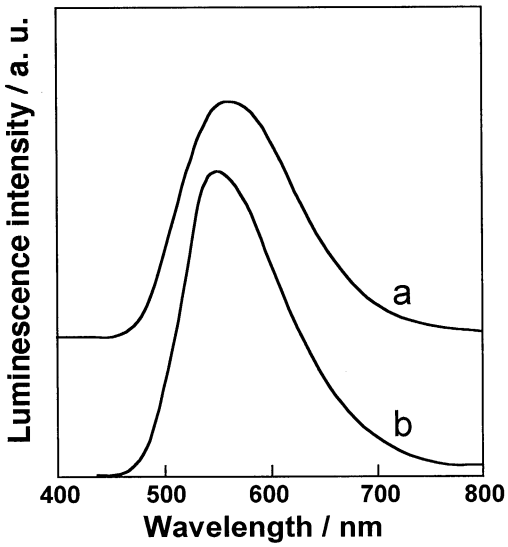


Figure 1. (a) EL spectrum of an ITO/TPD(400 Å)/$Alph_3$ (600 Å)/Mg:Ag device, and (b) PL spectrum of a vacuum deposited film of $Alph_3$ (λem=425 nm). Spectra are offset for clarity.

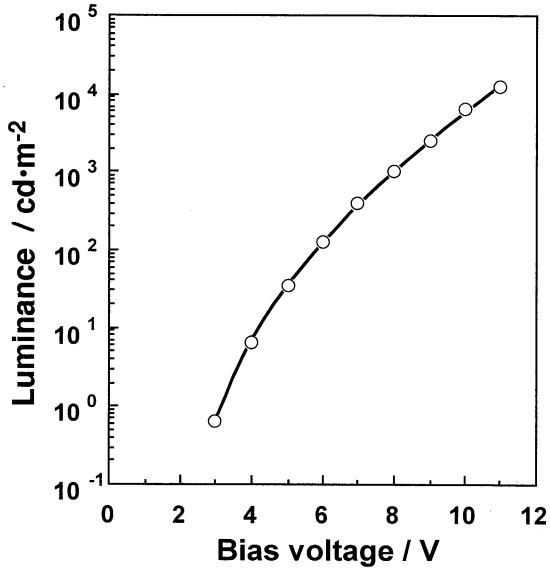


Figure 2. Luminance-voltage characteristics of an ITO/TPD (400 Å)/Alph (600 Å)/Mg:Ag device.

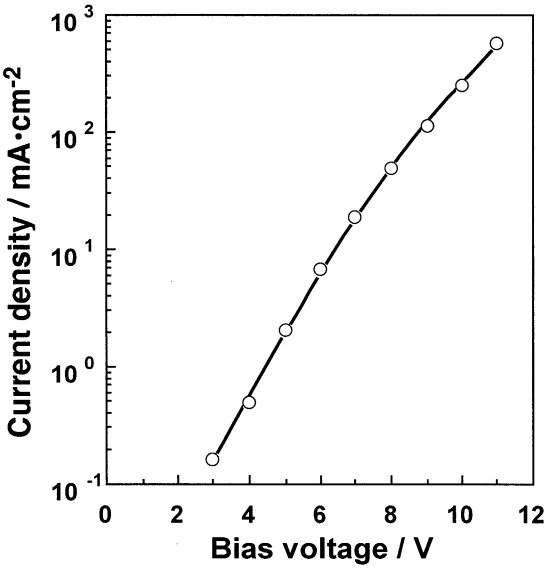


Figure 3. Current density-voltage characteristics of an ITO/TPD(400 Å)/Alph (600 Å)/Mg:Ag device.

increases with increasing injection current as well as bias voltage. The maximum luminance of the device is 13000 cd/m^2 at 11 V, which is comparable to that of Alq_3-based devices.

The current (I)-voltage (V) curve of the device is plotted in Figure 3. High current densities such as 570 mA/cm^2 at 11 V are observed, which may indicates that $Alph_3$ has high electron affinity. From the ionization potential of the complex (5.5 eV) and the optical energy gap (2.5 eV), the pseudo electron affinity (Ea) value of $Alph_3$ is estimated to be 3.0 eV, which is comparable to that of Alq_3 (3.0 eV). The external quantum efficiency of the device is calculated to be 0.75 % at 10V. At this drive voltage, the luminance is 6300 cd/m^2 and the current density 250 mA/cm^2.

In conclusion, we have demonstrated that $Alph_3$ is an excellent electron-transporting yellow light emitter. Lifetime of the $Alph_3$-based devices will be measured in the near future and reported elsewhere.

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