

Highly Efficient Phosphorescence Emitting Materials and Applications to Organic Light Emitting Diode

Lee Bum Sung, Jung Sang Yun, Byun Ki Nam, and Yu Han Sung
OLED Production Team, SKC Co. Ltd.

Lee Yoo-Jin, Kim Sung-Hyun

Nano-technology based Information and Energy Storage Research Center(NIES), Korea Electronics Technology

Abstract

Novel series of electron-transporting hosts, pentavalent aluminum complexes containing 8-hydroxyquinoline ligands and various phenolato ligands were synthesized, and organic light-emitting diodes (OLEDs) were fabricated using these complexes as host materials of phosphorescent emitting device and the fabricated phosphorescent emitting device showed low driving voltage, high efficiency at high current density and good stability under conventional driving condition.

1. Introduction

Organic electroluminescent materials have attracted a lot of attention, due to their intriguing physical properties and potential application in the flat-panel displays [1] Recently, OLED based on phosphorescent emitters can significantly improve electroluminescent performance because both of singlet (25%) and triplet (75%) excitons can be harvested for light emission. Theoretically internal quantum efficiency can approach 100%. [2]

When the phosphorescent emitting devices are applied to the display, however, they have several kinds of problems. Firstly, the quantum efficiencies of phosphorescent device dominantly decrease owing to their long emission duration of excitons, which leads to saturation of emissive sites and triplet-triplet (T-T) annihilation at high current density. [3] Especially, high peak luminance, over 10,000 cd/m² is required for passive matrix (PM) panel because of its driving method, aperture ratio and optical loss owing to transmission of polarizer film which is attached to glass substrate for better contrast.

In addition, the emission layer of phosphorescent OLED devices is generally composed of a carbazole-type host, 4,4'-N,N'-dicarbazol-biphenyl (CBP). The

exciton formation zone of the devices extends over 30 nm owing to the hole transporting ability of CBP. Therefore, in terms of the confinement of holes in the emission layer, a hole-blocking layer (HBL) has been generally used for effective recombination of holes and electrons [4], but the insertion of hole-blocking layer may give rise to several difficulties in application. For examples, the insertion of hole-blocking layer has tendency to increase driving voltage, directly causing a rise of power consumption, and drawback in mass production, in that it needs additional evaporation chamber.

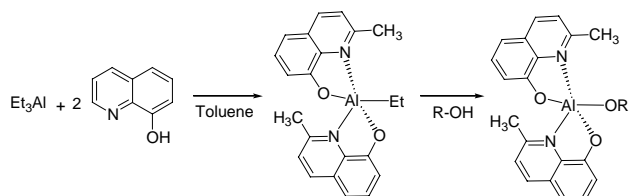
To alleviate these difficulties of insertion of hole-blocking layer, exciton formation zone of the host doped with phosphorescent emitting dopant should be narrow as much as holes can not pass through the emitting layer, but extremely narrow exciton formation zone tends to promote triplet-triplet (T-T) annihilation on the contrary. [4b] Recently, the electron-transporting hosts such as 2,9-dimethyl-4,7-diphenylphenanthroline (BCP), 1,3-bis(N, N-t-butylphenyl)-1,3,4-oxadiazole (OXD7), 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ) and aluminum (III) bis(2-methyl-8-quinolinato) 4-phenylphenolate (BALq) have been recommended to satisfy these requirements. [5]

In this communications, we wish to report to a series of remarkable hosts for phosphorescent emitting device, based on pentavalent aluminum complexes containing 8-hydroxyquinoline ligands and various phenolato ligands, and their strong electroluminescent brightness and efficiency.

2. Results and Discussions

As shown in Scheme 1, the series of BALq were synthesized from triethylaluminum, 8-hydroxyquinoline and phenol compounds. [6] At room temperature, a solution of triethylaluminum (50 mmol) in dried toluene was placed in a three-neck .

Scheme 1.



flask under an atmosphere of nitrogen. The solution of 8-hydroxyquinoline (100 mmol) in dried toluene was added drop-wise into the above solution with stirring at such a slow rate that a gentle reflux of the solvent was maintained. After the gentle reflux (1hr), a solution of phenol-compounds (100mmol) in dried toluene was added drop-wise. Then, the reaction was allowed to continue for overnight. The product was collected by filtration and recrystallized in methylene chloride. The structures of synthesized compounds outlined in the following Fig. 1.

Fig. 1 Host structures and optical properties

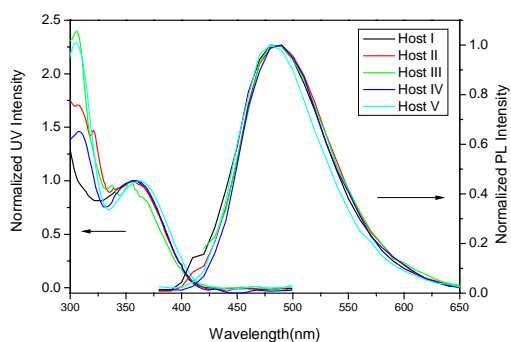
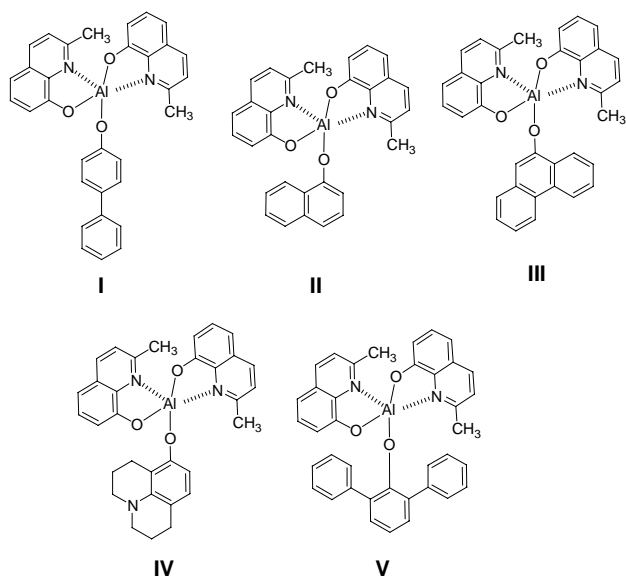


Table 1.

Host	I	II	III	IV	V
UV (nm)	362	362	362	362	362
PL (nm)	490	490	490	490	490
T _g (°C)	102	104	123	126	-
T _d (°C)	260	250	325	330	331
Band-Gap(eV)	2.8	2.8	2.8	2.8	2.8

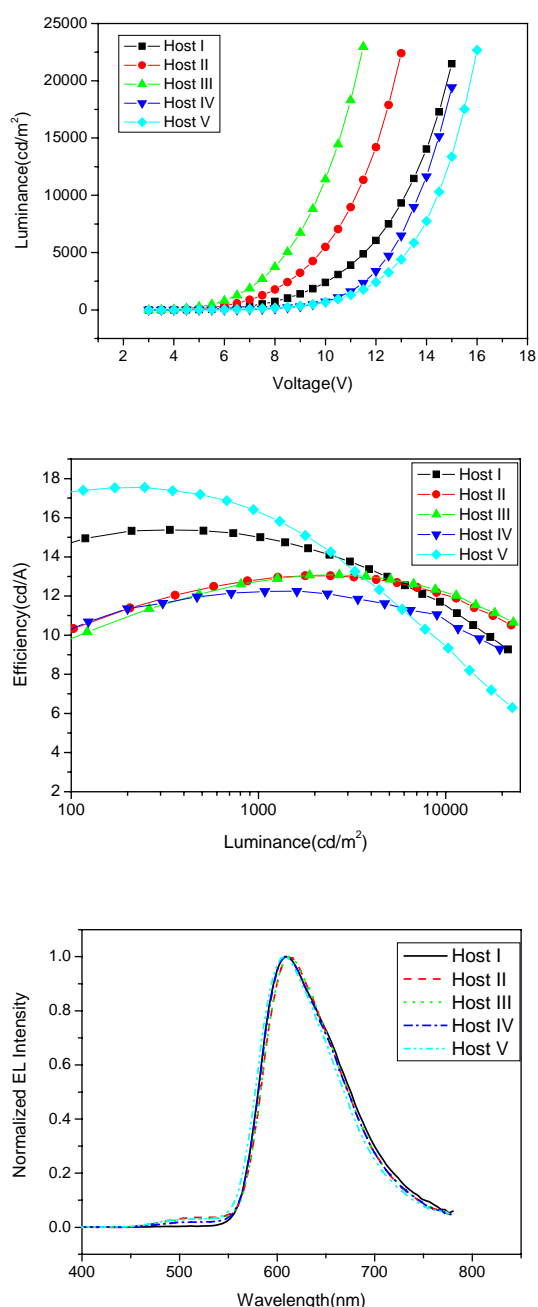
It was expected that BALq compound has wide band (2.9 eV) of HOMO (5.7 eV) and LUMO(2.8 eV) enough to be used as a host in red-phosphorescent emitting device. We made our efforts to find the appropriated hosts which have good thermal stability and charge mobility, and our efforts were focused on the only transformation of auxiliary ligands (R) to maintain its photoluminescent properties of BALq. As shown Table 1, the divergences of photoluminescence spectrum and HOMO/LUMO band-gap, calculated from edge of UV-Vis absorption were negligible but thermal stabilities (T_g and T_d) increased, depending on the size of auxiliary ligands. Both of host material (III) and host material (IV) have highest glass transition (T_g) temperature and decomposition temperature (T_d).

We used phosphorescent dopant, Pq (or Piq) which was reported by Mark E. Thompson' group. [7] It has several advantages, in that it can be easily obtained from commercial available starting materials and it has relatively short excitation lifetime (2.0 sec at 298K) compared to general red-phosphorescent emitting materials. It is very important that the phosphorescent emitting dopant has short excitation lifetime because excitation duration length of emitting dopant plays a role to bring about the roll off phenomena which the efficiency seriously decrease at high current density.

With these compounds, EL devices were fabricated on indium-tin oxide (ITO anode) substrates. Organic layers were deposited by conventional vacuum vapor deposition in 6×10^{-6} Torr. The emitting area is 2*2 mm. The device structure and layer thickness are follows. ITO (150nm) / 2-TNATA (60nm) / NPB (20nm) / Host + Dopant (40nm) / Alq₃ (30nm) / LiF (1nm) / Al (100nm) The current-voltage (I-V) and the luminance-voltage (L-V) characteristics were measured under forward bias using a Keithley 2400 source measurement with calibrated PR650 Spectra

Scan at room temperature and atmosphere. Current-voltage (I-V) and luminance-voltage (L-V) characteristics of phosphorescent emitting devices containing Host (I~V) were measured and summarized in Fig 2 and Table 2.

Fig 2. I-V-L Characteristics and EL Spectrum



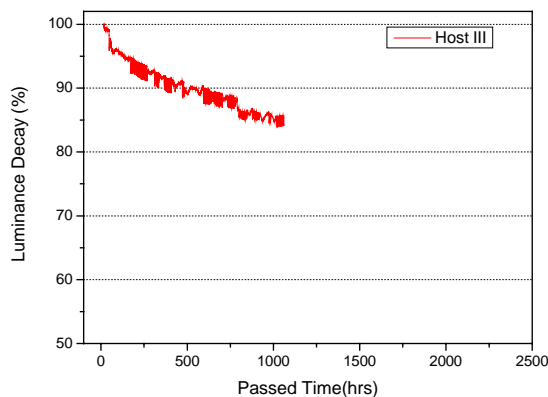
Host	Doping Ratio ^a	@ 10,000 cd/m ²		
		(V)	(cd/A)	CIE (x, y)
I	8 %	13.1	11.5	(0.6274, 0.3708)
II	10%	11.2	12.0	(0.6201, 0.3745)
III	12 %	9.7	12.2	(0.6209, 0.3737)
IV	8 %	13.7	10.7	(0.6202, 0.3784)
V	10%	14.4	9.4	(0.6201, 0.3736)

^a Optimized doping ratios which were evaluated between 5 and 15% with respect to color purity, efficiency and driving voltage.

As shown in EL spectrum (Fig. 2), emission from host materials was hardly observed, indicating good energy transfer from host excitons. The peak assignable to host material (I) at around 500 nm, not appeared in any degree and led to better red color (I, 0.6272, 0.3708). EL data were outlined on the basis of the luminance, 10,000 cd/m², since high efficiency and low driving voltage at high luminance region, are most essential for application of practical passive matrix display. It is noteworthy that host material (III) has lowest driving voltage (9.7 V at 10,000 cd/m²) and highest efficiencies (12.2cd/A at 10,000 cd/m²). Another feature that should be noted is that the host material (III) exhibited a very slow decrease in quantum efficiency with increasing current densities. It means that emitting region of the host material (III) layer, might be moderately narrow enough not to pass through the emission layer and not to promote triplet-triplet (T-T) annihilation.

Now, we turned to our attention to its practical application. Operational lifetime for host material (III) was measured under pulse driving method, which have been generally used for operation of passive matrix displays. The mono-color OLED panel (1 inch), contained 96(scan line) by 64(data line) was fabricated and the device structure was same as above the device (material III) and this panel operated under 1/64 duty-ratio pulse driving method. The initial luminance (251 cd/m²), equivalent to a peak luminance of 16067 cd/m² was set. The peak luminance was the calculated figure for the red pixel luminance (27cd/m²) of 1-inch full color panel to provide luminance of 80cd/m², considering aperture ratio, 1/64 duty, number of emitting pixels (3, R, G, B) at same scan line and transmittance of polarizer film (44%). The initial luminance decreased somewhat rapidly during initial 100hrs but decreased very slowly after 250hrs. It was expected that the

operational lifetime reached 4000 hrs by extrapolation to half-lifetime (50% decay) and its operational lifetime is attributed to be enough for practical application of displays.



3. Conclusions

In summary, we reported a series of aluminum complexes containing 8-hydroxyquinoline ligands and phenolato ligands, and these hosts have appropriate charge mobility to restraint triplet-triplet annihilation at high current density, then, successfully worked well without insertion of hole-blocking layer. Furthermore, the OLED device using host material (III), showed the low driving voltage, high-efficiency and long operational lifetime of panel enough to be used in practical display.

4 References

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