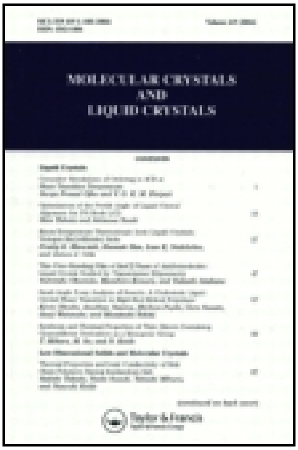

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Highly Efficient Red Phosphorescent OLEDs with Simple Device Structure

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We report high efficiency red phosphorescent OLEDs with a simple organic bi-layered structure. A host material bis(10-hydroxybenzo[h] quinolinato)beryllium complex (Bebq$_2$) having a good electron transporting and energy transfer characteristics and a good hole injection and transport material N,N′-di(4-(N,N′-diphenyl-amino)phenyl)-N,N′-diphenylbenzidine (DNTPD) lead to the fabrication of simplified high efficiency device. The driving voltage value of 3.5 V to reach luminance of 1000 cd/m^2 is reported. The maximum current- and power-efficiency values of 9.38 cd/A and 11.72 lm/W with real true red color of (0.67, 0.32) are demonstrated.

Keywords: efficiency; host; organic light-emitting diode; phosphorescent; red; simple

INTRODUCTION

Organic light-emitting diodes (OLEDs) have been widely recognized as a technology for flat panel display (FPD) products today and for potential future use in the lighting industry. A key goal of OLED researches is to achieve very high electroluminescent (EL) efficiency with low drive voltage. OLEDs with fluorescent dyes as the emissive layer, in which only the singlet states of the organic molecule contribute to the light emission, exhibit an upper limit on the external quantum efficiency of 5%. The efficiency of OLEDs can be improved by introduction of phosphorescent dyes, so-called electrophosphorescent OLEDs (or PHOLEDs), because of harvesting both singlet and triplet states.

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Extremely high external quantum and power efficiencies of PHOLEDs have been rapidly developed in recent years [1–5]. The device structure of PHOLEDs is required to be more complicate to confine long lifetime triplet excitons. Four or five organic layered structures have been commonly used to obtain high-efficiency PHOLEDs [6,7]. Such complicated structure enhances the drive voltage due to injection barriers from many hetero-interfaces. Therefore, the turn-on voltage of PHOLEDs is also relatively high about $1 \sim 2\,\mathrm{V}$ compared to that of fluorescent OLEDs [8,9]. These complicated structures and high turn-on voltage in PHOLEDs are limitation factors to be applied in display industry.

In our previous paper, we had reported a simple bilayered PHOLED structure with $\mathrm{Bebq_2}$ as host material and α-NPB (N,N′-bis (naphthalen-1-yl)-N,N′-bis(phenyl)benzi-dine) as hole transporting material [10,11]. In addition, improvement of driving voltage in this simple device was reported by minimizing injection barriers and reducing hetero-interfaces. Our reporting driving voltage to give $1000\,\mathrm{cd/m^2}$ was 4.5 V. In this simple red device, however, the injection barrier still needs to be improved because the injection barrier between NPB and indium tin oxide (ITO) was existed. Therefore, the driving voltage and power efficiency were not so satisfactory. In this paper, we report high power efficiency red PHOLEDs with significantly low driving voltage characteristics. A good hole injection and transporting material, DNTPD is introduced for reducing injection barrier from ITO and the doping concentration of $\mathrm{Ir(piq)_3}$ (tris(1-phenylisoquinoline)iridium) is optimized in our bi-layered structure. High efficiency and significantly low driving voltage characteristics of red PHOLEDs with a DNTPD/$\mathrm{Bebq_2}$: $\mathrm{Ir(piq)_3}$ structure are reported.

EXPERIMENTAL

Fabrication and Evaluation of OLED Devices

In this work, we have fabricated red PHOLEDs with a simple bilayerd structure of ITO/α-NPB (or DNTPD) (40 nm)/$\mathrm{Bebq_2}$:$\mathrm{Ir(piq)_3}$ (50 nm)/ LiF/Al. To optimize device performance, we fabricated several PHOLEDs by varying dopant concentration from 10% to 4% and studied. NPB and $\mathrm{Ir(piq)_3}$ were purchased from Gracel Corporation and DNTPD was purchased from Chemipro Corporation. To fabricate OLED devices, a clean glass substrate precoated with a 150-nm ITO layer with a sheet resistance of $10 \sim 12\ \Omega/\mathrm{sq}$ was used and the substrate size was $2\,\mathrm{cm} \times 2\,\mathrm{cm}$. The patterns of $2 \times 2\,\mathrm{mm^2}$ were formed by photolithography and wet etching processes and used as an anode.

The glass substrate was cleaned by sonification in an isopropyl alcohol, acetone, and methanol, rinsed in deionized water, and finally irradiated in a UV-ozone chamber. All organic materials were deposited by the vacuum evaporation technique under a pressure of $\sim 3.0 \times 10^{-7}$ Torr. Doping is carried out by co-evaporation from independent sources and effusion rates were monitored using a quartz crystal microbalance (QCM). Subsequently, Al with a deposition rate of ~5 Å/s was deposited in vacuum chamber without breaking the vacuum and used as a cathode. The current density-voltage (J-V) and luminance-voltage (L-V) data of PHOLEDs were measured with a Keithley SMU 238 and Minolta CS-100A, respectively. Electroluminescence (EL) spectra and CIE color coordinate were obtained using a Photo-research PR-650 spectroradiometer.

Cyclic Voltammetry Measurement

Cyclic voltammetry experiments were performed on BASi, Bioanalytical Systems Inc., analysis equipment (C-3 standard). Data were collected and analyzed by using Epsilon electrochemical work station. The platinum wire electrode and 150-nm ITO film on glass were used as counter and working electrodes respectively. Silver/silver ion (Ag wire in 0.1 M $AgNO_3$ solution) was used as a reference electrode. The Ag/Ag^+ ($AgNO_3$) reference electrode was calibrated at the beginning of experiments by running cyclic voltammetry on ferrocene as the internal standard. By means of the internal ferrocenium/ferrocene (Fc^+/Fe) standard, potential values were converted to the saturated calomel electrode scale. The coated films for measuring samples were made on ITO glasses by a solution drop coating or thermal deposition method and then dried in a vacuum oven at 80°C. An electrolyte solution of 0.1 M Bu_4NClO_4(tetrabutylammonium perchlorate) in acetonitrile was used all experiments. In order to confirm our measurement accuracy, Alq_3 also had measured and compared to reported results [12]. Alq_3 shows 5.54 eV oxidation potential in our system. Solid-state electrochemistry was performed at a scan rate of 150 mV/s.

RESULTS AND DISCUSSION

In order to know HOMO and LUMO energy levels of used organic materials, optical band-gap was calculated from absorption spectrum of each material. Figure 2 shows cyclovoltammogram results of DNTPD, $Ir(piq)_3$ and $Bebq_2$. The ferrocene having 4.8 eV HOMO energy shows on-set oxidation potential at 0 eV in our optimized cyclic-voltammetry system. From the on-set voltage of +0.3 eV oxidation curve, the HOMO energy level of the DNTPD estimated to be 5.1 eV. The DNTPD shows a good HOMO energy level to be matched to ITO anode and seems to have better hole injection ability compared with NPB. $Bebq_2$ shows about 5.5 eV HOMO energy and 2.8 eV LUMO energy levels, which are the same as previous reported values [13]. This beryllium complex has a very good LUMO energy level to transfer easily electrons from the cathode. General triplet red dopants such as $Ir(piq)_3$ and bis(2-phenylquinoline)(acetylacetonate)iridium ($Ir(phq)_2$ acac) had been reported that their HOMO levels were 4.8 eV and 5.1 eV and triplet energies were 2.2 and 2.4 eV range [14,15]. According to our measurement results, the HOMO energy level of $Ir(piq)_3$ is about 5.1 eV not to be 4.8 eV and LUMO energy level is 3.1 eV. Therefore, $Ir(piq)_3$ has about 2.0 eV triplet energy. The triplet energy of $Bebq_2$ host is estimated to be 2.5 eV by molecular modeling. The triplet energy of $Bebq_2$ is very adequate as a red triplet host material.

Simple bi-layered PHOLEDs have been composed an $Ir(piq)_3$ doped layer in $Bebq_2$ host and a NPB or DNTPD hole transport layer. Used organic materials and organic bi-layered device structure is shown in Figure 1. We have made a control device with NPB hole transport layer. Four DNTPD and $Bebq_2$ doped $Ir(piq)_3$ devices were fabricated to minimize hole injection barrier. Doping concentration was optimized by changing from 10% to 4%. Detailed device structures for these five devices are as follows:

Control device: NPB (40 nm)/$Bebq_2$:$Ir(piq)_3$ 8% (50 nm)/LiF (0.5 nm)/Al (100 nm)

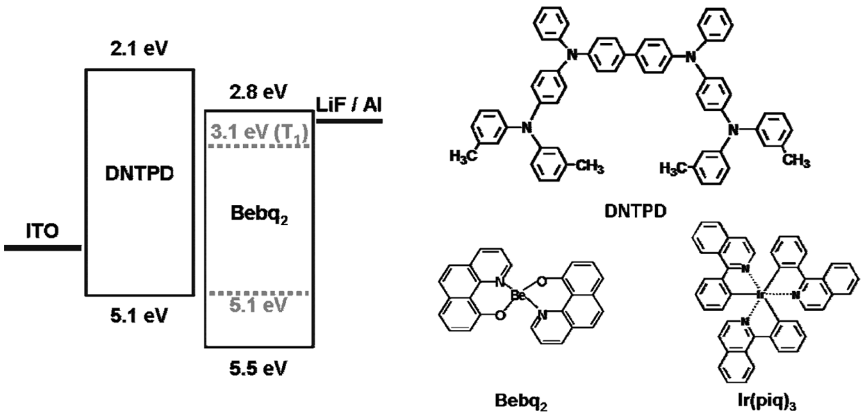


FIGURE 1 Device and molecular structures used in the present studies.

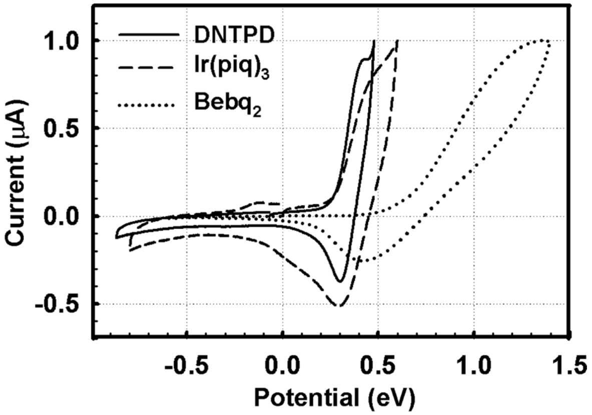
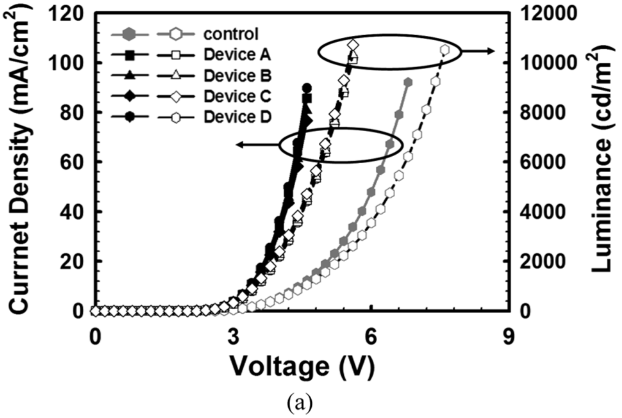


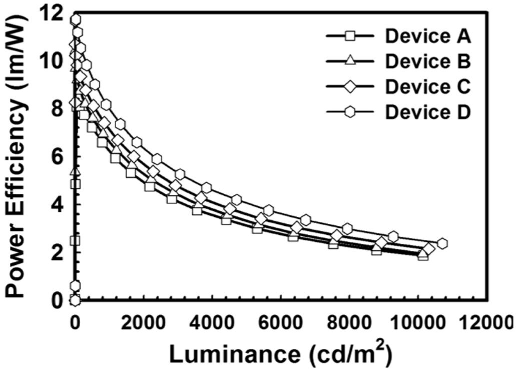
FIGURE 2 Cyclovoltammogram of used organic materials.

Device A: DNTPD (40 nm)/Bebq$_2$:Ir(piq)$_3$ 10% (50 nm)/LiF (0.5 nm)/Al (100 nm)
Device B: DNTPD (40 nm)/Bebq$_2$:Ir(piq)$_3$ 8% (50 nm)/LiF (0.5 nm)/Al (100 nm)
Device C: DNTPD (40 nm)/Bebq$_2$:Ir(piq)$_3$ 6% (50 nm)/LiF (0.5 nm)/Al (100 nm)
Device D: DNTPD (40 nm)/Bebq$_2$:Ir(piq)$_3$ 4% (50 nm)/LiF (0.5 nm)/Al (100 nm)

Figure 3 shows the J-V-L characteristics of fabricated red phosphorescent devices. At a given constant voltage of 4 V, current density values of 5.55, 31.84, 33.23, 34.55 and 36.10 mA/cm^2 in the fabricated control device and devices A-D are noticed as displayed in Figure 3, respectively. The driving voltages for all devices except for a control device to reach 1000 cd/m^2 are 3.5 V. A low turn-on voltage of 2.1 V in all devices with a simple bi-layered structure compared to control NPB/Bebq$_2$ 8% device (2.5 V) is observed. The resistance to current conduction in bilayered device A-D is significantly reduced. No significant variation of J-V characteristics among device A-D is noticed. As the HOMO energy of DNTPD is 5.1 eV, holes injected from the hole transport layer trap directly at the HOMO level (5.1 eV) of dopant. Barrier to hole injection in the device A-D is almost negligible. Also, electrons injected from the cathode move freely in the emitting layer as the low LUMO energy of host. The LUMO (triplet) of dopant and triplet of host has the almost same energy and finally captured at the trapped hole sites giving rise to phosphorescent emission.



(a)



(b)

FIGURE 3 J-V-L and efficiency characteristics of fabricated green PHOLED devices: (a) current-voltage and luminance-voltage characteristics and (b) current efficiency-luminance and power efficiency-luminance characteristics.

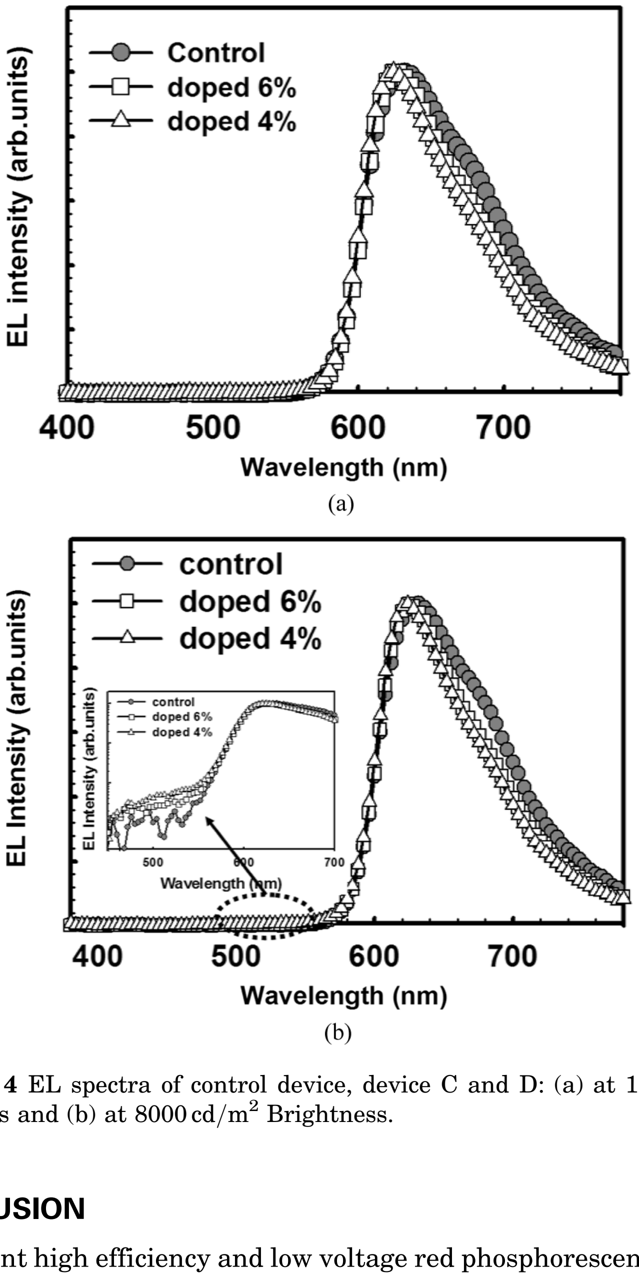
The current and power efficiency characteristics of fabricated devices are shown in Figure 3. At a given constant luminance of 1000 cd/m^2, the current and power efficiencies are 6.78 cd/A and 5.92 lm/W for the device A, 7.18 cd/A and 6.26 lm/W for the device B, 7.65 cd/A and 6.68 lm/W for the device C, 8.83 cd/A and 8.16 lm/W for the device D, 9.09 cd/A and 6.21 lm/W for the control device, respectively. Power efficiency values of device D is improved by a factor of 1.3 times compared with that of control NPB/Bebq$_2$ 8% device. The high efficiency device D with low doping concentration may be originated by efficient charge injection and energy transport between host and dopant. All device characteristics are summarized in Table 1.

TABLE 1 Electrical Characteristics of Fabricated Red Phosphorescent OLEDs

	Control device	Device A	Device B	Device C	Device D
Trun-on voltage (at 1 cd/m^2)	2.1 V	2.1 V	2.1 V	2.1 V	2.1 V
Operating voltage (1000 cd/m^2)	4.5 V	3.5 V	3.5 V	3.5 V	3.5 V
Efficiency (1000 cd/m^2)					
Current (cd/A)	9.09	6.78	7.18	7.65	8.83
Power (lm/W)	6.21	5.92	6.26	6.68	8.16
Maximum efficiency					
Current (cd/A)	9.83	7.38	7.82	8.37	9.38
Power (lm/W)	10.23	8.10	10.40	10.67	11.72
CIE (x,y) (1000 cd/m^2)	(0.67,0.23)	(0.67,0.32)	(0.67,0.32)	(0.67,0.32)	(0.67,0.32)

Figure 4 shows the electroluminescence (EL) spectra at different brightness (1000 cd/m^2, 8000 cd/m^2) of fabricated red PHOLEDs. A clean red light at 632 nm observed in all devices indicates the complete energy transfer from a narrow band gap $Bebq_2$ host material to $Ir(piq)_3$ dopant. The CIE coordinate of all red devices show the same coordinate as CIE (0.67, 032). In EL spectra of 4% doped device (device D) at 8000 cd/m^2 brightness value is observed very weak host emission peak together with dominant peak at 632 nm. No complete energy transfer occurs from $Bebq_2$ host to $Ir(piq)_3$ dopant when dopant concentration is under 4%, which indicate that recombination of injected holes and electrons occurs at the host molecules and then excited energy is rapidly transferred from host to the dopant. Clean EL peak in devices with concentration of $Ir(piq)_3$ over 4% indicates complete energy transfer from the host to the dopant.

Interesting and intriguing results on the performance of bi-layered device D have been obtained. The LUMO level of $Bebq_2$ material (2.8 eV), very close to LUMO values of LiF cathode, offers almost no barrier to electron injection between the emitting layer and LiF cathode. Furthermore, excellent electron transporting property of $Bebq_2$ material favors to mobility of electrons which provides a good charge balance in the emitting layer. HOMO levels of $Bebq_2$ host and DNTPD hole injection and hole transport layer in the fabricated devices are very close while LUMO energy levels of host and dopant are almost same. Therefore, the emission process in PHOLEDs via electron trapping at LUMO and hole trapping at HOMO seems to be minimized, giving to the low driving voltage value.



(a)

(b)

FIGURE 4 EL spectra of control device, device C and D: (a) at 1000 cd/m^2 Brightness and (b) at 8000 cd/m^2 Brightness.

CONCLUSION

We present high efficiency and low voltage red phosphorescent OLEDs with the DNTPD/Bebq$_2$:Ir(piq)$_3$ simple bi-layer organic structure. High current and power efficiency values of 9.38 cd/A and 11.72 lm/W at 4% doping concentration are obtained. The operating voltages of these bi-layered PHOLEDs at a luminance of 1000 cd/m^2 are 3.5 V. A simple bi-layered device structure with the narrow band-gap host and good hole transport layer could be a promising way to achieve efficient, economical, and ease manufacturing process, important for display and lighting production.

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