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# Efficient red electrophosphorescent devices based on starburst molecules

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## 1. Introduction

Since the fabrication of efficient phosphorescent organic light emitting diodes (PHOLEDs) using phosphorescent dyes have demonstrated high external quantum efficiencies. Those phosphorescent materials using a heavy metal containing phosphor showed radiative emission from triplet states has been successful for thermally evaporated small molecules [1]. To obtain high device performances, selecting a conductive host with a suitable triplet level of PHOLEDs are important. The host materials of organic light-emitting diodes (OLEDs) are distinguished into small organic molecules, conjugated polymers and dendrimers have been reported [2-3]. In contrast, polymers and dendrimers are fabricated devices by wet-process such as spin-coating and ink-jet printed from solution. Employing wet-process of organic materials is a useful processing for OLEDs fabrication and possibility of low-cost mass production and making large-size screens. We have employed a starburst molecule 1,3,5-tris[4-(diphenylamino) phenyl]-benzene (TDAPB) for the host of phosphorescent material because of the advantage to resist crystallization due to its steric hindrance by the high glass-transition and the excellent film forming properties by a wet-process.

In this work, we used TDAPB as a host material of phosphorescent dyes and fabricated simple structure OLEDs with a hole-injection and emitting layer by wet process.

## 2. Experimental Procedure

Organic layers were fabricated by spin coating onto a glass substrate coated with a patterned indium-tin-oxide (ITO) electrode. The substrate was degreased with solvents and cleaned in a UV-ozone chamber. First, a PEDOT:PSS hole injection layer was spun over the ITO-coated glass substrate with a 35nm-thick layer and baked in air at 120 °C for 10 min. TDAPB was used as the host for the phosphorescent material bis(2-(2'-benzo[4,5-a]thienyl)-pyridinato-N,$C^{3'}$) iridium(acetylacetonate) [Btp$_2$Ir(acac)]. The emitting layer which consisted of the host TDAPB, emissive phosphor Btp$_2$Ir(acac) and an electron-transport material 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4,-oxadiazole (PBD) and 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) were dissolved in 1,2-dichloroethane. The weight ratios of the various materials that the content of OXD-7, PBD and Btp$_2$Ir(acac) was 80, 80 and 8.0 wt% for TDAPB, respectively. The TDAPB

material containing Btp$_2$Ir(acac), PBD and OXD-7 was formed by a spin-coating method into 90 nm-thick layers. The solvent was removed by baking the samples in air at 110 °C for 10 min after spinning. The cathode, consisting of Cs/Al, was deposited in vacuum at a base pressure of $<10^{-4}$ Pa. Finally, the device was covered with a glass plate and encapsulated with epoxy resin in an argon gas atmosphere to prevent oxidation of the cathode and the organic layer. The active device area of 4 mm$^2$ was obtained using a shadow mask. The forward bias condition was a positive bias with respect to the Cs/Al cathode. All measurements were carried out at room temperature in an inert gas atmosphere.

The positions of the highest occupied molecular orbital (HOMO) levels of each material were estimated using a low-energy photoelectron spectroscopy instrument (Rikenkeiki, AC-1). The electroluminescent (EL) spectra were measured using a photonic multichannel spectral analyzer (Hamamatsu Photonic, PMA-11). The current-voltage-luminance (I-V-L) characteristics were obtained using a 2000 multimeter (Keithley), a regulated DC power supply (Kenwood, PW36-1.5AD) and a luminance meter (Minolta, LS-100). The external quantum efficiency was calculated from the luminance, current density and EL spectrum under the assumption of the Lambertian spatial emission pattern.
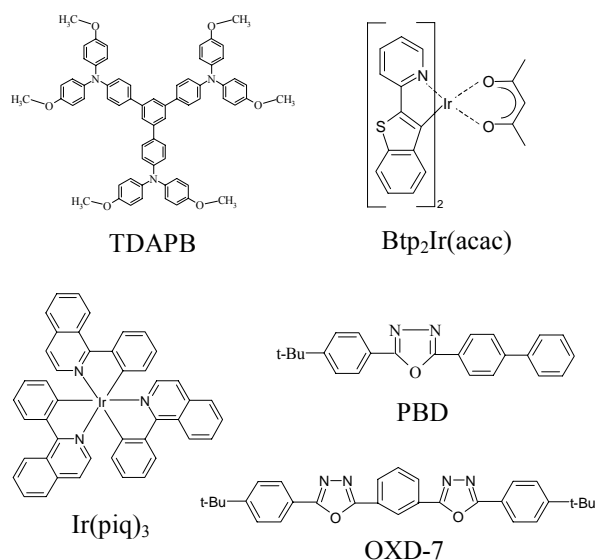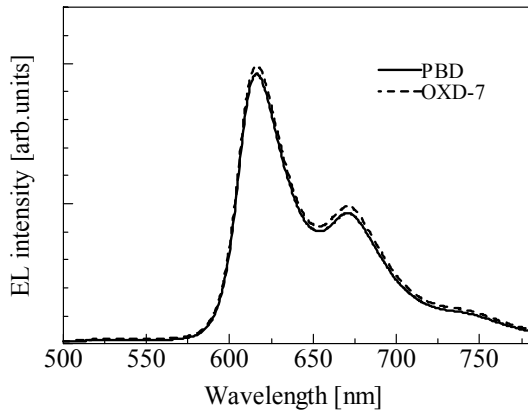


Fig.1 Chemical structure employed in this study.

Fig.2 EL spectra of PHOLEDs doped with two electron-transport materials in ITO/PEDOT:PSS (35 nm)/emitting layer (90 nm)/Cs/Al devices (here emitting layer is TDAPB:PBD:Btp$_2$Ir(acac) and TDAPB:OXD-7: Btp$_2$Ir(acac)).



Fig.3 The external quantum efficiency ($\eta_{ext}$)-current density (J) characteristics of PHOLEDs.

## 3. Results and discussion

Figure 2 shows the electroluminescence (EL) spectra of PHOLEDs using PBD and OXD-7. No change in the EL spectra for devices while the device performance was measured. The peak wavelength of emission was 616 nm at the current density of 2.5 mA/cm$^2$ which corresponds with the emission from the phosphorescent material Btp$_2$Ir(acac). The emission from TDAPB using as the host was not observed each device and the energy transfer from the host to dopant occurs successfully.

Figure 3 shows the dependence of the external quantum efficiency ($\eta_{ext}$)-current density (J) characteristics at 8.0 wt% Btp$_2$Ir(acac) doped into TDAPB for the different electron-transport materials at the content of 80 wt% for TDAPB. The solid line fits the triplet-triplet (T-T) annihilation theory to a data. Adachi et al. analyzed T-T annihilation for Ir(ppy)$_3$ doped CBP host devices and a best fit of the model to the data were obtained [4]. We tried to apply a T-T annihilation theory to our devices fabricated TDAPB as a host by a spin-coating method. All devices exhibit a gradual decrease in $\eta_{ext}$ at the high current density. The equation of the external quantum efficiency $\eta_{ext}$ is shown in the inset of Fig. 3, here $\eta_{ext}=\eta_0$ at J=0, and when J=J$_0$, then $\eta_{ext}=(1/2)\eta_0$. The experimental data and theoretical line in the Fig. 3 show a good fit at the high current density for all devices when $J_0$=50 mA/cm$^2$. It indicates the width of the exciton formation zone is almost same in all devices even if the electron-transport material changed. The peak external quantum efficiency $\eta_{ext}$ =3.2 % and 3.0 % were obtained for each device which was doped with PBD and OXD-7 at a current density of 12.1 and 5.6 mA/cm$^2$, respectively. At the low current density, however, the external quantum efficiency is low for the device using PBD compared w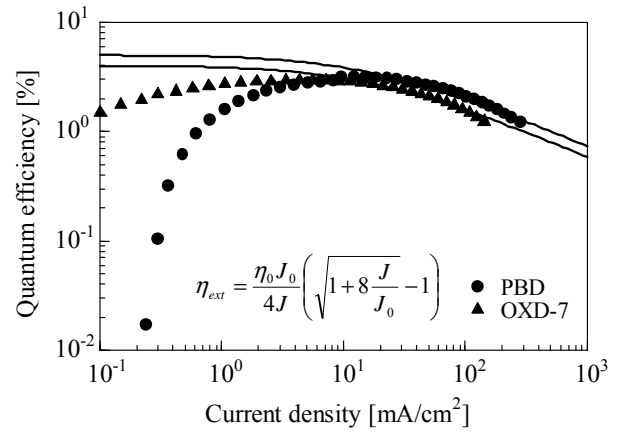ith that of the device using OXD-7. It means that holes and electrons recombine more efficiently by employing OXD-7 which has superior electron-transporting characteristics. However, the maximum luminance of the PBD doped device was about twice larger than that of OXD-7 device. The luminance of the devices was 3,300 cd/m$^2$ for the PBD and 1,700 cd/m$^2$ for the OXD-7 doped device at approximately 10 V. At the high current density, the external quantum efficiency of the PBD doped device is higher than that of the OXD-7 doped device. The carrier balanced at the emitting region with increasing the current. It is assumed that the carrier was confined efficiently in the emitting layer and high luminance was obtained by using PBD compared with the OXD-7 doped device. Consequently, the maximum luminance of the PBD doped device was about twice higher than that of the OXD-7 doped device. The other red emissive phosphor Tris(1-phenylisoquinoline) iridium(III) [Ir(piq)$_3$] is also investigated.

## 4. Conclusions

We demonstrated improvement in the efficiency of TDAPB-based red emitting OLEDs with two layered structure fabricated by spin-coating. The peak external quantum efficiency of 3.2 % and luminance of 3,300 cd/m$^2$ was obtained with the PBD doped device. The result in this study suggests that using starburst low molecule TDAPB for the host of emissive phosphor Btp$_2$Ir(acac) is effective to achieve high efficiencies and luminance in simple device structure.

## References

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