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Device characteristics of blue phosphorescent organic light-emitting diodes depending on the electron transport materials

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Iridium-(III)-bis[(4,6-di-fluorophenyl)-pyridinate-N,C$^{2'}$]picolinate-based blue phosphorescent organic light-emitting diodes with different electron transport materials were fabricated. Each electron transport material had different electron mobilities and triplet energies. The device with 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene had the highest external quantum efficiency (20.1%) and luminous current efficiency (33.1 cd/A) due to its high electron mobility and triplet energy. The operational stability of each device was also compared with that of the others. The device with 2,2′,2″(1,3,5-benzenetriyl)tris-(1-phenyl-1H-benzimidazole) was found to have a longer lifetime than the other devices.

Keywords: OLED; blue phosphorescent; electron transport layer

1. Introduction

Since the invention of the organic light-emitting diode (OLED) by Tang and VanSlyke [1], the performance of OLEDs has improved dramatically. Small OLED panels are already being used for some commercial electronic devices such as cellular phones and MP3 players. Especially, the usage of phosphorescence rapidly increases the efficiency of OLEDs because phosphorescence uses triplet and singlet excitons [2]. Blue phosphorescent OLEDs have been studied intensively because highly efficient blue phosphorescent OLEDs are required for OLED displays and for the white solid-state lighting source.

High triplet energy is required for high efficiency in phosphorescent OLEDs. Some papers reported that the triplet energy of the hole transport layer (HTL) can affect the efficiency of the phosphorescent OLEDs [3,4]. Therefore, the HTL, electron transport layer (ETL), and host should have much higher triplet energies than the blue phosphorescent dopant so that the efficiency of the blue phosphorescent OLEDs could be improved. (III)-bis[(4,6-di-fluorophenyl)-pyridinate-N,C$^{2'}$]picolinate (FIrpic) is widely used in blue phosphorescent OLEDs due to its high efficiency. As the triplet energy of FIrpic is about 2.7 eV, 1,1-bis[(di-4-tolyamino)phenyl]cyclohexane (TAPC) and *N*,*N*′-dicarbazolyl-3,5-benzene (mCP) are suitable for FIrpic-based OLEDs as an HTL and a host, respectively, because of their high triplet energies, which are 2.87 eV (TAPC) and 2.9 eV (mCP) [4]. In the case of ETL, the electron mobility should be considered along with the triplet energy because electron–hole balance is also a critical factor for high efficiency in OLEDs. Generally, the hole mobility of HTL is higher than the electron mobility of ETL in OLEDs. Therefore, ETL should have high electron mobility for efficient OLEDs.

In this paper, blue phosphorescent OLEDs with three different ETLs were fabricated. The electron transport materials had different electron mobilities, triplet energies, and hole-blocking barriers. The performance of each device was affected by these properties of each ETL. The device with 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB) had the highest external quantum efficiency (EQE) (20.1%) and luminous current efficiency (33.1 cd/A), whereas the device with 2,2′,2″(1,3,5-benzenetriyl)tris-(1-phenyl-1H-benzimidazole) (TPBi) was found to have a longer lifetime than the other devices.

2. Experiment

Devices were fabricated on indium-tin-oxide (ITO)-precoated glass substrates. The substrates were sequentially cleaned with acetone and isopropyl alcohol and rinsed with deionized water. After drying in a vacuum oven at 120°C, all the organic materials and cathode metals were deposited in succession, without breaking the vacuum. The blue phosphorescent OLEDs had the following structure, as shown in Figure 1: ITO/MoO$_3$ (10 nm) as a hole injection

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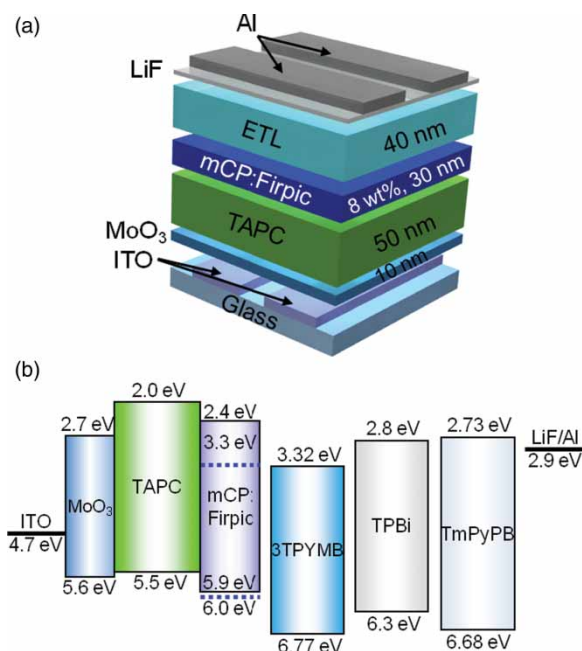†Member, KIDS.

Figure 1. (a) Device structure and (b) schematic energy level diagram of blue phosphorescent OLEDs with different ETLs.

layer, TAPC (50 nm) as an HTL/mCP layer doped with 8 wt% FIrpic (30 nm) as an emitting layer (EML), ETL (40 nm)/LiF (0.5 nm) as an electron injection layer, and Al (100 nm) as a cathode. Three electron transport materials – tris[3-(3-pyridyl)mesityl]borane (3TPYMB) [5] for device A, TPBi [6,7] for device B, and TmPyPB [8] for device C – were utilized. All the organic materials that were used in this work were purchased from Luminescence Technology Corporation and were used without further purification.

The current–voltage–luminance (I–V–L) characteristics were measured at room temperature using a Keithley-236 source measurement unit and a Keithley 2000 multimeter. The luminance and efficiencies were calculated from photocurrent measurement data obtained with a calibrated Si photodiode (Hamamatsu S5227-1010BQ) and a photomultiplier tube and from electroluminescence (EL) spectra obtained with a spectroradiometer (Model CS-1000A, Minolta). The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital, and triplet energy levels of all the materials that were used in this work were obtained from the references and from the measurement data acquired using a photoelectron spectrometer (Model AC-2, Riken Keiki Co., Ltd) and a UV/Vis spectrophotometer (Model DU-70, Beckman).

3. Results and discussion

Figure 2 shows the current density–voltage (J–V) and luminance–voltage (L–V) characteristics of the blue phosphorescent OLEDs with different ETLs. The current densities of all the devices were similar, but device B had a slightly higher current density than the other devices at a
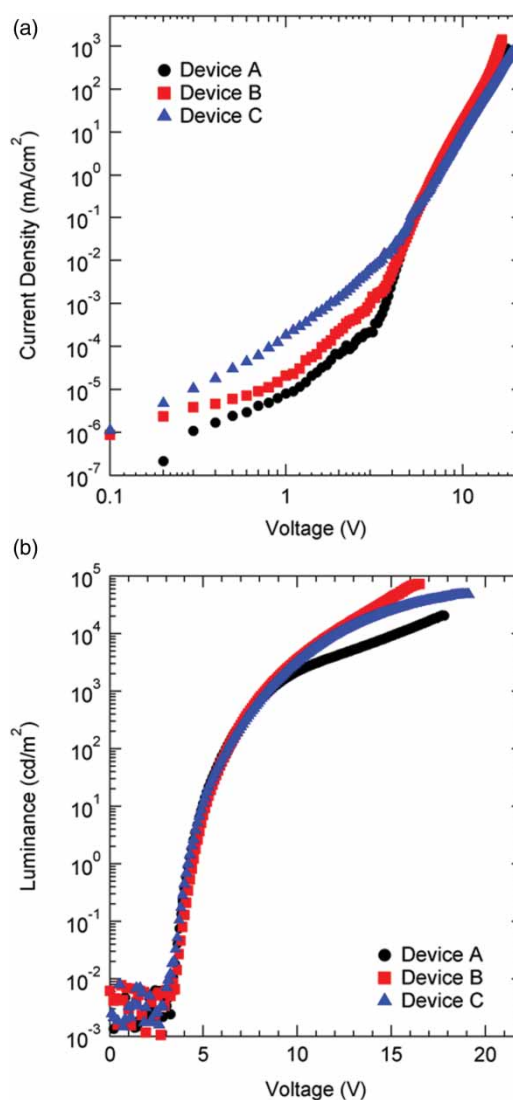

Figure 2. (a) Current density–voltage (J–V) and (b) luminance–voltage (L–V) characteristics of the blue phosphorescent OLEDs with different ETLs.

high voltage region. This may be due to the fact that the hole leakage current might have flown well in device B at a high voltage region because the hole-blocking barrier of TPBi was lower than that of the other ETLs. The turn-on voltages of the devices were about 3–3.5 V, depending on the electron transport material, and the driving voltages for 1000 cd/m^2 were about 8.5, 8.3, and 8.4 V in devices A, B, and C, respectively. The luminance was similar by about 9 V but was different at a high voltage region because each electron transport material had different electron mobilities, HOMOs, and triplet energies. In the case of device A, the luminance rapidly decreased at a high voltage region, unlike the other devices. 3TPYMB had lower electron mobility ($\mu_e = \sim 10^{-5}$ cm^2/V s), deeper HOMO, and higher triplet energy ($T_1 = 2.95$ eV) than the other electron transport materials that were used in this work. These conditions can cause triplet–triplet annihilation or
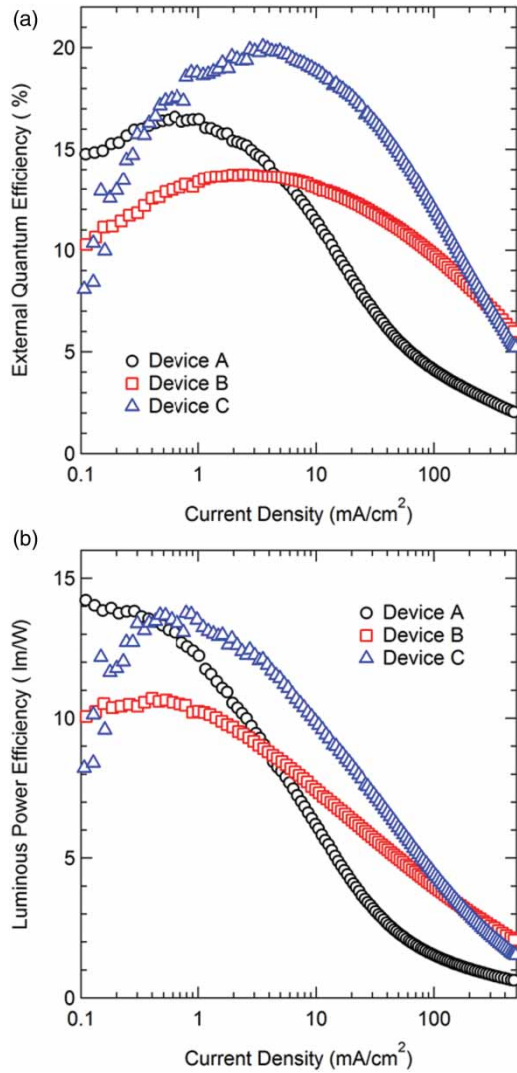
(a)

(b)

Figure 3. (a) EQE and (b) LPE of the devices with different ETLs as a function of current density.

triplet–polaron quenching, which decreases the luminance of the phosphorescent device at a high voltage region [9]. The maximum luminance values were 20,756, 72,791, and 48,071 cd/m^2 in devices A, B, and C, respectively. This tendency is the same as the sequence of the hole-blocking barrier and triplet energy.

Figure 3 shows the EQE and luminous power efficiency (LPE) of the devices with different ETLs as a function of current density. Device C had the highest EQE (20.1% at 3.53 mA/cm^2) because TmPyPB had higher electron mobility ($\mu_e = \sim10^{-3}$ $cm^2/V\,s$) than the other electron transport materials. Device A had a higher EQE compared with device B, at a low-current–density region, due to the higher triplet energy level and the lower electron injection barrier of 3TPYMB compared with TPBi ($T_1 = 2.6$ eV). The EQE of device B, however, was higher than that of device A at a high-current–density region because the electron mobility ($\mu_e = \sim3.3$–8×10^{-5} $cm^2/V\,s$) of TPBi was much higher than that of 3TPYMB. In addition, as 3TPYMB had a deeper
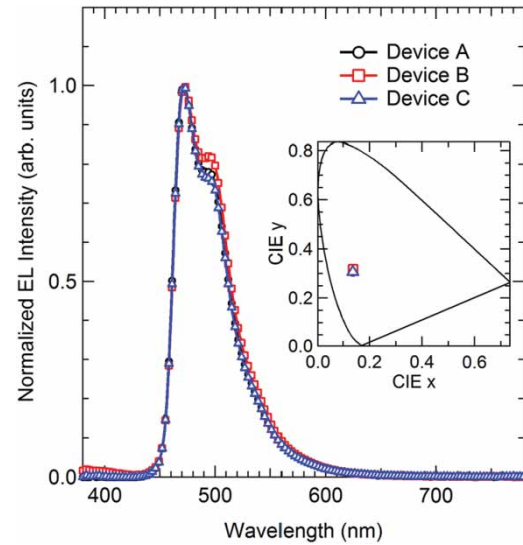

Figure 4. Normalized EL spectra and CIE color coordinates (inset) of three blue phosphorescent OLEDs measured at 5.1 mA/cm^2.

HOMO energy level than TPBi, triplet–polaron quenching easily occurred in device A due to the high hole carrier concentration in the interface between EML and ETL at a high-voltage region [10]. The LPEs of devices A, B, and C were 8.5, 8.7, and 12.3 lm/W at 1000 cd/m^2, respectively. These results indicate that the electron mobility of ETL is a critical factor affecting the power efficiency of phosphorescent OLEDs.

Figure 4 shows the normalized EL spectrum of each device measured at a driving current density of 5.1 mA/cm^2. All the devices had a main emission peak of 472 nm, with a vibronic peak of about 495 nm, which corresponds to the typical EL spectrum of FIrpic emission. The Commission Internationale de L'Eclairage (CIE) color coordinates of the devices were also similar, regardless of the ETL. The CIE color coordinates were (0.1361, 0.3086), (0.1368, 0.3184), and (0.1358, 0.306) in devices A, B, and C, respectively.

Figure 5 shows the operational stability of the devices with different ETLs. The measurements were carried out at room temperature by applying a constant current for an initial luminance of 1000 cd/m^2 to each device. It is well known that the operational stability of the FIrpic-based device is not good [6,11,12]. The fabricated devices also had short lifetimes, but Figure 5 shows relative operational stability for the devices with different ETLs. Device B shows a much longer operational lifetime compared with the other devices. As the hole mobility of mCP was higher than the electron mobility [13], holes could easily accumulate between the EML and the ETL with device operation. As the hole-blocking barrier of TPBi was lower than that of the other ETLs, the number of accumulated holes between the EML and the ETL in device B could be lower than that in the other devices; thus, the probability of triplet–polaron quenching in device B could also be lower than that in
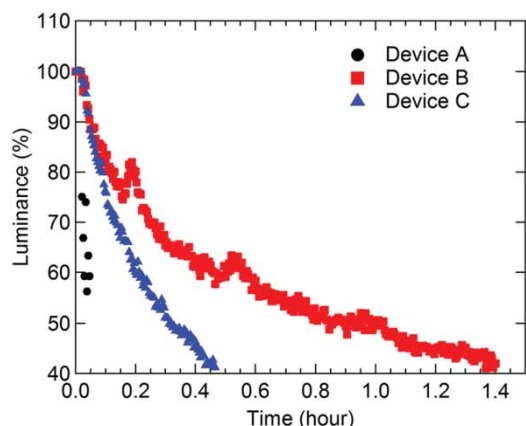
Figure 5. Operational stability of the devices with different ETLs, with an initial luminance of $1000\,\mathrm{cd/m^2}$, at room temperature.

the other devices [9,10]. Therefore, the luminance decrease ratio of device B as a function of time was lower than that of the other devices. Device A had poor operational stability due to the low electron mobility and high hole-blocking barrier of 3TPYMB. Although the electron mobility of TmPyPB was higher than that of TPBi, the lifetime of device C was shorter than that of device B. This is also due to the higher hole-blocking barrier of TmPyPB compared with that of TPBi. Consequently, the electron–hole balance in the EML is important for stable blue phosphorescent OLEDs. The higher glass transition temperature ($T_g = 127°C$) [14] of TPBi, compared with that of the other ETLs, may also affect the operational stability of the device.

4. Conclusions

The effects of electron mobility, triplet energy, and hole-blocking barrier of ETL on the performance of blue phosphorescent OLEDs were investigated using three electron transport materials: 3TPYMB, TPBi, and TmPyPB. It was found that these properties are very important for high-performance phosphorescent OLEDs. The device with TmPyPB as an ETL showed the highest efficiencies (about 20.1% EQE and 33.1 cd/A luminous current efficiency) due to its high electron mobility and triplet energy level as well as due to its deep HOMO energy level. In the case of operational stability, the device with TPBi had a longer

lifetime compared with the other devices because of its low hole-blocking barrier and high T_g compared with those of the other ETLs.

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