

Effect of Host Materials on Electrophosphorescence Properties of PtOEP-doped Organic Light-emitting Diodes

Gi-Wook Kang^{**a} and Changhee Lee^{*b}

Abstract

We have studied the effect of host materials on the electrophosphorescence properties by comparing three different host materials such as tris(8-hydroxyquinoline)-aluminum (III) (Alq_3), bis(8-hydroxyquinoline)-zinc (II) (Znq_2), and 4,4'-N,N'-dicarbazole-biphenyl (CBP) doped with a red-emissive phosphorescent dye, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum (II) (PtOEP). The EL spectra show a strong red emission (peak at 650 nm) from the triplet excited state of PtOEP and a very weak emission from an electron transport layer of Alq_3 and a hole transport layer of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1-biphenyl-4,4'-diamine (TPD). We find that the triplet exciton lifetime and the quantum efficiency decrease in the order of CBP, Alq_3 , and Znq_2 host materials. The results are interpreted as a poor exciton confinement in Alq_3 and Znq_2 host compared with in CBP. Therefore, it is very important for the triplet-exciton confinement in the emissive layer for obtaining a high efficiency.

Keywords : organic light-emitting device, electrophosphorescence, PtOEP, host materials

1. Introduction

Organic electrophosphorescent devices are recent research focus because they have in principle an internal quantum efficiency (QE) of 100 % [1-7], while the conventional organic light-emitting devices (OLEDs) using fluorescent materials waste triplet excitons and therefore they have a limit of the QE up to 25 % [8]. In organic electrophosphorescent devices, a light-emitting host layer is doped with organic phosphorescent dyes. A strong spin-orbit coupling in such materials allows the intersystem crossing between the singlet and triplet manifolds, leading to an efficient phosphorescence emission from the triplet excited states [9]. To enhance the quantum efficiency, it is important to optimize the energy transfer processes between the host and dopant molecules as well as charge carrier trapping on the dopant molecules. Furthermore, the efficiency and lifetime of OLEDs are affected by the

electron-hole balance and the confinement of excitons in the emissive layer [10, 11]. Since the diffusion length of a triplet exciton is very long, it is particularly crucial to prevent the leakage of triplet excitons into nearby charge transport layers [2, 3]. Therefore, it is important to investigate key parameters which affect the charge balance and exciton confinement in the phosphorescent OLEDs.

In this work, we studied the effect of host materials, where the red-emissive phosphorescent dye, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum (II) (PtOEP) is doped, on the electrophosphorescence characteristics of OLEDs. PtOEP molecules were doped into three different host materials such as *tris*(8-hydroxyquinoline)-aluminum (III) (Alq_3), bis(8-hydroxyquinoline)-zinc (II) (Znq_2), and 4,4'-N,N'-dicarbazole-biphenyl (CBP). Since each host material has different highest occupied molecular level (HOMO), lowest unoccupied molecular level (LUMO) and triplet exciton energy relative to PtOEP [1-7, 12], as shown in Fig. 1, we can expect that charge balance and exciton confinement behaviors were different. Therefore, this study will provide valuable information about the charge balance and exciton confinement in the phosphorescent OLEDs.

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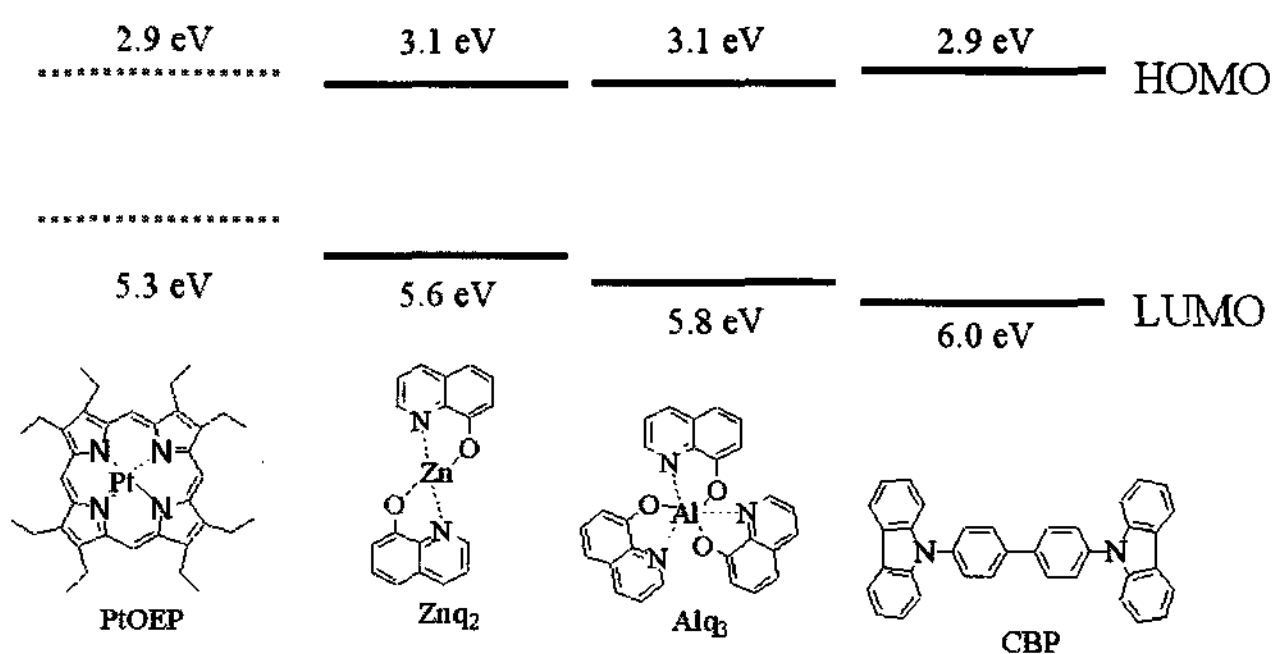


Fig. 1. The schematic energy levels and chemical structures of organic materials, PtOEP, TPD, Alq₃, Znq₂, and CBP.

2. Experimental

Organic electrophosphorescent devices were fabricated by vacuum deposition of organic materials and LiF/Al cathodes under a vacuum of about 2×10^{-6} Torr on ITO glass substrates (Samsung Corning Co., a sheet resistance of about $10 \Omega/\square$) which was cleaned with sequential ultrasonic cleaning in organic solvent (isopropyl alcohol, acetone and methanol), and rinsing in de-ionized water. The 300-Å-thick emissive layer was formed by doping PtOEP into the host organic materials (Alq₃, Znq₂, or CBP) with a doping concentration of about 8 %. N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1-biphenyl-4,4'-diamine (TPD) was used as a hole-transporting layer (HTL) and Alq₃ was used as an electron-transporting layer (ETL). After depositing organic materials, the Al cathode with a very thin (1 nm) layer of LiF was deposited without breaking vacuum. The overlap area of the Al and ITO electrodes was about 2.8 mm². The device structure was ITO/TPD(600 Å)/(PtOEP doped Alq₃, Znq₂, or CBP, 300 Å)/Alq₃ (200 Å)/LiF (10 Å)/Al. The Fig. 1 shows the schematic energy levels and chemical structures of organic materials (PtOEP, Alq₃, Znq₂, and CBP) used in the emissive layer.

The devices were mounted in the sample holder in vacuum and all measurements were taken at room temperature. The current-voltage (I-V) characteristics were measured with a Keithley 236 source-measure unit. The intensity of the EL emission was simultaneously measured with a Keithley 2000 multimeter equipped with a calibrated Si photodiode or a photomultiplier tube (ARC P2 PMT) by an ARC 275 monochromator. The transient EL response, which was detected by a fast PMT when the voltage pulse was applied using a Hewlett-Packard 214B pulse generator,

was digitized with a 500 MHz digital storage oscilloscope (Tektronix TDS 644B). The transient photoluminescence (PL) was measured after photoexcitation at 400 nm using the dye/nitrogen laser system (PTI Inc.) with a pulse width of 600 ps.

3. Results and Discussion

Fig. 2 shows the normalized EL spectra of the devices with the emitting layer (EML) of PtOEP-doped Alq₃, Znq₂, and CBP, measured under a constant current density of 36 mA/cm². The inset shows the same data in the semilog scale to clearly show the weak EL signal in the spectral region between 380 and 620 nm. All three devices show similar EL spectra with a very strong red emission peak at 650 nm, indicating that the triplet-excited state of PtOEP is very effective for the radiative recombination and the exciton energy transfer is very efficient between the host and PtOEP.

A peak around 520 nm is mainly due to the emission from Alq₃ that is used as an electron-transport layer since the peak wavelength and the EL intensity are very similar for three devices. Therefore, there is a fraction of holes that leaked into the ETL (Alq₃) layer where they recombine with electrons injected from a cathode. Since the HOMO level of TPD is about 5.5 eV [13], the HOMO level offset at the TPD/EML interface was about 0.1, 0.3, and 0.5 eV for Znq₂, Alq₃, and CBP, respectively. Therefore, the hole leakage

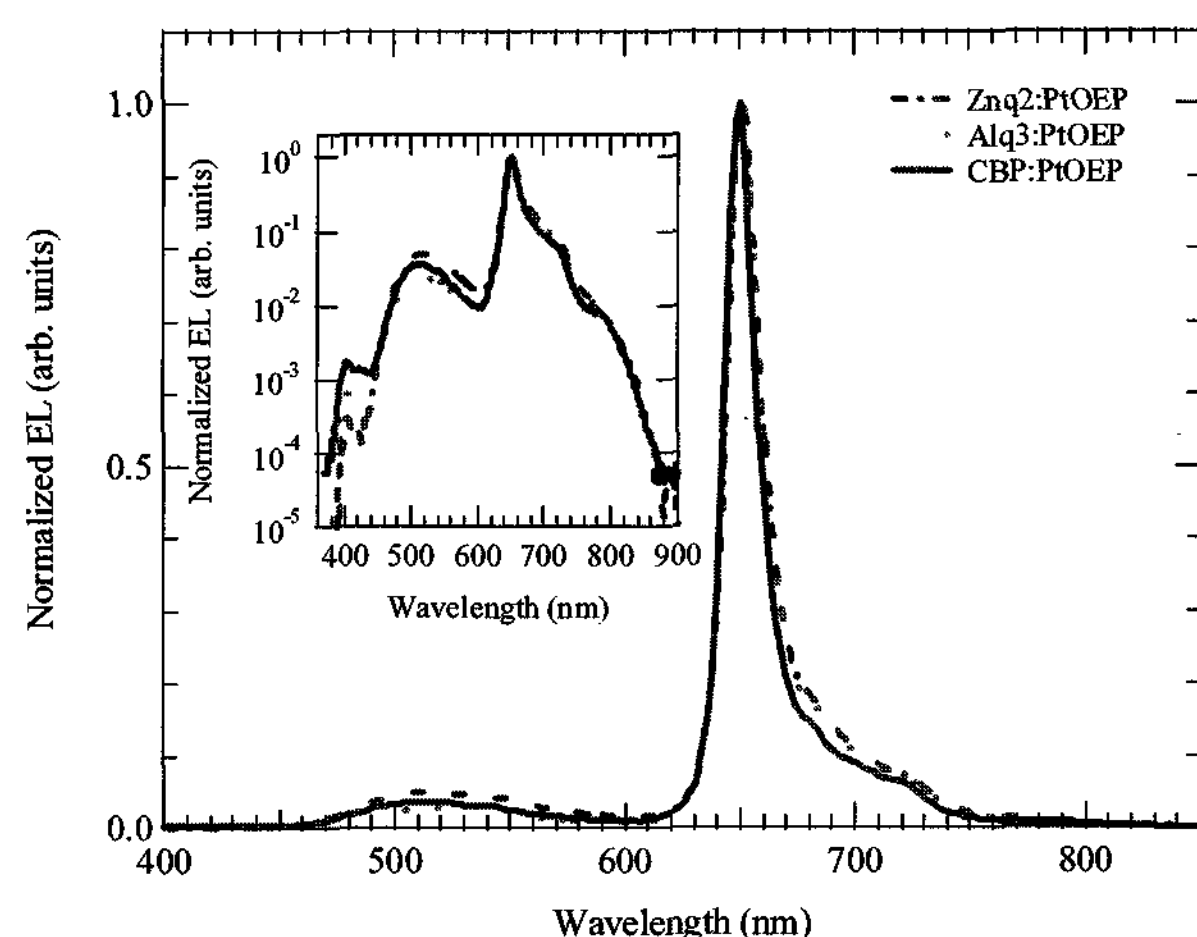


Fig. 2. Normalized EL spectra of devices with the light-emitting layer of 8%-PtOEP doped into Znq₂ (dot-dash), Alq₃ (dot), and CBP (solid line), measured at room temperature at current density of 36 mA/cm². The inset shows the same data in the semilog scale.

into the ETL layer is lowest for the CBP host. As a result, the Alq₃ peak around 520 nm is the lowest for the CBP host as shown in the inset of Fig. 1. It is also noted in the inset of Fig. 1 that the EL emission from TPD with a peak around 400 nm can be detected although it is very weak. The EL peak from TPD increases in the order of Znq₂, Alq₃, and CBP. This behavior is also consistent with the magnitude of the HOMO level offset at the TPD/EML interface. As the HOMO offset at the TPD/EML interface increases, more holes accumulate there and recombine with electrons injected from the PtOEP-doped host layer. Therefore, the EL emission from TPD is the highest for the CBP host.

Fig. 3 shows the I-V and luminescence-voltage (L-V) characteristics of the three devices shown in Fig. 2. Although the I-V characteristics are very similar for three host materials, the L-V characteristics show slight differences: The EL onset voltage of the device with an Alq₃ host is lower (~2.2 V) than for host materials of Znq₂ and CBP (~2.4 V). The device with a Znq₂ host shows smaller light intensity compared with the devices of Alq₃ and CBP hosts.

The external quantum efficiency (QE) of the EL is shown in Fig. 4 as a function of the current density. The QE is the highest (~2%) at low current density for the device with the Alq₃ host. At high current density the device with the CBP host shows a highest QE. In all three devices with

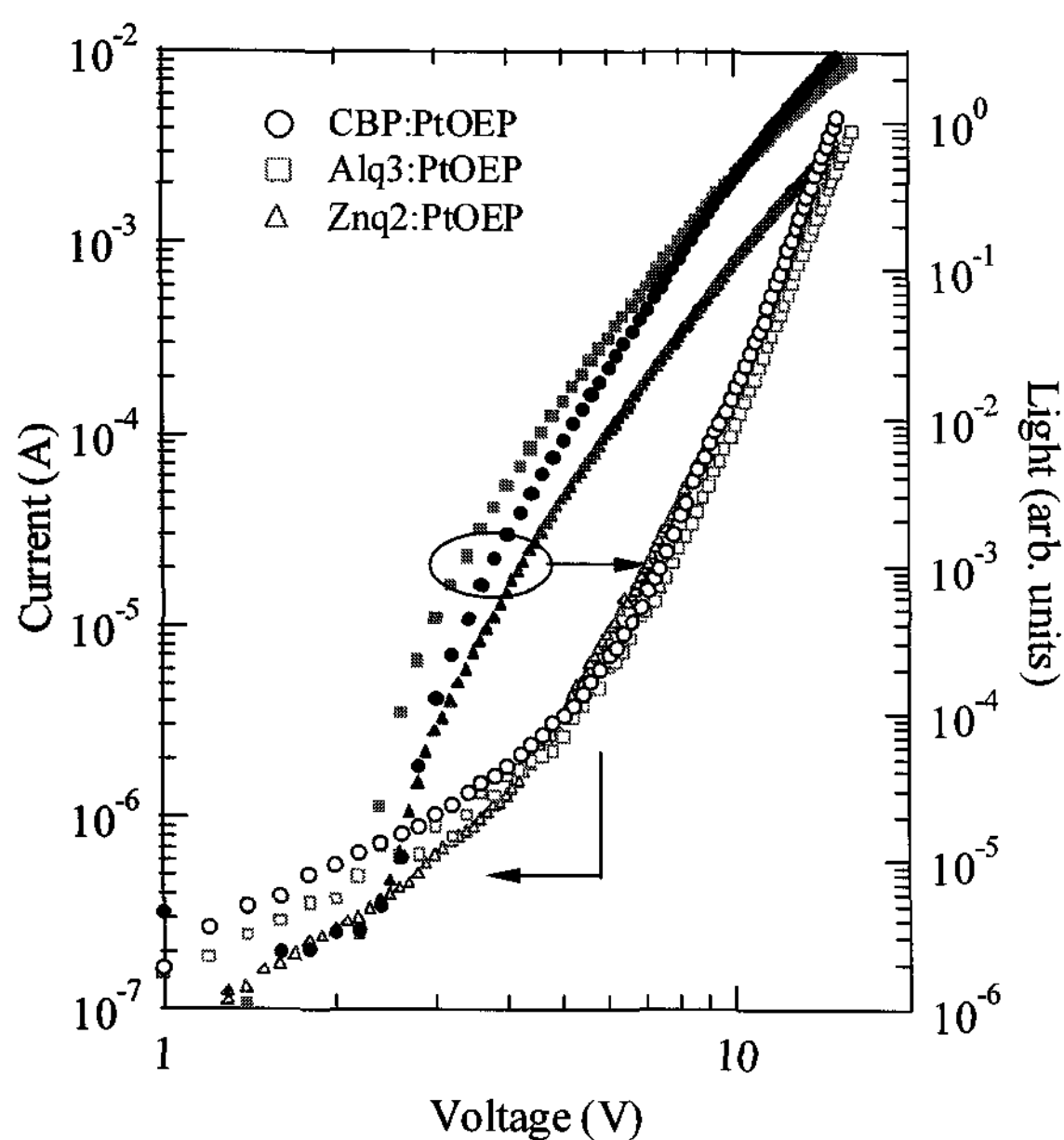


Fig. 3. I-V (open) and L-V (solid) characteristics for the devices with 8%-PtOEP doped into CBP (circle), Alq₃ (square), and Znq₂ (triangle) host layers at room temperature.

different host materials the QE decreases with increasing current density due to the triplet-triplet (T-T) annihilation [14, 15]. Since the QE of the device with the Alq₃ host rolls off faster than that of the CBP and Znq₂ host, the T-T annihilation process is more severe in the Alq₃ host. The device with the Znq₂ host shows about 5 times lower QE compared with the devices with the Alq₃ and CBP hosts, indicating higher quenching of the triplet excitons in the Znq₂ host. In addition, hole leakage into the ETL layer is higher for the Znq₂ host, as explained in Fig. 1.

These differences in Figs. 3 and 4 demonstrate the effect of host materials on the charge balance and exciton confinement in the phosphorescent OLEDs. Since HOMO level offsets at the TPD/EML and EML/ETL interfaces are the lowest for the Alq₃ host, its EL onset voltage is lowest, as shown in Fig. 3. The highest QE in the case of the device with the CBP host at high current density indicates better electron-hole balance and more efficient exciton energy transfer from CBP to PtOEP.

Fig. 5 compares the transient PL decays at the emission wavelength of 650 nm for the devices with PtOEP doped into CBP and Alq₃. The triplet lifetime of PtOEP is about 102 μ s and 62 μ s in CBP and Alq₃, respectively. These values are similar to the previously reported value by Baldo *et al.* [14]. In our previous study [16], the triplet lifetime of PtOEP doped into CBP and Alq₃ was found to be similar at low temperature, but it decreases significantly in the Alq₃ host compared with the CBP host as the tem-

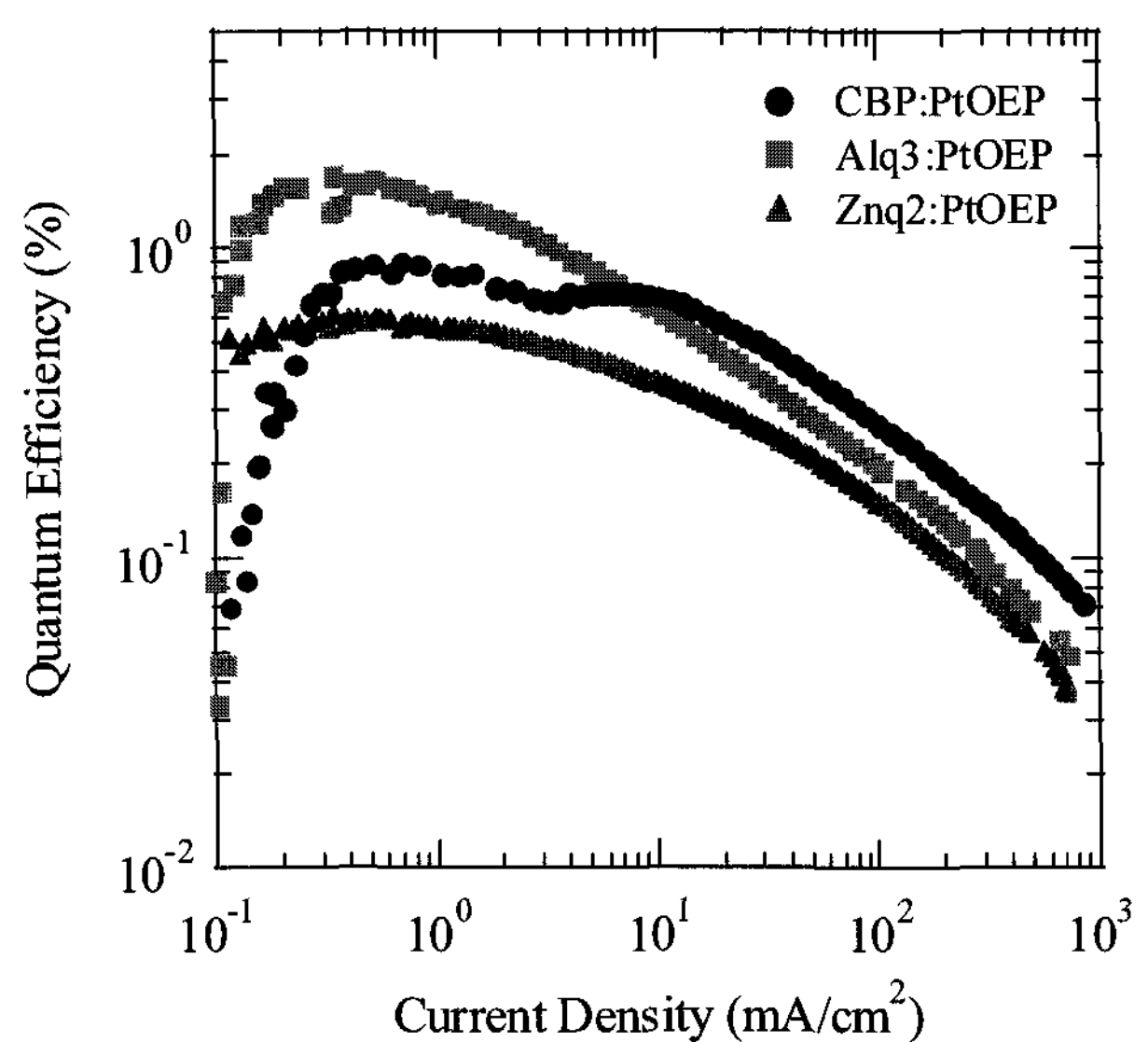


Fig. 4. The external quantum efficiency vs the current density of the same devices shown in Fig. 3.

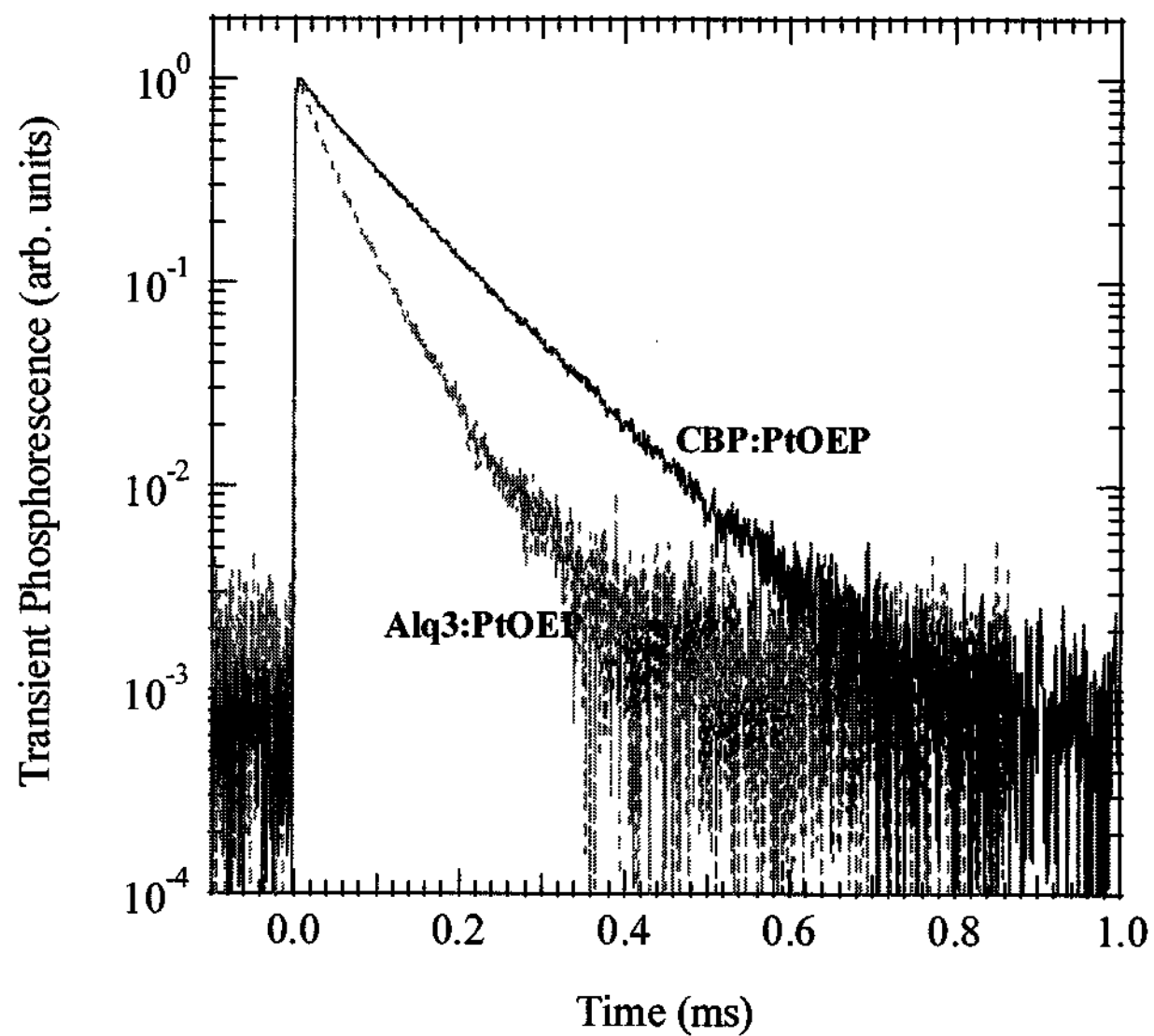


Fig. 5. The transient PL decays measured at the emission wavelength of 650 nm at room temperature for the devices with 8%-PtOEP doped into CBP and Alq₃ hosts.

perature increases. This result indicates that nonradiative recombination of triplet excitons is more severe for PtOEP doped in Alq₃.

Fig. 6 compares the transient EL decays at the emission wavelength of 650 nm for the devices with PtOEP doped into CBP, Alq₃ and Znq₂ host matrices at room temperature. The transient EL decays are fitted into the double exponential decay function, as previously reported [14]. The lifetime of the triplet state decreases in the order of CBP ($\tau \sim 52.3 \mu\text{s}$), Alq₃ ($\tau \sim 25.3 \mu\text{s}$), and Znq₂ ($\tau \sim 9.5 \mu\text{s}$). Similar with the transient PL result in Fig. 5, the triplet exciton lifetime in the Alq₃ host is smaller than in the CBP host. However, the lifetime measured from the transient EL decays is much smaller compared with the transient PL data. It is considered to be due to nonradiative quenching by the metal cathode [8, 16]. In the Znq₂ host, the lifetime is greatly reduced, indicating that the nonradiative decay of the triplet excitons is very significant in the Znq₂ host.

Different triplet exciton lifetime and QE with different host materials can be understood by considering the relative position of triplet energy levels of host and dopant molecules. The triplet energies of PtOEP, Alq₃ and CBP are reported as 1.9, 2.0 and 2.6 eV, respectively [14]. The small triplet energy difference between PtOEP and Alq₃ (only about 0.1 eV) leads to poor triplet exciton confinement [14, 15]. Therefore, the probability of the diffusion of triplet excitons to nonradiative sites increases in Alq₃. In contrast,

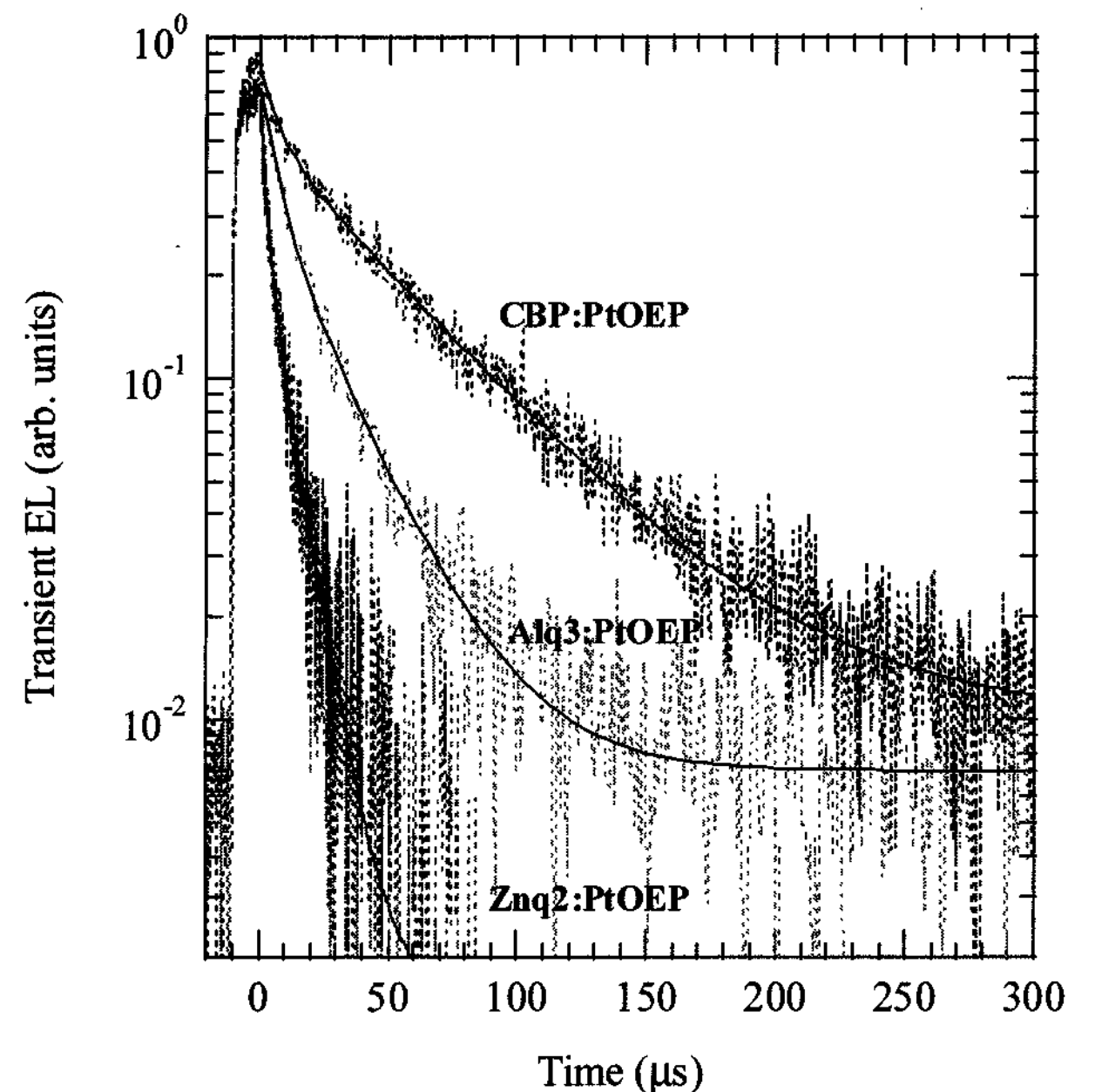


Fig. 6. The transient EL decays measured at the emission wavelength of 650 nm at room temperature for the devices with 8%-PtOEP doped into CBP (top), Alq₃ (middle), and Znq₂ (bottom). The solid line through the data is a fitting curve using the double exponential decay formula.

triplet excitons are difficult to diffuse in the CBP host due to the large difference in the triplet energies between PtOEP and CBP (~ 0.7 eV). Although the triplet exciton energy of Znq₂ is not known, it would be smaller than that of Alq₃ since Znq₂ have a slightly smaller energy band gap and ionization potential (IP) compared with Alq₃ [12]. Therefore, quenching of the PtOEP triplet exciton is more severe in Znq₂ compared with Alq₃, leading to a lower triplet lifetime and a substantial loss of quantum efficiency as shown in Figs. 4 and 6.

4. Conclusions

We have studied the effect of host materials on the electrophosphorescence properties by comparing three different host materials such as Alq₃, Znq₂, and CBP doped with PtOEP. All devices show a strong emission from the triplet-excited state at 650 nm, implying an efficient electrophosphorescence process. In addition, very weak EL emission from the ETL of Alq₃ and the HTL of TPD are observed, indicating the hole and electron leakages from the PtOEP-doped emissive layer. Difference in the EL spectra

and I-V-L characteristics for three hosts are discussed in terms of charge balance and the triplet exciton confinement. The triplet exciton lifetime and the QE of the EL decrease in the order of CBP, Alq₃, and Znq₂, indicating poor exciton confinement in Alq₃ and Znq₂ host compared with in CBP. Therefore, it is very important for the triplet-exciton confinement in the emissive layer for obtaining a high efficiency.

References

- [1] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature* **395**, 151 (1998).
- [2] D. F. O'Brien, M. A. Baldo, M. E. Thompson, S. R. Forrest, "Improved Energy Transfer in Electrophosphorescent Devices," *Appl. Phys. Lett.* **74**, 442 (1999).
- [3] M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **75**, 4 (1999).
- [4] C. Adachi, M. A. Baldo, S. R. Forrest, M. E. Thompson, *Appl. Phys. Lett.* **77**, 904 (2000).
- [5] M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, *Appl. Phys. Lett.* **79**, 156 (2001).
- [6] C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **79**, 2082 (2001).
- [7] Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, *Nature* **440**, 908 (2006).
- [8] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, *Nature* **397**, 121 (1999).
- [9] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals*, (Clarendon Press, Oxford, 1982).
- [10] B. D. Chin, M. C. Suh, S. T. Lee, H. K. Chung, and C. H. Lee, *Appl. Phys. Lett.* **84**, 1777 (2004).
- [11] B. D. Chin and C. H. Lee, *Adv. Mater.* (in press).
- [12] Y. Hamada, *IEEE Trans. on Electron Dev.* **44**, 1208 (1997).
- [13] J. Kalinowski, W. Stampor, J. Mezyk, M. Cocchi, D. Virgili, V. Fattori, and P. Di Marco, *Phys. Rev. B* **66**, 235321 (2002).
- [14] M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **62**, 10958 (2000).
- [15] M. A. Baldo, C. Adachi, and S. R. Forrest, *Phys. Rev. B* **62**, 10967 (2000).
- [16] G.-W. Kang, Y.-J. Ahn, and C. H. Lee, Proc. of the 2nd International Display Manufacturing Conference (2002. 1. 29-31, Seoul), pp. 289-292.