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Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Red Phosphorescent Dopant/Polymeric Host System as an Emitting Layer: Effect of Hole Blocking Materials

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Version of record first published: 18 Mar 2009

To cite this article: Hui Wang, Jeong-Tak Ryu, Yoon Soo Han & Younghwan Kwon (2009): Red Phosphorescent Dopant/Polymeric Host System as an Emitting Layer: Effect of Hole Blocking Materials, Molecular Crystals and Liquid Crystals, 499:1, 18/[340]-25/[347]

To link to this article: http://dx.doi.org/10.1080/15421400802618489

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Mol. Cryst. Liq. Cryst., Vol. 499, pp. 18/[340]–25/[347], 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802618489

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Phosphorescent OLEDs with the configuration of ITO/PEDOT/EML/HBL/Alq_3/LiF/Al were fabricated and their electroluminescent performance was investigated. Synthesized red phosphorescent iridium (III) bis(2-phenyl-isoquinoine) (2-acetyl-cyclohexane) (Ir-PIQCH) dopant and p{[N-(2-ethylhexyl)-3,6-bis(styryl) carbazole]-alt-[2,5-(4-biphenyl)-1,3,4-oxadiazole]} [P(CZ-OXD)] host were used as emitting layer in OLEDs. The devices showed red emission ($\lambda_{max.EL}$ about 660 nm), similar with PL emission of Ir-PIQCH dopant. EL properties of the phosphorescent OLEDs were measured to investigate the effect of hole blocking layers such as 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), bathocuproine (BCP), and bis(2-methyl-8-quinolinate)-4-phenylphenolate (BAlq) on luminescence and color purity of the devices. It was found that Device 3 using BCP as HBL showed pure red emission with CIE coordinates value as ($x = 0.6673$, $y = 0.3231$), due to higher energy barrier (1.03 eV) between P(CZ-OXD) host polymer and hole blocking BCP.

Keywords: dopant; hole blocking layer; phosphorescent OLEDs; polymeric host

INTRODUCTION

Organic light emitting diodes (OLEDs) have been paid much attention in recent years for their potential application in full color flat displays

This work was supported in part by Daegu University Research Grant, 2008.

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[1–2]. In order to fabricate an efficient OLED, one of the promising structures is multilayered OLEDs consisting of anode/hole injection layer (HIL)/hole transport layer (HTL)/emissive layer (EML)/electron ectron transport layer (ETL)/electron injection layer (EIL)/cathode. Generally, the mobility of holes is much faster than that of the electrons. Fast moving holes pass through ETL to the opposite electrode, which results in the imbalanced recombination of holes and electrons in the emitting layer. Moreover, the excitons can diffuse from EML to ETL. These two related factors were known to decrease the luminous efficiency of OLEDs [3–4]. Therefore, it is necessary to reduce the mobility of the holes and diffusion of excitons for increasing efficiency of OLEDs.

Many methods have been exploited to adjust the mobility of holes and diffusion of excitons, such as doping hole trap materials into the HTL, utilization of the hole blocking layer (HBL), and so on [4–9]. HBL plays an important role in improving the efficiency and color purity of the devices with the configuration as anode/HIL/HTL/EML/HBL/ETL/EIL/cathode, especially in phosphorescent OLEDs, where EML composed of phosphorescent dopant and host materials. Studies have been performed by using HBL materials such as BAlq, BCP, PBD, tris(*N*-arylbenzimidazole) (TPBI), triazine derivatives, SAlq, single-wall carbone nanotubes, poly(pyridine-2,5-diyl) and octaphenylcyclootatetraene [10].

In this work, phosphorescent OLEDs consisting of synthesized Ir-PIQCH and P(CZ-OXD) as an emitting layer were fabricated. The effect of hole blocking layers such as BAlq, PBD and BCP on EL performance of phosphorescent OLEDs was investigated in details, respectively.

EXPERIMENTAL

Materials

Host polymer, P(CZ-OXD), was synthesized and characterized as described previously [11]. Red phosphorescent doapnt, Ir-PIQCH, was synthesized according to the published paper [12]. PEDOT was received from LG electronics Co. BAlq, PBD, BCP, tri(8-hydroxylquinolate)aluminum (Alq_3) and lithium fluoride (LiF) were obtained from Tokyo Kasei Co. and used as received. Aluminum (99.99%) was purchased from CERAC, USA. Indium-tin oxide (ITO) coated glass with a sheet resistance of 50 $\Omega/\square$ was obtained from Sin'an SNP Co. The chemical structures of host polymer, dopant and HBL materials were presented in Figure 1.

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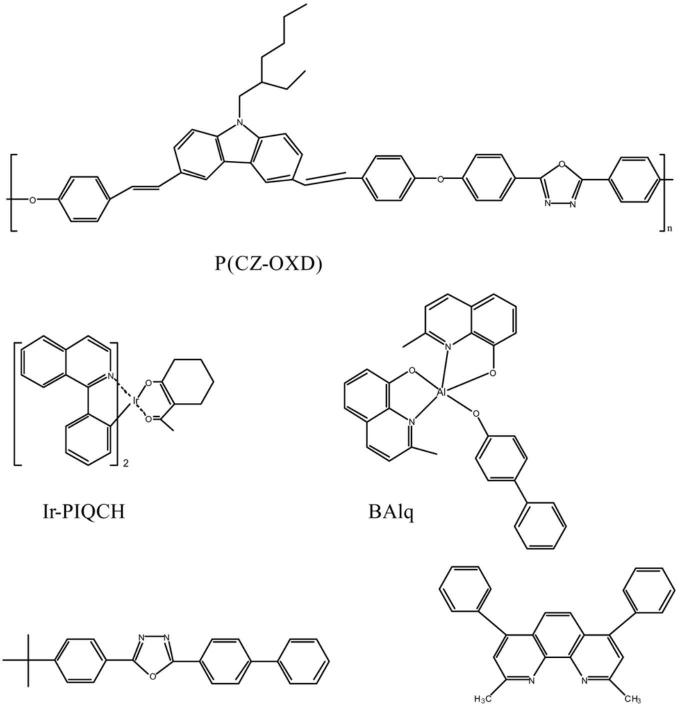

FIGURE 1 Chemical structures of host polymers, guest dopant and hole blocking materials.

Fabrication of Phosphorescent OLED

ITO coated glass was cut into 5.0 cm × 5.0 cm, and electrode area was prepared by photo-etching technique. It was sequentially cleaned in an ultrasonic bath of acetone, methanol, and mixture of isopropyl alcohol and water (1:1 v:v) solution. The hole injecting PEDOT layer was spin-coated with a solution of 1 wt% in isopropyl alcohol onto ITO substrate, and then baked on hot plate at 80°C for 10 min. Subsequently, an emissive layer was spin-coated with a solution (1 wt%) of P(CZ-OXD) and Ir-PIQCH in 1,1,2,2-tetrachloroethane, after filtration using MFS filter (0.45 μm pore size), and then dried at 100°C for 10 min. Finally, hole blocking BAlq (PBD or BCP), electron transporting Alq$_3$, and LiF/Al were successively deposited under pressure $<10^{-6}$ torr. The device structures are summarized as follows: ITO/PEDOT/P(CZ-OXD) and Ir-PIQCH (10 wt%)/HBL (30 nm)/Alq$_3$ (20 nm)/LiF (1 nm)/Al (120 nm).

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Characterization

UV-Visible absorption spectra were obtained by using Shimadzu UV-2100. The photoluminescence (PL) spectra excited by He-Cd laser at 325 nm were monitored by Optical Multichannel Analyzer (Laser Photonics, OMA system). Electroluminescence (EL) spectra were measured by using Spectroscan PR 650 (Photoresearch Inc). Current density-luminescence-voltage (*J-V-L*) profiles of devices were obtained by using dc power supply connected to Model 8092A Digital Multimeter and luminance meter (Minolta LS-100).

RESULTS AND DISCUSSION

Phosphorescent OLEDs have been reported because of their high efficiency [13–14]. To achieve a full-color display based on phosphorescent OLEDs, red phosphorescent dopants are very important to be developed with suitable host materials. In our previous study [17], red phosphorescent Ir-PIQCH dopant and P(CZ-OXD) host polymer were designed and synthesized. Therefore, device performance of phosphorescent OLEDs consisting of synthesized Ir-PIQCH and P(CZ-OXD) as an emitting layer will be investigated as a function of hole blocking layers in this article.

UV-Visible absorption spectrum of Ir-PIQCH, PL emission spectra of Ir-PIQCH and P(CZ-OXD) were measured, as shown in Figure 2.

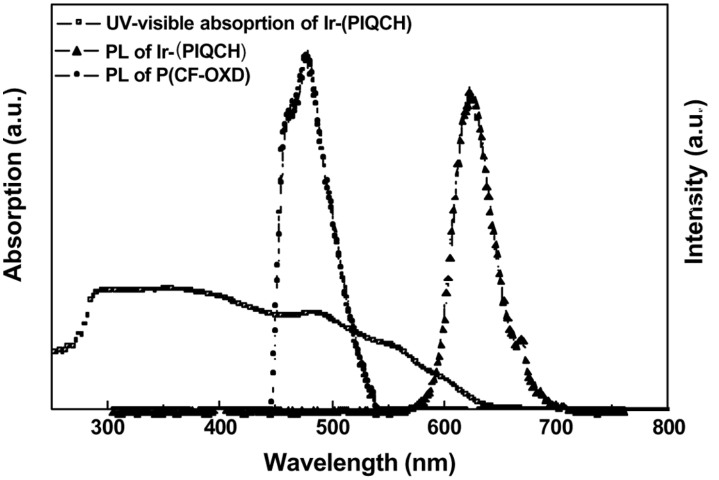

FIGURE 2 UV-Visible absorption spectra of Ir-PIQCH, and PL emission spectra of Ir-PIQCH and P(CZ-OXD).

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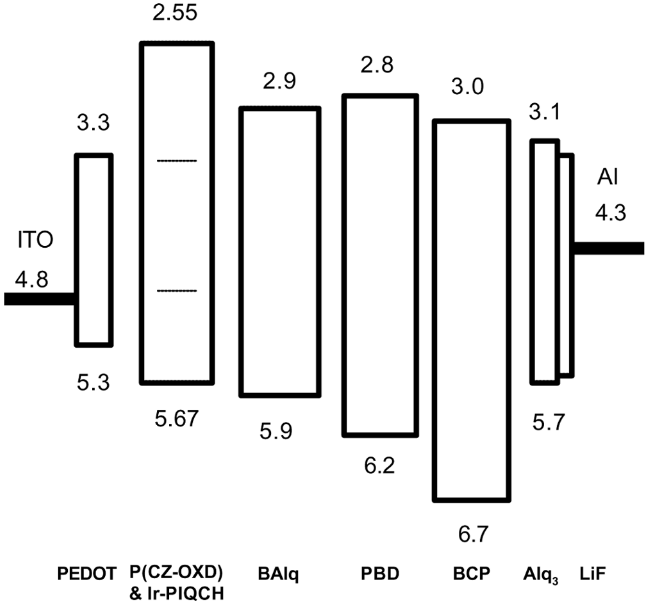

FIGURE 3 Schematic energy diagram of device (the dashed line is for the HOMO and LUMO energy level of Ir-PIQCH).

UV-Visible absorption peaks of Ir-PIQCH appeared at 300, 362, 487, and 563 nm, respectively. Ir-PIQCH showed PL emission in the range of red with $\lambda_{\mathrm{max,PL}}$ at 630 nm. P(CZ-OXD) host polymer exhibited $\lambda_{\mathrm{max,PL}}$ around 440 nm with narrow width. In addition, it can could be clearly seen that there were good overlap between UV-Visible absorption of Ir-PIQCH dopant and PL emission peak of P(CZ-OXD) host polymer. Such system could afford a necessary condition for the energy transfer from host polymer to dopant material [15–16].

Schematic energy diagram of the phosphorescent OLEDs is displayed in Figure 3. It was obviously seen that energy levels of each layers matched well in the device with the configuration of ITO/EML [P(CZ-OXD) & Ir-PIQCH]/HBL/Alq$_3$/LiF/Al. HOMO energy level of P(CZ-OXD) (– 5.67 eV) was higher than that of hole blocking materials such as BAlq (–5.9 eV), PBD (–6.2 eV) and BCP (–6.7 eV)], where these materials may block the exciton diffusion and hole transport from EML.

J-V-L plots of the phosphorescent OLEDs were presented in Figure 4, and the related data were summarized in Table 1. Their current density and luminescence increased generally with increasing the voltage. Device 1 with BAlq as HBL showed turn-on voltage at 12 V and

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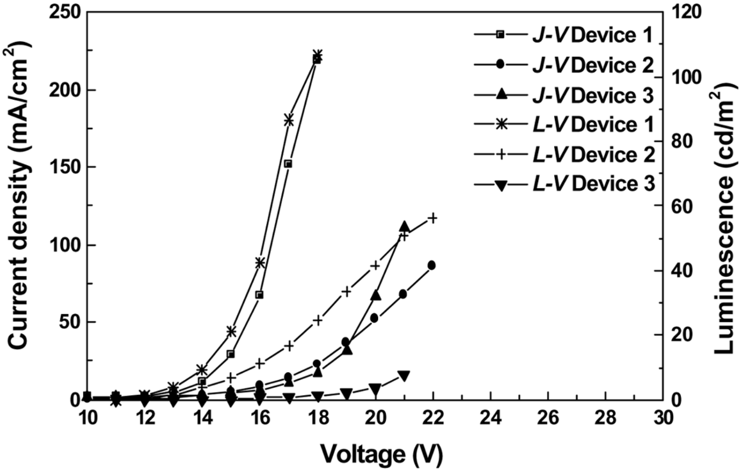

FIGURE 4 Current-luminescence-voltage (*I*-*V*-*L*) curves for the phosphorescent OLEDs.

maximum luminescence of 106.6 cd/m^2. Device 2 with PBD as HBL presented turn-on voltage at 13 V with maximum luminescence of 56.3 cd/m^2. Turn-on voltage at 16 V and maximum luminescence of 7.7 cd/m^2 were observed in Device 3 with BCP as HBL. The maximum luminescence efficiency were obtained as 0.08 cd/A, 0.03 cd/A and 0.01 cd/A for Device 1, Device 2 and Device 3, respectively.

EL spectra of three devices are shown in Figure 5. All devices showed red emission ($\lambda_{\mathrm{max.EL}}$ at about 660 nm), similar with PL emission of Ir-PIQCH dopant. The Commission International de L'Eclairage (CIE) coordinates for these devices were measured to be (x = 0.588, y = 0.359) for Device 1, (x = 0.616, y = 0.350) for Device 2, and (x = 0.668, y = 0.323) for Device 3, respectively. However, though Device 1 showed low turn-voltage with higher luminescence and luminescence efficiency, its color purity was low. Moreover, EL spectrum of

TABLE 1 EL Properties of the Phosphorescent OLEDs with Configuration of ITO/EML (Ir-PIQCH/P(CZ-OXD)/HBL/Alq$_3$/LiF/Al

Devices	HB	Turn-on voltage	Max. luminescence (cd/m^2)	CIE (x, y)	$\lambda_{\mathrm{EL,max}}$(nm)
Device 1	BAlq	12	106.6	0.588,0.359	660
Device 2	PBD	13	56.3	0.616,0.350	660
Device 3	BCP	16	7.7	0.667,0.323	655

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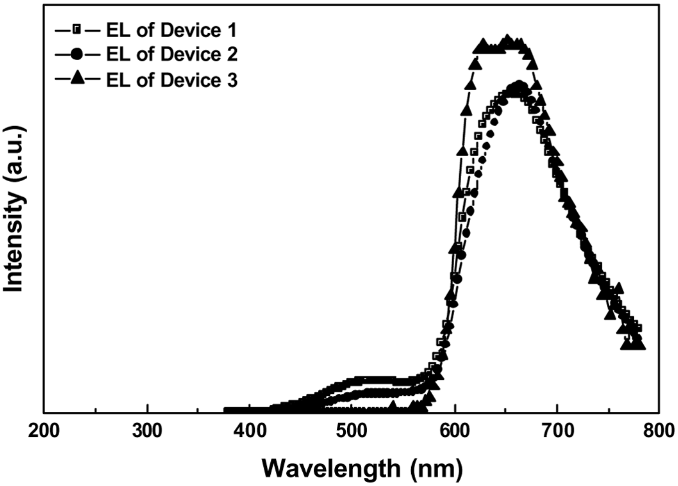

FIGURE 5 EL spectra of the phosphorescent OLEDs.

Device 1 exhibited emission peak at 520 nm, which was attributed to the emission of Alq_3. Because energy barrier (0.23 eV) between P(CZ-OXD) and BAlq was low, green emission from Alq_3 could be originated either by direct electron-hole recombination inside ETL or by the exciton diffusion from the EML to ETL [4,10]. Subsequently, in Device 2, with increasing the energy barrier (0.53 eV) between P(CZ-OXD) and PBD, the intensity of emission peak at 520 nm decreased and the color purity increased. It was observed from Figure 5 that Device 3 showed pure red emission without any green emission from Alq_3 in its EL spectrum, attributing to higher energy barrier (1.03 eV) between P(CZ-OXD) and BCP, which could block the diffusion of holes and excitons effectively. As a result, BCP with low HOMO energy level has good hole blocking property in this structure of phosphorescent OLEDs, resulting in improved color purity of the device. However, an exhaustive study of the device with BCP as HBL to increase other device performance such as decreasing the turn-on voltage, increasing the intensity of luminescence, luminescence efficiency and so on should be carried out in details.

CONCLUSIONS

Different hole-blocking materials afford the devices different device performance. Phosphorescent OLEDs with synthesized Ir-PIQCH dopant and P(CZ-OXD) host polymer as the emitting layer and BAlq, PBD or BCP as a HBL were fabricated. Red electroluminescence was observed in all the devices. It was found that BCP with low HOMO energy level presented excellent hole blocking property. With increasing the energy barrier between P(CZ-OXD) and hole blocking materials, the exciton diffusion and hole transporting from EML to ETL can be blocked effectively, resulting in increased color purity. Device 3 with BCP as HBL showed pure red emission with CIE coordinates value as ($x = 0.667$, $y = 0.323$). Other performance of Devices 3 will be improved further.

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