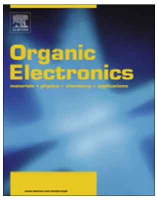
Organic Electronics 13 (2012) 586–592

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Soluble processed low-voltage and high efficiency blue phosphorescent organic light-emitting devices using small molecule host systems

Yoo Jin Doh [a], Jung Soo Park [a], Woo Sik Jeon [a], Ramchandra Pode [b], Jang Hyuk Kwon [a,*]

[a] Department of Information Display, Kyung Hee University, Dongdaemoon-ku, Seoul 130-701, Republic of Korea
[b] Department of Physics, Kyung Hee University, Dongdaemoon-ku, Seoul 130-701, Republic of Korea

ARTICLE INFO

Article history:
Received 10 June 2011
Received in revised form 27 December 2011
Accepted 1 January 2012
Available online 18 January 2012

Keywords:
Solution process
Blue
Phosphorescence
OLED

ABSTRACT

We report low voltage driving and highly efficient blue phosphorescence organic light emitting diodes (PHOLEDs) fabricated by soluble process. A soluble small molecule mixed host system consisting of hole transporting 4,4',4'' tris(N-carbazolyl)triphenylamine (TCTA) and bipolar carrier transporting 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy) exhibits high solubility with smooth surface properties. Moreover, this small molecule host shows the smoothest morphological property similar to a vacuum deposited amorphous film. A low driving voltage of 5.4 V at 1000 cd/m^2 and maximum external quantum efficiency 14.6% obtained in the solution processed blue PHOLEDs are useful for large area low cost manufacturing.

1. Introduction

Solution processed phosphorescence organic light emitting diodes (PHOLEDs) have been a great interest for displays and lighting applications due to their simple and low cost fabrication process and large area display applications [1,2]. Good device performances of PHOLEDs by solution process had been reported by several groups [3–5]. Although several solution processed PHOLEDs with very good performances were reported, high driving voltage, low efficiency, and short lifetime still remain crucial issues. Consequently, investigations on soluble materials, film characteristics of solution process, and device structures are very important and still open issues.

In order to achieve a low driving voltage and high efficiency in solution processed PHOLEDs, the solution processed emitting layer (EML) is more vital than other layers like carrier transport layers since carriers movements are mainly limited by the host-dopant situation. Usually, the host materials should have wide band gap and high triplet state energy for exciton confinement [6]. Also, the balanced hole and electron movement within an emitting layer is very important for the good charge balance [7]. In addition to these general requirements, solubility and amorphous-like film characteristics without crystallization are also critical factors to get the high efficiency device.

Many groups made attempts to explore the ways for improving the performance of solution processed blue PHOLEDs [8–10] in recent years. Mixed host system [3,11,12] such as a polyvinylcarbazole (PVK) hole transporting and 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxidiazolyl]phenylene (OXD-7) electron transporting host system is a well known approach for good charge balance in an EML. In mixed host system, the balanced carrier transportation, minimization of carrier trapping by dopants, and decreased crystallization by mixing two hosts are of great beneficial to solution processed PHOLEDs.

Based on this approach, the high efficiency blue PHOLEDs over 15% external quantum efficiencies (EQEs) by solution processing were reported [3,5]. Typically, non-conjugated polymer of PVK has high triplet energy and good film formation characteristics. Hence it used as hole transporting host due to a reasonable HOMO value of 5.8 eV. However, the PVK host always shows high driving voltage owing to its low carrier mobility [13]. Other small

---

[*] Corresponding author. Tel.: +82 2 961 0948; fax: +82 2 968 6924.
E-mail address: jhkwon@khu.ac.kr (J.H. Kwon).

1566-1199/$ - see front matter Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2012.01.003

Table 1
Performance summary of soluble processed blue PHOLEDs.

Host materials	Driving voltage (V) @1000 cd/m^2	EQE (%)	Current efficiency (cd/A)	Power efficiency (lm/W)	CIE coordinates	Ref.
PVK: OXD-7	7.5	–	22.0(max)	14.5(max)	0.17, 0.37	[11]
PVK: OXD-7	8.0	9.03(max)	20.3(max)	–	–	[12]
PVK: OXD-7	10.0	15.5(max)	28.3(max)	–	0.14, 0.28	[3]
TBCPF: OXD-7	12.4	–	12.5(max)	–	0.22, 0.44	[8]
DTCPFB	10.5	–	24.0(max)	8.8(max)	0.14, 0.23	[9]
PVK/SPPO13	7.5	14.1(max)	30.4(max)	–	0.17, 0.42	[4]
SimCP2	6.5	15.8(at 1000 cd/m^2)	31.1(at 1000 cd/m^2)	–	–	[5]
PTC: OXD-7	7.5	11.9(max)	25.7(max)	–	0.16, 0.38	[10]

Table 2
Performance summary of soluble processed Devices A–D.

Devices	Driving voltage (V)	EQE (%)	Current efficiency (cd/A)	Power efficiency (lm/W)	CIE coordinates
Device A	6.0(1000 cd/m^2)	12.0(max)	21.0(max)	13.0(max)	0.16, 0.33
Device B	5.6(1000 cd/m^2)	12.1(max)	21.8(max)	12.7(max)	0.17, 0.34
Device C	5.4(1000 cd/m^2)	14.6(max)	25.1(max)	15.7(max)	0.16, 0.34
Device D	6.0(1000 cd/m^2)	9.2(max)	15.9(max)	8.8(max)	0.15, 0.32

molecule host systems with both hole and electron carrier transporting characteristics were also tried to address this issue. However, the solution processed blue PHOLEDs still have high driving voltage due to its too wide band-gaps of host materials. Table 1 shows the reported driving voltages and efficiencies in soluble processed blue PHOLEDs. All reported blue PHOLEDs devices have driving voltages of more than 6.5 V.

In this paper, low driving voltage and high efficiency soluble blue PHOLEDs were fabricated by using the small molecule mixed host system. The mixed host with a blue dopant, which possesses a good solubility and morphological uniformity without crystallization issues, has an energetically minimized charge trapping situation by dopant molecules and high carrier mobility characteristics for holes and electrons. As a consequence, we achieved a driving voltage as low as 5.4 V (at 1000 cd/m^2) with a maximum current efficiency of 25.1 cd/A and a maximum quantum efficiency of 14.6% in the optimized solution processed blue PHOLEDs.

2. Experimental details

We have fabricated solution processed blue PHOLEDs using 1,3,5-tri[(3-pyridyl)-phen-3-yl)benzene (TmPyPB) and 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBI) electron-transporting materials. 4,4',4''-tris(carbazol-9-yl)-triphenylamine (TCTA) and 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzPPy) were used as the single or mixed host with bis(3,5-difluoro-2-(2-pytidyl)phenyl-(2-carboxypridyl)iridium(III) (FIrpic) as the blue dopant for an EML. Fig. 1 shows the molecular structure with the energy levels of materials.

To fabricate the blue PHOLEDs, a patterned indium-tin oxide (ITO) with a 150 nm thickness glass substrate having an emission area of 4 mm^2 with a sheet resistance of 10–12 Ω/□ were used. A line pattern of ITO and an insulating layer to make active areas were formed by the photolithography process. The ITO glass substrate was cleaned by sonication in isopropyl alcohol (IPA) and then rinsed in deionized water. Subsequently, the ITO-coated glass substrate was subjected to UV-ozone treatment prior to device fabrication. The PEDOT:PSS (CLEVIOSTM AI4083 (H.C. Stack)) as a hole injection layer was spin-coated on the ITO substrates and dried using a hot plate at 120 °C for 20 min to remove solvent. The emission layer dissolved in chloro-benzene was spin-coated and dried at 120 °C for 10 min. In case of mixed host, a blending ratio was fixed as 1:1 [14]. All solution depositions were performed in a glove box with nitrogen ambient at room temperature. After coating EML, TmPyPB or TPBI as an electron transporting layer (ETL) was thermally deposited at a base pressure of 10^{-7} torr and then LiF and Al cathode was deposited without breaking the vacuum.

The current density–voltage (*J*–*V*) and luminance–voltage (*L*–*V*) characteristics of the fabricated devices were collected using a Keithley 2635A and Minolta CS-100A luminance-meter. Also, the electroluminescence (EL) spectra and CIE color coordinates were obtained using a Minolta CS-1000A. For investigation of film surface morphology, atomic force microscopy (AFM) of Park systems XE-100 was used.

For the measurement of photoluminescence (PL) quantum yields, TCTA, 26DCzPPy, and TCTA: 26DCzPPy films doped with 10% FIrpic were made by spin coating and vacuum deposition process, respectively. Each layer thickness was adjusted to be 40 nm. UV–vis absorption spectra of these films were recorded with a Sinco S-3100 UV–vis spectrophotometer. Relative photoluminescence (PL) quantum yields of these films were measured by Jasco FP-6000 spectrophotometer. As a standard (Φ = 85%) sample [15], 1,3-bis(9-carbazolyl)benzene (mCP) film doped with 6% FIrpic by vacuum deposition process was used. Excitation wavelength of each film was 337 nm.