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Solution processed deep blue phosphorescent organic light-emitting diodes with over 20% external quantum efficiency

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ABSTRACT

Highly efficient solution processed deep blue phosphorescent organic light-emitting diodes (PHOLEDs) were developed using a solution processible high triplet energy host and deep blue dopant materials. Stable film morphology was observed from the spin coated deep blue emitting layer and a high quantum efficiency of 22.1% was achieved in the deep blue PHOLED with a color coordinate of (0.14, 0.19).

1. Introduction

Solution processed phosphorescent organic light-emitting diodes (PHOLEDs) have been developed to replace soluble fluorescent organic light-emitting diodes (FOLEDs). Soluble PHOLEDs can show four times higher quantum efficiency than soluble FOLEDs [1,2]. High quantum efficiency has already been achieved in soluble PHOLEDs [3–5] although the quantum efficiency and color coordinate of soluble blue PHOLEDs are not good enough for practical application. Therefore, there has been much effort to enhance the quantum efficiency and color coordinate of the soluble PHOLEDs.

Most studies to improve the quantum efficiency of soluble blue PHOLEDs were focused on developing high triplet energy host and charge transport materials [6–15]. Poly(N-vinylcarbazole) (PVK) has been typically used as the high triplet energy host material, but the efficiency of the soluble blue PHOLEDs with the PVK host was only 22 cd/A in sky blue PHOLEDs with *y* color coordinate over 0.30 [6–12]. Several soluble high triplet energy host materials were also synthesized and applied as the host for sky blue PHOLEDs [13–17]. Our group synthesized alcohol soluble high triplet energy host material based on spirobifluorene and reported high quantum efficiency of 14.1% [13]. Fluorinated PVK was also effective as the host for soluble blue PHOLEDs and a high efficiency of 27 cd/A was achieved in sky blue PHOLEDs [18]. Hole and electron transport layers were also critical to the quantum efficiency of blue PHOLEDs. The use of the PVK as the high triplet energy hole transport layer was effective to obtain better quantum efficiency in soluble blue PHOLEDs because of triplet exciton confinement in the emitting layer [13]. Other small molecule based host materials were developed, but the efficiency of the device was not high in spite of good morphological stability and bipolar charge transport properties. High triplet energy electron transport layers could also confine triplet excitons inside the emitting layer, resulting in high efficiency in blue PHOLEDs. The best efficiency value reported in the soluble blue PHOLEDs was 15.5% using a mixed host structure of PVK and 1,3-bis[(4-tertbutylphenyl)-1,3,4-oxadiazolyl]phenylene doped with sky blue emitting iridium(III) bis(2-(4,6-difluorophenyl)-pyridinato-N,C2)picolinate (FIrpic) [6].

Although a high quantum efficiency over 15.0% was achieved in sky blue PHOLEDs, the color coordinate of

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the soluble blue PHOLEDs is not suitable for display application. Deep blue color with *y* color coordinate below 0.20 is required for display application, but no solution processed deep blue PHOLED has been fabricated. High triplet energy host materials with a triplet energy over 2.90 eV and morphological stability after solution film coating are required to develop deep blue PHOLEDs. In addition, soluble deep blue emitting phosphorescent dopant materials are needed to obtain deep blue color. However, there has been no report fabricating soluble deep blue PHOLEDs because no soluble host and dopant material was available for application in deep blue PHOLEDs. Therefore, it is important to develop solution processed deep blue PHOLEDs using soluble host and dopant materials.

Phosphine oxide type compounds can be a candidate as a high triplet energy soluble host materials. Our group reported high external quantum efficiency in deep blue PHOLEDs using phosphine oxide type host materials [19–21]. In particular, *N*,*N*′-Dicarbazolyl-3,5-benzene based phosphine oxide compound showed above 20% external quantum efficiency in deep blue PHOLEDs [19]. Therefore, the phosphine oxide type host materials can be useful as the host materials for soluble deep blue PHOLEDs.

In this work, solution processed deep blue PHOLEDs were developed using a soluble high triplet energy host material and a deep blue emitting phosphorescent dopant. High quantum efficiency of 22.1% and a deep blue color coordinate of (0.14, 0.19) were demonstrated from solution processed deep blue PHOLEDs. The quantum efficiency is one of the best efficiency values reported in solution processed blue PHOLEDs and this work is the first paper reporting deep blue PHOLEDs fabricated by solution process.

2. Experimental

The synthesis of the mCPPO1 was described in our previous work [19]. The device structure of the blue PHOLED was indium thin oxide (ITO)/poly-3,4-ethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) (60 nm)/PVK (10 nm)/(9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl)-diphenylphosphine oxide (mCPPO1):bis((3,5-difluoro-4-cyanophenyl)pyridine) iridium picolinate (FCNIrpic) (20 nm, 3%)/4-(triphenylsilyl)phenyldiphenylphosphine oxide (TSPO1) (35 nm)/LiF(1 nm)/Al(200 nm). The soluble deep blue PHOLED with PVK host instead of mCPPO1 was also fabricated for comparison. The mCPPO1:FCNIrpic emitting layer was spin coated from toluene solution and the concentration of the mCPPO1 solution was 1.0 wt.%. The mCPPO1:FCNIrpic film was baked at 80 °C for 10 min to remove residual solvent after spin coating. PVK hole transport layer was formed by spin coating from 0.3 wt.% chlorobenzene solution at a spin speed of 1000 rpm. The PVK layer was baked at 110 °C for 10 min after spin coating. TSPO1 was vacuum deposited at a vacuum pressure of 8.0×10^{-7} torr at a deposition rate of 0.1 nm/s. All devices were encapsulated with a CaO getter and a glass lid after device fabrication. Current density–voltage–luminance performances of the soluble blue PHOLEDs were measured with a Keithley 2400 source measurement unit and a CS 1000 spectroradiometer. Surface morphology of the spin coated mCPPO1:FCNIrpic film was analyzed using atomic force microscope.

3. Results and discussion

There are several requirements for the soluble host materials for solution processed high efficiency deep blue PHOLEDs. The host material should form uniform film with low surface roughness less than 1 nm, which is comparable to that of vacuum deposited film. The solution coated film should also be stable and form amorphous film. In addition to the smooth surface morphology after coating, high triplet energy and bipolar charge transport properties are important to obtain high efficiency in soluble deep blue PHOLEDs. Other than these, good solubility in common aromatic solvents such as toluene, chlorobenzene and dichlorobenzene is also required for good mixing with blue phosphorescent dopant.

A high triplet energy host material, mCPPO1, was reported to be effective as the host material for vacuum deposited blue PHOLEDs [19]. It has a high triplet energy of 3.00 eV and bipolar charge transport properties. In addition, the asymmetric molecular structure of the mCPPO1 is suitable for amorphous film formation. Therefore, the mCPPO1 is suitable as the host material for solution processed deep blue PHOLEDs. A deep blue emitting phosphorescent dopant, FCNIrpic, was reported in other works and gave high efficiency [19]. It has highly polar substituents and picolinic acid as the ancillary ligand. Although the dopant with three main ligands without any ancillary ligand was not soluble in aromatic solvent, the FCNIrpic was soluble in chlorobenzene and dichlorobenzene. Therefore, the FNCIrpic can be used as the soluble deep blue emitting dopant in solution processed deep blue PHOLEDs. Chemical structures of host and dopant materials are shown in Fig. 1.

The mCPPO1 and FNCIrpic were mixed in toluene solvent and was spin coated on Si substrate and PVK film to study the morphology of the mCPPO1:FNCIrpic film. Atomic force microscope pictures of spin coated mCPPO1:FCNIrpic and PVK/mCPPO1:FCNIrpic films are shown in Fig. 1. The mCPPO1:FCNIrpic and PVK/mCPPO1:FCNIrpic films showed smooth morphology with a surface roughness of 0.47 and 0.48 nm, respectively. The mCPPO1:FCNIrpic film could be stably coated on the PVK layer with little intermixing because the high molecular weight PVK layer shows poor solubility in toluene. There was little aggregation of the FCNIrpic dopant and uniform morphology was observed in spin coated mCPPO1:FCNIrpic film. The surface roughness of the mCPPO1:FCNIrpic film was comparable to that of the vacuum deposited mCPPO1:FCNIrpic film. This indicates that the mCPPO1:FCNIrpic film forms stable morphology after spin coating from toluene solution. The low surface roughness of the mCPPO1:FCNIrpic film was maintained even after thermal annealing at 110 °C for 10 min, indicating morphological stability of the mCPPO1:FCNIrpic film. The high temperature morphological stability of the mCPPO1:FCNIrpic film is due to the thermal and morpho-