

## Small molecule interlayer for solution processed phosphorescent organic light-emitting device

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### Abstract

Using 4,4'4''-tris(N-carbazolyl)-triphenylamine (TCTA) small molecule interlayer, we have fabricated efficient green PHOLED by solution process. The maximum current and power efficiency values of 33.7 cd/A and 19.6 lm/W are demonstrated, respectively. Results reveal a way to fabricate the PHOLED using TCTA interlayer by solution process, promising for efficient and simple manufacturing.

### 1. Introduction

Solution processible organic light-emitting diodes (OLEDs) are attracting much attention as potential candidates for flat-panel displays and solid state lighting, owing to their easy processing and low manufacturing cost [1,2]. Requirement for use in these applications, the high luminance at lower current density and efficient operation, are realized by the balance charge carriers injection from the electrodes into the emitting layer. Poly(3,4-ethylenedioxythiophene)-poly(4-stylenesulfonate) (PEDOT:PSS) hole injection layer on the top of indium-tin-oxide (ITO) surface is most widely used to improve the hole injection [3,4]. Further, the insertion of a thin interlayer (thickness 10 ~ 30 nm) between the PEDOT:PSS and emission layer (EML) significantly improves the device efficiency and lifetime. Conjugated polymer materials such as poly(p-phenylene vinylene), poly(9,9-dioctylfluorene) (PFO) and poly(9,9'-dioctylfluorene-alt-benzothia-diazole) [5], poly(9,9-dioctylfluorene-co-N-(4-butyl-phenyl)-diphenylamine) (TF) [6,7], and poly(9,9-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine (PFB) [8] were used for this purpose. To date, non-conjugated materials,

poly(N-vinylcarbazole) (PVK) [8] and crosslinked non-conjugated materials [9-11] having hole transporting chemical units were mostly reported for this purpose. However, such interlayer polymers have several issues for use in practical devices such as considerably high exchange energy, 1.0 ~ 1.5 eV values [12], between singlet and triplet states. As a consequence, conjugated polymers generally are not suitable as phosphorescent host materials [13]. Further, these polymers in phosphorescent OLEDs may act as a potential quencher at the interface of EML. Owing to low solubility in several organic solvents, conjugated polymers also offer a serious difficulty for the printing process and in removing the undesired material from the substrate. Although TFB is a widely used interlayer material, its low triplet emission energy (2.2 ~ 2.3 eV) causes some quenching of phosphorescence emission in green phosphorescent emitting devices. While 4,4'4''-tris(N-carbazolyl)-triphenylamine (TCTA) small molecule has a good film forming properties, solubility, and high triplet emission energy (2.7 eV).

Therefore, we propose that the use of small molecule material interlayer may be a good approach in solution processed phosphorescent OLEDs. In the present work, phosphorescent green light emitting devices using solution process with a small molecule TCTA interlayer have been fabricated and studied.

### 2. Experimental

To fabricate OLED devices, clean glass substrates of size 2 cm x 2 cm precoated with a 150-nm-thick indium tin oxide (ITO) layer with a sheet resistance of 12  $\Omega/\square$  were used. The ITO glass was cleaned by

sonification in an isopropylalcohol (IPA) and acetone, rinsed in deionized water, and finally irradiation in a UV-ozone chamber. The line pattern of ITO was formed by photolithography process. The PEDOT:PSS was spin-coated on the ITO substrates pretreated with UV ozone to a thickness of 40 nm and the dried at 120 °C for 20 min on a hot plate to remove the solvent. Subsequently, the interlayer solution either TCTA or TFB 0.5 wt% in toluene (thickness of about 30 nm) was spin coated and later dried at 180 °C for 30 min on a hot plate. The 40 nm thick EML host of PVK:CBP(4,4-N,N-dicarbazolebiphenyl) system mixed in the proportion of 1:1 and doped with 13 wt% of 2-(4-biphenyllyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazol (Ir(mppy)<sub>3</sub>) in chlorobenzene was spin-coated on the top of interlayer film. The spin coated structures were then baked on a hot plate at 120 °C for 60 min to remove the solvent present, if any. The spin coating and baking processes were carried out in a nitrogen atmosphere in glove box. Subsequently, 2,2',2''-(1,3,5-phenylene) tris (1-phenyl-1H-benzimidazole) (TPBi) (30 nm) was deposited in organic chamber using vacuum thermal evaporation in a base pressure of 10<sup>-7</sup> Torr, while LiF (1 nm) and Al (100 nm) were deposited in a metal chamber without breaking the vacuum of the system. Following devices were fabricated:

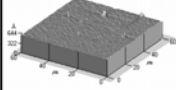
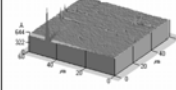
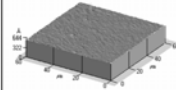
- Device-1: ITO/PEDOT:PSS (40 nm)/TFB (30 nm)/EML (40 nm)/ TPBi (30 nm)/LiF (1 nm)/Al (100 nm)
- Device-2: ITO/PEDOT:PSS (40 nm) /TCTA (30 nm)/ EML (40 nm)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm)

The emission area of devices was 2 mm × 2 mm. The current density-voltage (*I-V*) and luminance-voltage (*L-V*) characteristics of fabricated OLEDs were measured using a Keithley SMU 238 and Minolta CS-100A. Electroluminescence (EL) spectra and CIE color coordinate were obtained using a Photo-research PR-650 spectroradiometer.

### 3. Results and discussion

TCTA hole transport material (HTL) is known to have excellent exciton blocking performance and reported as a suitable host material in green phosphorescent OLEDs [14,15]. To acquire the knowledge about the amorphous nature of spin coated TCTA film, vacuum thermal evaporated TCTA and spin coated TCTA and well known TFB interlayer films (30 nm thick) were fabricated on glass substrates.

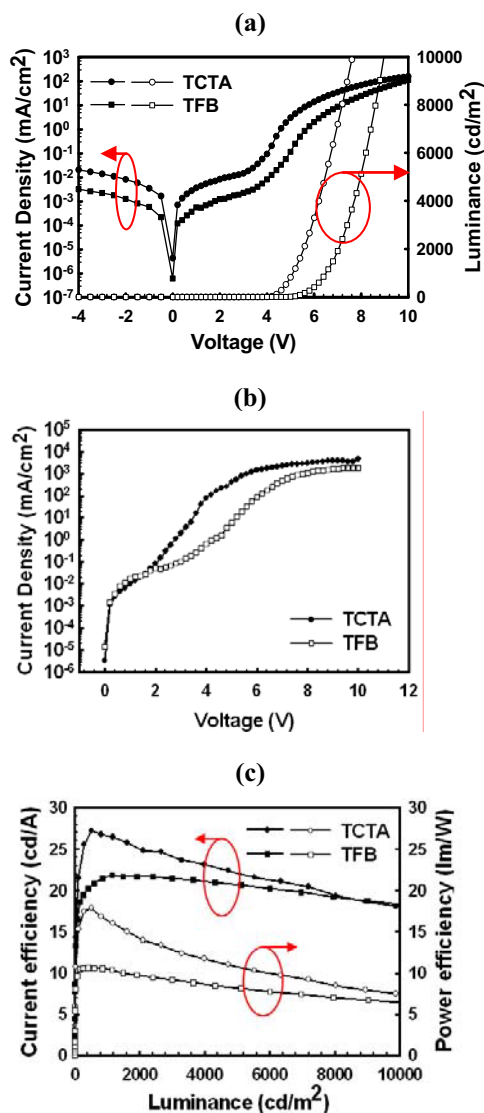
The average surface roughness ( $R_{ave}$ ) values of spin-coated and sublimated TCTA surface, measured using Atomic Force Microscopy (AFM), are about 4.17 Å and 3.38 Å, while the surface roughness value of 5.49 Å in spin-coated TFB interlayer is observed as shown in Fig. 1. Unlike value of surface roughness in spin coated TCTA film than vacuum thermal evaporated may be attributed to the solvent evaporation during the process of spin coating. A good amorphous film formation characteristic of TCTA has been ascribed to three dimensional molecular structure of TCTA. Half circle shape structure of TCTA molecule with coplanar two carbazole units and remaining one carbazole unit vertically orthogonal to the plane containing two carbazole units contributes to amorphous molecular packing, indicating that the crystallization of TCTA film during spin coating and baking process is practically missing. The good surface characteristic of spin-coated TCTA film is well suited for use as an interlayer material.

	TCTA Spin-coating	TFB Spin-coating	TCTA Thermal evaporation
image			
$R_{ave}$	4.17 Å	5.49 Å	3.38 Å

**Fig. 1. Surface morphology of sublimated TCTA, spin-coated TCTA and TFB.**

Fig. 2 (a) shows the luminance and current density as a function of applied voltage. The turn-on voltage value of 4.0 V to attain a luminance of 1,000 cd/m<sup>2</sup> in Device 1 with TFB interlayer is reported, while this value is 3.0 V in Device 2 with TCTA interlayer. Device 2 with TCTA interlayer seems to offer a low barrier for hole injection into emitting layer. To substantiate our argument, hole only devices, having configuration of ITO/PEDOT:PSS (40 nm)/TCTA or TFB (70 nm)/LiF (1 nm)/Al (100 nm), were fabricated. As evident from the results presented in Fig. 2 (b), low resistance to hole transport and conduction in hole only device with TCTA interlayer is noticed. Clearly, these results corroborate the superior electrical performance of device 2 with the TCTA interlayer. Fig. 2 (c) shows the current and power efficiencies as a function luminance. Current and power efficiency values of 21.5 cd/A and 10.5 lm/W in Device 1 with TFB interlayer at a luminance of 1,000 cd/m<sup>2</sup> are observed, respectively, whereas these values in Device 2 with TCTA interlayer are 26.5 cd/A and 16.0 lm/W.

The maximum current and power efficiency values with TCTA interlayer are 27.2 cd/A and 17.8 lm/W and 21.7 cd/A and 10.6 lm/W with TFB interlayer, respectively. Better performance of the Device 2 with TCTA interlayer, therefore, is of interest to manufacturers.

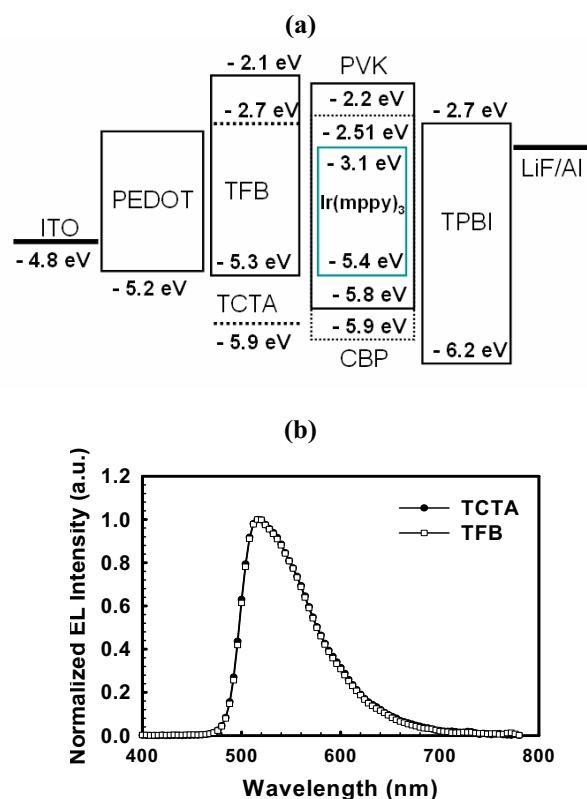


**Fig. 2.** *I-V-L* and efficiency characteristics of fabricated PHOLED devices (a) luminance and current density versus voltage devices 1 & 2 (b) current versus voltage characteristics of fabricated hole only devices (c) current and efficiency versus luminance in devices 1 & 2.

Furthermore, improvement of the device performance due to increase of the thickness of TCTA interlayer from 30 to 40 nm is observed. The values of current and power efficiencies of 32.0 cd/A and 15.9 lm/W at the luminance of 1,000 cd/m<sup>2</sup> were measured,

respectively. The maximum current and power efficiencies were 33.7 cd/A and 19.6 lm/W in this device, respectively.

Indeed, interesting and intriguing results on the device performance with the TCTA small molecule interlayer deposited using spin coating are obtained. These results may be explained on the basis of the knowledge of energy levels of materials used in device fabrication as following. Hole injection efficiency in TCTA interlayer based device is significantly improved, leading to better electrical & luminance characteristics. The highest occupied molecular orbital (HOMO) level of TCTA (-5.9 eV) is at low energy compared to TFB (-5.3 eV) as shown in Fig. 3 (a).



**Fig. 3.** (a) Device structure and energy band diagram of the devices using hole transporting interlayer. (b) electroluminescence spectra of fabricated devices.

As the HOMO energy of host layer (-5.8 eV in PVK and -5.91 eV in CBP) is very close to HOMO energy of TCTA, the hole charge carriers are efficiently injected into emitting host layers and enhance the hole-electron recombination probability. Besides, triplet emission energy of Ir(mppy)<sub>3</sub> (2.38

eV) much higher than the triplet energy levels of TFB (2.2 – 2.3 eV) but lower than TCTA triplet emission energy (2.7 eV) may quench some light emission of the TFB interlayer PHOLEDs as compared with TCTA interlayer ones.

Furthermore, clean emission peak in green region at 520 nm (CIE coordinates (0.33, 0.61) at 1,000 cd/m<sup>2</sup>) in the fabricated TCTA interlayer device reveals no leakage of electrons into HTL layer (Fig. 3 (b)), thereby confining electrons in the EML.

#### 4. Summary

We have fabricated TCTA small molecular interlayer based green phosphorescent devices using spin-coating process. TCTA has a good solubility in toluene and thin film forming properties by spin coating process. Low turn on voltage value of 3.0 V to obtain luminance of 1000 cd/m<sup>2</sup> and maximum current and power efficiencies values of 27.3 cd/A and 18.0 lm/W are reported in this device, respectively. The maximum current and power efficiencies of 33.7 cd/A and 19.6 lm/W with TCTA thickness of 40 nm are also demonstrated. In conclusion, demonstration of solution processible efficient green phosphorescent OLEDs using the TCTA small molecule interlayer could be a promising way for simple manufacturing process.

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