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Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Naoto Oda, Hirotake Kajii & Yutaka Ohmori (2013) Characteristics of Solution-Processed Phosphorescent Organic Light-Emitting Diodes Utilizing Low Molecular Carbazole Derivative as a Host Material, Molecular Crystals and Liquid Crystals, 581:1, 70-75

To link to this article: http://dx.doi.org/10.1080/15421406.2013.808538

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Mol. Cryst. Liq. Cryst., Vol. 581: pp. 70–75, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.808538

Characteristics of Solution-Processed Phosphorescent Organic Light-Emitting Diodes Utilizing Low Molecular Carbazole Derivative as a Host Material

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This study focused on the characteristics of solution-processed phosphorescent organic light-emitting diodes (PHOLEDs) by using a small molecular carbazole derivative, 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1) which has side chains for solubility in organic solvent and high triplet level as a host material for the PHOLEDs. The device with fac-*tris(2-phenylpyridine) iridium(III) doped in TCz1 emitted green light, and showed the maximum luminance of approximately 25,000 cd/m^2. Blending hole transport material into emissive layer, carrier balance factor in the device was optimized and the maximum current and the external quantum efficiency of 23 cd/A and 6.8% were achieved.*

Keywords Carbazole; organic light-emitting diode; phosphorescence; solution-process

1. Introduction

Organic light-emitting diodes (OLEDs) are capable of emission over a wide visible wavelength range, are highly efficient, and require only a low driving voltage [1–4]. The phosphorescent OLEDs (PHOLEDs) using phosphorescent dyes such as Ir complexes have demonstrated high external quantum efficiencies [3,4]. OLEDs with a long lifetime and excellent durability for flat-panel display applications have been realized. There are some requirements of OLEDs when they are used not only in display applications but also as various light sources [5–7].

Employing solution process of organic materials is useful for organic light emitting diodes (OLEDs) fabrication, and allows for the possibility of low cost mass production and for making high-sized screens. For solution process, polymer materials are mainly used. In these materials, a carbazole derivative, poly(9-vinylcarbazole) (PVCz) is generally used as a host material for PHOLEDs due to its high triplet level for some phosphorescent complexes [8,9]. However, compared to polymer materials, small molecular materials have a high purity and can be easily purified.

In this study, we focused on a small molecular carbazole derivative, 3,6-di(9-carbazolyl)-9-(2-ethylhexyl)carbazole (TCz1) [10–12] which has side chains for solubility

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*Address correspondence to Yutaka Ohmori, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. Tel.:/Fax: +81-6-6879-4212. E-mail: ohmori@oled.eei.eng.osaka-u.ac.jp in organic solvent. Besides, it can be used as a host for PHOLEDs due to its high triplet level (2.9eV). Therefore, we investigated the characteristics of solution processed PHOLEDs with TCz1 as a host material for *fac*-tris(2-phenylpyridine) iridium(III) [Ir(ppy)$_3$].

2. Experimental

The glass substrate was degreased with solvents and cleaned in a UV ozone chamber. First, a 40-nm-thick poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT: PSS) hole-injection layer was spin-coated on an indium tin oxide (ITO)-coated glass substrate and baked. Next, poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)- diphenylamine) (TFB) as a hole transport layer (HTL) was fabricated by the spin-coating method and then annealed at 200°C for 1 hour in a glovebox and followed by spin rinsing with 1,2-dichloroethane in order to remove the remaining soluble part of TFB. After rinsing, a thin ($\sim$10 nm) TFB layer was remained on the PEDOT: PSS layer [13]. The materials were dissolved in 1,2-dichloroethane and the emissive layers, which consisted of the host small molecular of TCz1 blended with hole transport material of 1,1-bis((di-4-tolylamino) phenyl) cyclohexane (TAPC) and electron transport material of 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) and emissive dopant of Ir(ppy)$_3$, were formed by spin-coating method into 90 nm-thick layers on PEDOT: PSS or TFB layer. Different compositions of TCz1: TAPC: PBD: Ir(ppy)$_3$ in weight ratio were prepared (100: x: 60: 6, x = 0, 20, 30, 50, 100). The solvent was removed by baking films. The cathode consisting of CsF (2 nm)/Mg: Ag/Ag was deposited in vacuum at a chamber base pressure of about 10^{-4} Pa. The active area was 4 mm^2.

The photoluminescence (PL) spectra and absolute PL quantum yields (PLQYs) were measured using an absolute PL quantum yield measurement system (HAMAMATSU, Quantaurus-QY). The film for the PL spectrum measurement was formed on quartz glass substrate. The electro-luminescence (EL) spectra were measured using a photonic multi-channel spectral analyzer (Hamamatsu Photonics, PMA-11). The current density-voltage-luminance (J-V-L) characteristics were obtained using a digital multimeter (Keithley 2000), a regulated DC power supply (Kenwood PW36-1.5AD), and a luminance meter (Minolta LS-100). Transient EL measurements were measured by applying square-wave voltage pulses and were observed using a photomultiplier tube detector, (Hamamatsu Photonics). The EL and voltage waves were monitored by a Lecroy 104Xi oscilloscope. All of the measurements were carried out at room temperature.

3. Results and Discussion

External quantum efficiency(η_{ext}) of OLEDs follows: $\eta_{\text{ext}} = \gamma \times \eta_{\text{r}} \times \varphi_{\text{p}} \times \eta_{\text{p}}$, where γ is carrier balance factor, η_{r} is efficiency of exciton formation, φ_{p} is the radiative quantum efficiency of the emitting material and η_{p} is the light outcoupling efficiency [4]. PLQY of an emissive layer is one of the important factors to achieve the high φ_{p}. Figure 1 shows TAPC concentration dependence of PL spectra in 90-nm-thick TCz1: TAPC: PBD: Ir(ppy)$_3$ blend films. The PL intensity slightly decreased with increasing the TAPC concentration. The PLQYs of up to approximately 70% were obsereved in blend films with TAPC. These results suggest that high efficiency PHOLEDs can be fabricated.

There is high barrier for hole injection due to a wide band gap between PEDOT: PSS which has the work function of -5.1 eV and TCz1 which has the ionized potential of -5.8 eV [11]. TFB, which has highest occupied molecular orbital (HOMO) level of

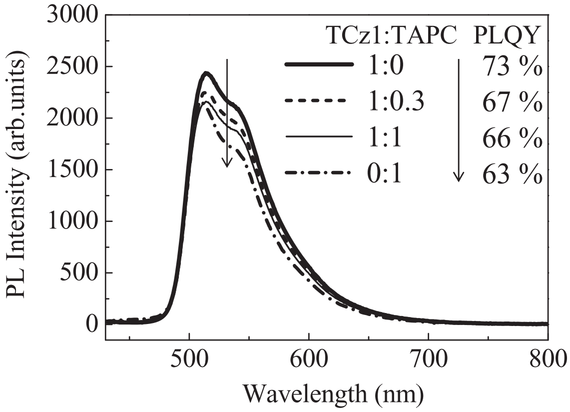

Figure 1. TAPC concentration dependence of PL spectra in 90-nm-thick TCz1: TAPC: PBD: Ir(ppy)$_3$ blend films.

−5.3 eV [13], was used to modify the interface between the PEDOT:PSS layer and the emissive layer. The J-V-L characteristics of the PHOLEDs with and without TFB are shown in Fig. 2. The device without the TFB interlayer showed the maximum luminance of 19,000 cd/m^2. By insertion of the TFB layer which acts as the hole transport and electron blocking layer and improves heat stability of the device, the maximum luminance of 25,000 cd/m^2 was obtained, and the current efficiency at low current densities was improved. However, the maximum current efficiency of 15 cd/A in the device with TFB is almost the same as that without TFB as shown in the inset of Fig. 2. It is suggested that the low efficiency is caused as a result of triplet energy transfer from host to HTL due to low triplet level of TFB.

The performance of OLEDs is often limited by injection. To investigate the blend effect of a hole transport material, TAPC which has a high triplet level and lower HOMO level of −5.5 eV into an emissive layer, Fig. 3 shows the J-V-L characteristics and current efficiencies of the PHOLEDs with and without TAPC. The blend of TAPC results in the low driving voltage and the improvement of current efficiency. For the weight ratio of TCz1

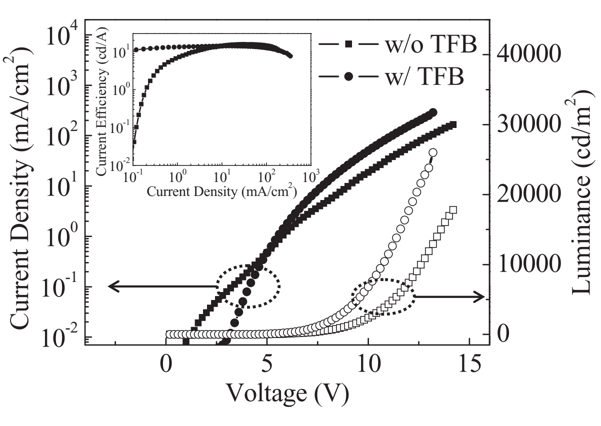

Figure 2. J-V-L characteristics of the devices of ITO/PEDOT:PSS(40 nm)/TFB(0 or 10 nm)/TCz1: PBD:Ir(ppy)$_3$ (90 nm)/CsF/Mg:Ag/Ag with and without TFB. Inset the current density dependence of current efficiencies in the devices with and without TFB.

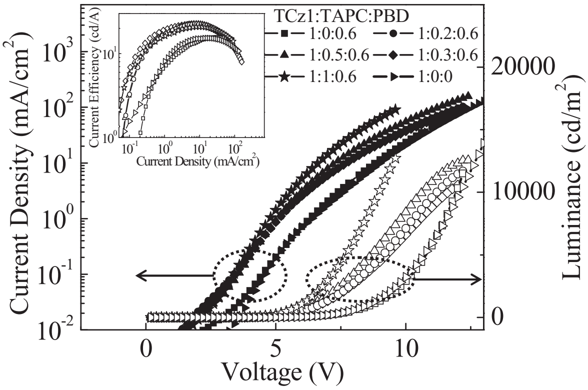

Figure 3. J-V-L characteristics of the devices of ITO/PEDOT:PSS(40 nm)/TCz1:TAPC:PBD:Ir(ppy)$_3$ (90 nm)/CsF/Mg:Ag/Ag with and without TAPC. Inset: the current density dependence of current efficiencies in the devices with and without TAPC.

and TAPC as 1: 0.3, the maximum current and external quantum efficiency of 23 cd/A and 6.8% at the current density of 6.9 mA/cm^2 were achieved. By contrast, the measured PLQY values as shown in Fig. 1 for these emissive layers were slightly decreased from 73 to 63% with increasing TAPC. Therefore, by blending TAPC, hole injection ability was improved and lower driving voltage was obtained. The devices in this study have a single layered structure, and the charge balance of holes and electrons injected in the emissive layer might be influenced carrier transport characteristics of each material. Hence, good hole injection leads to the improvement of carrier valance factor, and this is reason why the current efficiencies were improved. While an adequate amount of TAPC can improve carrier balance, large amount of TAPC may cause an imbalance in carrier transport and lowering the properties of the device due to its high hole transport ability. In addition, the device with only TAPC as a host instead of TCz1 might be very difficult to fabricate the uniform film as the emissive layer due to low solubility of TAPC, which results in high leakage current and low current efficiency in the device.

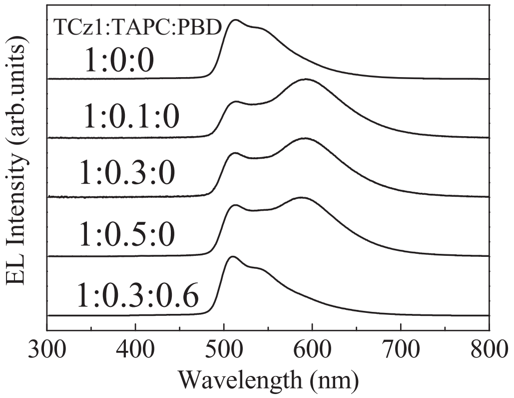

Figure 4. TAPC concentration dependence of EL spectra of PHOLEDs with and without PBD.

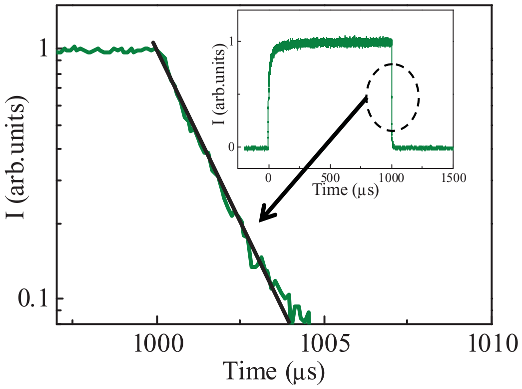

Figure 5. EL decay transient response of the device driven at 1-ms-wide rectangular voltage pulse of 8 V on a semilogarithmic scale. Inset: EL transient response.

Figure 4 shows TAPC concentration dependence of EL spectra of PHOLEDs with and without PBD. For the device of ITO/PEDOT:PSS/TCz1:TAPC:PBD:Ir(ppy)$_3$ (100:30:60:6 wt%)/CsF/Mg:Ag/Ag with PBD, the green emission based on Ir(ppy)$_3$ with a peak wavelength at 515 nm was obtained. TCz1 has been reported to exhibit the bipolar carrier transport with hole and electron motilities of 10^{-4} and 10^{-3} cm^{2}V^{-1}s^{-1}, respectively.[12] Then, the current efficiency can be expected to be independent of the concentration of PBD. As shown in Fig. 3, the J-V-L characteristics and current efficiencies of devices without PBD were almost the same as those with PBD. However, for the devices without PBD, the strong exciplex emission with a peak wavelength at 590 nm related with TCz1 and TAPC was observed. The intensity of exciplex emission increased with increasing TAPC. From these results, blended PBD inhibited the formation of exciplex related with TCz1 and TAPC.

Figure 5 shows EL transient response of the device driven at 1-ms-wide rectangular voltage pulse of 8 V. Decay profile of the device was fitted by a single exponential component (solid curves in Fig. 5), and the radiative lifetime (τ_r) was also estimated to be 1.5 μs from the decay profile fitted with $I(t) = \exp(-t/\tau_r)$, which is almost the same as the phosphorescence lifetime of Ir(ppy)$_3$. For this device, the contributing ratio of delayed fluorescence is small. η_r can approach 1 by using the phosphorescent material which harvest both singlet and triplet excitons. Then, these results in this study suggest that using a small molecular carbazole derivative, TCz1 which has a high triplet level as the host of the phosphorescent materials allows easy and stable fabrication for lighting applications by PHOLEDs including white color.

4. Conclusion

We have demonstrated improvement in the efficiency of solution-processed TCz1-based PHOLEDs. By optimizing the carrier balance factor, a current efficiency of 23cd/A and an external quantum efficiency of 6.8% which represented the low-voltage drive were achieved. It is considered that by the TAPC and PBD, TAPC leads to the improvement of the carrier balance factor in the emissive layer due to its hole transport ability. Then, electron transport material, PBD inhibited formation of exciplex related with TCz1 and TAPC.

Acknowledgments

Part of this work was supported by Grant-in-Aid for Scientific Research, from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This research was also partially supported financially by a Grant in Aid of Special Coordination Funds for Promoting Science and Technology.

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