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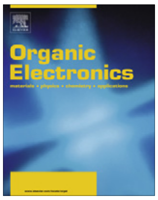

Extremely low driving voltage electrophosphorescent green organic light-emitting diodes based on a host material with small singlet–triplet exchange energy without p- or n-doping layer

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ABSTRACT

In order to achieve low driving voltage, electrophosphorescent green organic light-emitting diodes (OLEDs) based on a host material with small energy gap between the lowest excited singlet state and the lowest excited triplet state (ΔE_{ST}) have been fabricated. 2-biphenyl-4,6-bis(12-phenylindolo[2,3-a] carbazole-11-yl)- 1,3,5-triazine (PIC–TRZ) with ΔE_{ST} of only 0.11 eV has been found to be bipolar and used as the host for green OLEDs based on tris(2-phenylpyridinato) iridium(III) (Ir(ppy)$_3$). A very low onset voltage of 2.19 V is achieved in devices without p- or n-doping. Maximum current and power efficiencies are 68 cd/A and 60 lm/W, respectively, and no significant roll-off of current efficiency (58 cd/A at 1000 cd/m^2 and 62 cd/A at 10,000 cd/m^2) have been observed. The small roll-off is due to the improved charge balance and the wide charge recombination zone in the emissive layer.

1. Introduction

Organic light-emitting diodes (OLEDs) have now been accepted as a dream display owing to their attractive features such as thin feature, flexibility, low power consumption and so on [1–4]. Low driving voltage devices are of great interest to researchers from the point view of energy saving. Leo et al [5] proposed that a theoretical voltage necessary to reach 100 cd/m^2 is 1.95 V for green-emitting OLED in an idealized device where the gap energy between the electron and hole quasi-Fermi-levels is identical to the voltage applied to the contacts of the device. Like such a low operating voltage, the onset voltage at which the OLED starts the emission is expected to correspond to the photon energy ($h\upsilon$) of the emitted photons in the idealized device. However, typical phosphorescent devices always require higher driving voltages than the theoretical value since the carrier concentration is quite low, leading to Ohmic losses and a high field required [6].

The p- and n-doping techniques (p-i-n) have been used to reduce the operating voltages of phosphorescent organic light-emitting diodes (PHOLEDs) [7–10]. In such a device, due to the high conductivity of these highly n- and p-doped transport layers, the Ohmic losses are very small and the band edges are nearly flat since there is nearly no voltage drop and then the operating voltage of the device is close to the photon energy of the light emitted [6]. Earlier, a very low onset voltage of 2.4 V was achieved in Ir(ppy)$_3$ based p-i-n device with the maximum current and power efficiencies of 53.3 cd/A and 61.4 lm/W, respectively [11]. However, hole and electron block layers have to be introduced to prevent dopants from diffusing into the emitting layer (EML) which is not good for reducing the driving voltage. Except the above strategy, low driving voltage can also be realized by using electron transporting materials with much lower-lying lowest unoccupied molecular orbital (LUMO) level which can greatly improve electron injection without n-doping. Recently, Kido et al [12] reported that Ir(ppy)$_3$ based devices show an onset voltage of 2.18 V by using the undoped new electron transporting materials with much lower-lying LUMO level. Such

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a very low onset voltage, however, was achieved by using p-doped layers.

In devices without p- or n-doping layer, the injection at the contact has a large barrier and the carrier transport in the undoped layer is less efficient than the doped layer, leading to quite high driving voltage [5]. A new strategy that using host materials with small ΔE_{ST} has been proposed [13–17]. Very recently, Kido [18] reported a host material of 2,4,6-tris(3-(carbazol-9-yl)phenyl)-triazine (TCPZ) with ΔE_{ST} of 0.14 eV and the turn-on voltage of the Ir(ppy)$_3$ based device is 2.11 V. Although very low driving voltage was achieved, the device also adopted the p-doped hole transporting layer because the highest occupied molecular orbital (HOMO) (6.18 eV) of the host TCPZ was too low to inject holes from the adjacent layer. We think that by using hosts with extremely small ΔE_{ST} and appropriate HOMO and LUMO energy levels, low voltage devices without p- or n-doping can be obtained. Commonly the smaller ΔE_{ST} of the host is, the easier charge injection and transportation between layers become. Recently, thermally activated delayed fluorescent (TADF) materials with especially small ΔE_{ST} have aroused researchers' interest [19–21] since they have the potential to achieve 100% internal quantum efficiency through up-conversion from triplet state to singlet state. If such materials with lager triplet energies possess high charge mobilities, then, they can be used as host materials to fabricate low driving voltage PHOLEDs without p- or n-doping.

In this article, we choose 2-biphenyl- 4,6-bis(12-phenylindolo[2,3-a] carbazole-11-yl)- 1,3,5-triazine (PIC–TRZ), which was reported to possess a very small ΔE_{ST} of 0.11 eV [22], to demonstrate our idea. PIC–TRZ was determined to be a bipolar material with high charge mobilities and was used as the host doped with Ir(ppy)$_3$ to fabricate OLEDs without p- or n-doping. The most used 4,4′-Bis(9-carbazolyl)-1,1′-biphenyl (CBP) (ΔE_{ST} = 0.84 eV [13]) was also introduced as the host for comparison.

2. Experimental

2.1. General

PIC–TRZ was synthesized according to the report [22]. It was purified by silica gel chromatography and thermal gradient vacuum sublimation before device fabrication. Differential scanning calorimetry (DSC) was performed using a DSC 2910 modulated calorimeter under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was undertaken using a STA 409PC under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. UV absorption spectra were obtained from CH_3CN solutions with a UV–vis spectrophotometer (Agilent 8453). PL spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3).

2.2. The cyclic voltammogram measurement

The HOMO energy level was calculated from the oxidation potential onset of the cyclic voltammogram (CV) measured in CH_2Cl_2 (Pt electrode with 0.1 M n-Bu4NPF6 as the supporting electrolyte). The voltages are referenced to an Ag/Ag + standard. The energy level of the ferrocene (F_c) reference (4.8 eV) and calibrated using $E1/2$ (F_c/F_c+) = 0.70 V. Energy bandgap between HOMO and LUMO (E_g) is calculated from the onset wavelength of the absorption spectrum of PIC–TRZ. From the formula E_g = LUMO–HOMO, the LUMO energy level can be got.

2.3. Crystal structure determination

Single crystals of PIC–TRZ were grown from slow evaporation of dichloromethane/petroleum ether (1:4) solutions. The room temperature single-crystal X-ray experiments were performed on a RIGAKU SATURN 724 + CCD diffractometer equipped with a graphite monochromatized Mo Kα radiation. The structure was solved by direct methods and refined with a full-matrix least-squares technique based on F2 with the SHELXL-97 crystallographic software package [23].

Selected Crystal Data of PIC–TRZ: Space group P21/c with a = 12.973(4) Å, b = 13.179(4) Å, c = 27.480(8) Å, α = 92.968(6)°, β = 91.663(4)°, γ = 103.559(6)°, V = 4557(3) Å3, Z = 4, dcalcd = 1.303 g cm^{-3}, R1 = 0.1275 (R1 all data = 0.1397), ωR2 = 0.2336 (ωR2 all data = 0.2378) for observed reflections [$I \geqslant 2\sigma$(I)].

2.4. Device fabrication and characterization

Indium-tin-oxide (ITO) substrates with sheet resistance of 15 Ω/□ were sufficiently cleaned using chemical and UV–ozone methods before the deposition of organic layers. Then the organic materials were sequentially deposited onto the cleaned ITO glass substrates through thermal evaporation. The layer thickness of the deposited material was monitored in situ using an oscillating-quartz thickness monitor. Finally a LiF buffer layer and an Al cathode were deposited onto the organic films. The background pressure of the chamber was less than 10^{-5} Torr during the deposition process. The luminance-current characteristics of devices were measured using a PR650 spectroscan spectrometer and the current–voltage characteristics were studied using a Keithley 2400 sourcemeter. All the measurements were carried out at room temperature under air atmosphere.

3. Results and discussion

As the triplet energy of PIC–TRZ is 2.55 eV [22], and the triplet energy of Ir(ppy)$_3$ is 2.42 eV, it is concluded that the triplet excitons can be effectively confined on the guest.

From the cyclic voltammetry (CV) measurement (Fig. 1), the HOMO energy level of PIC–TRZ is determined to be 5.37 eV, while the LUMO energy level is calculated from the HOMO level and the E_g (2.81 eV, calculated from the UV–vis absorption spectrum) to be 2.56 eV. Compared with the host CBP (HOMO = 6.1 eV), PIC–TRZ possesses much high lying HOMO energy level as it introduces indolocarbazole unit as the hole transporting moiety. The high lying HOMO energy level of PIC–TRZ enables the holes transportation between EML and hole transporting layer