

High-efficiency conjugated-polymer-hosted blue phosphorescent light-emitting diodes

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Highly-efficient blue phosphorescent light-emitting diodes were fabricated based on a conjugated-polymer host by doping bis(2-(4,6-difluorophenyl)-pyridinato-N,C2') picolinate (FIrpic) into poly(9,9-dioctylfluorene) (PFO). Previously, conjugated polymers were not considered as potential hosts for blue phosphorescent dyes because of their low-lying triplet energy levels. Energy back transfer would occur and lead to poor luminescent efficiency in both photoluminescence (PL) and electroluminescence (EL) processes. However, by inserting a hole-transporting layer of poly(*N*-vinylcarbazole) (PVK), the energy back transfer was suppressed. At low FIrpic-doping concentrations, PFO emissions were completely quenched; with 8 wt% FIrpic, a maximum luminous efficiency of 11.5 cd/A was achieved.

polymer light-emitting diode, phosphorescent, organic electroluminescence, back energy transfer

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Despite thirteen years of extensive research attention, phosphorescent organic/polymer light-emitting diodes (OLEDs/PLEDs) still generate considerable interest as potential candidates for use in flat panel displays and solid-state lighting [1–5]. Either a small organic molecular material or a polymer can be adopted as a phosphorescent dye host [6]. Of these, polymer hosts are more promising for use in large-sized flexible products due to the underlying solution processing technology [7,8].

Non-conjugated polymer poly(*N*-vinylcarbazole) (PVK) has been a commonly used polymer host for phosphorescent dyes [9–12]. As a host polymer, PVK has however an inherent defect in that its electron and hole mobility difference is too large. To improve the electron mobility, PVK must be doped with an electron-transporting material [13]. However, in fabricating functional layer on top of the emissive layer (EML), electron-transporting material would be selectively removed resulting in poor luminescent efficiency [14,15]. For example, Xu et al. [14] found that the spin-

coating of the electron-injection layer from the methanol solution was capable of selectively extracting the electron-transporting material, 1,3-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-5-yl]benzene (OXD-7), of the EML, PVK:OXD-7:FIrpic:(piq)₂Ir(acac), leading to poor PLED performance.

Poly(9,9-dioctylfluorene) (PFO) is a commonly-used blue material and host polymer for red phosphorescent dyes in PLEDs industry [16–19]. Previously, PFO was thought to be a bad choice as a host for blue or green phosphorescent dyes because of its low-lying triplet energy level. Although energy back transfer happened in both PL and EL processes, efficient green phosphorescent PLEDs were fabricated recently with a PFO host [20,21]. In contrast to PVK-hosted PLEDs, the performances of PFO-hosted PLEDs could be enhanced from the selective removal of the electron-transporting material during fabrication of the functional layer [22]. In this manner, PFO becomes a promising polymer host for phosphorescent dyes. Obtaining efficient blue phosphorescent PLEDs on a PFO host will not only offer greater selection of polymer host but extend the approaches towards generation of white light that would boost the application of

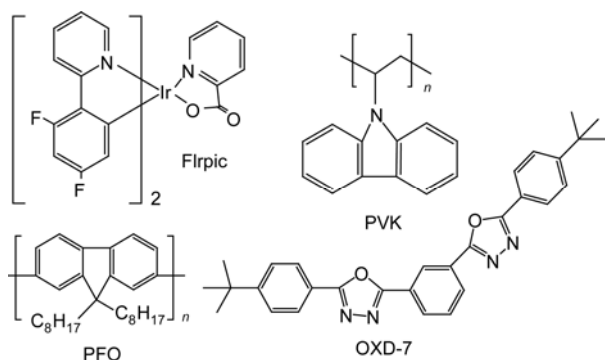
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phosphorescent PLEDs.

In this article, we report on the fabrication of high-efficiency blue phosphorescent EL with the conjugated-polymer PFO as a FIrpic host. The triplet energy level of PFO lies lower than that of FIrpic, causing energy back transfer from FIrpic to PFO that leads to poor PLEDs performances. However, by inserting PVK as a hole-transporting layer (HTL), the energy back transfer was suppressed because of the higher triplet energy level of PVK than FIrpic. At low FIrpic-doping concentrations, PFO was quenched completely. A luminous efficiency of 11.5 cd/A was achieved, which was comparable with that of the PVK hosted PLED, 9.1 cd/A.

1 Experimental

The device structure consists of ITO/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (40 nm)/PVK (40 nm)/PFO:OXD-7 (30 wt%):FIrpic (x wt%) (70 nm)/CsF (1 nm)/Al (100 nm), where OXD-7 was incorporated to improve the electron current in the EML. The chemical structures of the relevant materials are shown in Scheme 1. Prior to device fabrication, an ITO-coated glass substrate was subjected to wet-cleaning in an ultrasonic bath sequentially filled with acetone, detergent, deionized water, and isopropanol. Next, the substrate was baked in a vacuum oven at 80°C for 2 h. Before the coating with PEDOT:PSS, the substrate was treated for 10 min with O₂ plasma. The 40 nm of PEDOT film (P4083) was spun-cast onto the ITO surface, and then baked in a vacuum oven at 90°C for 12 h to remove residual water. Subsequently, HTL and EML were sequentially spun-coated to a thickness of about 40 and 70 nm, respectively, as determined by profilometry (XP-2). Finally, cathodes of CsF (1 nm) and then Al (200 nm) were thermally evaporated at a basic pressure of 3×10^{-4} Pa. The active emission area defined by a shadow mask was 0.15 cm². Except for the coating process of the PEDOT layer, all processes were performed in a N₂ atmosphere dry box (Mikrouna) with water and oxygen concentration less than



Scheme 1 The chemical structures of PFO, PVK, OXD-7 and FIrpic.

1 ppm. PVK-PLEDs doped with 30 wt% OXD-7 as host at 10 wt% FIrpic were also fabricated and tested under the same conditions.

Data of the current density, operating voltage, and luminous efficiency were recorded using a Keithley 2400 source measurement unit coupled with a calibrated silicon photodiode. Emission spectra were measured with a PR-705 SpectraScan Spectrophotometer (Photo Research).

2 Results and discussion

Figure 1 shows the PL spectra of various PFO thin films doped with FIrpic at different weight ratios: 0.1%, 1%, 8%, 10% and 100%. The PL spectrum of FIrpic peaked at 475 nm. In the spectra of the blended thin films, the peak at 425 nm originated from PFO, and no FIrpic emission was observed. That is to say, FIrpic was completely quenched even at high doping concentrations. Similar quenching phenomena have been observed before for conjugated polymers [20,21,23]. Previous studies showed that the lower triplet energy level of the polymer host would cause energy back transfer from phosphorescent dye to polymer, leading to phosphorescent quenching [20,21,23–25]. A schematic diagram of the energy levels for PFO, FIrpic and PVK is displayed in Figure 2. Since the triplet energy level of PFO (2.3 eV) [20] is lower than that of FIrpic (2.65 eV) [26], energy back transfer occurs from the triplet excitons on the FIrpic to the low-lying triplet states of PFO that causes the FIrpic quenching. Therefore, in the PL process, FIrpic was quenched by PFO because of the low-lying triplet energy level of PFO.

FIrpic quenching also occurs in the EL process, as inferred from the EL spectra of the devices without the PVK interlayer, ITO/PEDOT/PFO:OXD-7 (30 wt%):FIrpic (x wt%)/CsF/Al, with FIrpic weight ratios varying from 0, 0.1%, 1%, 8%, 10% to 16%, as seen in Figure 3. With no more than 1 wt% FIrpic, only the PFO emission was observed,

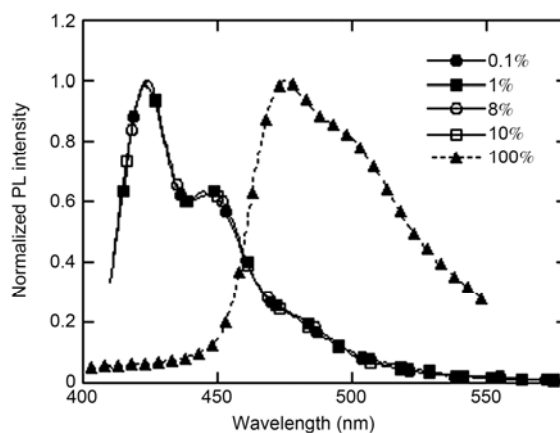


Figure 1 PL spectra of thin films, PFO doped with FIrpic at different weight ratios: 0.1%, 1%, 8%, 10% and 100%.

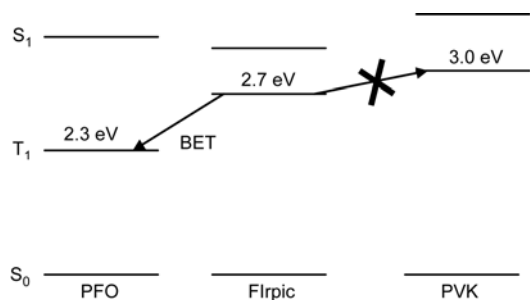


Figure 2 Schematic diagram of energy levels of PFO, Flrpic and PVK.

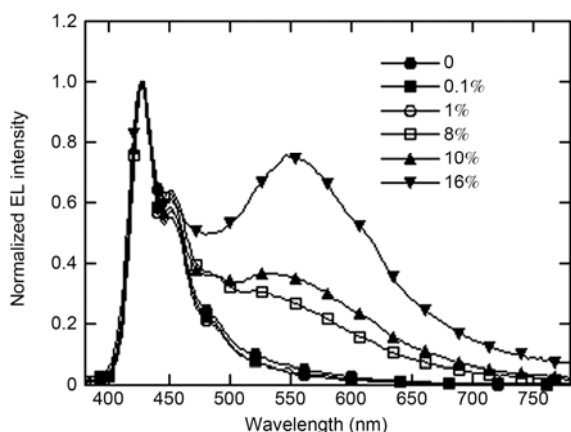


Figure 3 EL spectra of the devices without PVK layer, with Flrpic concentrations varying from 0, 0.1%, 1%, 8%, 10% to 16%.

the emission peak being located at 427 nm, along with a shoulder peak at 450 nm. In contrast to PL spectra, at high Flrpic concentrations of 8%, 10%, and 16%, Flrpic emissions were detected simultaneously with a peak at 547 nm that can be attributed to charge trapping of Flrpic in the EL process. Nevertheless, the relative intensity of Flrpic was much weaker than that of PFO, suggesting Flrpic quenching by PFO [20,21]. Therefore, in PFO matrix, Flrpic quenching has occurred in both PL and EL processes.

Device structures of PLEDs were modified by inserting

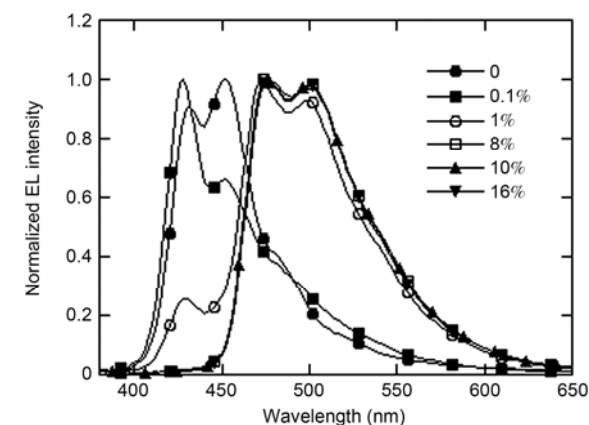
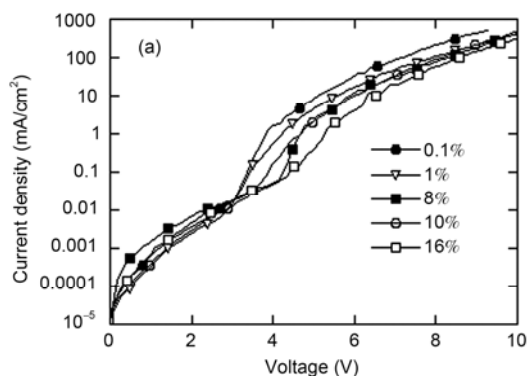


Figure 4 EL spectra of the devices with PVK layer, with Flrpic weight ratios varying from 0 to 16%.

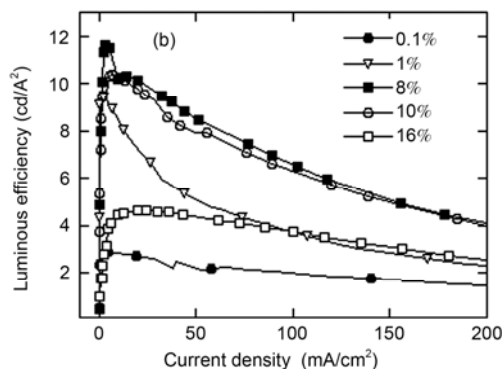


Figure 5 Characteristics of current density-voltage (a) and luminous efficiency-current density (b) of the PFO hosted devices at 0.1%, 1%, 8%, 10%, and 16% Flrpic.

HTL PVK between PEDOT and the EML. Figure 4 shows the EL spectra of devices with PVK interlayer, ITO/PEDOT/PVK/PFO: OXD-7 (30 wt%): Flrpic (x wt%)/CsF/Al, with Flrpic weight ratios of varied from 0 to 16%. With the exception of the PFO emission, another emission band was also observed clearly from Flrpic. Differing from the EL spectra of devices without PVK layer, here PFO was almost quenched at the low Flrpic concentration of 1 wt%, indicating the PVK layer suppressed the energy back transfer. Similar to previous research of ours on the host-guest combination of PFO and Ir(ppy)₃, exothermal energy-transfer quenching from the excited state of Ir(ppy)₃ was circumvented by inserting a PVK interlayer [20,21]. According to previous studies, two features of PVK were responsible for the minimization of phosphorescent quenching, the high lowest unoccupied molecular orbit (LUMO) level, and the high triplet energy level [20,21,27]. Since the LUMO of PVK (-2.0 eV) is much higher than that of PFO (-2.4 eV), electrons can be blocked by PVK at the PVK-EML interface. Thus, the recombination zone is located at the PVK-EML interface and excitons form on PVK at the interface [21]. As seen in Figure 2, PVK has a triplet energy level of 3.0 eV

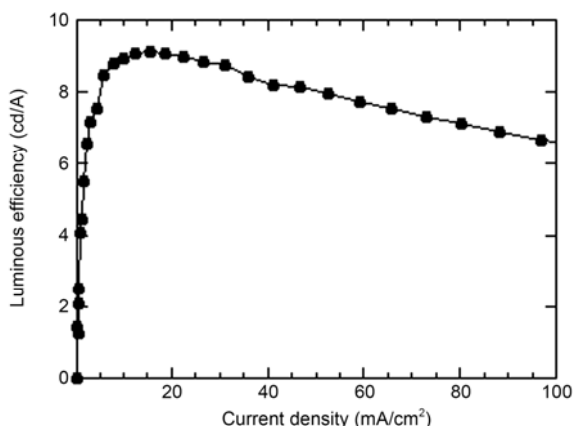


Figure 6 Luminous efficiency-current density characteristics of the PLED with PVK: OXD-7 (30 wt%) doped with 10 wt% FIrpic.

[27], which is much higher than the FIrpic level (2.65 eV), energy back transfer from FIrpic to PVK would not occur. The PVK excitons can be readily transferred to FIrpic, via Förster or Dexter energy transfer, leading to efficient blue electrophosphorescence [27]. Thus, quenching of the excited state of FIrpic to the triplet state of PFO is circumvented.

Current density-voltage and luminous efficiency-current density characteristics of the PLEDs with PVK interlayer and various FIrpic concentrations are shown in Figure 5. The luminous efficiencies show strong FIrpic concentration dependence, that increased with increasing FIrpic concentration up to 8 wt% and then decreased. The optimum device showed a maximum luminous efficiency of 11.5 cd/A with the 1931 CIE coordinates of (0.18, 0.41). PVK hosted PLED with the structure of ITO/PEDOT/PVK: OXD-7 (30 wt%): FIrpic (10 wt%) was tested [28], for which luminous efficiency-current density characteristic is shown in Figure 6. The maximum luminous efficiency was 9.1 cd/A, which was slightly lower than that of the PFO hosted device.

3 Conclusion

Highly-efficient blue phosphorescent PLEDs based on a PFO host were fabricated. Because of the low-lying triplet energy of PFO, energy back transfer occurred from FIrpic to PFO in both PL and EL processes. At high FIrpic-doping concentrations in PFO, only a weak emission from FIrpic was observed. By inserting a PVK interlayer, energy back transfer was suppressed; at low doping concentrations, PFO was completely quenched. A maximum luminous efficiency of 11.5 cd/A was achieved with 8 wt% FIrpic.

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