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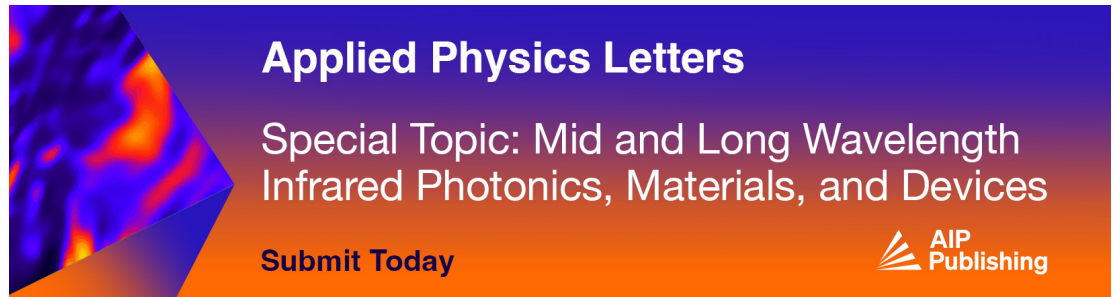


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Polymer electrophosphorescence devices with high power conversion efficiencies

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We demonstrate efficient single-layer polymer phosphorescent light-emitting devices based on a green-emitting iridium complex and a polymer host co-doped with electron-transporting and hole-transporting molecules. These devices can be operated at relatively low voltages, resulting in a power conversion efficiency of up to 24 lm/W at luminous efficiencies exceeding 30 cd/A. The overall performances of these devices suggest that efficient electrophosphorescent devices with acceptable operating voltages can be achieved in very simple device structures fabricated by spin coating. © 2004 American Institute of Physics. [DOI: 10.1063/1.1691194]

Intense research activities are currently being undertaken on organic light-emitting devices because of their potential for applications in flat panel displays and solid state lightening.^{1,2} Light-emitting materials for these devices can be divided into two general classes, those that are fluorescent and those which are phosphorescent. Phosphorescent light-emitting devices are particularly interesting for being able to utilize all the injected charges for emission.^{3–19} Among the phosphorescent dopants, iridium complexes are the most promising for their relatively short excited state lifetime and high photoluminescence (PL) efficiency. In fact, highly efficient green electrophosphorescence devices (30–70 lm/W) have been demonstrated in devices based on evaporated multilayer structures.^{5,6}

For the preparation of polymer phosphorescent light-emitting devices (PPLEDs), the commonly used concept is to blend a low molecular weight phosphorescent dye into a proper polymer matrix.^{8–18} Because a polymer host with a triplet state energy above that of the phosphorescent dye is required to guarantee the confinement of the triplet excited state on the guest, large band gap polymers such as poly(N-vinyl carbazole) (PVK) are commonly used in PPLEDs. However, the electron-transporting properties of PVK are poor and electron-transporting materials such as 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) have been blended with PVK to insure good efficiencies and low driving voltages.^{13–15,17} In those PVK-based PPLEDs, the guest emission in electroluminescence (EL) spectrum is far more intense than in the PL spectrum. This effect suggests that carrier trapping and subsequent recombination on the guest rather than energy transfer is the dominant excitation path of the triplet excited state of the phosphorescent guest.^{13–15,17} Even though the direct formation of the guest triplet state is the most elegant way to achieve good color purity and high efficiency, it is often accompanied by a high operating voltage due to the buildup of a space-charge field.

We have recently shown that improving the injection and transport of electrons via proper thermal treatment of the polymer layer and modification of the cathode avoids the

buildup of significant space charges in devices based on a PVK:PBD host.¹⁷ Moreover, at a sufficiently large PBD concentration, the current was mainly injection limited. But though these improvements resulted in a luminous efficiency of up to 27 cd/A, driving voltages were still high, which limited the maximum power conversion efficiency (PCE) to ~14 lm/W. This result can be explained in part by the rather large hole-injection barrier of ~0.7 eV from the used poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDT:PSS) anode into the highest occupied molecular orbital (HOMO) level of PVK at –5.8 eV.¹²

It has been realized that direct hopping of holes between Ir dyes becomes possible at higher guest concentrations.^{17–19} The fact that holes can be transported through the layer without the need for detrapping of charges to the PVK host suggests the possibility of improving hole injection and transport by introducing hole-transporting molecules with an ionization potential lower than that of PVK into the emission layer.

In this letter we report the performances of single-layer PPLEDs, co-doped with the hole-transporting molecule N,N'-diphenyl-N,N'-(bis(3-methylphenyl)-[1,1-biphenyl]-4,4'-diamine (TPD). TPD is particularly suitable because the HOMO level of TPD at –5.5 eV²⁰ is similar to that of Ir(ppy)₃ (–5.4 eV),¹⁹ but significantly higher than that of PVK. In fact, TPD was earlier shown to function as a hole trap at low concentration and a hole-transporting moiety at high loading when doped into PVK.²¹

Tris(2-(4-tolyl)phenylpyridine)iridium (Ir(mppy)₃) was obtained from American Dye Sources. PVK, TPD and PBD were purchased from Sigma-Aldrich. All the materials were used as received. A blend of PVK, PBD, TPD and Ir(mppy)₃ in chlorobenzene solution was spin coated on top of indium tin oxide substrates, precoated with PEDT:PSS layers. An ultrathin CsF interfacial layer with a nominal thickness of 1 nm was incorporated between the polymer layer and the aluminum metal cathode to promote electron injection.^{22–24} Details about the device preparation and characterization can be found in Ref. 17.

Figure 1 shows the current density-brightness-voltage properties of a device, based on a PVK emission layer containing 25 wt% PBD, 1 wt% Ir(mppy)₃ and 10 wt% TPD, compared to a control device without TPD. The turn-on volt-

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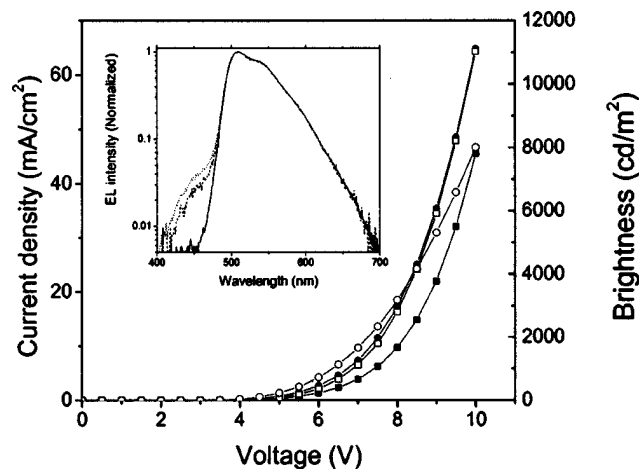


FIG. 1. Current density (solid symbols)-brightness (open symbols)-voltage characteristics of a single-layer PPLED device with a PVK(0.64)+PBD(0.25)+Ir(mppy)₃(0.01)+TPD(0.1) emission layer (circles) and of a corresponding control device without TPD (squares). The inset shows EL spectra of a device containing TPD driven at 10 mA/cm² (dashed line) and 40 mA/cm² (dotted line) and without TPD (solid line) driven at 40 mA/cm².

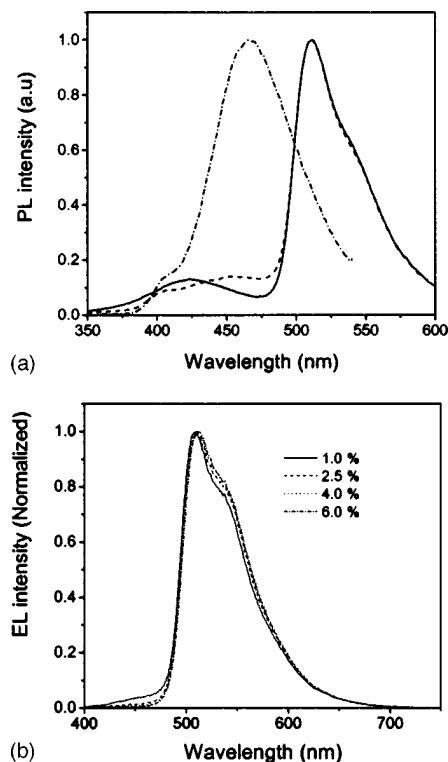


FIG. 2. (a) PL spectra of doped PVK films with the same composition as described in Fig. 1, either without TPD (solid line) or with TPD (dashed line); Also shown is the PL spectrum of TPD and PBD doped into polystyrene (PS) at a weight ratio TPD(0.4)+PBD(0.4)+PS(0.2) (dash-dot line). (b) EL spectra of devices with different Ir(mppy)₃ concentrations driven at 40 mA/cm². The TPD concentration was ~10 wt%

age (0.1 cd/m²) is significantly lowered upon addition of TPD, and the current remains larger for the TPD-doped device throughout the whole bias range. This suggests that addition of TPD improves the hole injection and transport. But though the brightness at a given bias is larger for the TPD-containing device at low current densities, it falls below that of the control device for large driving voltages. In order to understand this phenomenon, we have examined the EL spectra at different current densities. As shown in the inset of Fig. 1, the EL spectra of the devices with TPD reveal a weak but well-resolved blue emission contribution, which becomes more pronounced with increasing current density. Note that pure guest-emission in EL was observed in devices not containing TPD at an Ir(mppy)₃ concentration of as low as 0.3%.¹⁷ The blue emission band, deduced through subtracting the EL spectrum of a control device from that of the TPD-containing devices, shows a peak at ~470 nm and a shoulder at ~400 nm, similar to the PL spectrum of a film with the same composition as used in EL devices [Fig. 2(a)]. The shoulder at ~400 nm can be attributed to the emission of TPD or PVK while the peak at ~470 nm most likely originates from the emission of (TPD⁺PBD⁻)* exciplexes. The latter conclusion is supported by the PL spectrum of PBD+TPD blended in an inert polystyrene matrix [Fig. 2(a)]. Since the HOMO level of TPD is comparable to that of the Ir dyes, the holes will not be confined on the dye. Also, the lowest unoccupied molecular orbital level of TPD (-2.4 eV)²⁰ is similar to that of the dye (-2.4 eV),¹⁹ indicating that

the electron confinement on the dye is weak. Therefore, inefficient recombination of charges involving TPD is expected at low Ir(mppy)₃ concentrations. In order to circumvent this problem, we have systematically increased the Ir(mppy)₃ concentration. Figure 2(b) shows EL spectra of devices with a constant TPD concentration of ~10 wt% but different Ir(mppy)₃ concentrations, measured at an operating current density of 40 mA/cm². The intensity of blue emission band decreases with increasing Ir(mppy)₃ concentration and at an Ir(mppy)₃ concentration of ~4 wt%, the blue contribution has almost vanished. Concurrently, the efficiency of the devices increases significantly with increasing Ir(mppy)₃ concentration. We also found that the current densities of the devices increased with increasing Ir(mppy)₃ concentration, especially at large driving voltages. This implies that Ir(mppy)₃ itself participates in charge transport,¹⁷⁻¹⁹ especially in presence of the TPD co-dopant. In fact, in a series of devices with an Ir(mppy)₃ concentration of ~6 wt% and different amounts of TPD (Table I), the peak luminous effi-

TABLE I. Performances of PVK:PBD based single-layer devices with ~6% Ir(mppy)₃ and different TPD concentrations.

TPD concentration	Peak luminous efficiency	Voltages at 10 ² , 10 ³ , 10 ⁴ cd/m ²	PCE at 1000 cd/m ²	Brightness at 10 V
0%	23.7 cd/A	5.0 V, 6.9 V, >10 V	10.5 lm/W	8920 cd/m ²
6%	35.5 cd/A	4.4 V, 5.9 V, 8.8 V	17.6 lm/W	17 900 cd/m ²
9%	38.1 cd/A	4.3 V, 5.8 V, 8.6 V	19.8 lm/W	18 600 cd/m ²
12.5%	37.1 cd/A	4.2 V, 5.6 V, 8.4 V	19.8 lm/W	21 400 cd/m ²
19%	27.6 cd/A	4.1 V, 5.4 V, 8.2 V	15.2 lm/W	22 100 cd/m ²

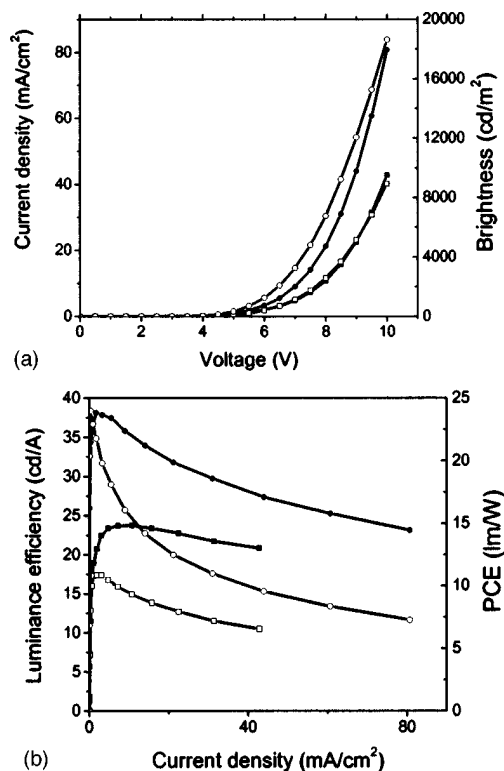


FIG. 3. (a) Current density (solid symbols)-brightness (open symbols)-voltage characteristics of a device containing PVK(0.61)+PBD(0.24)+Ir(mppy)₃(0.06)+TPD(0.09) (circles) and a control device without TPD (squares). (b) The corresponding luminous efficiency (solid symbols) and power conversion efficiency (open symbols) curves as a function of current density.

ciency increases largely when adding ~6 wt% of TPD, but further addition of TPD affects the driving voltages and peak efficiencies only slightly. Moreover, the luminous efficiency begins to decrease for TPD concentrations larger than 13 wt%, indicating that a large concentration of TPD disturbs the balance of carrier injection and transport.

Figure 3 shows the current density-brightness-voltage properties of a device with ~6 wt% Ir(mppy)₃ and 9 wt% TPD, compared to that of a control device without TPD. The peak luminous efficiency of the TPD-doped device is 38 cd/A at a current density of 1.8 mA/cm², a voltage of 5.5 V and a brightness of 700 cd/m², corresponding to an external quantum efficiency of 10.7%. The luminous efficiency of the devices is comparable to the best value of PPLEDs in literature.^{25,26} Moreover, the maximum PCE is 24 lm/W, with a current density of 0.4 mA/cm², a voltage of 4.4 V and a brightness of 136 cd/m². The operating voltages for 10², 10³, 10⁴ cd/m² are 4.3, 5.8, 8.6 V, respectively. These performances are approaching those of multilayer devices based on a 4-4'-N,N'-dicarbazole-biphenyl host, the low molecular weight counterpart to PVK.^{4,27-29} Finally, we would like to note that co-doping TPD was shown to improve the efficiency of multilayer devices based on europium complex doped into a PVK:PBD host.³⁰ We, therefore, expect that co-doping with hole-transporting moieties such as TPD may be a general scheme to improve the efficiency of PVK:PBD based devices.

In conclusion, we have been able to decrease the driving voltage of single-layer PPLEDs by co-doping the emission

layer with TPD. In this case, a high Ir(mppy)₃ concentration is required to ensure emission solely from the Ir(mppy)₃. As a result, PPLEDs with a peak external quantum efficiency of 10.7% and a power conversion efficiency of 24 lm/W at ~100 cd/m² was achieved in a simple device structure fabricated by spin coating.

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