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Highly efficient green phosphorescent organic light-emitting diodes with simplified device geometry

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We report on the performance of green phosphorescent organic light-emitting diodes based on the well-known host 4,4'-di(carbazol-9-yl)-biphenyl and the green phosphor emitter *fac* tris(2-phenylpyridinato-N,C^{2'}) iridium. Using a spin-coated hole-injection/transport layer of poly(*N*-vinyl-carbazole) and a hole-blocking/electron-transport layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, devices with efficiencies of 21.2% and 72 cd/A at 100 cd/m² were obtained in a simplified device geometry that requires the deposition of only two organic layers from the vapor phase. © 2008 American Institute of Physics. [DOI: 10.1063/1.2952452]

Since the report of efficient organic light-emitting diodes (OLED) based on phosphorescent emitters,¹ there has been a strong interest in these devices because singlet and triplet excited states can contribute to light emission, which can lead to an internal quantum efficiency of 100%. Therefore, much higher external quantum efficiencies (EQEs) can be achieved than with fluorescent OLEDs. In one of the first reports of an electrophosphorescent OLED, Baldo *et al.* used the green phosphorescent emitter *fac* tris(2-phenylpyridinato-N,C^{2'}) iridium, Ir(ppy)₃, as the emissive center and obtained a record high EQE of 7.5% (26 cd/A) at 100 cd/m².² Their device structure consisted of 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (α -NPD) as a hole-transport layer, 4,4'-di(carbazol-9-yl)-biphenyl (CBP) as a host for Ir(ppy)₃, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole-blocking layer, and tris(8-hydroxyquinolinato-N,O) aluminum (Alq₃) as an electron-transport layer. The device was capped with a Mg:Ag cathode.

Generally, OLEDs have higher efficiencies when alkali metal compounds, especially lithium compounds, are used as a buffer layer between the organic layer and the cathode.^{3,4} Such buffer layers enhance electron injection, which leads to lower turn-on voltages and higher efficiencies. For example, Tsutsui *et al.* have been able to improve the performance of the previously mentioned devices by using a Li₂O/aluminum cathode instead of the Mg:Ag cathode.⁵ EQEs of 13.7% at 105 cd/m² were measured.

Since then, several teams have modified the structure and the nature of the materials in those devices to improve efficiency, light output, and turn-on voltage.^{6–11} Most of the cited references report efficiencies of up to 19.0% for optimized devices while Tanaka *et al.* reach efficiencies of up to 29%.⁶ However, the most efficient devices (higher than 20% EQE) are based on complex device structures with at least four organic layers, three of which are deposited from the vapor phase. The rather slow deposition rate of organic lay-

ers (1 Å/s) can be a limiting factor in the manufacturing cost of such devices. Therefore, device geometries in which fewer organic materials and fewer layers are deposited from the vapor phase and in which high efficiency is maintained are desirable.

In this paper, we show that the efficiency of phosphorescent OLEDs based on the well-known host-guest matrix CBP:Ir(ppy)₃ can be significantly improved by tuning the ionization potential (I_p) and the hole-mobility (μ_h) of the hole-injection/transport layer. In addition, the device structure is simplified by using a wet-processable material and by reducing the number of subsequent evaporated layers without compromising the performance. For this study, we used a series of cross-linkable side-chain copolymers based on *N,N'*-bis(*m*-tolyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD).¹² The ionization potentials of these copolymers can easily be tuned by using differently substituted TPD side-chain moieties (Fig. 1). The estimated ionization potential of these TPD copolymers (P1–P4) ranges from 5.2 to 5.5 eV while the hole mobilities, characterized by the time-of-flight technique at an applied electric field of 4×10^5 V/cm and at room temperature, decrease from 1.8

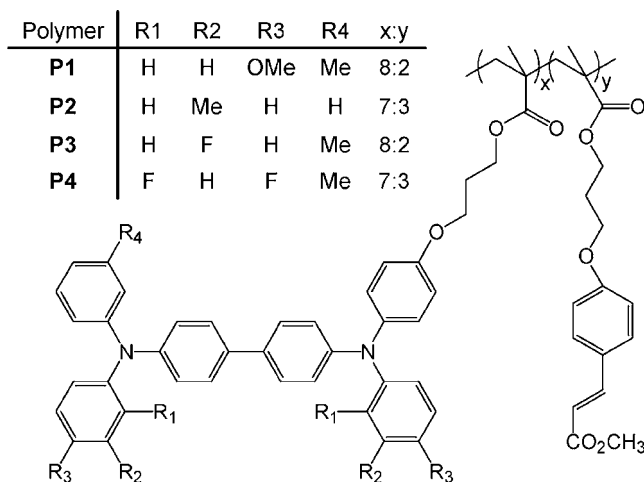


FIG. 1. Structure of cross-linkable TPD-based copolymers.

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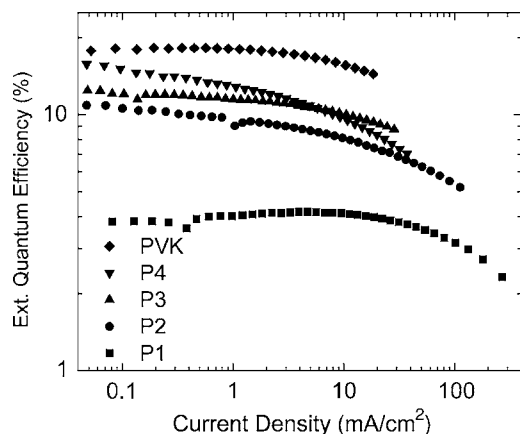


FIG. 2. EQE as a function of the current density for OLEDs with device structure ITO/HTM (25–35 nm)/CBP:Ir(ppy)₃ (6%, 20 nm)/BCP (6 nm)/Alq₃ (20 nm)/LiF (1 nm)/Al.

$\times 10^{-5}$ to 5.9×10^{-7} cm²/V s.¹³ To complete the study, we also tested poly(*N*-vinyl-carbazole) (PVK) which has a higher ionization potential of 5.8 eV (Ref. 14) and a lower mobility in the range of 10^{-8} – 10^{-7} cm²/V s.¹⁵

TPD-copolymer films of 35 nm thickness (25 nm for PVK) were spin coated from toluene onto air-plasma treated indium tin oxide (ITO) coated substrates in a nitrogen inert atmosphere. The TPD-polymer films were cross-linked for 1 min under $700 \mu\text{W}/\text{cm}^2$ of a broadband UV light. The substrates were then loaded into a Kurt J. Lesker Spectros vacuum system without being exposed to atmosphere. For all subsequent organic layers, materials were first purified using gradient zone sublimation, and were then thermally evaporated at a rate of $1 \text{ \AA}/\text{s}$ and at a pressure below 1×10^{-7} Torr on top of the hole-transport layers. For the emitting layer, a concentration of 6% Ir(ppy)₃ was coevaporated into a 20-nm-thick film of CBP. A 6-nm-thick layer of BCP was used as a hole-blocking layer, followed by a 20-nm-thick layer of Alq₃ as an electron-transport layer. Finally, a 1-nm-thick layer of lithium fluoride (LiF) was deposited as an electron injection layer, followed by a 200-nm-thick Al cathode. The testing was done in inert atmosphere after fabrication without exposing the devices to air.

The EQEs are shown as a function of the current densities in Fig. 2 for the devices with the five different hole-transport materials (HTMs). EQE, luminous efficiency, and power efficiency at 100 cd/m² are listed in Table I. While devices with P1 ($I_p=5.2$ eV, $\mu_h=1.8 \times 10^{-5}$ cm²/V s) show the lowest EQE of 4.0% at 100 cd/m², devices with PVK ($I_p=5.8$ eV, $\mu_h=4.5 \times 10^{-7}$ cm²/V s) exhibit an EQE of up to 18.1% at 100 cd/m². These results indicate that the efficiency increases with an increasing ionization potential and a decreasing hole mobility of the HTM. These two effects both lead to a reduction of the injected hole current relative to the electron current, resulting in an improved charge balance. This hypothesis is in agreement with previous studies.^{16–20} We note that results obtained in other studies did not support this explanation.^{21–23} To further investigate the observed effect, we prepared and characterized hole carrier devices with the structure ITO/HTM (25–35 nm)/CBP:Ir(ppy)₃ (6%, 20 nm)/aluminum (200 nm). A significant decrease in current density was observed in devices using HTMs with increasing ionization potential and decreasing hole mobility,

TABLE I. Ionization potentials, hole-mobility values, and triplet energy of the five different HTMs used in this study, and device performance at 100 cd/m² of OLEDs with device structure ITO/HTM/CBP:Ir(ppy)₃/BCP/Alq₃/LiF/Al.

HTM	I_p (eV)	Hole mobility ^a (cm ² /Vs)	Triplet energy (eV)	EQE (%)	Luminous efficiency (cd/A)
P1	5.25 ^b	1.8×10^{-5}	2.48 ^c	4.0	14
P2	5.34 ^b	6.4×10^{-6}	2.49 ^c	10.2	35
P3	5.45 ^b	7.2×10^{-7}	2.51 ^c	12.0	41
P4	5.47 ^b	5.9×10^{-7}	2.56 ^c	14.3	49
PVK	5.8 ^d	4.5×10^{-7}	3.0 ^e	18.1	62

^aMeasured at 4×10^5 V/cm and T=297 K. The mobilities of P1–P4 were reported by Domercq *et al.* (see Ref. 13). The hole mobility of PVK was measured by a time-of-flight experiment.

^bCalculated from electrochemistry (see Ref. 13).

^cCalculated in a similar framework as Ref. 28.

^dEstimated from photoemission spectroscopy (see Ref. 14).

^eSee Ref. 25.

therefore further supporting the charge balance optimization explanation.

However, another possible origin of the increase in device efficiency can be attributed to an increase in the triplet energy of the HTM that can reduce nonradiative recombination through energy transfer from the emissive excited state of Ir(ppy)₃ to the triplet state of the HTM.²³ As shown in Table I, the calculated triplet level energies of polymers P1–P4 vary only by 0.08 eV. However, their average value is close to that of Ir(ppy)₃ (2.4 ± 0.1 eV).²⁴ Hence, small variations could lead to changes in efficiency. On the other hand, when using PVK with a triplet energy of 3.0 eV,²⁵ the non-radiative loss mechanism should be significantly reduced.

The fabrication process for a highly efficient electrophosphorescent OLED was further simplified and improved by increasing the thickness of the BCP layer and removing Alq₃ as the electron-transport layer. It has been shown that BCP has an electron mobility that is at least an order of magnitude larger than that of Alq₃,^{26,27} and, therefore, better charge balance can be expected with a BCP electron-transport layer. OLEDs with the structure ITO/PVK (35 nm)/CBP:Ir(ppy)₃ (6%, 20 nm)/BCP (40 nm)/LiF (2.5 nm)/aluminum (200 nm) showed lower turn-on voltage and higher efficiencies than the devices reported above with an Alq₃ electron-transport layer (Fig. 3). An optimized PVK and LiF thickness of 35 and 2.5 nm, respectively, were used to reduce leakage current at low applied voltage. An EQE of 21.2% at 100 cd/m² was obtained, leading to a luminous efficiency of 72 cd/A. This is the highest efficiency achieved in a device comprised of less than four organic layers. It should also be noted that all of the materials used for this high-efficiency device are commercially available while other reports with high efficiencies typically include some specialty compounds. Furthermore, the hole-transport layer is processed from solution, which reduces the overall deposition time of the remaining two organic layers that are deposited from the vapor phase at low deposition rates ($1 \text{ \AA}/\text{s}$).

In conclusion, we show that the efficiency in devices based on CBP:Ir(ppy)₃ can be improved by using HTMs with increased ionization potential and lower hole mobility. Using BCP as hole-blocking and electron-transport material, the efficiency could be further increased. Devices structures

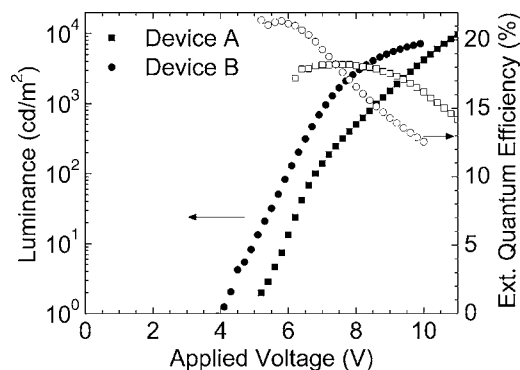


FIG. 3. Luminance (solid shapes) and EQE (empty shapes) as a function of the applied voltage for device A (squares): ITO/PVK (25 nm)/CBP:Ir(ppy)₃ (6%, 20 nm)/BCP (6 nm)/Alq₃ (20 nm)/LiF (1 nm)/Al, and for device B (circles): ITO/PVK (35 nm)/CBP:Ir(ppy)₃ (6%, 20 nm)/BCP (40 nm)/LiF (2.5 nm)/Al.

with ITO/PVK/CBP:Ir(ppy)₃/BCP/LiF/Al showed an improved EQE of 21.2% (72 cd/A) at 100 cd/m². These high efficiencies have been obtained using a simplified device structure requiring the deposition of only two organic layers from the vapor phase.

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