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Very high-efficiency green organic light-emitting devices based on electrophosphorescence

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We describe the performance of an organic light-emitting device employing the green electrophosphorescent material, *fac* tris(2-phenylpyridine) iridium [Ir(ppy)₃] doped into a 4,4'-N,N'-dicarbazole-biphenyl host. These devices exhibit peak external quantum and power efficiencies of 8.0% (28 cd/A) and 31 lm/W, respectively. At 100 cd/m², the external quantum and power efficiencies are 7.5% (26 cd/A) and 19 lm/W at an operating voltage of 4.3 V. This performance can be explained by efficient transfer of both singlet and triplet excited states in the host to Ir(ppy)₃, leading to a high internal efficiency. In addition, the short phosphorescent decay time of Ir(ppy)₃ (<1 μs) reduces saturation of the phosphor at high drive currents, yielding a peak luminance of 100 000 cd/m². © 1999 American Institute of Physics. [S0003-6951(99)00127-8]

The recent demonstration^{1,2} of high-efficiency red electrophosphorescence from a platinum porphyrin foreshadowed a breakthrough in organic light-emitting device (OLED) performance. Unlike fluorescence,³ phosphorescence makes use of both singlet and triplet excited states, suggesting^{1,2,4} the potential for reaching a maximum internal efficiency of 100%. However, at the benchmark luminance of 100 cd/m², the porphyrin of the initial studies exhibits an external quantum efficiency of 2.2%, substantially less than its quantum efficiency at low currents (5.6%). Although its efficiency at 100 cd/m² is highly competitive with red fluorescent dyes of comparable color saturation,² that phosphor is hampered by a long decay time, causing saturation of emissive sites and a decrease in efficiency at high drive currents. Consequently, it fails to realize the potential of phosphorescence: external quantum efficiencies of ~10% with correspondingly high power efficiencies.

In this work, we describe OLEDs employing the green, electrophosphorescent material *fac* tris(2-phenylpyridine) iridium [Ir(ppy)₃].⁵⁻⁸ The coincidence of a short triplet lifetime and reasonable photoluminescent efficiency allows Ir(ppy)₃-based OLEDs to achieve peak quantum and power efficiencies of 8.0% (28 cd/A) and 31 lm/W, respectively. At an applied bias of 4.3 V, the luminance reaches 100 cd/m², and the quantum and power efficiencies are 7.5% (26 cd/A) and 19 lm/W, respectively.

Fluorescence is limited to radiative relaxations of organic molecules that conserve spin symmetry. These processes are extremely rapid (~1 ns), and typically involve transitions between singlet excited and ground states. In con-

trast, phosphorescence results from “forbidden” transitions where symmetry is not conserved, for example, transitions between triplet excited states and singlet ground states. Under electrical excitation, excitons are formed in both symmetry states; thus, harvesting luminescence from all excitons has the potential to yield significantly higher efficiencies than is possible in purely fluorescent devices.

To maximize performance, electrophosphorescent devices should employ a conductive host material with a phosphorescent guest sufficiently dispersed to avoid “concentration quenching.” Although some phosphorescent guests may trap charge and form excitons directly, it is likely that if host emission is to be avoided, then some form of energy transfer to the guest is necessary. Since the triplet energy levels in the host and the absorption of the guest triplet state are frequently unknown and, moreover, are difficult to quantify, optimizing guest–host systems for resonant triplet transfer is problematic. Comparisons of the absorption of the guest and the emission spectrum of the host are relevant only to the transfer of singlet states, but may nevertheless give a general indication of the likelihood for triplet transfer. Based on this assumption, the blue (λ ~ 400 nm peak) emissive material 4,4'-N,N'-dicarbazole-biphenyl (CBP)⁹ was chosen as the host for Ir(ppy)₃. In previous work,² it was found that CBP formed a suitable host for the red phosphor 2,3,7,8,12,13,17,18-octatethyl-21H,23H-porphine platinum (PtOEP).

A proposed energy level¹⁰ diagram, together with the molecular structural formulas of some of the materials used in the OLEDs, is shown in Fig. 1. Organic layers were de-

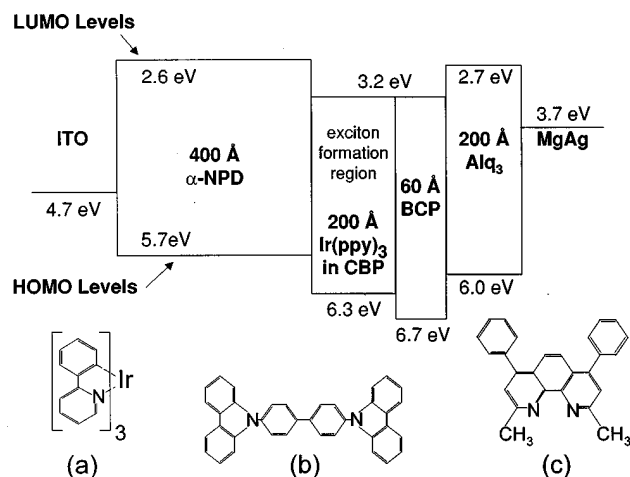


FIG. 1. Proposed energy level structure of the electrophosphorescent device. The highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy are also shown (see Ref. 10). Note that the HOMO and LUMO levels for Ir(ppy)_3 are unknown. The inset shows the chemical structural formulas of (a) Ir(ppy)_3 , (b) CBP, and (c) BCP.

posited by high-vacuum (10^{-6} Torr) thermal evaporation onto a cleaned glass substrate precoated with transparent, conductive indium–tin–oxide. A 400-Å-thick layer of 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino] biphenyl (α -NPD) is used to transport holes to the luminescent layer consisting of Ir(ppy)_3 in CBP. A 200-Å-thick layer of the electron transport material tris-(8-hydroxyquinoline) aluminum (Alq_3) is used to transport electrons into the Ir(ppy)_3 :CBP layer, and to reduce Ir(ppy)_3 luminescence absorption at the cathode. A shadow mask with 1-mm-diam openings was used to define the cathode consisting of a 1000-Å-thick layer of 25:1 Mg:Ag, with a 500-Å-thick Ag cap. As previously,² we found that a thin (60 Å) barrier layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, or BCP)¹¹ inserted between the CBP and the Alq_3 was necessary to confine excitons within the luminescent zone and hence maintain high efficiencies. In Ref. 2, it was argued that this layer prevents triplets from diffusing outside of the doped region. It was also suggested that CBP may readily transport holes and that BCP may be required to force exciton formation within the luminescent layer. Transient studies of triplet exciton diffusion within CBP are currently in progress in an effort to resolve this question. In either case, the use of BCP in the structure in Fig. 1 clearly serves to trap excitons within the luminescent region.

Figure 2 shows the external quantum efficiencies of several Ir(ppy)_3 -based OLEDs. The doped structures exhibit a slow decrease in quantum efficiency with increasing current. Similar to the results for the Alq_3 :PtOEP system, the doped devices achieve a maximum efficiency ($\sim 8\%$) for mass ratios of Ir(ppy)_3 :CBP of approximately 6%–8%. Thus, the energy transfer pathway in Ir(ppy)_3 :CBP is likely to be similar to that in $\text{PtOEP}:\text{Alq}_3$,^{1,2} i.e., via short-range Dexter transfer of triplets from the host. At low Ir(ppy)_3 concentrations, the lumophores often lie beyond the Dexter transfer radius of an excited Alq_3 molecule, while at high concentrations, aggregate quenching is increased. Note that dipole–dipole (Förster) transfer is forbidden for triplet transfer, and

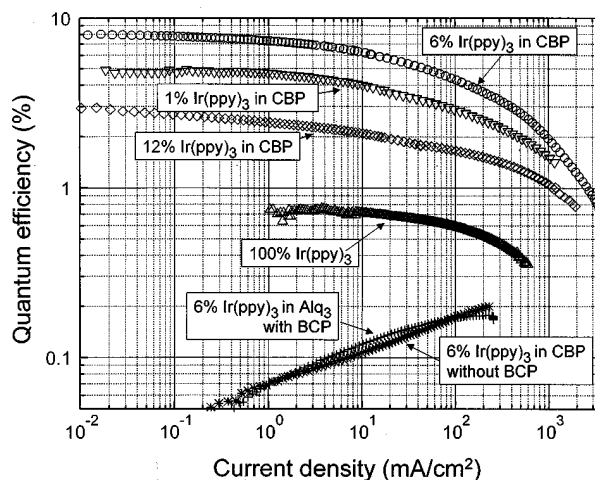


FIG. 2. The external quantum efficiency of OLEDs using Ir(ppy)_3 :CBP luminescent layers. Peak efficiencies are observed for mass ratio of 6% Ir(ppy)_3 :CBP. The 100% Ir(ppy)_3 device has a slightly different structure than shown in Fig. 1: the Ir(ppy)_3 layer is 300 Å thick and there is no BCP blocking layer. The efficiency of a 6% Ir(ppy)_3 :CBP device grown without a BCP layer is also shown.

in the $\text{PtOEP}:\text{Alq}_3$ system direct charge trapping was not found to be significant.

In addition to the doped device, we fabricated a heterostructure where the luminescent region was a homogeneous film of Ir(ppy)_3 . The reduction in efficiency (to $\sim 0.8\%$) of neat Ir(ppy)_3 is reflected in the transient decay, which has a lifetime of only ~ 100 ns, and deviates significantly from mono-exponential behavior. A 6% Ir(ppy)_3 :CBP device without a BCP barrier layer is also shown together with a 6% Ir(ppy)_3 : Alq_3 device with a BCP barrier layer. Here, very low quantum efficiencies are observed to increase with current. This behavior suggests a saturation of nonradiative sites as excitons migrate into the Alq_3 , either in the luminescent region or adjacent to the cathode.

In Fig. 3, we plot luminance and power efficiency as functions of voltage. The peak power efficiency is 31 lm/W with a quantum efficiency of 8%, (28 cd/A). At 100 cd/m², a power efficiency of 19 lm/W with a quantum efficiency of 7.5% (26 cd/A) is obtained at a voltage of 4.3 V. The tran-

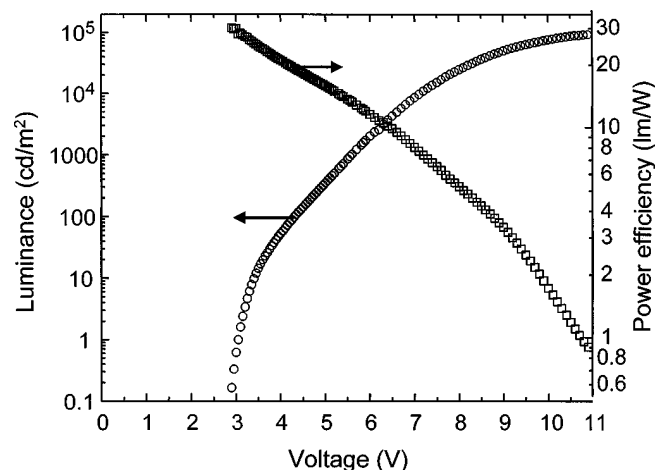


FIG. 3. The power efficiency and luminance of the 6% Ir(ppy)_3 :CBP device. At 100 cd/m², the device requires 4.3 V and its power efficiency is 19 lm/W.

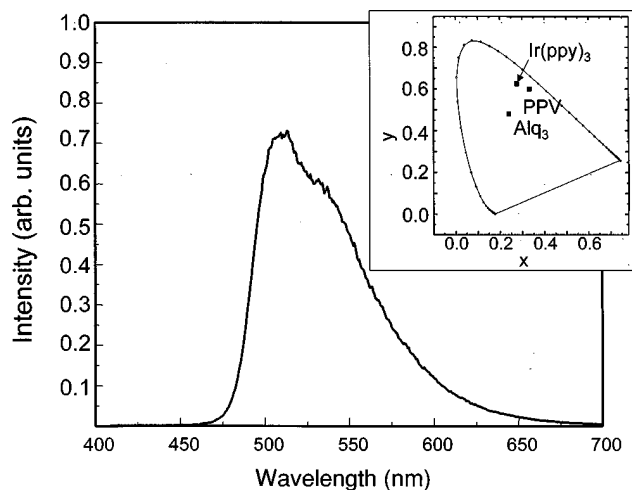


FIG. 4. The electroluminescent spectrum of 6% Ir(ppy)₃:CBP. Inset: the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates of Ir(ppy)₃ in CBP are shown relative to the fluorescent green emitters Alq₃ and poly(*p*-phenylenevinylene) (PPV).

sient response of Ir(ppy)₃ in CBP is a mono-exponential phosphorescent decay of ~ 500 ns, compared with a measured lifetime^{5,6,8} of 2 μ s in degassed toluene at room temperature. These lifetimes are short and indicative of strong spin orbit coupling, and together with the absence of Ir(ppy)₃ fluorescence in the transient response, we expect that Ir(ppy)₃ possesses strong intersystem crossing from the singlet to the triplet state. Thus, all emission originates from the long-lived triplet state. Unfortunately, slow triplet relaxation can form a bottleneck in electrophosphorescence and one principal advantage of Ir(ppy)₃ is that it possesses a short triplet lifetime. The phosphorescent bottleneck is thereby substantially loosened. This results in only a gradual decrease in efficiency with increasing current, leading to a maximum luminance of $\sim 100\,000$ cd/m².

In Fig. 4, the emission spectrum and Commission Internationale de L'Eclairage (CIE) coordinates of Ir(ppy)₃ are shown for the highest efficiency device. The peak wavelength is $\lambda = 510$ nm, and the full width at half maximum is 70 nm. The spectrum and CIE coordinates ($x = 0.27, y = 0.63$) are independent of current. Even at very high current densities (~ 100 mA/cm²), blue emission from CBP is negligible—an indication of complete energy transfer.

We note that the device structure has the potential for further optimization. For example, the use of LiF cathodes,^{12,13} shaped substrates,¹⁴ and novel hole transport materials¹⁵ that result in a reduction in operating voltage or increased quantum efficiency are also applicable to this work. These methods have yielded power efficiencies of ~ 20 lm/W in fluorescent small molecule devices.¹⁵ The quantum efficiencies in those devices¹⁶ at 100 cd/m² is typically $\leq 5\%$, and hence green-emitting electrophosphorescent devices with power efficiencies of > 40 lm/W can be expected.

Given the performance advantage inherent to phosphorescence, new phosphors deserve intensive investigation. It has been noted¹⁷ that, since triplet emission is typically red-shifted from singlet emission, it may be difficult to find guest/host systems where the phosphorescent guest emits in the blue or green. Indeed, although fluorescent energy trans-

fer in the blue has been demonstrated using CBP and perylene,¹⁸ the additional exchange energy loss must be overcome at some stage in energy transfer to the triplet state of the phosphorescent guest. This may be a problem in the blue, where wide-gap (~ 3.5 eV) host materials are necessary. However, it is clear from this work that the efficiency improvements offered by phosphorescence outweigh the slight increase in voltage that results from the use of large-energy-gap materials. The alternative is to employ the phosphorescent material as an undoped film, with an attendant loss in efficiency.

Of the few phosphorescent compounds investigated to date, the purely organic materials¹⁹ possess insufficient spin orbit coupling to show strong phosphorescence at room temperature. While one should not rule out the potential of purely organic phosphors, the most promising compounds may be transition-metal complexes with aromatic ligands. The transition metal mixes singlet and triplet states, thereby enhancing intersystem crossing and reducing the lifetime of the triplet excited state. As demonstrated in this work, reasonable photoluminescent efficiencies and lifetimes on the order of 1 μ s are sufficient for high-performance devices.

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