

High-performance polymer light-emitting diodes doped with a red phosphorescent iridium complex

Fang-Chung Chen and Yang Yang^{a)}

Department of Materials Science and Engineering, University of California at Los Angeles, Los Angeles, California 90095

Mark E. Thompson

Department of Chemistry, University of Southern California, Los Angeles, California 90089

Junji Kido

Graduate School of Science and Engineering, Yamagata University, Yamagata 992-8510, Japan

(Received 28 November 2001; accepted for publication 21 January 2002)

High efficiency has been achieved in polymer light-emitting diodes (PLEDs) exhibiting red emission by doping a fluorescence host material, poly(vinylcarbazole) (PVK), with an iridium(III) complex, bis[2-(2'-benzothienyl)-pyridinato-N,C^{3'}]iridium(acetylacetonate) (BtpIr). The electroluminescence spectrum has a maximum wavelength of 614 nm. The highest external quantum efficiency is 3.3%. Due to its short triplet excited lifetime ($\sim 5 \mu\text{s}$), the quenching of the triplet exciton in BtpIr-doped PVK PLEDs has been shown to be suppressed compared to platinum(II)-2,8,12,17-tetraethyl-3,7,13,18-tetramethylporphyrin-doped PVK PLEDs. 65% of the peak efficiency can be sustained at high-current density and at the very high brightness of 1350 cd/m^2 . We suggest that both triplet-triplet annihilation and polaron-triplet annihilation involves exciton quenching. © 2002 American Institute of Physics. [DOI: 10.1063/1.1462862]

Polymer light-emitting diodes (PLEDs) are promising candidates for the next-generation displays, particularly for portable electronic devices such as cellular phones.¹ One of the major concerns for the displays on portable devices is the quantum and power efficiencies of the PLEDs, since these are directly related to the battery usage. One common way to enhance the quantum efficiency of a PLED is to dope polymer host materials with dyes having high-photoluminescence (PL) efficiency.² This way significantly cuts down the concentration quenching by isolating emitting sites. Recently, phosphorescent dopants have been successfully used in organic light-emitting diodes (OLEDs) to improve the device performance by breaking the spin conservation rule. The harvesting of both singlet and triplet excitons has led to very high-efficiency OLEDs.³⁻⁵ The high efficiency of red PLEDs doped with the phosphorescent dopant, platinum(II) porphyrins, have also been demonstrated.⁶⁻⁸ However, for most of these LEDs, the device quantum efficiencies drop rapidly with increasing current density, and consequently with the brightness, due to the long phosphorescent lifetime. Triplet excitons relax much more slowly and can potentially cause saturation of the emission sites. In addition, two possible triplet exciton quenching mechanisms, triplet-triplet (TT) annihilation⁹ and polaron-triplet (PT) annihilation^{9,10} have been proposed. For phosphorescent OLEDs, the major quenching has proved to be TT annihilation.⁹ The longer lifetime for triplet excitons actually diminishes one of the advantages of dye doping of organic light-emitting devices, the ability to eliminate concentration quenching. One way to remedy these problems is to use dopants with shorter triplet exciton lifetime.³

By virtue of the strong spin-orbit coupling of the heavy metal center, Ir complexes usually have efficient phosphorescence and short lifetimes, which typically range from 1 to 14 μs .¹¹ The shorter exciton lifetime makes Ir complexes more attractive candidates than platinum porphyrins, which usually have about one order of magnitude longer lifetime. By lowering the ligand triplet³ ($\pi-\pi^*$) energy level, Ir complex, bis[2-(2'-benzothienyl)-pyridinato-N,C^{3'}]iridium(acetylacetonate) (BtpIr), with red emission has been synthesized and successfully used as the dopant to fabricate high-efficiency small-molecule organic electroluminescent devices.^{11,12} In this study, the high performance of BtpIr-doped polymer light-emitting diodes is reported. The high efficiencies have been achieved at both low- and high-current-density regimes. Exciton quenching is also investigated and discussed in this manuscript.

Two polymers, poly(vinylcarbazole) (PVK) and poly[9,9-bis(octyl)-fluorene-2,7-diyl] (PF) were chosen as the host materials for the PLEDs. For comparison, BtpIr and PtOX were used as dopants. To achieve charge balance, two types of PLED structures were designed for the two different host materials, respectively;¹³ type I: ITO/PEDOT/PVK-PBD-dopant/Ca/Al and type II: ITO/PEDOT/PVK/doped PF/Ca/Al. Bilayer electrodes, consisting of indium-tin-oxide (ITO)/glass substrate coated with a thin layer of conducting polymer (PEDOT 3,4-polyethylenedioxythiophene-polystyrenesulfonate), were used as the anode in all of our devices. For optical measurements, such as photoluminescence spectra, thin films of polymers were spin coated from solution onto quartz substrates. For type-I devices, a single layer of polymer (PVK) consisting of 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD), an electron transport medium, at 1:1 weight ratio and light-emitting dopants

^{a)}Electronic mail: yangy@ucla.edu

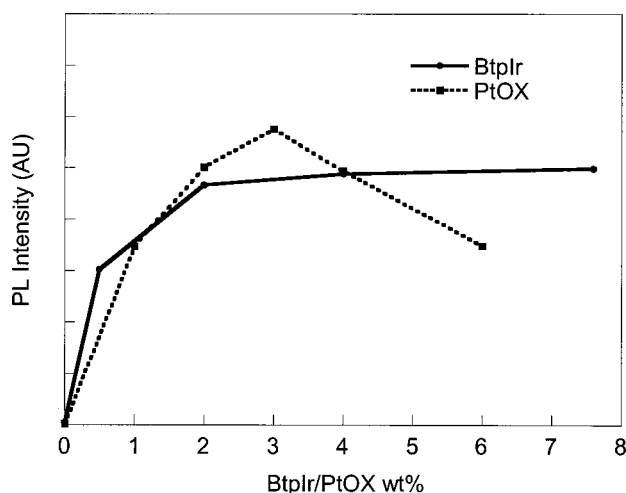


FIG. 1. The photoluminescence intensities of dopants, PtOX and BtpIr, in the PVK/PBD matrix as a function of dopant concentration. The PL intensities were measured at 647 nm and 614 nm for PtOX and BtpIr emission, respectively.

were used as the active material. For type-II devices, bilayer polymer films consisting of a 20-nm-thick hole-transporting layer (PVK) and a second layer of PF doped by iridium complexes were used as the active medium.^{6,13} The thicknesses of these two types of devices are ~ 100 nm. Calcium (500 Å)/aluminum (1000 Å) bilayer cathodes were used in all of our devices. Thermal evaporation of the calcium was carried out at 1×10^{-6} Torr vacuum, followed by an overcoating of the aluminum layer. All devices were fabricated and tested under nitrogen environment.

The self-quenching of PtOX in PF thin films has been reported.^{6,7} Similar phenomena can also be observed when PtOX is doped into PVK films. Figure 1 shows the PL intensities of the host and of the dopant at different PtOX concentrations in the PVK:PBD thin films. As expected, energy transfer from the host to the guest was observed. However, when the dopant concentration exceeded 3 wt %, the emission from PtOX went down. The long lifetime of the PtOX exciton increases the probability of self-quenching, such as by excimer formation or TT annihilation. On the contrary, when BtpIr, which has a shorter lifetime (~ 5 μ s), was doped into PVK/PBD mixing thin films, the emission from BtpIr increased with dopant concentration in the beginning of the doping process and then steadily saturated. By comparing these two different results, we conclude that the self-quenching can be suppressed for BtpIr-doped PVK thin films due to the shorter lifetime of BtpIr excitations. Thus, we expect the BtpIr-doped PLEDs will have the better performance.

Figure 2 shows the I - L - V curve of the PVK device doped with 4% BtpIr. The light turn-on voltage, defined arbitrarily as the brightness of 0.1 cd/m^2 , was 6.5 V. The maximum external quantum efficiency and the highest brightness were 3.3% and 1400 cd/m^2 , respectively. The inset of Fig. 2 shows the electroluminescence (EL) spectrum of a BtpIr-doped PVK device. The EL spectrum maximum was at a wavelength of $\lambda_{\text{max}}=614$ nm, and the red electroluminescence is identical to the PL emission. The Commission Internationale de L'Eclairage chromaticity coordinate is (0.66,0.33), which is very close to the NTSC standard for red

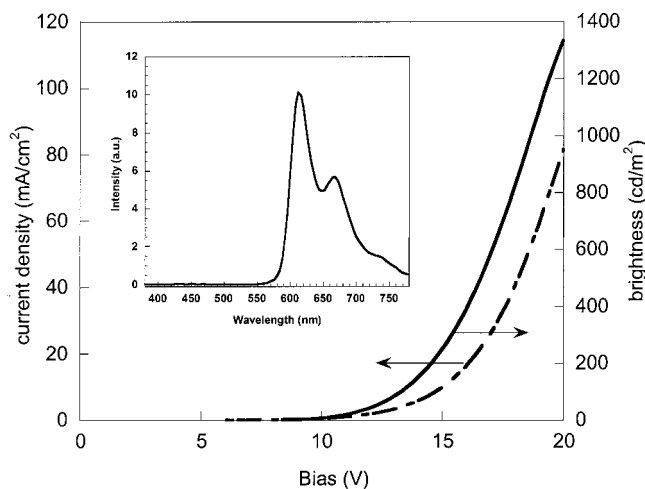


FIG. 2. Current-light-voltage curves of PLEDs with 4% BtpIr-doped PVK as the emitting medium. Inset shows electroluminescence from the same device.

subpixels of CRT displays. The EL emission spectrum was independent of the current density, and no host emission was observed. This implies that there was efficient energy transfer from PVK to BtpIr under electrical excitation. On the other hand, the optimized dopant concentration for the BtpIr-doped PF device was 5 wt %. The highest quantum efficiency obtained was 2.4%, while the maximum brightness was about 800 cd/m^2 . All the device performances are summarized in Table I. PtOX-doped devices with corresponding concentrations are listed for comparison. From Table I, one can clearly see that the PVK devices have a better performance than PF devices, which we attribute to the more efficient energy transfer from the host to dopants and better triplet exciton confinement on the dopants.¹³ The fluorescence of PVK comes from excimer emission, and hence, has a longer lifetime (~ 35 ns).¹⁴ The host triplet exciton lifetimes of PVK and PF are about 100 and 2.5 ms, respectively.¹⁵ It was reported earlier that a longer lifetime of the host material can facilitate the energy transfer.^{3,13}

As shown in Fig. 3, the quantum efficiencies of these

TABLE I. Device performance of type-I and type-II devices.

Host	Dopant (wt %)	Maximum QE at mA/cm^2 brightness (cd/m^2)	QE at high-current density at mA/cm^2 QE/maximum QE	Maximum brightness (cd/m^2)
PVK	BtpIr(4%)	3.3%	2.2%	1400
		5.7	80	
		147	65%	
PVK	PtOX(4%)	2.5%	0.79%	270
		3.1	60	
		28	32%	
PVK	BtpIr(5%)	2.4%	1.0%	800
		1.3	80	
		25	43%	
PF	PtOX(5%)	1.2%	0.26%	125
		1.7	80	
		12	21%	

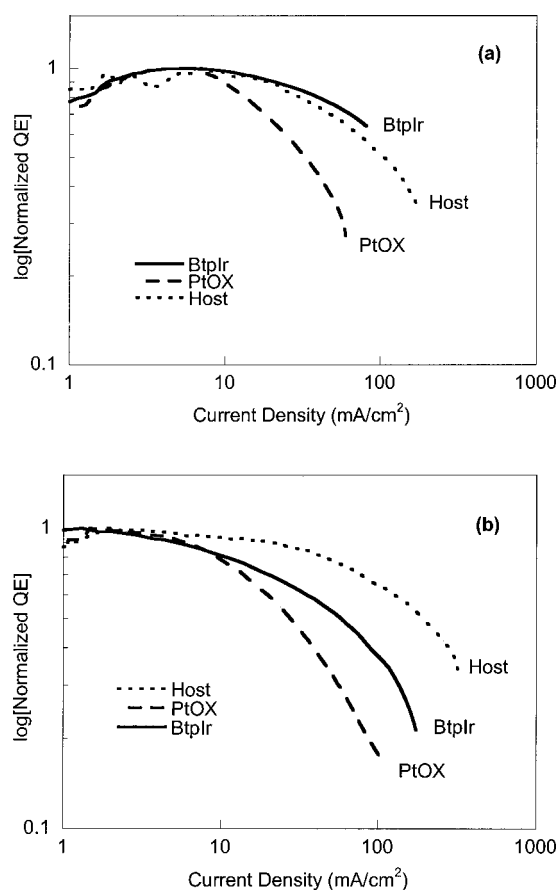


FIG. 3. Normalized external quantum efficiencies vs current density for (a) doped and undoped PVK devices and (b) doped and undoped PF devices using different dopants.

phosphorescence PLEDs decreased with increasing current density. For easier comparison, we normalized the device's quantum efficiencies. In the low-current region, the efficiency increased with current density because better charge balance was achieved. After reaching the maximum value, quantum efficiencies went down with current densities, indicating that saturation of dopant emission sites and/or exciton quenching begins to occur. The maximum quantum efficiency of the 4 wt % PtOX-doped PVK device [Fig. 3(a)] occurred at 3 mA/cm², this current density is far below the current density^{3,9} required to excite all the dopant molecules. In addition, we could not observe strong dopant concentration dependence at the onset of the quantum efficiency (QE) rolloff. They should have a linear relationship if the saturation is an important factor. These observations suggest that saturation of emission sites is not the dominant factor, which restricts the QE at high-current densities. For exciton quenching, on the other hand, two exciton quenching mechanisms are possible, TT annihilation and PT annihilation. Both mechanisms can be suppressed by utilizing dopants with shorter lifetimes. From Figs. 3(a) and 3(b), we can clearly see that, for both types of devices, BtpIr-doped devices have a slower decrease of QE than PtOX-doped devices. The one order of magnitude of shorter lifetime of BtpIr ($\sim 5 \mu\text{s}$) over PtOX ($\sim 80 \mu\text{s}$) leads to improved quantum efficiency at high-current densities. It has been shown that the decrease of QE at high-current densities is mainly due to TT annihilation for phosphorescence OLEDs.⁹ How-

ever, unlike the phosphorescence OLEDs, in which quantum efficiencies of host-only devices either increase with or are independent of current densities in the operation current region,^{16,17} quantum efficiencies of host-only PLEDs decrease with current density after reaching the maximum value (Fig. 3). Comparing with the curves in Fig. 3 of PVK host-only device and BtpIr-doped PVK devices, a similar rolloff of the quantum efficiency can be observed. This implies that the limitation of QE in the device does not only come from the TT annihilation at the dopants, but is also associated with the host material. The quenching of excitons by polarons or at the cathode are equally important.

In conclusion, high efficiency in a red polymer light-emitting diode has been achieved by doping with BtpIr, an Ir complex, into PVK. Due to the short triplet excited state lifetime of BtpIr, 65% of the peak efficiency can be sustained at high-current densities and high brightness, 1350 cd/m². The limitation of the QE probably comes from the host materials itself. While the PT annihilation model has been proved not to be the major quenching mechanism in triplet-emitter-doped small molecular OLEDs,⁹ it is likely to be an important quenching pathway for the PLEDs studied here. Both TT and PT mechanisms probably play an equal role of limiting the performance of phosphorescence PLEDs. Details of the quenching mechanisms are under investigation.

This research is supported by the National Science Foundation (ECS-9733355), the Air Force Office of Scientific Research (F49620-00-1-0103), DARPA, and Universal Display Corporation.

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