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Energy transfer in polymer electrophosphorescent light emitting devices with single and multiple doped luminescent layers

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We study energy transfer in efficient polymer electrophosphorescent organic light emitting diodes (PHOLEDs) using poly(9-vinylcarbazole) (PVK) host doped with one or more phosphorescent cyclometalated Ir(III) complexes. Single dopant double heterostructure PHOLEDs exhibited saturated color luminescence due to emissive triplet metal-to-ligand charge-transfer to ground state transitions of the Ir(III) dopants. Blue PHOLEDs, excited by an endothermic process from the host polymer, exhibited an emission maximum at a wavelength of $\lambda_{\text{max}}=474$ nm, with an external quantum efficiency of $\eta_{\text{ext}}=1.3\pm0.1\%$ and luminous power efficiency of $\eta_p=0.8\pm0.1$ lm/W. The green PHOLED exhibited $\eta_{\text{ext}}=5.1\pm0.1\%$, with $\eta_{\text{ext}}>2\%$ for both red and yellow emission. Resonant energy transfer between green emitting *fac*-tris (2-phenylpyridyl)Ir(III) and red emitting bis[2-(2'-benzothienyl)-pyridinato-N,C^{3'}](acetylacetonate)Ir(III) was observed to nearly double the efficiency of red emission when both dopants were simultaneously blended in a PVK host. PHOLEDs containing a blend of red, yellow, and blue Ir(III) complex dopants produced white light emission with $\eta_{\text{ext}}=2.1\pm0.1\%$. Our results suggest that deep lying energy states in the PVK conductive matrix may limit the energy transfer efficiency in phosphor doped polymer OLEDs. © 2002 American Institute of Physics. [DOI: 10.1063/1.1479751]

I. INTRODUCTION

Polymer-based organic light emitting diodes (OLEDs) have been investigated for many years due to their potential application to electroluminescent displays.^{1,2} Based on their compatibility with solution processing and relatively high materials strength, the exploration of their suitability for organic electronic devices has primarily been motivated by the need for low cost production which these attributes make possible. To date, nearly all polymer OLED emission is based on fluorescence from either the functionalized polymer itself, or from emissive dopants blended with the polymeric conducting matrix. While several researchers^{3–5} have suggested that the number of electronically generated fluorescent singlet states in polymers is higher than is suggested by simple statistical arguments (in which only 25% of the states would be singlets), it remains a common observation that the highest external quantum efficiency (η_{ext}) obtained to date in the most efficient polymer systems is only 5%. Given the fact that only 20% of the emitted light from a lambertian source (which is approximately consistent with OLED light emission) exits a glass substrate, 5% external efficiency is yet consistent with the 25% singlet generation fraction.

Recently, it has been demonstrated that nearly 100% internal quantum efficiency (corresponding to the harvesting of

all singlet as well as triplet states) can be achieved in small molecule based devices using metalorganic phosphor complexes based on either Pt or Ir heavy metals.^{6–9} These so-called electrophosphorescent OLEDs (or PHOLEDs) have been demonstrated to emit across the visible spectrum, and most recently have been used to produce high efficiency white light emission either by direct triplet emission, or via the formation of a triplet excimer between phosphor molecules.¹⁰ To improve the quantum efficiency of polymer OLEDs using a similar strategy, PHOLEDs consisting of a polymer host and small molecular weight Pt- and Ir-based phosphor dopants have been the source of considerable recent attention.^{11–14} In this case, the Pt(II) porphyrin complexes emit via the $^3\pi-\pi^*$ transition,¹⁵ and cyclometalated Ir(III) complexes emit via the triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) transition.¹⁶ We note that these emissive processes are inherently different from those leading to emission in lanthanide(III) complexes, which are based on the inner $f-f$ metal transitions made accessible via intramolecular triplet energy transfer.¹⁷ To our knowledge, the highest reported external quantum efficiencies obtained for polymer PHOLEDs employ poly(9-vinylcarbazole) (PVK) doped with Ir(ppy)₃, attaining¹¹ $\eta_{\text{ext}}=5\%-7\%$. Here, PVK is employed as a host due to its high energy blue-emissive singlet excited state host,¹⁸ its favorable film-forming properties and

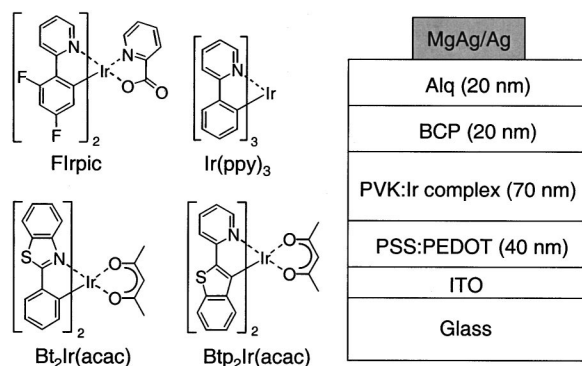


FIG. 1. Chemical structural formulas of compounds and device configurations employed in this study.

durability at high temperature, and hole mobility of $\sim 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁹

In this work, we study the energy transfer processes leading to red, green and blue emission in polymer PHOLEDs. Specifically, we find that phosphor molecules with triplet state energies intermediate between that of the host and the emitting dopant, can be successfully employed as “sensitizers,” allowing for efficient energy transfer from the host to the dopants.^{20,21} This process of phosphor sensitization has also previously been demonstrated in small molecular weight materials,²² and can significantly extend the applicability of a single host material to obtain efficient emission from dopants over a wide spectral range. We show that energy transfer to multiple dopants can also be used to generate efficient white light emission. Note that the efficiencies reported here are still well below the best efficiencies reported for small molecular weight PHOLEDs. We discuss this observation in terms of differences in the energy transfer mechanisms of these two systems.

II. EXPERIMENTAL PROCEDURE

Chemical structures of the materials and the device structure are shown in Fig. 1. The Ir(III) dopant complexes^{16,23} used are bis[(4,6-difluorophenyl)pyridinato-N,C^{2'}](picolinato)Ir(III) (or Flrpic) for blue emission, fac-tris(2-phenylpyridyl)Ir(III) [Ir(ppy)₃] for green, bis(2-phenylbenzothiazolato-N,C^{2'})(acetylacetonate) Ir(III) [Bt₂Ir(acac)] for yellow, and bis[2-(2'-benzothienyl)pyridinato-N,C^{3'}](acetylacetonate) Ir(III) [Btp₂Ir(acac)] for red. Bathocuproine (BCP), employed as a hole and exciton blocker,^{6,12,24} was purified by train sublimation prior to use. It has been shown that the use of a hole/exciton blocker in electrophosphorescent devices is necessary for confining long lived triplet states in the luminescent region. Inclusion of this layer, thereby forming a double heterostructure OLED, has been shown to increase the efficiency of small molecular weight PHOLEDs by as much as a factor of ten as compared with devices lacking this layer.^{8,22} More recently, similar efficiency improvements have also been realized in double heterostructure polymer PHOLEDs.^{11,12}

The PHOLEDs were prepared as follows: pre-cleaned ITO-coated (sheet resistance $20 \Omega/\square$) glass substrates were

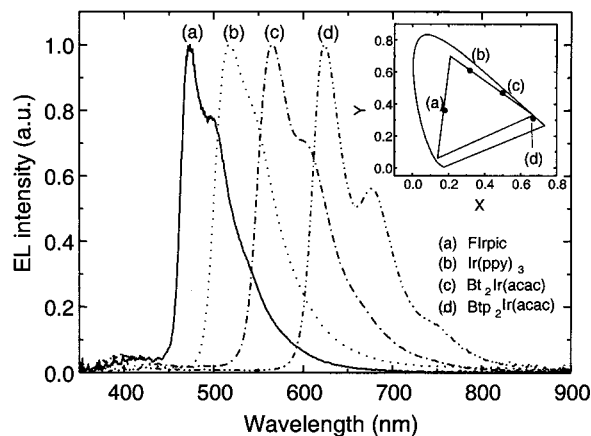


FIG. 2. EL spectra of blue, green and red PHOLEDs employing the following Ir(III) complexes doped at 5 wt % in PVK: Flrpic, Ir(ppy)₃, Bt₂Ir(acac), and Btp₂Ir(acac). Spectra are measured at a current density of $J = 10 \text{ mA/cm}^2$. Inset: CIE coordinates of the four devices. The triangles show the National Television Standards Committee recommended blue, green, and red coordinates.

first coated with a 40-nm-thick layer of poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) spun on at 4000 rpm, used to improve hole injection and substrate smoothness. Next, a mixture of the Ir(III) complex and PVK layer was spin-coated at room temperature under ambient conditions from a CHCl₃ solution, resulting in 70-nm-thick films. The conductive polymer host, PVK, was obtained from a commercial supplier and was used as supplied without purification. Prior to spinning, each solution was filtered through a $0.4\text{-}\mu\text{m}$ pore membrane to remove aggregates, and other impurities or inhomogeneities. The solvent was removed by baking the samples *in vacuo* at 120°C for 10 min after spinning. Following solvent evaporation, a 20-nm-thick BCP hole blocking layer and a 20-nm-thick tris(8-quinolinolato)Al(III) (Alq₃) electron transporting layer were applied by thermal vacuum evaporation at a chamber base pressure of $<10^{-6}$ Torr. Finally, a 100-nm-thick 10:1 Mg:Ag cathode capped by a 20-nm-thick Ag layer was also deposited in vacuum through a shadow mask with 1 mm-diameter circular openings. The layer thicknesses were determined using a crystal thickness monitor, and an ellipsometer for the evaporated and spin coated films, respectively.

All measurements were carried out in air at room temperature. Current density (J)–voltage (V)–luminance (L) measurements were obtained using a Hewlett-Packard 4145B semiconductor parameter analyzer, with the optical response obtained by placing the PHOLED directly onto the surface of a calibrated Si photodiode (Newport, 818UV). Electroluminescence (EL) spectra were recorded with an Ocean Optics USB2000 fiber optic spectrometer.

III. RESULTS AND DISCUSSION

A. Blue to red electrophosphorescence in single dopant devices

The EL spectra of PHOLEDs with 5 wt % Ir(III) complexes [Flrpic, Ir(ppy)₃, Bt₂Ir(acac), Btp₂Ir(acac)] are shown in Fig. 2. The Commission Internationale de L'Eclairage

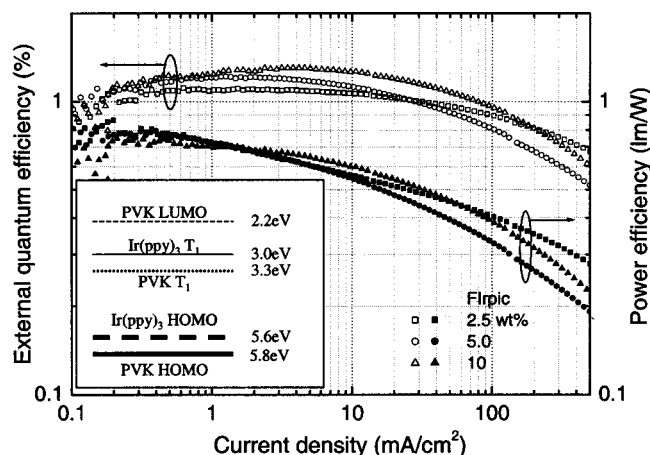


FIG. 3. Dependence of external quantum efficiency (η_{ext}) and luminous power efficiency (η_p) on current density of FIrpic PHOLEDs, with doping concentration in PVK varied. Inset: Energy level scheme of PVK doped with $\text{Ir}(\text{ppy})_3$.

(CIE) coordinates of these PHOLEDs are shown in inset of Fig. 2. Each device exhibited emission due to $^3\text{MLCT}$ or [in the case of $\text{Btp}_2\text{Ir}(\text{acac})$] ligand to ground state transitions of the dopants peaked at wavelengths of $\lambda_{\text{max}}=474$, 517, 565, and 623 nm for FIrpic, $\text{Ir}(\text{ppy})_3$, $\text{Bt}_2\text{Ir}(\text{acac})$, and $\text{Btp}_2\text{Ir}(\text{acac})$, respectively.^{16,25}

Figure 3 shows the dependence of the external quantum efficiency (η_{ext}) and luminous power efficiency (η_p) on current density for several doping concentrations of FIrpic in PVK. Blue EL with $\eta_{\text{ext}}=1.1\pm0.1\%$ was achieved for 2.5 wt % FIrpic. At a doping of 10 wt % FIrpic, the maximum η_{ext} increases to $1.3\pm0.1\%$. The increased doping also increases the turn-on voltage somewhat (e.g., at 1 mA/cm^2 , the voltage increases from 10 V for 2.5 wt % to 11 V for 10 wt % FIrpic), achieving a maximum $\eta_p=0.8\pm0.1$ lm/W and a brightness of 9500 cd/m^2 ($J=960$ mA/cm^2). The maximum η_{ext} is a factor of six higher than that of blue fluorescent polymer OLEDs based on poly(9,9'-dioctylfluorene),²⁶ although it is significantly less than that of 4, 4'-N, N'-dicarbazole-biphenyl (CBP) based small molecular weight devices, where η_{ext} between 5.6% and 7% have been achieved with this Ir(III) complex.^{25,27} From Fig. 3, we observe that η_{ext} gradually decreases at high current due to triplet-triplet (TT) annihilation.²² As in CBP small molecu-

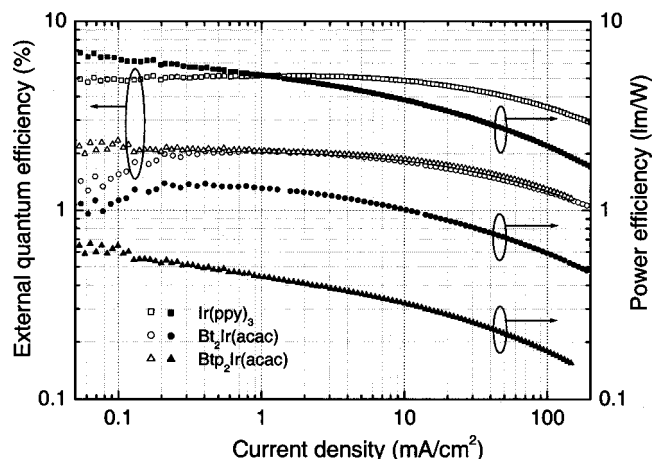


FIG. 4. Dependence of η_{ext} and η_p on current density of PVK PHOLEDs doped with $\text{Ir}(\text{ppy})_3$ (squares), $\text{Bt}_2\text{Ir}(\text{acac})$ (circles), $\text{Btp}_2\text{Ir}(\text{acac})$ (triangles).

lar weight devices, the energy gap between the lowest excited triplet states of PVK (~ 2.5 eV)²⁸ and FIrpic²⁵ (2.62 eV) suggests that endothermic energy transfer from the host to the dopant is the dominant energy transfer process.^{25,29}

Green $\text{Ir}(\text{ppy})_3$ -doped PHOLED results are shown in Fig. 4. Here, the maximum $\eta_{\text{ext}}=5.1\pm0.1\%$ is comparable to that reported by Yang and Tsutsui, where a similar double heterostructure was employed.¹¹ In contrast to that report, however, the drive voltage in the device in Fig. 4 was reduced by insertion of PEDOT:PSS layer, resulting in $\eta_p=6.0\pm0.5$ lm/W at 8 V. Finally, the characteristics of both red and yellow polymer PHOLEDs are also shown in Fig. 4. The red emitting $\text{Btp}_2\text{Ir}(\text{acac})$ device exhibited maximum $\eta_{\text{ext}}=2.1\pm0.1\%$ and $\eta_p=0.6\pm0.1$ lm/W .

Table I summarizes the results obtained for the monochromatic PHOLEDs employing only a single Ir(III) complex dopant. The characteristic current (J_0) at which η_{ext} falls to 50% of its peak value is also provided, and for green emitting devices is found to be somewhat lower than comparable small molecular weight devices employing CBP as a host (e.g., $J_0=260$ mA/cm^2 for $\text{Ir}(\text{ppy})_3$ in PVK compared with 630 mA/cm^2 when doped into CBP).²² In contrast, the trend is reversed for red emitting, $\text{Btp}_2\text{Ir}(\text{acac})$ devices (in which $J_0=190$ mA/cm^2 for a PVK host, compared with 27 mA/cm^2 for a CBP host).⁹

TABLE I. Characteristics of PHOLEDs doped with phosphorescent Ir(III) complexes (5 wt %). External quantum efficiency (η_{ext}) and power efficiency (η_p) are given as functions of current density. Peak wavelength is λ_{max} in electrophosphorescent spectrum. The characteristic current (J_0) is a measure of the TT annihilation rate.

| | FIrpic ^a | $\text{Ir}(\text{ppy})_3$ | $\text{Bt}_2\text{Ir}(\text{acac})$ | $\text{Btp}_2\text{Ir}(\text{acac})$ |
|---|---------------------|---------------------------|-------------------------------------|--------------------------------------|
| λ_{max} (nm) | 474 | 517 | 565 | 623 |
| CIE (x, y) | (0.18, 0.36) | (0.32, 0.61) | (0.50, 0.47) | (0.67, 0.31) |
| $\eta_{\text{ext}}(\%)$ [η_p (lm/W)] at 0.1 mA/cm^2 | 0.96 (0.69) | 4.9 (6.3) | 1.5 (1.1) | 2.2 (0.60) |
| 1 | 1.2 (0.70) | 5.1 (5.2) | 2.0 (1.3) | 2.1 (0.44) |
| 10 | 1.2 (0.60) | 4.8 (3.8) | 1.8 (1.0) | 1.8 (0.32) |
| 100 | 0.96 (0.39) | 3.5 (2.2) | 1.2 (0.59) | 1.3 (0.18) |
| J (mA/cm^2) for 100 cd/m^2 | 3.4 | 0.55 | 1.7 | 6.1 |
| J_0 (mA/cm^2) | 410 | 260 | 190 | 190 |

^a10 wt % doped device.

It has previously been shown²⁹ that $J_0 = 4qd/(k_{TT}\tau^2)$, where q is the electronic charge, d is the luminescent zone thickness, k_{TT} is the TT annihilation rate constant, and τ is the triplet natural lifetime. This suggests that the product, $k_{TT}\tau^2$, is larger in the green emitting polymer PHOLED as compared to those using small molecular weight hosts, possibly due to trapping of triplets at low lying states along the polymer backbone. Trapping would tend to increase the rate of annihilation since it localizes triplets at low energy sites within the conducting matrix prior to energy transfer, encouraging interactions with other, diffusing triplets. Indeed, this may be an *intrinsic* property underlying the processes of energy transfer and multiparticle interactions. Conformational disorder along the polymer backbone leads to a large variation in possible energy states. The lowest lying energy configurations therefore serve as traps.³⁰ This can impede energy transfer to the high energy dopant resulting in reduced external emission efficiency, and at the same time provide a site for interparticle collisions, leading to enhanced TT annihilation or other lossy recombination processes as compared with small molecular weight systems.

The transfer mechanisms from PVK to $\text{Ir}(\text{ppy})_3$ is likely initiated by a combination of hole trapping and hopping (Dexter) from the polymer. The possibility for both processes is inferred from the relative positions of the PVK triplet (T_1) relative to highest occupied molecular orbital (HOMO) state of 2.5 eV,²⁸ the ionization potential of 5.8 eV (referenced to vacuum), as well as the lowest unoccupied molecular orbital position of 2.2 eV³¹ (see inset, Fig. 3). The $\text{Ir}(\text{ppy})_3 T_1$ energy lies at 3.0 eV and its ionization potential at 5.6 eV.⁶ Hence, the $\text{Ir}(\text{ppy})_3$ HOMO lies 0.2 eV above that of the PVK, suggesting that holes are readily trapped by the dopant.

Note that the effects on energy transfer efficiency due to energetic dispersion are reduced, as evidenced by the higher J_0 (but not eliminated), for red dopants whose energies lie well below the range of energies spanned by these traps. Hence, for sufficiently low dopant energies, energy transfer from the host polymer to the dopant is not as strongly affected by trapping, resulting in a shorter residence time of triplets on the polymer (with the concomitant reduction in TT annihilation). Here, resonant Dexter-related energy transfer is more likely to dominate than in the case of higher energy dopants where charge trapping also plays a role. As will be discussed later, transfer to the blue dopant is endothermic, leading to a somewhat different energy transfer process.

From these considerations we conclude that, provided the statistics for singlet and triplet exciton formation are identical in both polymers and small molecular weight devices, the efficiency of PVK, and perhaps other polymer PHOLEDs can be limited to values less than can be obtained in small molecular weight systems. This conclusion is consistent with observations of these two phosphor doped light emitting device types, where small molecular weight PHOLED efficiencies remain substantially higher (19% versus 5%) than similarly doped polymer PHOLEDs.

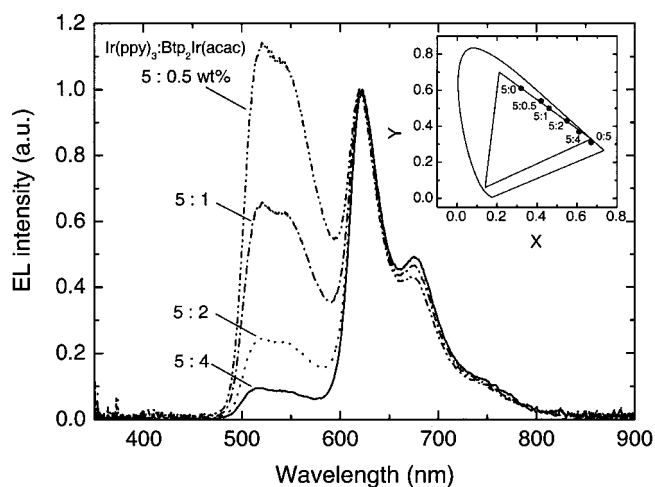


FIG. 5. EL spectra of $\text{Ir}(\text{ppy})_3\text{:Btp}_2\text{Ir}(\text{acac})\text{:PVK}$ sensitized PHOLEDs at a current density of $J = 10 \text{ mA/cm}^2$. Inset: the CIE coordinates of each device.

B. Enhanced red electrophosphorescence via phosphor sensitization in double-doped devices

Previously, we have shown that phosphor sensitizers can be used to effectively transfer both singlet and triplet excited states from a host with a high excited state energy to a dopant at a considerably lower energy where transfer between these two species would otherwise be inefficient.^{20–22} For example, energy transfer from PVK to a red dopant such as $\text{Btp}_2\text{Ir}(\text{acac})$ results in a red emission efficiency of only 2% (see Fig. 4) due to the poor energetic overlap between the PVK host and the dopant. Here, the requirement for sensitized phosphorescence is that the excited and ground states of the host and sensitizer be resonant, and that a similar condition obtains between these same levels on the sensitizer and dopant. Then efficient energy transfer between species can occur via either Dexter, or dipolar (Förster) processes.

To examine sensitized phosphorescent energy transfer, we fabricated devices employing $\text{Ir}(\text{ppy})_3$ as a sensitizer for $\text{Btp}_2\text{Ir}(\text{acac})$ codoped in PVK. Two series of devices were investigated: one with 5 wt % $\text{Ir}(\text{ppy})_3$ and 0.5–4 wt % $\text{Btp}_2\text{Ir}(\text{acac})$, and the other with 1–5 wt % $\text{Ir}(\text{ppy})_3$ and 5 wt % $\text{Btp}_2\text{Ir}(\text{acac})$. As inferred from the spectra and CIE coordinates of the several devices in Fig. 5, the emission color changed from greenish yellow [for 5% $\text{Ir}(\text{ppy})_3$ in 0.5% $\text{Btp}_2\text{Ir}(\text{acac})$] to reddish orange [for 5% $\text{Ir}(\text{ppy})_3$ in 4% $\text{Btp}_2\text{Ir}(\text{acac})$]. This spectral change with the proportional decrease of the green emission as the concentration of $\text{Btp}_2\text{Ir}(\text{acac})$ increases indicates the existence of energy transfer between the two phosphors. The current dependence of η_{ext} and η_p for this series is shown in Fig. 6. Here, a maximum efficiency for the red device [corresponding to 5% $\text{Ir}(\text{ppy})_3$ in 4% $\text{Btp}_2\text{Ir}(\text{acac})$] is $\eta_{\text{ext}} = 3.3 \pm 0.2\%$, or approximately 1.5 times higher than obtained for the unsensitized device in Fig. 4. Furthermore, at $\eta_p = 1.2 \text{ lm/W}$, the power efficiency is approximately doubled. This is a result of the increased quantum efficiency of the sensitized device, coupled with its lower operating voltage which is due to the improved hole transporting characteristics of $\text{Ir}(\text{III})$ complex doped devices, as discussed previously.¹⁶

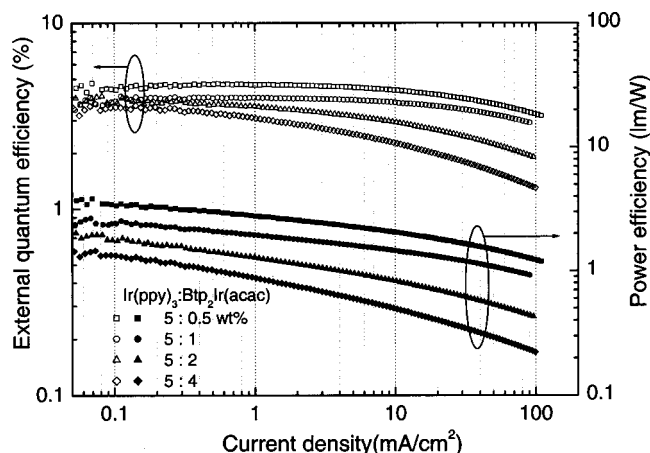


FIG. 6. Dependence of η_{ext} and η_p for the sensitized Ir(ppy)_3 : $\text{Btp}_2\text{Ir(acac)}$ (squares: 0:5, circles: 5:1, triangles: 5:2, diamonds: 5:4 wt %) doped PVK PHOLED on current density.

The sensitization pathway is most likely due to direct triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) state transitions of the sensitizer. This is inferred from the excitation spectrum of Ir(ppy)_3 , whose maximum efficiency lies near to the $^3\text{MLCT}$ bands,¹⁶ as well as the lack of emission from higher excited states, such as intraligand transitions and $^1\text{MLCT}$. This results from rapid intersystem crossing to the triplet state effected by the heavy metal ion. The transfer then excites the purely ligand-based state of the sensitized phosphor,¹⁶ $\text{Btp}_2\text{Ir(acac)}$. Consistent with other results involving phosphor dopants, a much higher doping concentration (~ 5 – 10 wt %) was required for pure red emission from $\text{Btp}_2\text{Ir(acac)}$ than is generally required for fluorescent dyes (<1 wt %).³² This is due to the higher transition probability of “naturally allowed” $^1\pi-\pi^*$ and “acquired allowed” $^3\text{MLCT}$ transitions, with energy transfer of phosphor systems occurring primarily via Dexter, short-range hopping.

Further evidence for the dominance of Dexter transfer is provided by the enhancement of η_{ext} for red emission as the concentration of Ir(ppy)_3 is increased, while the concentration of $\text{Btp}_2\text{Ir(acac)}$ is fixed at 5 wt %, as shown in Fig. 7.

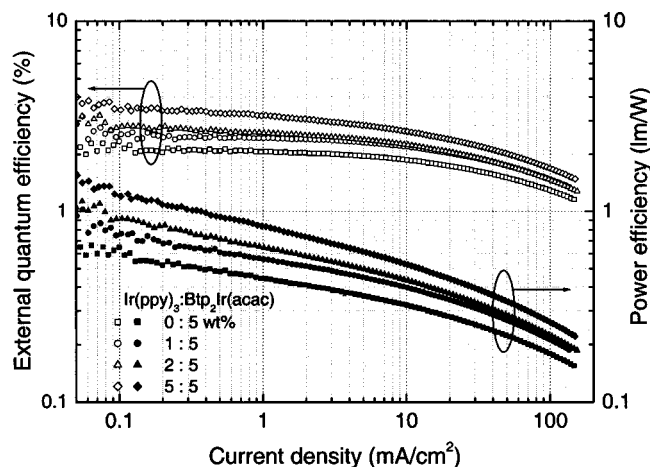


FIG. 7. Dependence of η_{ext} and η_p for PHOLED Ir(ppy)_3 : $\text{Btp}_2\text{Ir(acac)}$ (squares: 0:5, circles: 1:5, triangles: 2:5, diamonds: 5:5 wt %) doped PVK PHOLED on current density.

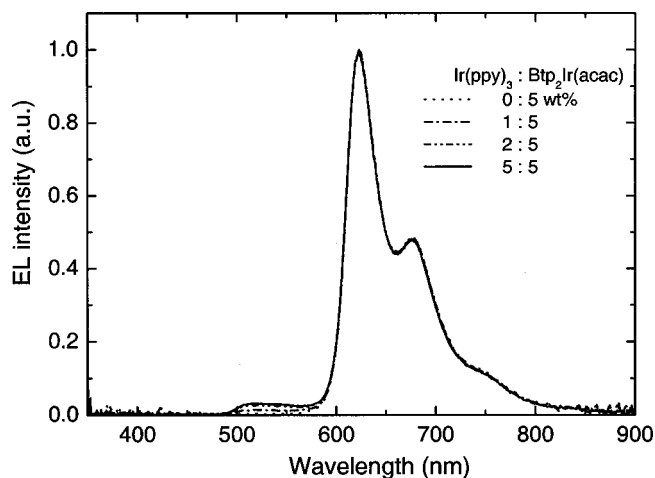


FIG. 8. EL spectra of red emitting Ir(ppy)_3 : $\text{Btp}_2\text{Ir(acac)}$ sensitized PVK PHOLEDs at a current density of $J = 10$ mA/cm^2 .

The maximum η_{ext} obtained is $3.5 \pm 0.1\%$ obtained at 5 wt % Ir(ppy)_3 concentration. The EL spectra of the devices in Fig. 7 are shown in Fig. 8. It is evident that at all Ir(ppy)_3 concentrations studied, very little green emission is observed, with the CIE coordinates of (0.66, 0.33) maintained even at 5 wt % Ir(ppy)_3 concentrations. Furthermore, no significant change of color is observed even at very high current densities of 100 mA/cm^2 (see Fig. 9), suggesting that at these concentrations, no saturation of either the sensitizing or emissive centers occurs.

C. White electrophosphorescence in triple-doped PHOLEDs

To further test the mechanism of sensitization and energy transfer, we triply doped the PVK emissive region with Flrpic for blue, $\text{Bt}_2\text{Ir(acac)}$ for yellow, and $\text{Btp}_2\text{Ir(acac)}$ for red emission. Doping concentrations of Flrpic , $\text{Bt}_2\text{Ir(acac)}$, and $\text{Btp}_2\text{Ir(acac)}$ were 10 wt %, (0.25 or 0.5) wt %, and (0.125 or 0.25) wt %, respectively. The EL spectra at 10 mA/cm^2 for devices with differing combinations of dopant concentrations are shown in Fig. 10. As expected, each PHOLED exhibits white luminescence due to mixed emis-

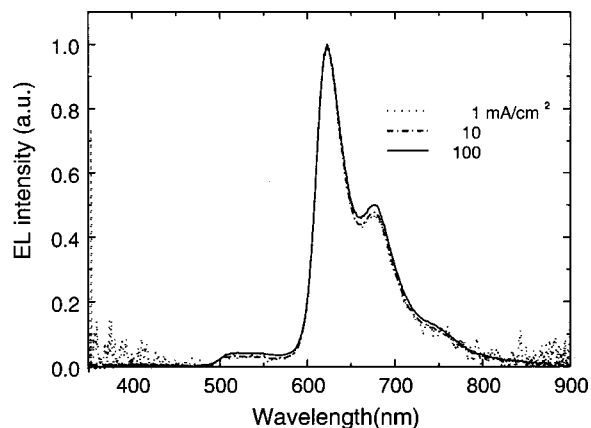


FIG. 9. EL spectra of Ir(ppy)_3 : $\text{Btp}_2\text{Ir(acac)}$ sensitized PVK PHOLEDs at 5:5 wt % at current densities of $J = 1$, 10 , and 100 mA/cm^2 .

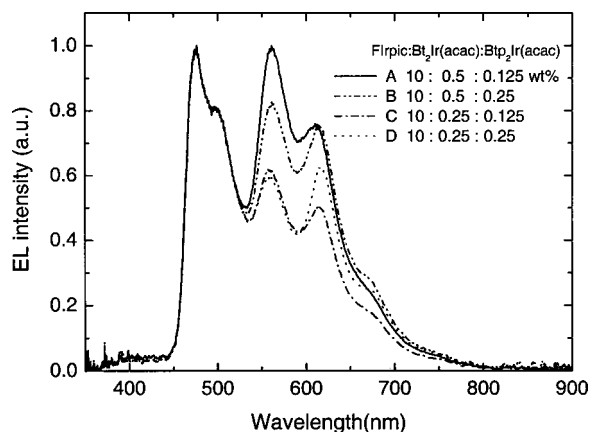


FIG. 10. EL spectra of white emitting FIrpic:Bt₂Ir(acac):Btp₂Ir(acac) PHOLEDs at a current density of $J = 10 \text{ mA/cm}^2$ (doping in wt % of device A: 10:0.5:0.125; device B: 10:0.5:0.25; device C: 10:0.25:0.125; device D: 10:0.25:0.25).

sion from the three constituent phosphors. The CIE coordinates of devices with 0.5 wt % Bt₂Ir(acac) (device A and B) are (0.37, 0.42), whereas the 0.25 wt % Bt₂Ir(acac) device has closer to an “ideal” white emission at (0.33, 0.41). The color rendering index (CRI), which is a measure of the color shift that an object undergoes when illuminated by the light source as compared with the color of the same object when illuminated by a reference source of comparable color temperature,³³ was also obtained for each PHOLED. The value of CRI ranges from 0 to 100, with 100 representing no shift in color. The 0.25 wt % Btp₂Ir(acac) devices (B, D) exhibited a higher CRI=77 as the result of the enhancement of red peak than that of the 0.125 wt % devices (A and C) with CRI=72 and 71, respectively.

Figure 11 shows the current dependence of both η_{ext} and η_p for the white PHOLEDs of Fig. 10. The current characteristics of the devices were categorized into two types by the concentration of the red dopant, Btp₂Ir(acac). The maximum $\eta_{\text{ext}} = 2.1 \pm 0.1\%$ was achieved in device D, also having the closest to ideal CIE and CRI for white emission. When compared with the peak efficiencies obtained using these dopants

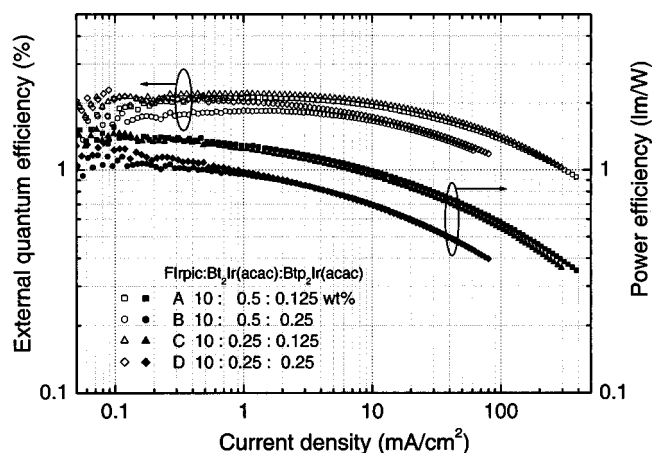


FIG. 11. Dependence of η_{ext} and η_p on current density for the white emitting PHOLEDs in Fig. 10 (squares: device A, circles: device B, triangles: device C, diamonds: device D).

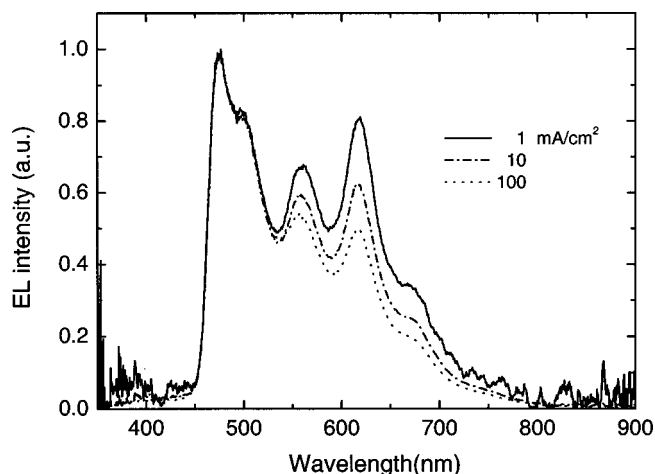


FIG. 12. EL spectra of FIrpic:Bt₂Ir(acac):Btp₂Ir(acac) triple-doped device D (cf. Fig. 10) at a current density of $J = 10 \text{ mA/cm}^2$.

in monochromatic devices (see Table I), this high η_{ext} indicates very efficient energy transfer from the host, to the several dopants in the blended luminescent layer. Note that the sensitization due to the blue dopant is minimal since its energy levels are more displaced from those of the red and yellow dopants by a larger energy than the host, PVK. Indeed, given the range of low trap energies available to the polymer backbone as discussed in Sec. III A, the most likely energy transfer mechanism is via direct hopping from the polymer to the three, individual dopants, with little interaction between the several dopants themselves. The maximum power efficiency obtained was $\eta_p = 1.4 \pm 0.1 \text{ lm/W}$ at 10 V for device D. Further, the maximum brightness was $L = 6800 \text{ cd/m}^2$ achieved at $J = 295 \text{ mA/cm}^2$ for device C. These results for nonoptimized PHOLEDs show the advantage of phosphorescence compared with previous reports for fluorescent polymer white devices having $\eta_p = 0.83 \text{ lm/W}$ at 10 V,¹ and for polymer blends where $\eta_{\text{ext}} = 1.2\%$.³⁴

The emission color of each PHOLED is slightly blue-shifted as the current density increases due to the relative decrease of yellow and red emission, shown in Fig. 12 for device D. This provides additional evidence for preferred energy transfer to the dopant directly from the polymer. Given that the number of states at low energies is limited, at higher current densities, excitons formed on the polymer backbone will migrate toward these states, where they will remain until they are transferred directly to the dopant. Hence, at high current densities, the high energy states will be populated in preference to the already filled low energy states, making energy transfer to the blue dopant more probable. This accounts for the blue shift in emission with current—energy transfer to FIrpic, which is generally endothermic at low current densities, becomes increasingly likely as the high energy polymer states become populated, allowing for exothermic transfer to dominate. Further, direct trapping on FIrpic (avoiding transfer from PVK completely) is also likely for this heavily doped system. Also contributing to the blue shift is the saturation of lightly doped red phosphor sites in the PVK matrix.

IV. CONCLUSIONS

In summary, we have demonstrated high efficiency blue to red electrophosphorescence in polymer PHOLEDs using an exciton confining PVK double heterostructure doped with several different Ir(III) complexes. These various devices were employed to study energy transfer from the polymer to the phosphor dopants, and in particular the applicability of such mechanisms as sensitized phosphorescence to polymer systems. In a double-doped PHOLED with Btp₂Ir(acac) and Ir(ppy)₃ as a sensitizer, a significant enhancement of red emission was observed. We also demonstrated white electrophosphorescence from triple-doped PHOLED. These results should show the importance of energy transfer via ³MLCT state for optimizing devices employing heavy metal phosphorescent dopants.

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