

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/234883451>

# Lee, C. L., Lee, K. B. & Kim, J. J. Polymer phosphorescent light-emitting devices doped with tris(2-phenylpyridine) iridium as a triplet emitter. Appl. Phys. Lett. 77, 2280-2282

ARTICLE *in* APPLIED PHYSICS LETTERS · OCTOBER 2000

Impact Factor: 3.3 · DOI: 10.1063/1.1315629

---

CITATIONS

210

---

READS

166

3 AUTHORS, INCLUDING:



Chang-Lyoul Lee

Gwangju Institute of Science and Technology

82 PUBLICATIONS 1,431 CITATIONS

SEE PROFILE

# Polymer phosphorescent light-emitting devices doped with tris(2-phenylpyridine) iridium as a triplet emitter

Chang-Lyoul Lee, Kyung Bok Lee, and Jang-Joo Kim<sup>a)</sup>

Department of Materials Science and Engineering, Kwangju Institute of Science and Technology,  
1 Oryong-Dong, Buk-Gu, Kwangju 500-712, Korea

(Received 9 June 2000; accepted for publication 14 August 2000)

We have fabricated phosphorescent polymer light-emitting devices with tris(2-phenylpyridine) iridium  $[\text{Ir}(\text{ppy})_3]$  as a triplet emissive dopant in poly(vinylcarbazole) (PVK) host. The device with 8% doping concentration of  $[\text{Ir}(\text{ppy})_3]$  in PVK showed the external quantum efficiency of 1.9% and the peak luminance of 2,500  $\text{cd/m}^2$ . The emission spectrum of the device exhibited no emission from PVK, indicating that the energy transfer from PVK to  $[\text{Ir}(\text{ppy})_3]$  is efficient. This work demonstrates that efficient electrophosphorescent light-emitting devices can be realized with polymers. © 2000 American Institute of Physics. [S0003-6951(00)00141-8]

Organic light emitting devices (OLEDs) are under active research lately because of their application to flat panel displays. Much effort has been focused on the improvement of the emission efficiency either by developing high efficiency materials or efficient device structures. In OLEDs, the electron and hole are injected from opposite electrodes and combined to form excitons. The operation of LEDs generates spin-symmetric triplet and spin-antisymmetric singlet in the ratio of 3:1. Radiative decay from singlet excitons is fast (fluorescence), but that from triplet (phosphorescence) is inhibited by the requirement of the spin conservation and is often very inefficient.<sup>1</sup> Until recently, materials adopted for the device fabrication have been mostly fluorescent dyes and polymers, which utilize the emission from a singlet exciton. Energy in triplet exciton in the materials is wasted by non-radiative decay. The nature of the emission from the fluorescent organic materials has set the limit in quantum efficiency to 25% in OLEDs, even though the ratio of the singlet to the triplet excitons is still under dispute.

Phosphorescence is a way to overcome the limit, since phosphorescent material can generate emission from both triplet and singlet excitons.<sup>2,3</sup> Utilization of triplet excitons in OLEDs was proposed several years ago and lanthanide chelates have been examined for the devices.<sup>4,5</sup> They show high quantum efficiency if photoexcited, but low quantum efficiency and luminance if incorporated in OLEDs. It is only recently that efficient phosphorescent LEDs are reported. Baldo and his co-workers reported high efficiency phosphorescent LEDs by doping phosphorescent materials such as platinum octaethylporphine (PtOEP) and tris(2-phenylpyridine) iridium  $[\text{Ir}(\text{ppy})_3]$  in host materials to utilize the energy transfer.<sup>2,6-8</sup> Remarkably high external quantum and power efficiencies of 7.5% and 19  $\text{lm/W}$  at 100  $\text{cd/m}^2$  were reported using the iridium complex  $[\text{Ir}(\text{ppy})_3]$  as the phosphorescent material for green light emission. The results have been reproduced and an even higher quantum efficiency of 13.7% and 38.3  $\text{lm/W}$  was obtained using the same material.<sup>9</sup>

Most of the efficient phosphorescent LEDs were fabri-

cated using organic materials.<sup>2,6-8</sup> Phosphorescent dyes were doped in organic molecules such as tris(8-hydroxyquinolinato) aluminum ( $\text{Alq}_3$ ) and 4,4'-N,N'-dicarbazole-biphenyl (CBP) to utilize the energy transfer. In contrast, there are only few reports on LEDs utilizing polymer host doped with phosphorescent dyes.<sup>3</sup> It is interesting to use polymer matrix instead of organic materials because polymer devices have potentials for large area devices, simple processes, and so on. It would be worth evaluating that the same concept of the Dexter energy transfer can be applied between polymer host and phosphorescent dyes.

In order to utilize both Forster and Dexter energy transfer in dye doped organic LEDs, a proper guest-host system must be selected. With a highly efficient emitting guest, the energy levels of both singlet and triplet excitons in the host must lie above the corresponding levels in the guest, and efficient energy transfer requires an overlap of emission in the host and absorption in the guest for both Forster and Dexter transfers to work out.<sup>10</sup> As pointed out by Cleave *et al.*, the procedure of finding the proper system involves trial and error<sup>3</sup> since the triplet exciton energy levels of most light emitting materials are not available.

Exciton lifetime of the host may be also an important factor for phosphorescent dye doped LEDs where the triplet exciton energy transfer from the host is used by Dexter transfer. The efficiency of either Forster or Dexter energy transfer from the host can be described by:<sup>8</sup>

$$\eta_{\text{ET}} = \frac{k_{\text{ET}}}{k_{\text{ET}} + k_{\text{R}} + k_{\text{NR}}} \quad (1)$$

Here  $k_{\text{ET}}$  is the rate of energy transfer from the donor to the acceptor and  $k_{\text{R}}$  and  $k_{\text{NR}}$  are the radiative and nonradiative rate of the donor, respectively. This equation suggests that energy transfer is efficient if  $k_{\text{ET}} > k_{\text{R}} + k_{\text{NR}}$ . While the Forster energy transfer between singlet excitons takes place in the nanosecond time scale, the triplet-triplet Dexter energy transfer is often in the microsecond range. Therefore the exciton lifetime must be longer than the microsecond range to have an efficient triplet-triplet energy transfer by the Dexter mechanism. Even though the triplet exciton lifetime is known to be longer than that of the singlet exciton and data

<sup>a)</sup>Electronic mail: jjk@kjist.ac.kr

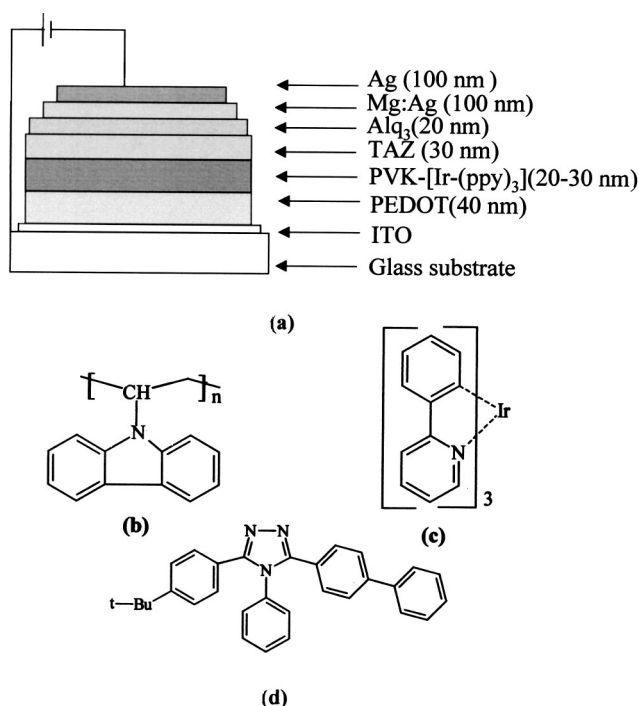


FIG. 1. Configuration of the electrophosphorescent polymer LED (a) and molecular structures of materials used. (b) PVK (host material), (c)  $[\text{Ir}(\text{ppy})_3]$  (phosphorescent dye) and (d) TAZ (hole blocking material).

on the triplet lifetime are not available for most light emitting materials, it would be important to keep the triplet exciton lifetime in mind when selecting a host material.

In this letter, we report on highly efficient polymer phosphorescent LEDs, where  $[\text{Ir}(\text{ppy})_3]$  is doped in a host polymer matrix of poly(vinylcarbazole) (PVK). PVK is selected as it is known as a good hole transporting material with high hole mobility.<sup>11</sup> It is also known to possess a large exciton lifetime.<sup>12</sup> The device showed the maximum external quantum efficiency of 1.9% and light output in excess of 2,500  $\text{cd}/\text{m}^2$ .

Figure 1 shows the device structure and chemical structure of the materials used in the fabrication of the LEDs. The fabricated multilayer polymer LEDs have the structure of indium tin oxide(ITO)/poly(3,4-ethylene dioxythiophene) (PEDOT)(40 nm)/PVK- $[\text{Ir}(\text{ppy})_3]$ (20–30 nm)/TAZ(30 nm)/ $\text{Alq}_3$ (20 nm)/Mg:Ag(100 nm)/Ag(100 nm) as shown in Fig. 1(a). ITO was obtained from Samsung SDI and cleaned in an ultrasonic bath of trichloroethylene, followed by acetone, and then methanol, and was dried in vacuum oven at 100 °C. The hole injecting the PEDOT layer was spin coated on the ITO with the thickness of 40 nm and baked at 150 °C for 10 min in the oven. The  $[\text{Ir}(\text{ppy})_3]$  doped PVK layer was spin coated on the PEDOT layer and used as the hole transporting and emitting layers. The doping concentrations were 6%, 8%, 10%, and 12% and the thickness of the emitting layer ranges from 20–30 nm. The phosphorescent dopant,  $[\text{Ir}(\text{ppy})_3]$  was synthesized according to the literature.<sup>13</sup> The 3-(4-Biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazole (TAZ) and  $\text{Alq}_3$  layers were grown sequentially by thermal sublimation in a vacuum of  $1 \times 10^{-6}$  Torr and used as the hole-blocking and electron transporting layers, respectively. TAZ is known as a good electron transporting and hole-blocking layer. It is also an exciton blocking layer because of

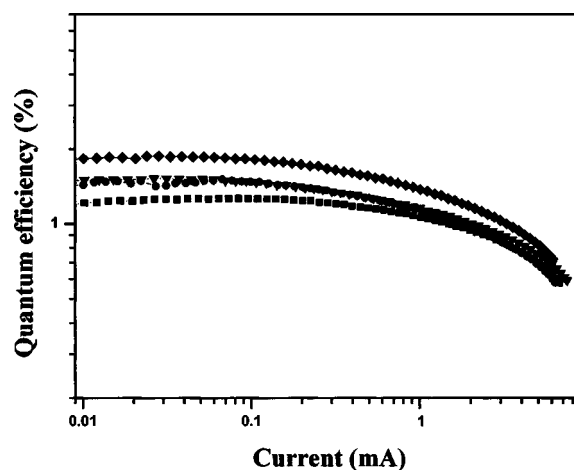


FIG. 2. The external quantum efficiencies as a function of the current density for the four devices with different doping concentration of  $[\text{Ir}(\text{ppy})_3]$  in PVK; ITO/PEDOT/PVK- $[\text{Ir}(\text{ppy})_3]$ /(6%)/TAZ/ $\text{Alq}_3$ /Mg:Ag/Ag (■), ITO/PEDOT/PVK- $[\text{Ir}(\text{ppy})_3]$ /(8%)/TAZ/ $\text{Alq}_3$ /Mg:Ag/Ag (◆), ITO/PEDOT/PVK- $[\text{Ir}(\text{ppy})_3]$ /(10%)/TAZ/ $\text{Alq}_3$ /Mg:Ag/Ag (●), ITO/PEDOT/PVK- $[\text{Ir}(\text{ppy})_3]$ /(12%)/TAZ/ $\text{Alq}_3$ /Mg:Ag/Ag (▼), respectively.

the large band gap.<sup>14</sup> The thicknesses of the TAZ and  $\text{Alq}_3$  layers were 30 nm and 20 nm, respectively. Finally, a Mg:Ag cathode with 10:1 ratio was formed through a shadow mask by co-evaporation of Mg and Ag with the deposition rate of 0.3–0.4 nm/s. The light output was measured by a calibrated silicon photodiode and the current–voltage characteristics were measured by using a Keithley 237 Source Measurement Unit. All the devices doped with  $[\text{Ir}(\text{ppy})_3]$  showed emission from  $[\text{Ir}(\text{ppy})_3]$  peaked around 510 nm.

Figure 2 shows the external quantum efficiency as a function of the current density for the four devices with different doping concentration of  $[\text{Ir}(\text{ppy})_3]$  in a PVK layer. The external quantum efficiency was slowly decreased with increasing current similar to the results in  $[\text{Ir}(\text{ppy})_3]$ :CBP.<sup>6</sup> This may result from the saturation of the emission site at high current densities due to the long lifetime of the phosphorescent dye.<sup>2,6,7</sup> The highest quantum efficiency was obtained from the device with 8% doping concentration in the host PVK. This result is similar to the result in  $[\text{Ir}(\text{ppy})_3]$ :CBP system, suggesting that the energy transfer pathway in  $[\text{Ir}(\text{ppy})_3]$ :PVK is similar to that in the  $[\text{Ir}(\text{ppy})_3]$ :CBP, i.e., via short-range Dexter transition of triplet excitons from the host. The doping concentration of 8% is a little higher than a doping concentration of 6.5% giving the highest efficiency in the organic electrophosphorescent devices.<sup>9</sup> The external quantum efficiency was 1.9% at 15  $\text{cd}/\text{m}^2$  and 1.7% at 100  $\text{cd}/\text{m}^2$ . The efficiency is lower than the organic electrophosphorescent LED. However, it is much higher than the device with the similar device structure without the dye dopant reported by Kido *et al.*,<sup>11</sup> demonstrating the effectiveness of the doping of the phosphorescent dye in PVK.

Luminance of the device doped with 8%  $[\text{Ir}(\text{ppy})_3]$  in PVK is displayed in Fig. 3 with the power efficiency as a function of driving voltage. Luminance as high as 2,500  $\text{cd}/\text{m}^2$  at 23 V was obtained from the device. The peak power efficiency is 2  $\text{lm}/\text{W}$  at a voltage of 10 V. At 100  $\text{cd}/\text{m}^2$ , a power efficiency of 1.4  $\text{lm}/\text{W}$  was obtained at a voltage of 15 V.

Figure 4 shows the normalized electrophosphorescence

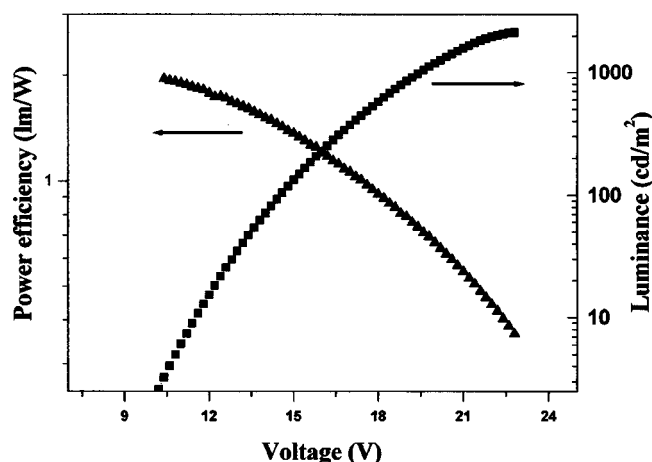


FIG. 3. Luminance and the power efficiency as a function of driving voltage of the device when doped with 8%  $[\text{Ir}(\text{ppy})_3]$  in PVK.

spectrum of the device. No emission from PVK and  $\text{Alq}_3$  even at high current density indicates efficient energy transfer from PVK to  $[\text{Ir}(\text{ppy})_3]$  and the effectiveness of the TAZ layer in blocking the exciton diffusion to the  $\text{Alq}_3$  layer. Emission from  $\text{Alq}_3$  is expected without the blocking layer, since the exciton lifetime in PVK is expected to be long and the transfer rate between triplet excitons is slow.

Our devices showed the lower quantum efficiencies compared to the devices that used the low molecular organic materials as the host.<sup>9</sup> It cannot be ruled out that the use of a polymeric material, PVK, as a host matrix may have some effects on the energy transfer process. Since this effect has been reported, using PVK as the host material for the phosphorescent  $[\text{Ir}(\text{ppy})_3]$ , this would explore the concept of different behavior of polymeric material in energy transfer than

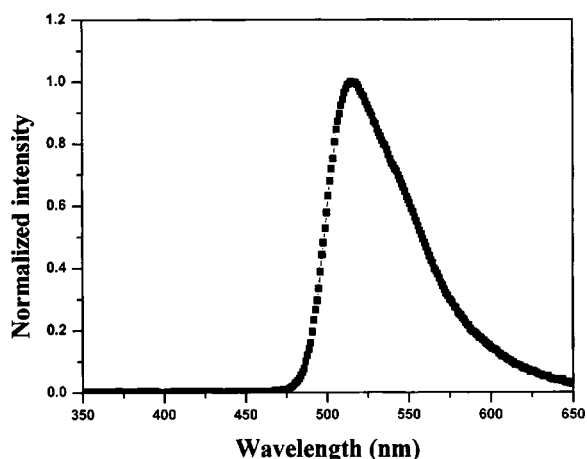


FIG. 4. Electroluminescence spectrum of  $[\text{Ir}(\text{ppy})_3]$  doped PVK device.

discrete organic molecules in OLEDs where metal complexes are used as the light-emitting material. This would open the window for the study of other polymeric materials as host molecules for the emitting materials. Another reason for low quantum efficiency compared to other groups lies in the fact that the measurements had been performed in an air equilibrated condition rather than in a deaerated environment in our case, which is to be checked in our further studies. It is also worthwhile to note that there is a lot of room for the improvement in the device performance since the device structure and the fabrication process have not been optimized yet. These may include ITO cleaning process, proper choice of cathode, optimization of the device structure, and proper purification of the constituent materials.

In summary, we fabricated high efficiency electrophosphorescent polymer LEDs. An efficient phosphorescent dye  $[\text{Ir}(\text{ppy})_3]$  was doped in a host polymer of PVK. The exhibition of the highest external quantum efficiency at 8% doping concentration of  $[\text{Ir}(\text{ppy})_3]$  in PVK indicates that Dexter energy transfer between triplet excitons is operating. The device showed the maximum external quantum efficiency of 1.9% and the peak luminance of  $2,500 \text{ cd/m}^2$ . Although not optimized, our devices demonstrate the potential that highly efficient electrophosphorescence LEDs can be realized with polymers as with organic molecules.

This work was financially supported by the Ministry of Education of Korea through the BK21 program.

- <sup>1</sup>M. Klessinger and J. Michi, *Excited States and Photochemistry of Organic Molecules* (VCH, New York, 1995).
- <sup>2</sup>M. A. Baldo, D. F. Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).
- <sup>3</sup>V. Cleave, G. Yahiogulu, P. L. Barny, R. H. Friend, and N. Tessler, *Adv. Mater.* **11**, 258 (1999).
- <sup>4</sup>J. Kido, H. Haromichi, K. Hongawa, K. Nagai, and K. Okuyama, *Appl. Phys. Lett.* **65**, 2124 (1994).
- <sup>5</sup>T. Sano, M. Fujita, T. Fujii, Y. Hamada, K. Shibata, and K. Kuroki, *Jpn. J. Appl. Phys., Part 1* **34**, 1883 (1995).
- <sup>6</sup>M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **75**, 4 (1999).
- <sup>7</sup>D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **74**, 442 (1999).
- <sup>8</sup>M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Nature (London)* **403**, 750 (2000).
- <sup>9</sup>T. Tsutsui, M. J. Yang, M. Yaihiro, K. Nakamura, T. Watanabe, T. Tsuji, Y. Fukuda, T. Wakimoto, and S. Miyaguchi, *Jpn. J. Appl. Phys., Part 2* **38**, L1502 (1999).
- <sup>10</sup>A. A. Shoustikov, Y. You, and M. E. Thompson, *IEEE J. Sel. Top. Quantum Electron.* **4**, 3 (1998).
- <sup>11</sup>J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, *Appl. Phys. Lett.* **63**, 2627 (1993).
- <sup>12</sup>J. W. Yu, K. K. Kim, H. N. Cho, D. Y. Kim, C. Y. Kim, N. W. Song, and D. Kim (unpublished).
- <sup>13</sup>K. A. King, P. J. Spellane, and R. J. Watts, *J. Am. Chem. Soc.* **107**, 1431 (1985).
- <sup>14</sup>J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, *Appl. Phys. Lett.* **64**, 815 (1994).