Highly efficient polymer light-emitting devices using a phosphorescent sensitizer

Gufeng He,[a] Shun-Chi Chang, Fang-Chung Chen, Yongfang Li,[a] and Yang Yang[b]
Department of Materials Science and Engineering, University of California at Los Angeles, Los Angeles, California 90095

Highly efficient single-layer polymer light-emitting diodes that employ Nile Red as a fluorescent dye, with a green phosphorescent-sensitizer, bis(2-phenyl pyridinato-N,$C^{2\prime}$) iridium (acetylacetonate) doped in a PVK/PBD host are demonstrated. The function of the phosphorescent sensitizer is to convert the triplet exciton into a singlet exciton during the energy transfer process. Therefore, ideally, all the excitons can be utilized. For comparison, devices with the same structure, but using a fluorescent sensitizer instead of a phosphorescent sensitizer, were fabricated. The efficiency of the phosphor-sensitized device is 6.4 cd/A, almost triple that of lumophor-sensitized or nonsensitized devices. This result indicates that not only singlet excitons but also triplet excitons are efficiently transferred from the host to the fluorescent dye when a phosphorescent material is used as a sensitizer. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1502442]

Polymer-based light-emitting diodes (PLEDs) have attracted wide interest, partially because of their applications in display technology.[1,2] Conjugated polymers can be coated onto large areas by simple low-cost wet coating processes and form large-area thin films with high quality,[3–7] which makes them considerably attractive for many applications.[8,9] However, due to the broad range of molecular weight distribution of polymers and electron–phonon interaction, the electroluminescence (EL) spectra are usually quite broad. This limits their applications in high quality full color flat panel displays. In addition, the internal quantum efficiency of a PLED is limited to 25% of the fluorescence efficiency from the thin film, due to the requirement of spin-symmetry conservation.[10] To achieve higher quantum efficiency, phosphorescent organic LEDs (OLEDs), which harvest both singlet and triplet excitons, have been demonstrated.[11,12] Similar approaches have also been successfully demonstrated in PLEDs.[13,14] However, phosphorescent dopants also have some disadvantages, despite their high performance. They are expensive to synthesize, the position of triplet is not always compatible with the host polymer, the device operating lifetime is still not long enough, and there is possible triplet–triplet annihilation at high brightness conditions.[11] An alternative method by which to solve this problem is to transfer all the excitons, both singlet and triplet, from the host, to singlets and triplets on the phosphorescent intermediary. The singlets on the intermediary intersystem cross to triplets. The triplets on the intermediary are efficiently transferred to singlets in the fluorescent dye. This approach is particularly attractive since many organic dyes have shown strong fluorescence during the past 10 years of research on OLEDs.

In this letter, we report high-efficiency red polymeric light-emitting devices using a phosphorescent sensitizer approach. The device fabrication process and material preparation are described. Poly (9-vinylcarbazole) (PVK) M_w $\sim 1\,100\,000$ g/mol) was selected as the host material (and hole-transport material), and 2-(4-biphenylyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD) as the electron-transport molecule. Both compounds were purchased from Aldrich and used as received. PVK and PBD were dissolved in dichlorobenzene (DCB) with weight ratio of 1:1. Phosphorescent dye, bis(2-phenyl pyridinato-N,$C^{2\prime}$) iridium (acetylacetonate) (PPIr), and fluorescent dye Alq_3 and Nile Red were also dissolved in DCB, respectively. These solutions were then mixed at various ratios to give the appropriate weight percentages. The mixed solution passed through 0.45 μm filters before spin coating. PPIr is a commonly used green phosphorescent dye.[15] The heavy metal atom Ir enhances the spin–orbit coupling of the ligand and the triplet states gain additional singlet character. So triplet excitons can radiatively decay to ground states efficiently. Hence both singlet and triplet excited states contribute to luminescence and very high EL efficiency can be reached.[11] When another fluorescent dye, Nile Red, was added, the emission was dominated by fluorescent dye instead of PPIr. The device structure used was Indium tin oxide (ITO)/3,4-polyethylenedioxythiophene-polystyrenesulfonate (PEDOT)/polymer film/Ca/Al. The ITO substrates were precleaned by ultrasonic treatment in detergent, de-ionized water, acetone and isopropanol, respectively. The ITO substrates were pretreated with UV ozone cleaner before coating a hole-injection layer of PEDOT (Bayer, Germany), and then thermally annealed at 120 °C for 2 h. The blend solution was spin coated onto the PEDOT to form an emissive layer and the film thickness was controlled by the solution concentration and the spin rate. Uniform, dense, pinhole free films of about 100 nm were routinely achieved at a typical spin rate of 2000 rpm. Finally, the cathode, a double layer of calcium (Ca) and aluminum (Al), was thermally evaporated with pressure of $\sim 10^{-6}$ Torr to finish device construction. UV–visible absorption spectra were recorded with an HP 8453

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[a]Permanent address: Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China.
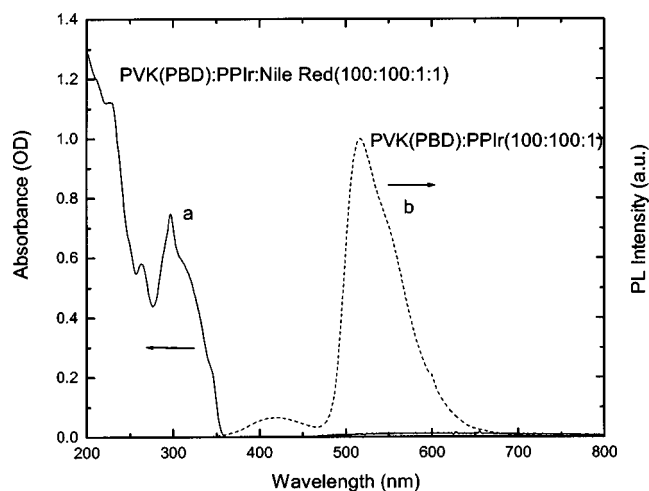[b]Author to whom correspondence should be addressed; electronic mail: yangy@ucla.edu

FIG. 1. (a) Absorption spectra of thin film of PVK:PBD:PPIr:Nile Red (100:100:1:1) blends and (b) PL spectrum of PPIr doped PVK (PBD) excited at 300 nm.

FIG. 2. Energy diagram and proposed energy transfer mechanism in this blend system.

spectrophotometer. Photoluminescence emission (PL) was measured using a Jobin-Yvon Spex Fluorolog-3 double-grating spectrofluorometer. And an ocean optics spectrometer with an optical fiber attachment was used to record electroluminescence of the devices.

Figure 1 [curve (a)] shows an absorption spectrum of a thin film of PVK:PBD:PPIr:Nile Red (100:100:1:1). The absorption spectrum of the blends can be fitted by weighted superposition of the spectrum of individual components, suggesting no ground state interaction between the materials.[16] For the very low concentration of PPIr and Nile Red, their absorption in the blend film can hardly be identified. When pumped by light of 300 nm wavelength, however, emissions mainly come from PPIr and Nile Red instead. Figure 1 [curve (b)] shows the PL spectrum of PPIr doped PVK(PBD) excited at 300 nm. This wavelength was selected because its photon energy is above the PVK and PBD absorption onset energies while it contributes little to the emission of PPIr. Almost all emission is from PPIr even though all excited energy is absorbed by PVK. Little host emission from the photoluminescence indicates that the energy transfer from host to dopant is nearly complete, i.e., the lifetime of excitons in the PVK is long enough so that they can transfer energy to the dyes before their radiative decay. The maximum PL of PPIr is at about 520 nm, while the λ_{max} of Nile Red absorption is 550 nm. The good overlap between the spectra benefits the efficient energy transfer between PPIr and Nile Red. The excitons created in the PVK can be transferred to either the PPIr triplet or Nile Red singlet. Then PPIr triplets can be transferred to the Nile Red singlet again, so almost all emission from Nile Red was found.

However, energy transfer between triplet and singlet is usually prohibited for the requirement of spin-symmetry conservation. There are two known energy transfer mechanisms from the donor to the acceptor: Dexter transfer and Förster transfer.[17] Dexter transfer is a short-range process which requires overlap of the molecular orbital of adjacent molecules. The symmetry of the donor and acceptor pair is preserved unless the donor exciton breaks up and reforms on the acceptor by incoherent electron exchange. However, sufficiently high energy (sometimes ~1 eV) is required to disso-
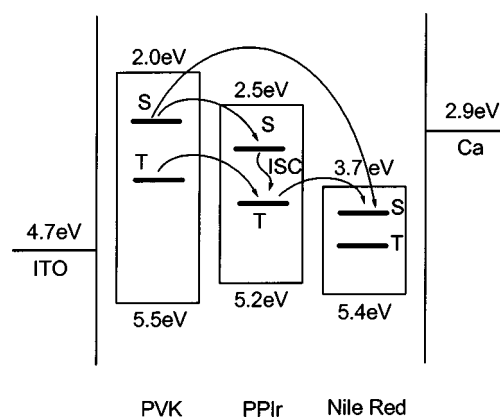
ciate the exciton for most molecules.[17] So this process is considered unlikely for triplet–singlet energy transfer. The alternative mechanism, Förster transfer, is instead a long-range process, which can occur between molecular entities separated by distances considerably exceeding the sum of their van der Waals radii. It is described in terms of interaction between the transition dipole moments (a dipolar mechanism).

In our system, a possible energy transfer mechanism is proposed (Fig. 2). After the injection of electrons and holes from the cathode and anode, respectively, excitons form in the host material PVK with a ratio of 25% singlet to 75% triplet. Then, the singlet excitons and triplet excitons are transferred to the singlet states and the triplet states in PPIr by a combination of Förster and Dexter processes along with carrier trapping. In the PPIr, the singlet excitons transfer to the triplet states through the intersystem crossing (ISC) process. With the presence of Nile Red dopant, the triplet excitons in the PPIr can transfer to the singlet exciton in Nile Red through Förster transfer by dipole–dipole coupling. The Nile Red singlets then decay radiatively and give out light.

Of course, there are some other energy transfer processes involved. First, the PVK host singlet excitons can directly transfer to Nile Red singlet states and host triplet excitons can directly transfer to Nile Red triplet states by Dexter
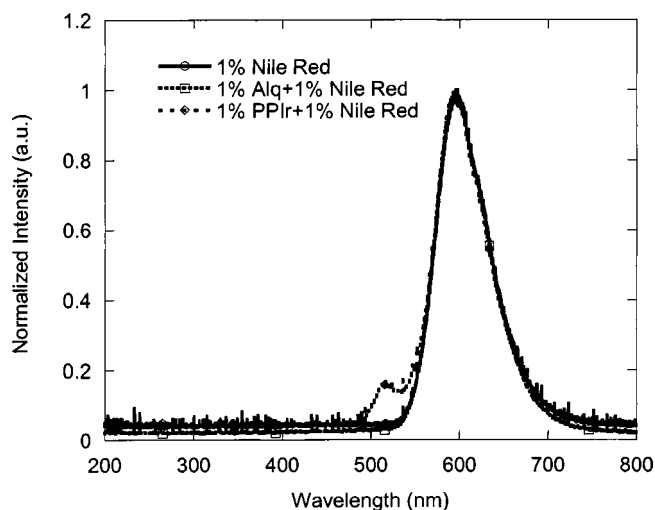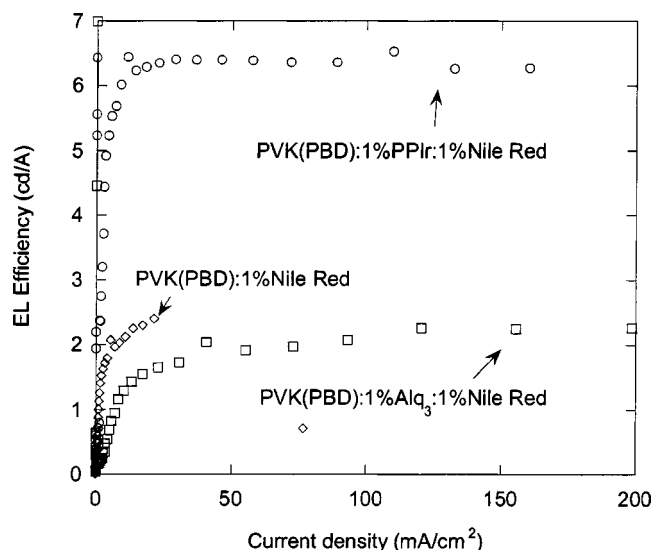

FIG. 3. EL spectra of the doped devices.

FIG. 4. EL efficiency (cd/A) of the devices in different structures vs current density.

transport. And the triplet excitons on the phosphor may transfer to Nile Red triplet states too. The last two processes are sources of emission loss since the triplet excitons in fluorescent dye cannot efficiently radiatively decay. They must be avoided to increase the emission efficiency. Here we use low concentrations of phosphor and fluorescent dye to increase the distance between them. Hence Dexter transfer is prohibited while little influence results from Förster transfer.

To verify the proposed energy transfer mechanism, two controlled devices were fabricated: ITO/PEDOT/PVK(PBD) +1% Nile Red/Ca/Al and ITO/PEDOT/PVK(PBD) +1% Alq_3+1% Nile Red/Ca/Al. Here Alq_3 is used for comparison because Alq_3 and PPIr are both green-emitting materials and have similar spectra except that Alq_3 is a fluorescent dye whereas PPIr is a phosphorescent dye. Figure 3 shows the EL spectra for these two devices. That there is no host emission observed in either case indicates full energy transfer from the host to fluorescent dyes. The host singlet excitons transfer to both fluorescent sensitizer singlet states and fluorescent dye by the Förster process. Having gotten the energy from the PVK host, Alq_3 singlets would rather transfer energy to Nile Red again than decay to their ground states directly, since there is good overlap between Alq_3 emission and Nile Red absorption. Hence, Alq_3 emission was not shown in the EL spectrum of the device using PVK(PBD):Alq_3:Nile Red blends as active materials.

Figure 4 shows the current efficiency versus current density curves for these two devices plus a third device using a phosphorescent dye, PPIr, as a sensitizer. The efficiency of ITO/PEDOT/PVK(PBD)+1% Nile Red/Ca/Al device is about 2.2 cd/A. When another fluorescent dye Alq_3 was added to the system, the efficiency of the device remains almost unchanged. However, dramatic enhancement of the EL efficiency was observed after adding phosphorescent material, PPIr. PPIr was used just like a sensitizer, and harvests

both singlets and triplets of the host and then transfers to the fluorescent dye. The efficiency of the device increased two times than that of the controlled devices. Ideally, the efficiency of the device in the presence of phosphorescent sensitizer should be quadruple that without it if the phosphorescent sensitizer transfers all host excitons to the fluorescent dye. The insufficiency of the enhancement shows that there is still some energy loss during the whole transfer process as discussed above.

In summary, we have demonstrated a highly efficient red emission single layer polymer light-emitting diode by doping 1% PPIr phosphorescent sensitizer and 1% Nile Red fluorescent dye and have considerably improved the EL efficiency of a PLED. The device exhibits 6.5 cd/A external efficiency, which is nearly triple that of controlled devices. The results show that the phosphorescent sensitizer can harvest both singlet and triplet excitons and then transfer to the fluorescent dopant.

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature (London) **347**, 539 (1990).
[2] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, Nature (London) **357**, 477 (1992).
[3] S. Aratani, C. Zhang, K. Pakbaz, S. Hoger, F. Wudl, and A. J. Heeger, J. Electron. Mater. **22**, 745 (1993).
[4] Y. Yang and A. J. Heeger, Appl. Phys. Lett. **64**, 1245 (1994).
[5] E. Westerweele, P. Smith, and A. J. Heeger, Adv. Mater. **7**, 788 (1995).
[6] Y. Cao, G. Yu, C. Zhang, R. Menon, and A. J. Heeger, Synth. Met. **87**, 171 (1997).
[7] Y. Yang, S.-C. Chang, J. Bharathan, and J. Liu, J. Mater. Sci. **11**, 89 (2000).
[8] X. L. Chen and S. A. Jenekhe, Appl. Phys. Lett. **70**, 487 (1997).
[9] G. Yu, C. Zhang, and A. J. Heeger, Appl. Phys. Lett. **64**, 1540 (1994).
[10] M. A. Baldo, D. F. O'Brien, M. E. Thompson, and S. R. Forrest, Phys. Rev. B **60**, 14422 (1999).
[11] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature (London) **395**, 151 (1998).
[12] M. A. Baldo, V. G. Kozlov, P. E. Burrows, S. R. Forrest, V. S. Ban, B. Koene, and M. E. Thompson, Appl. Phys. Lett. **71**, 3033 (1997); M. A. Baldo, M. E. Thompson, and S. R. Forrest, Nature (London) **403**, 750 (2000).
[13] T. F. Guo, S. C. Chang, Y. Yang, R. C. Kwong, and M. E. Thompson, Org. Electron. **1**, 15 (2001); F. C. Chen and Y. Yang, Appl. Phys. Lett. **80**, 2308 (2002).
[14] B. W. D'Andrade, M. A. Baldo, C. Adachi, J. Brooks, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **79**, 1045 (2001).
[15] C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, and R. C. Kwong, Appl. Phys. Lett. **78**, 1622 (2001).
[16] C. C. Wu, J. C. Sturm, R. A. Register, J. Tian, E. P. Dana, and M. E. Thompson, IEEE Trans. Electron Devices **44**, 1269 (1997).
[17] M. M. Klessinger, *Excited States and Photochemistry of Organic Molecules* (VCH, New York, 1995).