[19] D. J. Eaglesham, A. E. White, L. C. Feldman, N. Moriya, D. C. Jacobson, *Phys. Rev. Lett.* **1993**, *70*, 1643.

[20] S. B. Zhang, S. H. Wei, *Phys. Rev. Lett.* **2004**, *92*, 86 102.

[21] J. M. Howe, H. Saka, *MRS Bull.* **2004**, *29*, 951.

Achieving High-Efficiency Polymer White-Light-Emitting Devices**

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The external electroluminescence (EL) quantum efficiency (QE_{EL}) of a polymer light-emitting diode (PLED) can be affected by the following four factors: a) charge balance, b) the efficiency of producing singlet excitons, c) photoluminescence quantum efficiency (QE_{PL}), and d) the output coupling effect.[1] The QE_{PL} can approach unity and the efficiency of producing singlet excitons can be high in long-chain polymers.[2,3] Therefore, the dominating factor for achieving high efficiency for a given polymer is the balance and confinement of electrons and holes. Unfortunately, most conjugated polymers have unbalanced charge-transport properties as the hole mobility is much larger than the electron mobility. In this manuscript, we report a general method to significantly increase the efficiency of PLEDs by controlling the charge injection and distribution through material processing and interface engineering in the device. By blending high-bandgap and low-bandgap polymers in proper ratios, we were able to introduce charge traps in the light-emitting polymer (LEP) layer. Similarly, by introducing an electron-injection/hole-blocking layer, we were able to enhance the minority carrier (electron) injection and confine holes to the emissive layer. Efficient and balanced charge injection, as well as charge confinement, are attained simultaneously, and as a result high-efficiency devices can be achieved. This is a simple yet powerful concept in enhancing the overall efficiency of PLEDs. To illustrated our concept, we have blended 0.25–2 % of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with

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poly(9,9-dioctylfluorene) (PFO) as the active polymer layer for PLEDs. A Cs_2CO_3 electron-injection (and hole-blocking) layer is used at the cathode interface. The emission from the device covers colors from white to yellow, depending on the blend ratio, with the highest peak efficiency being $16\,lm\,W^{-1}$. To the best of our knowledge, this is the highest reported efficiency for a white-light emitting PLED.

There are several benefits to using a polymer blend: 1) the low-bandgap LEP behaves as a dopant for energy transfer from the higher-bandgap LEP, 2) the low-bandgap LEP behaves as a charge-trapping site to trap (and confine) the injected charges, which is particularly important in the low-voltage regime where only one type of charge is often present, and 3) the trapped electrons in the low-bandgap LEP will eventually help with the injection of holes and lead to self-balanced charge injection. When this LEP blend system is coupled with an electron-injection (and hole-blocking) layer of $Ca(acac)_2$[4] (acac: acetylacetonate) or Cs_2CO_3[5] at the cathode interface, holes are blocked within the LEP layer as well. As a result, both electrons and holes are effectively confined in the LEP layer rather than being extracted directly at the electrodes. Hence, efficient recombination occurs due to the overlapping distribution of electrons and holes (through formation of excitons). All of these factors can help to increase the efficiency of PLED devices. The schematic profile of the energy structure is shown in Figure 1.
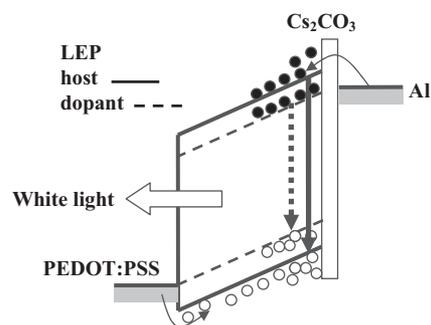

Figure 1. Schematic electronic-energy profile for the proposed device architecture. ITO: indium tin oxide; PEDOT:PSS: poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid).

In the past, a threefold improvement in efficiency has been observed in green PLEDs based on the PFO and poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) blend polymer system when $Ca(acac)_2$ was used as the cathode interface modification layer.[4] However, the actual mechanism has never been fully understood, and attempts to create similar efficiency improvements failed in other single polymer systems ranging from PFO to poly(phenylenevinylene) (PPV) derivatives. In this manuscript, due to understanding the mechanism, we report a general method to improve the PLED efficiency by both materials engineering and interface modification. In this method, the polymer blend plays an important role. It must satisfy both energy transfer and morphol-

ogy considerations. PFO and MEH-PPV have been extensively studied and have proven to form very smooth polymer blends when the concentration of MEH-PPV is less than 4 %.[5,6] Hence, a PFO and MEH-PPV blend has been selected for this study, and Cs_2CO_3 was chosen to replace $Ca(acac)_2$. One interesting property of the PFO:MEH-PPV system is that white-light emission can be realized by incomplete transfer of energy from PFO to MEH-PPV at low MEH-PPV concentrations. Cs_2CO_3 has been shown to be a better electron-injection material than LiF.[7] This is consistent with our observation that the green PLED device based on the PFO:F8BT system has a lower working voltage using a Cs_2CO_3 cathode than a device using a $Ca(acac)_2$ cathode (the operation voltage at 25 mA cm^{-2} decreases from 5.3 V to 4 V when other parameters are kept the same). This suggests that improved charge balance and conductivity in the interfacial layer is obtained using Cs_2CO_3.

Four types of devices with the structure of ITO (indium tin oxide)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/PFO:MEH-PPV/Cs_2CO_3/Al were fabricated. In order to obtain the electron-injection and hole-blocking layer through solution processing, Cs_2CO_3 was dissolved in 2-ethoxyethanol to form a dilute solution. The three layers of PEDOT:PSS, PFO:MEH-PPV, and Cs_2CO_3 were formed sequentially by spin-coating one layer on top of another. The thickness of the polymer blend layer was between 80 to 100 nm. The EL color can be modulated from yellow to white by changing the concentration of MEH-PPV from 2 to 0.25 wt.-%.

Figure 2 shows the normalized EL spectra of devices at 25 mA cm^{-2} for four different ratios of the components in the blend. All EL spectra show emission from both MEH-PPV
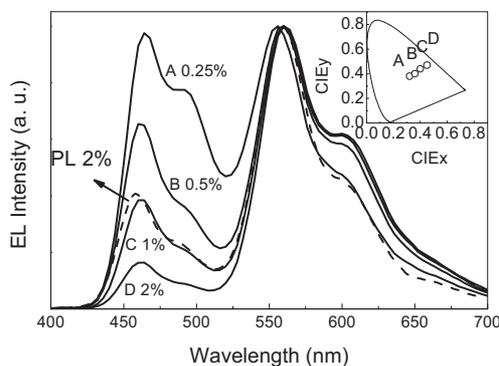
Figure 2. EL spectra of PLED devices with four different compositions; the photoluminescence spectra for the 2 wt.-% device is also shown by a dashed line. In the inset, the Commission Internationale de l'Éclairage (CIE) *x,y* color coordinates of EL emission are shown for these four devices.

and PFO. With increasing concentration of MEH-PPV in PFO, the relative emission intensity from PFO decreased due to the energy transfer from PFO to MEH-PPV. Yellow emission from MEH-PPV was observed from the sample with the high MEH-PPV concentration of 2 wt.-%, and white-light

emission was obtained at a lower MEH-PPV concentration. The Commission Internationale de l'Éclairage (CIE) *x,y* color coordinates of the emission are shown in the inset of Figure 2. The white-light emission PLED device with 0.25 wt.-% MEH-PPV has CIE coordinates of (0.32, 0.38). The energy-transfer process from PFO to MEH-PPV is proved by the decreasing emission from PFO with increasing MEH-PPV concentration, and is also illustrated by comparing photoluminescence (PL) and EL spectra of the polymer films and devices, shown in Figure 2 for the 2 wt.-% sample. In both the PL and EL spectra, two peaks appear that correspond to the emission of PFO and MEH-PPV. Significant differences in the peak intensities (as well as the ratios) between the PL spectrum and EL spectrum were observed, which is common in blended material systems. This is due to the fact that the PL emission process, which is an instant excitation and recombination process, does not involve the charge-transport process.[8] Hence, the possibility that the charges (photon-excited or electrically injected) are trapped by low-bandgap MEH-PPV is less in the PL emission process than the EL emission process.

Direct evidence of the energy-transfer process comes from the lifetime measurement obtained from the picosecond time-resolved PL spectra, shown in Figure 3. For excitons in PFO, the lifetime decreases from 0.57 to 0.48 ns when MEH-PPV is introduced as the dopant. This is due to the energy-transfer
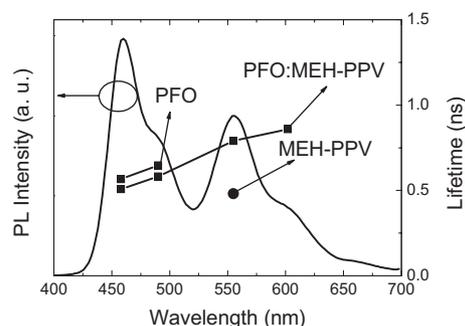
Figure 3. Exciton lifetimes at the selected wavelengths for PFO, MEH-PPV, and PFO:MEH-PPV films.

process between PFO and MEH-PPV. On the other hand, for excitons in MEH-PPV, the lifetime increases from 0.48 to 0.78 ns. The actual reason is unknown, but it is likely that the MEH-PPV has been significantly diluted, and the PL originated from the energy transferred from PFO. This observation is important in light of improving device performance, which is discussed in detail in the following paragraph.

Our devices show very good performance. The leakage current before light turn-on was low (~ 10^{-5} mA cm^{-2}), which is ideal for large-area illumination applications. Light emission was observed at a low applied external voltage of 2.3 V. Our single-emission-layer structure assures a low operating voltage; the emitting intensity reaches 3000 and 10000 cd m^{-2} at voltages of 4.3 and 5.4 V, respectively, for the 0.5 wt.-% de-

vice. These are the lowest operating voltages reported for a white PLED. The high performance of the device is attributed to the excellent balance of electrons and holes, as well as charge confinement; in addition, the polymer system has a high PL efficiency. The power efficiency versus current density of the four devices is shown in Figure 4a. The forward external quantum efficiency (η_{ex}) is calculated according to the luminous efficiency and EL spectra at a current density 25 mA cm^{-2}, which is also shown in Figure 4a. The maxima η_{ex} are 6 % for the white device (device C in Fig. 2) at 110 cd m^{-2} and 4.3 % for the yellow device (device D) at 300 cd m^{-2}. The peak power efficiencies for the white and yellow devices are 16 lm W^{-1} (device B,C) and 12.5 lm W^{-1} (device D), respectively, at low current density. The power efficiency at 100 cd m^{-2} is still as high as 15.3 lm W^{-1} (device B) and 12.1 lm W^{-1} (device D) for the white and yellow devices, respectively. To our knowledge, this is significantly higher than previously reported power efficiency values for white PLEDs, including fluorescence and phosphorescence. The power efficiency of 12.6 lm W^{-1} at 1000 cd m^{-2} is even higher than the reported highest efficiency phosphorescent OLED.[9] A comparison between the performance of our device and those previously reported is presented in Table 1.

The voltage dependence of the EL spectra, shown in Figure 4b, was measured to demonstrate the color stability of the white PLEDs. The EL spectra were obtained from 0.25 % doped devices operated from 3 to 7 V, corresponding to a nearly three orders-of-magnitude variation of current densities (or brightness). As one can see, the spectrum changes slightly with applied voltage, and the ratio of emission from PFO to that from MEH-PPV increases with the increasing current density. This is due to the low concentration of MEH-PPV in the blend, which results in the partial saturation of emission from MEH-PPV at high current densities.

According to our assumption, the improvement of the devices' performance results from the combination of two factors: self-balanced efficient charge injection and charge confinement. A minor increase in luminous efficiency can be obtained if only one condition is satisfied. This is illustrated by the comparison of luminous efficiencies for three groups of devices, as shown in Figure 5. For devices with the same device structure, the luminous efficiency reflects the degree of charge balance giving the same EL spectra. The three groups of devices are MEH-PPV, PFO, and 2 wt.-% MEH-PPV:PFO devices, using Ca or Cs$_2$CO$_3$ as the cathode for each. The reason we chose the high-percentage MEH-PPV sample for comparison is because the EL emission of this sample was contributed mainly from MEH-PPV, and the contribution for the improved efficiency from PFO emission is excluded. For devices with Ca cathodes, the doped MEH-PPV:PFO device has an efficien-
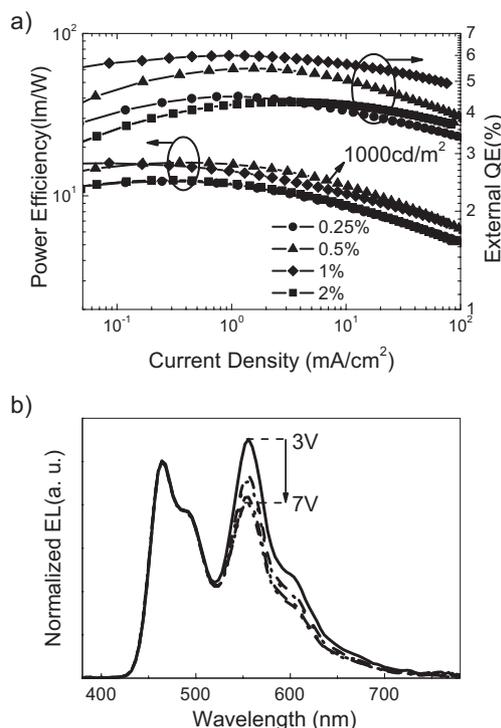

Figure 4. a) Characteristics of external efficiency and power efficiency as functions of current density for the four PLEDs. b) Normalized EL spectra of a device with 0.25 wt.-% MEH-PVV doped into PFO at voltages varying from 3 to 7 V, which corresponds to a variation of current density from 0.28 to 267 mA m^{-2}.

cy 3.5 times higher than the MEH-PPV device, which should be partially attributed to the increased PL efficiency of the polymer film. The increase of MEH-PPV PL efficiency in the blend can be explained by the suppression of interchain species.[5,6] In the diluted MEH-PPV:PFO solid solution, the MEH-PPV chains are effectively isolated by the PFO molecules, and interchain interactions are significantly reduced, which otherwise will decrease the PL efficiency of MEH-PPV film by aggregation. For the MEH-PPV and PFO devices with two different cathodes, the luminous efficiencies of devices

Table 1. Selected white polymer light-emitting devices (WPLEDs) (or white organic light-emitting devices, WOLEDs) with their corresponding performance characteristics. PAP-NPA: 4-{4-[N-(1-naphthyl)-N-phenylaminophenyl]}-1,7-diphenyl-3,5-dimethyl-1,7-dihydrodipyrazolo[3,4-b4'3'-e]pyridine; DPVBi: 4,4′-bis(2,2-diphenylvinyl)biphenyl; TPBI: 2,2′,2″-(1,3,5-phenylene) tris(1-phenyl-1H-benzimidazole); Alq$_3$: aluminum tris(8-hydroxyquinoline).

Methods	Cathode	η_{ext} [%]	η_{power} [lm W^{-1}]	CIE	Reference
PFO doped by MEH-PPV	Cs$_2$CO$_3$/Al	6	16	(0.36,0.40)	This work
PFO doped by fluorescent material	Ca/Al	–	2.8	(0.26,0.36)	[10]
PFO doped by fluorescent material	LiF/Ca/Al	–	1.6	(0.32,0.36)	[11]
dye-dispersed polyfluorene derivative	Ca/Ag	0.82	–	(0.34,0.34)	[12]
PAP-NPA doped with rubrene (OLED)	TPBI/Mg:Ag	–	2.51	(0.32,0.34)	[13]
Dye doped into PAP-Ph (OLED)	Alq/Mg:Ag	–	1.93	(0.34,0.35)	[14]
doped rubrene into blue anthracene derivatives	Alq/Mg:Ag	2.4	–	(0.32,0.34)	[15]
rubrene-doped DPVBi.	Alq$_3$/CsF/Al	4.6	6	(0.35,0.41)	[16]
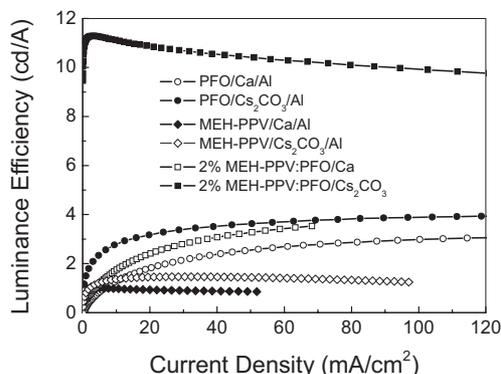
Figure 5. Luminance efficiencies of three groups of devices.

Legend:
- PFO/Ca/Al
- PFO/Cs$_2$CO$_3$/Al
- MEH-PPV/Ca/Al
- MEH-PPV/Cs$_2$CO$_3$/Al
- 2% MEH-PPV:PFO/Ca
- 2% MEH-PPV:PFO/Cs$_2$CO$_3$

Axes: Luminance Efficiency (cd/A) vs Current Density (mA/cm^2)

with Cs$_2$CO$_3$ cathodes increased to be 1.4 and 1.3 times higher than the devices with Ca cathodes; when both dopant and hole-blocking layer are used, the efficiency improved to 11.2 cd A^{-1}, which is more than three times that of the MEH-PPV:PFO/Ca device. We note that the efficiency improvement ratios are different after cathode modification for the single-component and blend material (three times improvement in the blend system compared to 1.3 times in the single-component polymer system). This apparent difference could be explained by the following scenario: because the Cs$_2$CO$_3$ hole-blocking layer is only a few nanometers thick, it can only partially block the holes, and thus hole accumulation is limited. For devices using the polymer blend, on the other hand, the charge-trapping effect occurring on MEH-PPV molecules enhances the hole accumulation more than the interface-blocking effect. The combined result is a better balance of electrons and holes confined inside the LEP layer, and subsequently much higher EL efficiency is achieved. This argument agrees with our statement that the considerable improvement of efficiency for PLEDs can only be achieved when two conditions are simultaneously satisfied: 1) the use of a polymer blend system, and 2) self-balanced electrons and holes by the interface-modification layer (Cs$_2$CO$_3$).

In conclusion, we have demonstrated a general method to significantly boost the efficiency of PLEDs by introducing an electron-injection and a hole-blocking layer, as well as using a polymer blend system as the active material. In this structure, efficient and self-balanced charge injection and charge confinement are achieved simultaneously. White polymer light-emitting devices (WPLEDs) can be realized by the incomplete transfer of energy from PFO to MEH-PPV, and the color is modulated from yellow to white by changing the concentration of MEH-PPV. The device shows excellent performance, and the highest power efficiency reported, of 16 lm W^{-1}, is obtained for our fluorescent WPLED. The method can be a universal method for achieving ultrahigh efficient polymer LEDs.

Experimental

The PLEDs were fabricated on pre-cleaned indium tin oxide (ITO) substrates with a sheet resistance of 20 Ω per square. A buffer layer of 30 nm poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was used as a hole-injection layer at the anode interface between ITO and the emissive polymer layer. Spin-coated polymer films were baked at 70 °C to remove the solvent. The Cs$_2$CO$_3$ layer was spin-coated on top of the existing polymer films. The devices were completed by the evaporation of an Al metal cathode.

The current–voltage and light–voltage curves were recorded with a Keithley 2400 source-measure unit and a calibrated silicon photodiode. The luminance was further measured by a Photo Research PR650 spectrophotometer. CIE (1931) coordinates were used to describe the color of the devices, including hue and saturation. The PL and EL spectra of the polymer doped with different weight ratios were studied with a Jobin Yvon Spex Fluorolog-3 double-grating spectrofluorometer and a Photo Research PR650 spectrophotometer, respectively.

For time-resolved photoluminescence (TRPL) measurements, the PL was excited by frequency-doubled ($\lambda = 375$ nm) laser pulses from a Ti:sapphire mode-locked femtosecond laser, and the time-correlated signals were analyzed by a two-dimensional synchronous streak camera with an overall resolution of better than 15 ps.

[1] W. Brutting, S. Berleb, A. G. Muckl, *Org. Electron.* **2002**, *2*, 1.
[2] J. S. Wilson, A. S. Dhoot, A. J. A. B. Seeley, M. S. Khan, A. Kohler, R. H. Friend, *Nature* **2001**, *413*, 828.
[3] M. Wohlgenannt, X. M. Jiang, Z. V. Vardeny, R. A. J. Janssen, *Phys. Rev. Lett.* **2002**, *88*, 197 401.
[4] Q. Xu, J. Ouyang, Y. Yang, *Appl. Phys. Lett.* **2003**, *83*, 4695.
[5] J. Liu, Y. Shi, Y. Yang, *Appl. Phys. Lett.* **2001**, *79*, 578.
[6] G. He, Y. Li, J. Liu, Y. Yang, *Appl. Phys. Lett.* **2002**, *80*, 4247.
[7] T. Hasegawa, S. Miura, T. Moriyama, T. Kimura, I. Takaya, Y. Osato, H. Mizutani, *Dig. Tech. Pap.—Soc. Inf. Disp. Int. Symp.* **2004**, *35*, 154.
[8] M. Suzuki, T. Hatakeyama, S. Tokito, F. Sato, *IEEE J. Sel. Top. Quantum Electron.* **2004**, *10*, 115.
[9] B. W. D'Andrade, R. J. Holmes, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 624.
[10] G. Tu, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, *Appl. Phys. Lett.* **2004**, *85*, 2172.
[11] Q. Xu, H. M. Duong, F. Wudl, Y. Yang, *Appl. Phys. Lett.* **2004**, *85*, 3357.
[12] J. H. Kim, P. Herguth, M.-S. Kang, A. K.-Y. Jen, Y.-H. Tseng, C.-F. Shu, *Appl. Phys. Lett.* **2004**, *85*, 1116.
[13] C. H. Chuen, Y. T. Tao, *Appl. Phys. Lett.* **2002**, *81*, 4499.
[14] C. W. Ko, Y. T. Tao, *Appl. Phys. Lett.* **2001**, *79*, 4243.
[15] L. Wang, L. Duan, G. Lei, Y. Qiu, *J. Appl. Phys.* **2004**, *43*, L560.
[16] G. Li, J. Shinar, *Appl. Phys. Lett.* **2003**, *83*, 5359.