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Citation: *Applied Physics Letters* **85**, 4576 (2004); doi: 10.1063/1.1813643

View online: <http://dx.doi.org/10.1063/1.1813643>

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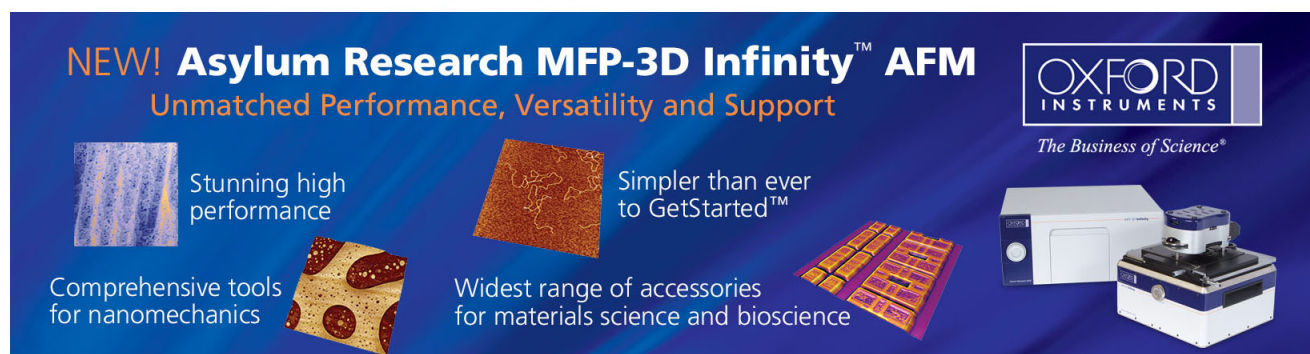
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Efficient white light emission in conjugated polymer homojunctions

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(Received 8 March 2004; accepted 16 September 2004)

We study polymer light-emitting diodes with a homojunction, i.e., junction between two layers with the same host material. One layer is poly (9,9-dioctylfluorene-2,7-diyl) (PFO) host blended with a small amount of poly (2-methoxy-5 (2'-ethyl-hexyloxy)-1,4-phenylene vinylene), another layer is either pure PFO or PFO host blended with green-emitting polyfluorene copolymers. Such homojunction devices are solution processed and show efficient white light emission. The peak luminance 3000 cd/m² is reached at 10 V with Internationale de L'Eclairage (CIE) coordinate (0.34, 0.34). © 2004 American Institute of Physics. [DOI: 10.1063/1.1813643]

Large area white light-emitting diode (LED) is of paramount importance to the full-color flat-panel displays. It can also be combined with color filters to give red, green, and blue light-emitting pixels. Small-molecule organic LEDs have shown quite high efficiency in white light.¹ However, the vacuum deposition of the small molecules makes it costly for large area fabrications. Conjugated polymers have the advantage of solution processability. Large area of polymer films can be easily made with spin coating. Many ways to achieve white polymer LEDs have been reported, including polymer blend;²⁻⁴ exciplex in bilayers;^{5,6} mixing with phosphorescent Ir complex;⁷ single polymer with aggregates;⁸ and polymer doped with dyes.⁹ So far the peak luminance of the white polymer LED is less than 1000 cd/m², far below small-molecule LEDs. The only exception is the case of dye-dispersed poly (*N*-vinylcarbazole) (PVK),⁹ in which 4100 cd/m² is reached. However high driving voltage is required. This letter proposes a method for white polymer LED using a homojunction between two emissive layers. Homojunction is the interface between two regions with different impurity conditions in the *same* host semiconductor. Such a junction has been extensively studied and applied in inorganic semiconductor devices, e.g., *p-n* junctions. Surprisingly, while heterojunction organic semiconductor devices have been intensively investigated,¹⁰⁻¹² there are very few reports on the homojunctions in organic semiconductors.

In our homojunction polymer LED the first emissive layer, counting from the anode, is a blue-emitting polymer host blended with orange-emitting polymer guest. The emission mainly comes from the guest due to exciton energy

transfer. The second emissive layer is the pure blue polymer used as the host in the first layer. The first layer has dual purposes. It provides the orange emission to compensate for the blue emission from the second layer. It also serves as the hole-transport layer with hole-blocking at the homojunction to improve the balance of electron-hole injection.^{10,13} Peak luminance of 3000 cd/m² is achieved at only 10 V with peak yield of 1.6 cd/A. In order to enhance the green emission required for potential application with color filter, we add green guest polymer to the pure blue polymer of the second layer. White emission with distinct red, green, and blue peaks is achieved with peak luminance of 1500 cd/m² at 10 V. No small-molecule dyes or triplet emitters like Ir complex are used. The whole device involves only the commonly used conjugated polymers.

Three kinds of devices are studied in this work. Device A is a single layer LED with a polymer blend emissive layer. Poly (9,9-dioctyl-fluorene) (PFO) purchased from American Dye Source is used as the host. Poly [2-methoxy-5 (2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) synthesized in our laboratory is used as the guest. PFO is dissolved in xylene with 2 wt %. Dissolution is improved by heating the solution at 100 °C for 1 min. MEH-PPV guest is added to the solution with MEH-PPV to PFO weight ratio equal to 1/60. The blend solution is spin-coated over an indium-tin-oxide (ITO) glass with poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonated acid (PEDOT:PSS) hole-transport layer at 4000 rpm. The PFO:MEH-PPV film thickness is 500 Å. The film is baked in vacuum (60 mtorr) for 60 min. Ca/Al cathode is then evaporated. For device B, on top of the first PFO:MEH-PPV layer we add the second layer of pure PFO by spin-coating in xylene solution with 2 wt %. The thickness of the second layer is 300 Å. Prior to the spin-coating of the pure

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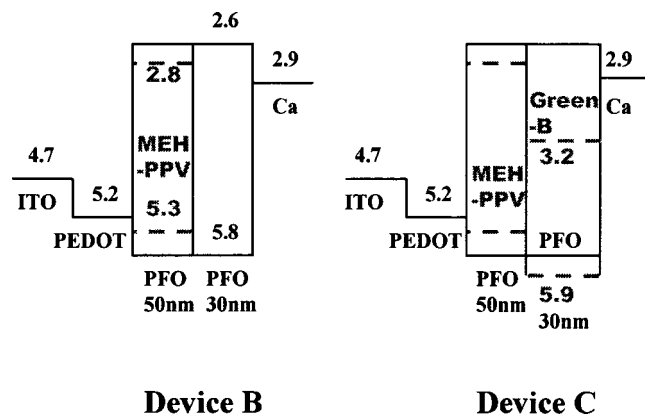


FIG. 1. The structures of homojunction devices B and C with PFO host are shown. The EA and IP of the energy bands are given in electron-volts. Device A is the same as device B except that the pure 30 nm PFO layer is removed. The EA and IP of MEH-PPV and Green-B guest are indicated by grey broken lines. Note the large hole barrier between MEH-PPV and PFO.

PFO, the first layer is baked for 60 min to reduce dissolution by the second layer as much as possible. By spinning pure xylene on the baked film and measuring the resulting film thickness reduction, it is determined that 50% of the first layer is dissolved during deposition of the second layer. The second layer is baked in vacuum for 60 min before the evaporation of the Ca/Al cathode. Various MEH-PPV to PFO ratios are studied for the double layer device B. The energy bands are shown in Fig. 1. Ionization potential (IP) and electron affinity (EA) are indicated. In device C the first layer is still PFO host blended with MEH-PPV guest with fixed ratio 1/60. The second layer is PFO host blended with green-emitting Dow Chemical LUMATION¹⁴ Green-B polyfluorene copolymer¹⁵ with various blending ratios. The energy bands are indicated in Fig. 1.

In Fig. 2(a) the normalized emission spectra of device A at various voltages are shown. The band peaked at 430 nm is due to PFO host, while the peak at 560 nm is due to the MEH-PPV guest. At lower voltage, the emission is dominated by the guest due to the efficient exciton energy transfer. The photoluminescence (PL) spectrum of the blend film is similar to the EL at lower voltage. As the voltage increases the PFO band rises rapidly. At 10 V the PFO blue emission is as strong as the MEH-PPV orange emission. Because the 430 nm emission and the MEH-PPV emission at 560 nm happen to compensate each other, the emission becomes white with Internationale de L'Éclairage (CIE) coordinate (0.34, 0.35) at 10 V. PL spectrum implies that the energy transfer is nearly complete without the voltage bias. The rise of the host emission in electroluminescence (EL) suggests a reduced energy transfer to the guest by the electric field. The LED characteristics of device A are shown in Fig. 3. Peak brightness of 1700 cd/m² is reached at 10 V, which is also the voltage closest to the ideal white CIE coordinate of (0.33, 0.33). Peak yield is 0.6 cd/A at 5 V. The emissive film thickness 500 Å is the optimal value for device A. The characteristic single layer LED of pure PFO is shown for comparison. Both the current density and luminance are similar to device A for a given voltage. It implies that the carriers are not localized in the guest polymers. For device B we use various blend ratios for the MEH-PPV guest in the first layer. The EL spectrum depends on both the voltage and the blend ratio. For fixed ratio, the PFO 430 nm band rises with volt-

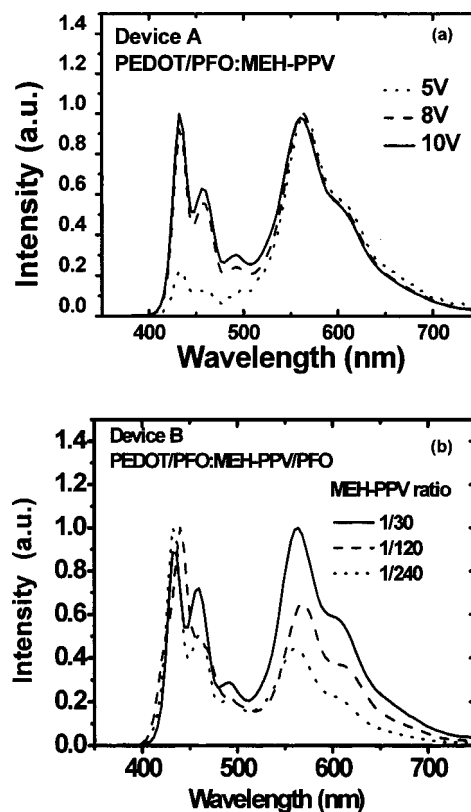


FIG. 2. (a) The normalized EL spectrum of single layer device A is shown for various voltages. The 430 nm PFO peak grows with the voltage. (b) The normalized EL spectrum at peak luminance of homojunction device B is shown for various MEH-PPV blending ratios in weight. The optimal ratio is 1/30.

age as in the case of device A. The voltage dependence of the spectrum is however weaker because the second layer emits only pure blue light regardless of the voltage. The EL spectra for device B with various blending ratios at their individual peak luminance are shown in Fig. 2(b). There is an optimal ratio of 1/30 at which the spectrum can be tuned as white with CIE coordinate (0.34, 0.34). The LED characteristics of device B are shown in Fig. 3. Compared with device A, the peak luminance of device B is doubled to 3000 cd/m² at optimal film thickness of 500 Å for the PFO:MEH-PPV layer and 300 Å for PFO layer. The yield is tripled to 1.6 cd/A. Apparently the improvement is due to the homojunction between PFO:MEH-PPV and PFO layers. Such improvement suggests that the junction has a major effect on the carrier transport and exciton formation process. We therefore expect carrier distribution and recombination in not only

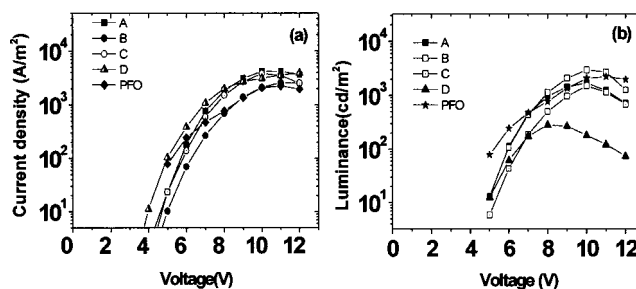


FIG. 3. (a) The current–voltage relations of devices A, B, C, D and pure PFO LED are plotted. (b) The luminance–voltage relations of the devices are shown. The peak white-light luminance of device B is 2928 cd/m².

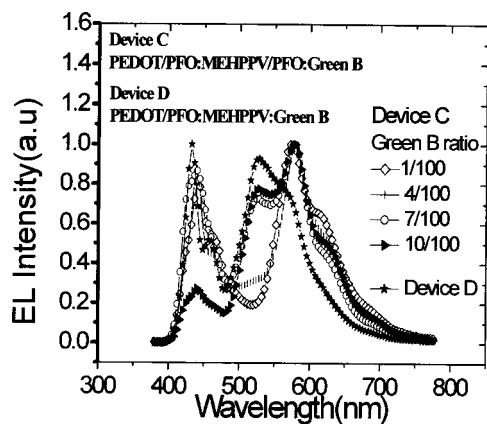


FIG. 4. The normalized EL spectrum at peak luminance of homojunction device C is shown for various Green-B blending ratios in the second layer. The MEH-PPV blending ratio of the first layer is fixed at 1/60. The optimal ratio is 7/100. The EL spectrum of device D is also shown. PFO:Green-B:MEH-PPV blending ratio is 100:10:7.

the host but also the guest. This is quite reasonable because the IP of MEH-PPV (5.3 eV) is 0.5 eV smaller than the IP of PFO (5.8 eV). Most of the holes injected from the PEDOT will be in the MEH-PPV guest while the electrons are uniformly distributed between MEH-PPV and PFO. The holes in MEH-PPV meet an energy barrier of 0.5 eV at the homojunction and are accumulated there. The accumulation enhances the recombination and balances the carrier injections in polymers.¹³ Another advantage of the hole barrier is to keep the recombination away from the cathode to avoid exciton quenching. The homojunction is superior to the heterojunction of pure MEH-PPV and pure PFO because in the heterojunction LED the blue emission from the PFO will be absorbed by the MEH-PPV before it comes out of the ITO glass. There is no such reabsorption problem in the homojunction since the absorption of the first layer is determined by the high band-gap PFO host instead of the low band-gap MEH-PPV.

Even though by compensating orange and blue emission the spectrum of device B is very close to the CIE white, it is not ideal for the application in full-color display with color filters due to lack of green emission. In order to solve the problem we study device C with Dow Chemical LUMATION¹⁴ Green-B polyfluorene copolymers blended into the second layer as the green guest. Both sides of the homojunction are blends in this case. The EL spectrum of device C for various green blending ratios is shown in Fig. 4. The optimal Green-B to PFO ratio at peak luminance is 7/100 while the MEH-PPV:PFO ratio is fixed at 1/60 as in device A. The CIE coordinate is (0.34, 0.34). The LED characteristics of device C are shown in Fig. 3. Peak luminance achieved at 10 V is 1500 cd/m², about half of device B. The reason for the reduction is probably due to the electron barrier of 0.6 eV between Green-B and PFO (see Fig. 1). Because the ratio of MEH-PPV is small in the first layer, the majority of the electron will be injected into the PFO conduction band initially at the homojunction. The large energy barrier makes this injection difficult. The balance of electron-hole injection provided by the hole barrier in device B is therefore weakened. Nevertheless, luminance of 1500 cd/m² is one of the best in polymer LEDs with three peaks at the

TABLE I. The performance of all the devices are summarized. The luminance and yield are peak values. CIE coordinates are taken at the peak luminance.

Device	Yield (cd/A)	Luminance (cd/m ²)	CIE
A	0.62	1690	(0.34, 0.35)
B	1.63	2928	(0.35, 0.34)
C	0.4	1496	(0.34, 0.34)
D	0.1	300	(0.29, 0.38)

primary colors. In order to further emphasize the effect of the homojunction, we compare device C with device D which is a single layer LED with both Green-B and MEH-PPV blended in the PFO host. The nearly white EL spectrum of device D is shown in Fig. 4. The yield of device D is reduced by a factor of 4 as shown in Fig. 3 and Table I. This is similar to the case that the yield of device A is three times lower than device B. In general, the efficiency of the homojunction LED is always much higher than the single-layer blend LED with the same composition due to carrier accumulation at the junction.

In conclusion, strong white emission is achieved in polymer LED with a homojunction between two layers with the same host blue polymer. This LED is based only on commonly used conjugated polymers MEH-PPV and PFO. No dye or phosphorescent molecules are involved. The homojunction both facilitates the color control and improve the efficiency by hole blocking. Without synthesizing any new material, our work demonstrates a new easy method to fabricate large-area efficient white LED.

The authors thank the Dow Chemical Company for supplying the LUMATION¹⁴ Green-B polymers. This work is supported by the National Science Council of the Republic of China, Industrial Technology Research Institute of ROC, and the Excellence Project of the ROC Ministry of Education.

¹C. W. Ko and Y. T. Tao, Appl. Phys. Lett. **79**, 4234 (2001).

²M. Granström and O. Inganäs, Appl. Phys. Lett. **68**, 147 (1996).

³B. Hu and F. Karasz, J. Appl. Phys. **93**, 1995 (2003).

⁴J. I. Lee, H. Y. Chu, S. H. Kim, L. M. Do, T. Zyung, and D. H. Hwang, Opt. Mater. (Amsterdam, Neth.) **21**, 205 (2002).

⁵C. L. Chao and S. A. Chen, Appl. Phys. Lett. **73**, 426 (1998).

⁶J. S. Kim, B. W. Seo, and H. B. Gu, Synth. Met. **132**, 285 (2003).

⁷I. Tanaka, M. Suzuki, and S. Tokito, Jpn. J. Appl. Phys., Part 1 **42**, 2737 (2003).

⁸M. L. Tsai, C. Y. Liu, M. A. Hsu, and T. J. Chow, Appl. Phys. Lett. **82**, 550 (2003).

⁹J. Kido, H. Shionoya, and K. Nagai, Appl. Phys. Lett. **67**, 2281 (1995).

¹⁰R. Friend, R. Gymer, A. Holmes, J. Burroughes, R. Marks, C. Taliani, D. Bradley, D. Dos Santos, J. Brédas, M. Lögdlund, and W. Salaneck, Nature (London) **397**, 121 (1999).

¹¹P. E. Burrows, G. Gu, V. Bulović, Z. Shen, S. R. Forrest, and M. E. Thompson, IEEE Trans. Electron Devices **44**, 1188 (1997).

¹²C. C. Huang, H. F. Meng, G. K. Ho, C. H. Chen, C. S. Hsu, J. H. Huang, S. F. Horng, B. X. Chen, and L. C. Chen, Appl. Phys. Lett. **84**, 1195 (2004).

¹³B. K. Crone, P. S. Davids, I. H. Campbell, and D. L. Smith, J. Appl. Phys. **87**, 1974 (2000).

¹⁴Trademark of The Dow Chemical Company.

¹⁵T. Bernius, M. Inbasekaran, J. O'Brien, and W. Wu, Adv. Mater. (Weinheim, Ger.) **12**, 1737 (2000).