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# Electroluminescent Devices Using Polymer Blend Thin Films

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## Abstract

We report the thin film electroluminescent devices made from polymer blends composed of the luminescent conjugated polymer poly(3-n-butyl-*p*-pyridyl vinylene) (Bu-PPyV), a hole-transporting polymer poly(9-vinyl carbazole) (PVK), and an electron-transporting material 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD). Through the blends, we show that the self-quenching of the luminescence of the luminescent polymer is reduced and the luminescent efficiency is much increased. Carrier transport materials provide better match of hole and electron injection into the blends and therefore raise the electroluminescent efficiency by over one order of magnitude higher than the pure material. By tuning the composition of the blends, the emission color can be changed across the whole visible spectrum.

## Introduction

That luminescent polymers deposited by spin-coating can be used to fabricate thin film electroluminescent devices has been known for several years [1,2]. The basic structure of a luminescent polymer contains alternation of single and double bonds along the polymer chain. The interaction of  $\pi$  bonds along the polymer chain results in the formation of  $\pi$  and anti- $\pi$  bands and the energy gap between them. As shown in Fig. 1, a simplest polymer LED is formed by spin-coating the polymer on an ITO-coated (transparent electrode) glass substrate, followed by the evaporation of a top metal contact. The performances of such simple devices are usually poor due to some basic limitations. First, an efficient luminescent polymer does not necessarily have both good electron and hole transport properties. Also, due to the self-quenching or interchain interaction, the luminescent efficiencies of these polymers in the form of solid thin films are much lower than those in their dilute solvent solutions [3]. To overcome the carrier transport problems, various approaches have been adopted, including the use of reactive low work function metal electrodes[2] and the incorporation of carrier

transport layers to form a multilayer device structure[4]. Making devices with several spin-coated polymer layers is not easy because the solvent carrying a second layer might dissolve a layer which has already been deposited. In our studies, we investigated LEDs made from polymer blends composed of the luminescent conjugated polymer Bu-PPyV, the hole-transporting polymer PVK and the electron-transporting material PBD, whose chemical structures are shown in Fig. 2. Instead of using separate carrier-transporting and emitting layers, we mixed all materials as a blend in a solvent and then deposited it in a single step, simplifying the device fabrication. The effects of blending on optical and electrical properties of polymers were then studied.

## Processing

Bu-PPyV used in this study was synthesized by cross-coupling the corresponding 2,5-dibromopyridine and E-1,2-bis(tributylstannylethylene) in the presence of a palladium catalyst, as described in the references [5,6,7,8]. As a result of the butyl side group, Bu-PPyV is soluble in its conjugated form in conventional organic solvents, such as chloroform, THF, etc. Solutions containing different amounts of Bu-PPyV, PVK, PBD in chloroform were prepared to give PVK/Bu-PPyV or PVK/Bu-PPyV/PBD blends of different ratios. The solutions were then spin-coated onto quartz substrates for optical measurements and onto glass substrates with 2mm wide ITO stripes for device fabrication. The typical film thicknesses range from 800-2000Å, depending on the concentration and the spin rate. The devices were then finished by thermally evaporating 2mm wide Al stripes perpendicular to the ITO stripes on top of the polymer blend films to form an array of 2mmX2mm LEDs.

## Results and Discussions

### A. PVK/Bu-PPyV Blends

Though Bu-PPyV is a very efficient luminescent polymer in dilute solutions (photoluminescence quantum efficiency >90%), its luminescence in concentrated solutions or solid thin films is much weaker, along with the red-shift and broadening of the spectra [7,8]. The difference is attributed to the interchain interaction of Bu-PPyV, due to its rigid chain structure and quite planar geometry of polymer chains. The interchain interaction leads to the formation of excimers between Bu-PPyV chromophores, which emit at lower energies and have low radiative efficiency. Diluting Bu-PPyV with higher energy-gap PVK in solid thin films eliminates the formation Bu-PPyV excimers and thus recovers the Bu-PPyV monomer emission (green) and its much higher luminescent efficiency (Fig. 3). Fig. 4 shows the PL spectra of blends excited at 340nm, where the photon energy is beyond PVK absorption onset and there is minimal absorption from Bu-PPyV. Due to the lower energy gap of Bu-PPyV, excitons formed in the blend can efficiently transfer to Bu-PPyV chromophores. Therefore, with Bu-PPyV content as much as 1 wt.%, almost all emission is from Bu-PPyV. The emission from PVK is purple and can only coexist with Bu-PPyV emission at extremely low Bu-PPyV content. The optimal PL intensity is obtained around 2 wt% and is about 10 times higher than that of pure Bu-PPyV.

The electroluminescence (EL) spectra of the LEDs made from these blends are similar to their 340nm PL spectra, as shown in Fig. 5. Pure PVK emits purple light, blends with extremely low Bu-PPyV content (<1 wt%) emit blue light, which is the combination of PVK emission and Bu-PPyV monomer emission; above 1 wt%, the Bu-PPyV monomer emission is dominant and the emission is green; Further increase of the Bu-PPyV content in the blend increases the interaction of Bu-PPyV chromophores and causes the redshift of spectra to yellow and finally to red emission of Bu-PPyV excimers. Therefore, by tuning the composition of the blends, the full visible color range of polymer LEDs has been spanned with a single series of polymer blends.

The I-V characteristics of LEDs made from PVK and Bu-PPyV are shown in Fig. 6. The LEDs made from the pure Bu-PPyV have relatively high turn-on voltage due to the difficulty for carrier injection. As shown in Fig. 7, in the dilute PVK/Bu-PPyV blends, the I-V characteristics are not significantly different from those of pure PVK devices, suggesting that the current transport occurs through PVK, leading to a lower turn-on voltage. But at much higher Bu-PPyV contents, the I-V curves will noticeably shift to a higher voltage, indicating that the carrier transport is more complicated. The external EL quantum efficiency vs. Bu-PPyV content is shown in Fig. 8. The quantum efficiency of blends first increases rapidly with the Bu-PPyV content and reaches the 0.01% level of

pure Bu-PPyV around 5 wt%, then saturates around that level. That the dilute 5 wt% blend has similar efficiency to 100wt% Bu-PPyV is believed to be due to the much higher luminescent efficiency of Bu-PPyV monomers than Bu-PPyV excimers.

### *B. PVK/Bu-PPyV/PBD Blends*

Though at the optimal PVK/Bu-PPyV blend ratio, a lower turn-on voltage is achieved, the EL quantum efficiency is just slightly higher than pure Bu-PPyV. It is believed to be due to the poor electron transport or injection ability of the PVK, though it is a good hole transport material. Adding an electron transport material into the blends is therefore considered. PBD, which has been used as electron transport material in layered organic EL devices [4] or polymer blends with other polymers [9,10], was used in our study. Similar to PVK, it also has a larger energy gap than Bu-PPyV, with absorption onset around 350nm and PL peak around 390nm.

As shown in Fig. 3, the relative PL efficiency of Bu-PPyV in the PVK/Bu-PPyV/PBD blend has the same trend with the Bu-PPyV content, as in the PVK/Bu-PPyV blend. The PL spectra of PVK/Bu-PPyV/PBD blends, excited at 340nm, are also similar to those of PVK/Bu-PPyV blends, showing similar exciton transfer to Bu-PPyV, Bu-PPyV monomer emission and transition to Bu-PPyV excimer emission.

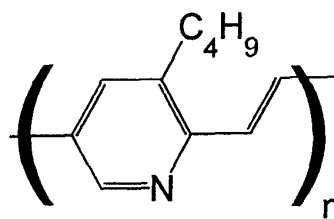
The performances of LEDs made from these PVK/Bu-PPyV/PBD, however, is much better than the PVK/Bu-PPyV devices. The EL external quantum efficiency vs. Bu-PPyV content is shown in Fig. 8. The composition PVK:Bu-PPyV:PBD is 100:X:100, where the ratio between PVK and PBD is about optimal. The highest EL efficiency is around 0.2%, over one order of magnitude higher than that of pure Bu-PPyV or the best two-component blend without PBD. Fig. 9 shows the light intensity vs. dc drive current for the best PVK/Bu-PPyV and PVK/Bu-PPyV/PBD devices. As shown in Fig. 7, the turn-on voltage of PVK/Bu-PPyV/PBD is higher than PVK, but still lower than pure Bu-PPyV. The I-V characteristics up to 10 wt.% are not significantly different from those of PVK/PBD blend. It indicates that now the current transport occurs through PVK and PBD, holes through PVK and electrons through PBD. For our optimal devices, the brightness is about 220cd/m<sup>2</sup> at 25V, 30mA/cm<sup>2</sup>. The estimated luminous efficiency is about 0.1 lumen/watt, not as high as the values of the commercial thin film EL displays, which are usually on the order of 1 lumen/watt. But the threshold voltage of commercial EL displays are so high that they have to be driven by pulses of high voltages (>100V) and therefore the typical brightness is only tens of cd/m<sup>2</sup> to 100 cd/m<sup>2</sup>.

## Conclusion

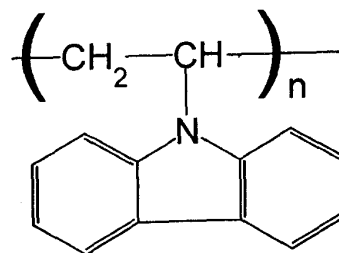
In summary, we have presented the results of the EL devices made from Bu-PPyV blended with PVK and PBD. Diluting Bu-PPyV with higher energy gap PVK and PBD in the thin films reduces the interchain interaction and improves the luminescence efficiency of Bu-PPyV. Along with better match of hole and electron injection through PVK and PBD, the EL quantum efficiency can be as high as 0.2%. Adjusting the blend compositions allows one to cover the visible spectra.

## Reference

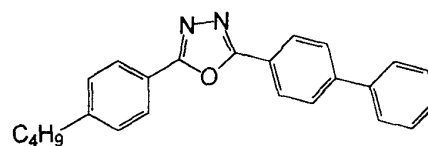
- [1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A. B. Holmes, *Nature* **347**, 539 (1990)
- [2] D. Braun, A.J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991)
- [3] Jenekhe, J.A. Osaheni, *Science* **265**, 765 (1994)
- [4] A.R. Brown, D.D.C. Bradley, P.L. Burn, J.H. Burroughes, R.H. Friend, N. Greenham, A.B. Holmes, A. Kraft, *Appl. Phys. Lett.* **61**, 2793 (1992)
- [5] M.J. Marsella, T.M. Swager, *Polymer Preprints* **33**(1), 1196 (1992)
- [6] J. Tian, M.E. Thompson, C.C. Wu, J.C. Sturm, R.A. Register, M.J. Marsella, T.M. Swager, *Polymer Preprints* **35**(2), 761 (1994)
- [7] J. Tian, C.C. Wu, M.E. Thompson, J.C. Sturm, R.A. Register, *Adv. Mater.* **7**, 395 (1995)
- [8] J. Tian, C.C. Wu, M.E. Thompson, J.C. Sturm, R.A. Register, *Chem. Mater.*, in press
- [9] C. Zhang, H. von Seggern, B. Kraabel, H.W. Schmidt, A.J. Heeger, *Synth. Met.* **72**, 185 (1994)
- [10] C. Zhang, S. Hoyer, K. Pakbaz, F. Wudl, A.J. Heeger, *J. Electron. Mater.* **23**, 453 (1994)



Bu-PPyV



PVK



PBD

Fig. 2: Chemical structures of Bu-PPyV, PVK and PBD

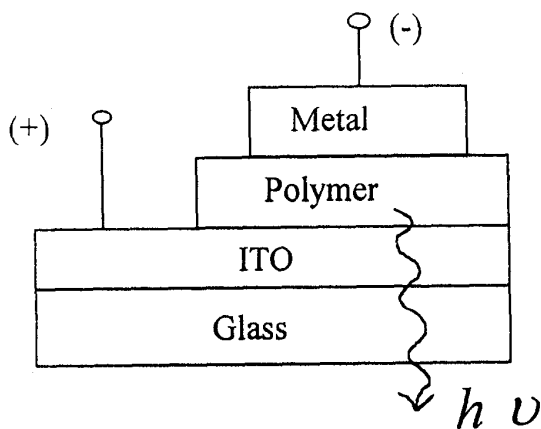


Fig. 1: Device structure of polymer LED

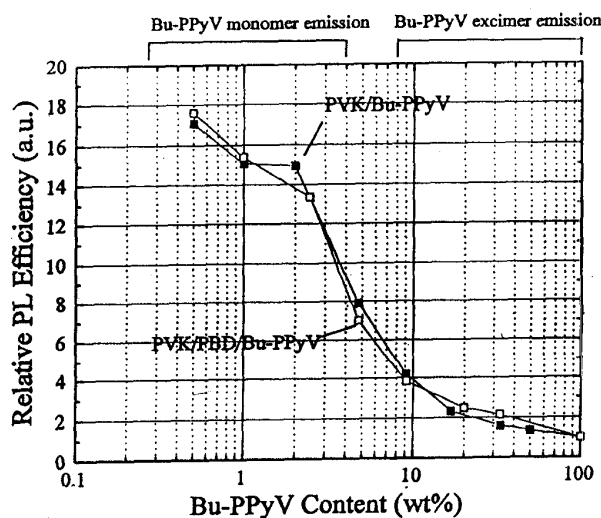


Fig. 3: Relative PL efficiency of Bu-PPyV in blends vs. Bu-PPyV content, using excitation wavelength 420nm (absorbed by Bu-PPyV only)

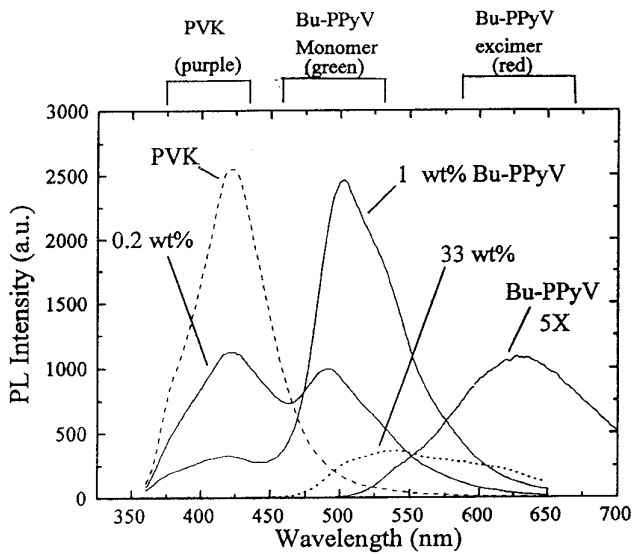


Fig. 4: PL spectra of PVK, Bu-PPyV and blends, using excitation wavelength 340nm (most absorbed by PVK)

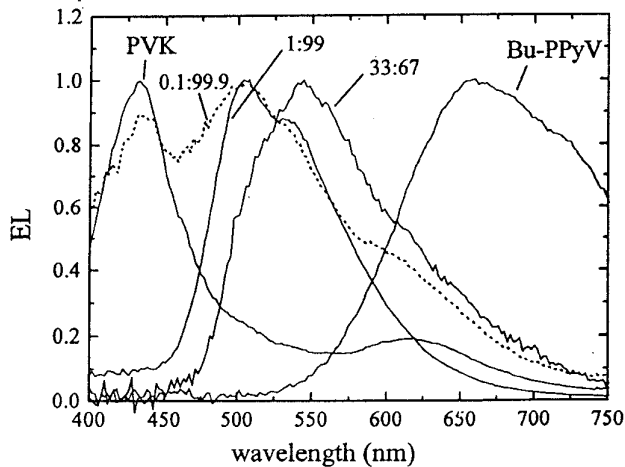


Fig. 5: EL spectra of PVK, Bu-PPyV and PVK/Bu-PPyV blends.

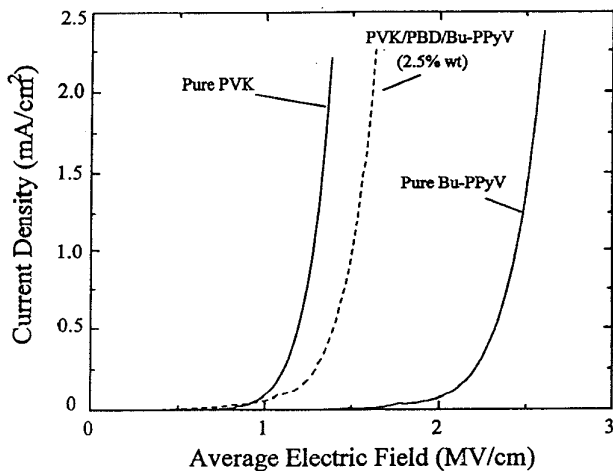


Fig. 6: Forward current vs. average field (V/tnfilm thickness) of polymer LEDs.

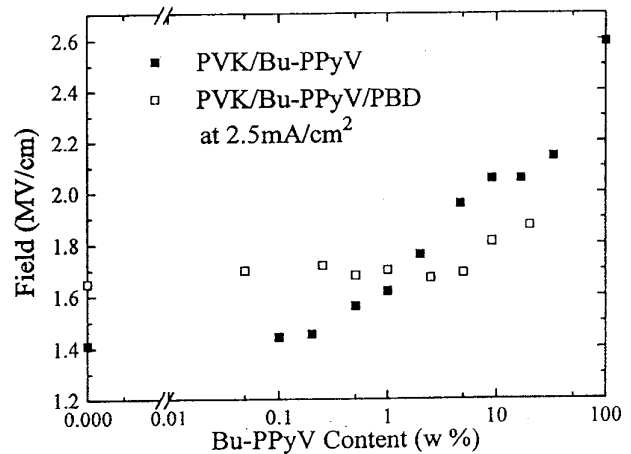


Fig. 7: Average field (at  $J=2.5\text{mA/cm}^2$ ) vs. Bu-PPyV content

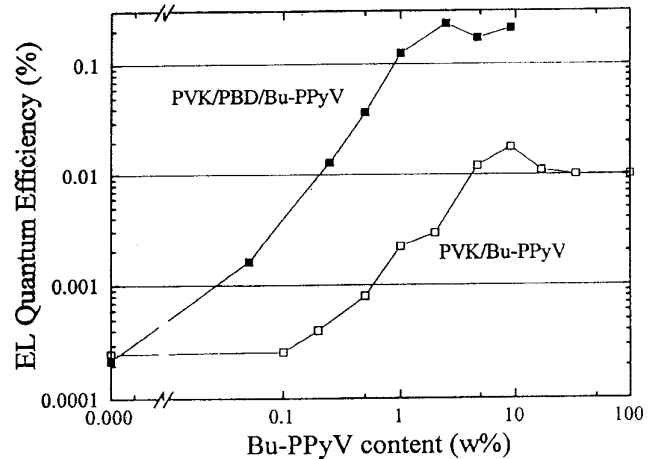


Fig. 8: External EL quantum efficiency of blend LEDs vs. Bu-PPyV content.

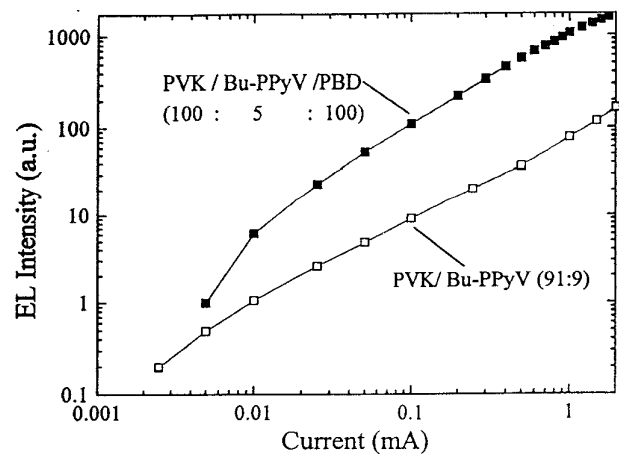


Fig. 9: Light intensity vs. dc drive current