

# Blue polymer light emitting diode based on ladder poly(para-phenylene)<sup>☆</sup>

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## Abstract

A blue polymer light emitting diode was prepared by inserting an electron transport layer between cathode and poly (N-vinylene carbazole) (PVK) doped by ladder poly (para-phenylene) (LPPP) layer. In comparison with the single layer LPPP device, the brightness of the device was improved by about one order of magnitude. An explanation based on energy diagram of the devices was presented. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Ladder poly(para-phenylene), Polymer light emitting diode

## 1. Introduction

Polymer light-emitting diodes (PLED) have attracted considerable interest due to the ease of their production, high achievable electroluminescence (EL) efficiency at relatively low drive voltage, especially possibility of obtaining emission in blue region [1,2]. To date blue emission has already been demonstrated in a wide range of conjugated polymers, non-conjugated polymers and polymer blends [1,3,4]. Among them, ladder poly(para-phenylene) is one of the best blue emitter for excellent solubility in organic solvent, low subgap absorption, high photoluminescence (PL) efficiency, good resistance to moisture and oxygen. However due to its co-planar structure of molecules, relatively large interaction among molecules causes redshift of emission spectra and decrease of the efficiency of the device [2,5]. Chemical tailoring methods have been adopted to interrupt regular conjugated length and decrease the coplanar degree of molecules, in addition incorporation high energy gap spacer group results in retarding the exciton from migrating to quenching centers [6,7]. We note that doping LPPP into a polymer matrix may be an alternative way to solve the above mentioned problems, since interaction between LPPP molecules would be decreased with reduced LPPP concentration in a polymer matrix. First of all we measured PL spectrum of LPPP, and the excitation spectrum of LPPP has a large overlap with emission spec-

trum of poly(N-vinylene carbazole) (PVK), which may imply the possibility of energy transfer from PVK to LPPP molecules when we doped LPPP in PVK matrix. Combining doping LPPP in PVK matrix and incorporating electron transport layer to build trilayer structure device as initially reported by Kido [3], we obtained about 5–8 folds improvement of device brightness in comparison with that of the single layer LPPP device.

## 2. Experimental

PVK and LPPP were dissolved in chloroform, the concentration of PVK and LPPP solution was about 5 and 1 mg/ml, respectively. PVK:LPPP blending solution with different concentration LPPP was spin-coated on conducting glass and quartz substrate for constructing electroluminescence (EL) device and PL measurement, respectively. Electron transport material, 1,3-bis(4-tert-butylphenyl)-1,3,4-oxadiazoyl (OXD) and (8-hydroxyquinolino) aluminium (Alq<sub>3</sub>) were thermally evaporated in a vacuum with about  $2 \times 10^{-5}$  Torr. The thickness of evaporating layer and deposition rate was monitored by quartz crystal thickness monitor placed near the substrate. The front electrode, about 100 nm thick aluminium, patterned by a shadow mask, was deposited by thermal evaporation in a vacuum of  $6 \times 10^{-5}$  Torr. All the measurements were then carried out in air at room temperature without any subsequent processing.

<sup>☆</sup> Supported by Key National Natural Science Foundation of China, granted code: 29992530.

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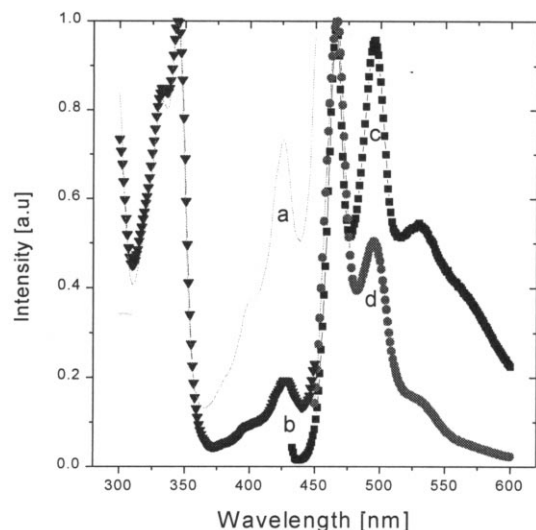


Fig. 1. Photoluminescence measurements of blending sample (a) excitation spectrum of PVK:LPPP (10%) monitored at 467 nm, (b) excitation spectrum of PVK:LPPP (1%) monitored at 467 nm, (c) excitation spectrum of PVK:LPPP (10%) excited at 425 nm, (d) excitation spectrum of PVK:LPPP (10%) excited at 425 nm.

### 3. Results and discussion

Emission spectrum of LPPP film (100–200 nm) sample excited by light of 425 nm wavelength has two peaks located at 468, 495 and a shoulder at 530 nm. PL excitation spectrum of LPPP film monitored at 468 nm has peaks at 456, 426 and 401 nm. The PL emission spectrum of PVK film has a peak at about 420 nm with half height full width about 70 nm. From these data we presume that there might be energy transfer from PVK to LPPP molecules since emission spectrum of PVK greatly overlaps with excitation spectrum of LPPP.

PL of blending film proved this assumption. Fig. 1 shows PL spectra of blending film with the concentration of LPPP by weight about 10 and 1%. Emission spectra of blending films have almost the same peaks when excited by light of 425 nm corresponding excitation peak of LPPP. But the

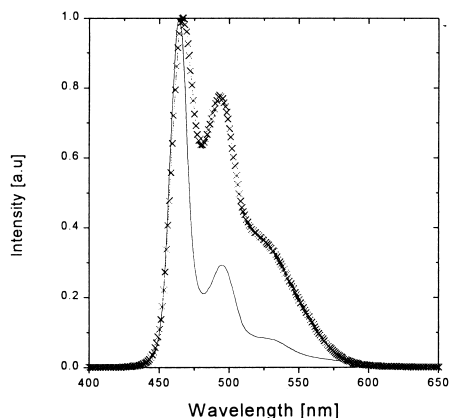


Fig. 2. EL spectrum of doping device (line), EL of single layer LPPP device was also presented for comparison (symbol).

contour of spectrum is different, the peak at 468 nm becomes more dominant when the concentration of LPPP decreases, which can be attributed to the decrease of self-absorption since absorption spectrum of LPPP overlaps partly with emission spectrum of LPPP. The excitation spectra of blending film (monitored at 468 nm) are attributed to both PVK and LPPP, the ratio of intensity of excitation peaks from PVK to that from LPPP becomes larger with decreasing concentration of LPPP. This clearly shows the energy transfer from PVK to LPPP molecules, however, at relatively large concentration of LPPP energy transfer from PVK to LPPP molecules was limited in PL study since PVK emission appeared when we excited the sample by the light with wavelength at excitation peaks of PVK, in contrast to system like dye doped Alq [7].

EL spectrum of freshly fabricated single layer LPPP device (ITO/LPPP/Al) was essentially identical to PL spectrum of LPPP film. Turn-on voltage of the single layer device was about 5 V. Light emission can be observed in normally lighted room when the applied voltage was increased up to 9 V. EL spectra of the doped multilayer device were also the characteristic spectra of LPPP as presented in Fig. 2. We didn't observe emission from PVK in contrast to PL experiment, indicating other energy transfer process or charge transfer process may take place in this case. We think the reabsorption process is not the main process in this case under such low LPPP concentration (1%). We also found LPPP concentration dependent turn-on voltage and different increment of PL efficiency and EL efficiency in this device, we believe direct carrier recombination at dopant sites or charge transfer among PVK and LPPP molecules may be responsible in this case. In EL experiment we also observe emission with better chromaticity in the blue region in the doped device comparing with single layer LPPP owing to decreased self-absorption effect.

In the LPPP doped PVK device with electron transport layer, we found turn-on voltage of device was almost independent on the thickness of OXD layer and Alq layer at rather large range, indicating large part of driven voltage was applied on PVK:LPPP layer. In our experiments the optimized thickness of OXD layer and Alq layer were about 15 and 40 nm, respectively. Emission from both PVK:LPPP layer and Alq layer was observed in the devices with thinner OXD layer, indicating in these devices carrier recombination zone lies both at PVK:LPPP layer and Alq layer. Without Alq layer we found current under the same driven voltage decreased due to relative lower carrier mobility of OXD layer as reported by Kido et al. [2], in addition we also found inferior contact between OXD layer and Al cathode. The turn-on voltage of multilayer device (doping ratio about 1%) was about 7 V, under the similar driven current the light emission was about 5–8 times higher than that of the single layer device. Fig. 3 shows current-voltage characteristic of the device and brightness-voltage characteristic of the device.

Two factors can be attributed for the improvement of

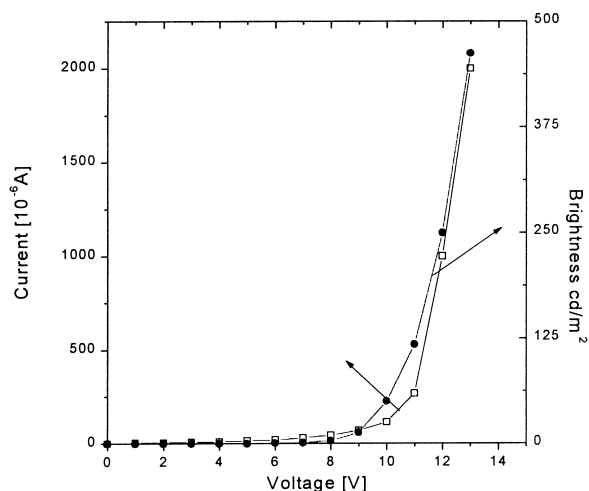


Fig. 3. Current–voltage and brightness–voltage of the device.

efficiency of the device, namely chromophore diluted effect and balanced carrier injection and transportation. The first factors can be proved by following facts: In case of single PVK:LPPP layer there was 2–3 times improvement of efficiency of the device and the peak at 590 nm attributed to emission of aggregated state wasn't observed in contrast to the case in single layer LPPP device. This may imply that interaction between LPPP molecules was decreased in blending film. Fig. 4. shows energy level diagram of multi-layer device: energy level value of organic material were cited from literature [8]. In single layer LPPP device unbalanced carrier injection and carrier transport decreases efficiency of the device owing to larger electron injection barrier and small electron mobility in LPPP [7], furthermore quenching of the luminescence through irradiative paths may occur for carrier recombination zone locates near the cathode. While in multilayer device electron transport may be improved by inserting electron transport layers, while holes are hold in PVK:LPPP layer due to relative larger ionization potential of OXD layer, bigger exciton energy in OXD layer and enough thickness of OXD layer, as result carrier recombination zone locates at the region far from cathode effectively avoiding quenching near the cathode region. In the device with thinner OXD layer holes injected from ITO can tunnel through OXD layer, and recombine with electrons in Alq<sub>3</sub> layer resulting in emission from Alq layer.

#### 4. Conclusion

We have demonstrated energy transfer process (Frost) from PVK to LPPP molecules when we doped LPPP into

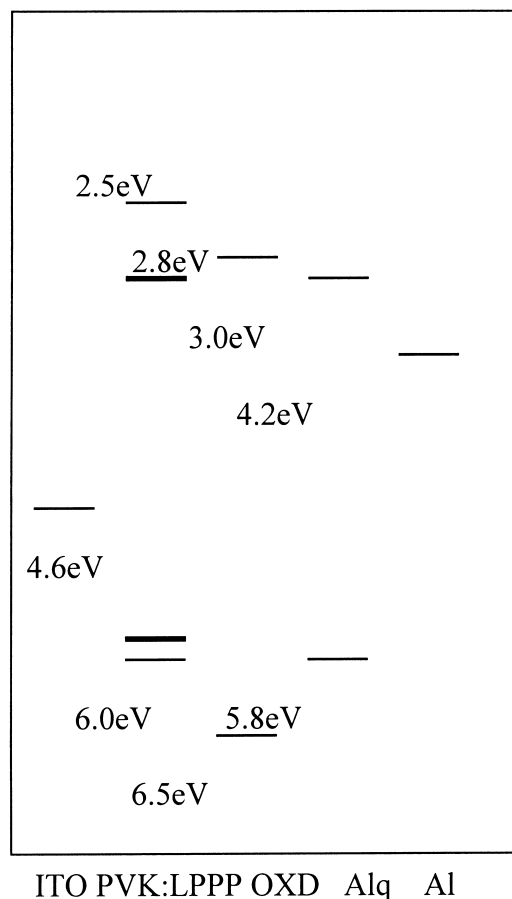


Fig. 4. Energy level diagram of the device.

PVK matrix. The better chromaticity of blue emission both in PL and EL measurement is attributed to the decrease of self-absorption effect. The improved brightness was attributed to the balance of carrier injection and recombination.

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