JOURNAL OF
Materials
CHEMISTRY

Enhancing emission of poly(*p*-phenylenevinylene) by sandwiching an energy transferable layer

Horng-Long Cheng and King-Fu Lin*

Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan, 10617, Republic of China. E-mail: kflin@ccms.ntu.edu.tw; Fax: +886-2-2363-4562; Tel: +886-2-2392-8290

Received 24th April 2002, Accepted 19th May 2002
First published as an Advance Article on the web 28th June 2002

Photoluminescent (PL) and electroluminescent (EL) efficiencies of poly(*p*-phenylenevinylene) (PPV) film were found to be significantly increased by sandwiching an energy-transferable poly(2-carboxyphenylene-1,4-diyl) (PCPD) layer. Energy transfer from PCPD to PPV in the prepared PPV/PCPD/PPV trilayer film was detected by photoluminescence excitation (PLE) spectroscopy and time-resolved fluorescence decay profiles, and was attributed to the chemical-interlocking between two polymers in the interfacial regions. It resulted in a strong increase of the PL intensity, a ~250-times increase of the maximum external EL quantum efficiency (up to 1.3% photon/electron), and a ~500-times increase of the maximum light output for the ITO/PPV/PCPD/PPV/Al device compared to the neat PPV. The significant increase of EL was also attributed to the higher energy bandgap of inserting PCPD layer that trap the holes and electrons in the interfacial regions, facilitating the formation of excitons *in situ* and energy transfer.

Introduction

Polymeric light-emitting diodes (PLEDs) have become an active research area since the discovery of the electroluminescent (EL) properties of poly(*p*-phenylenevinylene) (PPV).[1] As a result of low reflective index and easy processing, PLEDs are considered as a potential candidate for large flat surface display. Efforts to pursue a higher luminescent efficiency through the innovation of emitting mechanisms have been one of the major approaches for the development of PLEDs. Recent research[2–6] has shown that it is possible to obtain an energy transfer of excitations in a host–guest (or donor–acceptor) polymeric pair contributing to the enhancement of both photoluminescent (PL) and EL efficiencies.

Poly(2-carboxyphenylene-1,4-diyl) (PCPD) is a conjugated polymer with an emission spectrum within the optical absorption region of PPV.[7] A good spectral overlap between the emission of PCPD and the absorption of PPV was believed to have an efficient energy transfer if they were miscible. Unfortunately, poly(xylylene tetrahydrothiophenium chloride) (PXT, also dubbed as PPV-precursor) and PCPD can not be mixed in solution because of formation of a polyion complex. In our previous work, we have prepared the PPV/PCPD bilayer films by sequentially spin-coating the PXT aqueous solution and PCPD pyridine solution, followed by heat treatment to transform the PXT to PPV. The resulting bilayer films had an energy transfer efficiency of ~36%, measured by the time-resolved PL decay profile.[7] The PL intensity was much higher than that of the neat PPV and the maximum external EL quantum yield of the prepared ITO/PPV/PCPD/Al device was $8.3 \times 10^{-2}\%$ at 9.5 V, ~16 times that of the neat PPV ($5.3 \times 10^{-3}\%$ at 5.5 V). If PXT was transformed to PPV by heat treatment before the PCPD layer was applied, the quality of the bilayer film was poor, resulting in the inconsistent PL and EL emissions.[8] The energy transfer efficiency was also significantly reduced when detectable.

In this study, a PPV/PCPD/PPV trilayer film was prepared by alternately spin-coating the PPV-precursor aqueous solution and the PCPD pyridine solution, followed by heat treatment. An arrangement of adjacent positive and negative polyion layers in preparation of a trilayer film resulted in better contact between the two polymers in the interfacial regions (see Fig. 1), where they were further chemically interlocked by subsequent heat treatments. As a result, near 100% energy transfer from PCPD to PPV was obtained with a stronger PL emission than the PPV/PCPD bilayer film. The external EL quantum efficiency of the ITO/PPV/PCPD/PPV/Al device was ~16 times that of the bilayer films and $\sim 16^2 = 256$ times that of the neat PPV.

Experimental

Materials

PXT, with a weight average molecular weight ($\bar{M}_w$) of 1.2×10^6 and a dispersity of 3.2 relative to the polystyrene standards (measured by GPC), was prepared *via* a modified sulfonium precursor route.[9,10] The detailed description has been reported elsewhere.[11] PCPD with a $\bar{M}_w$ of $\sim 1.3 \times 10^3$ and a dispersity

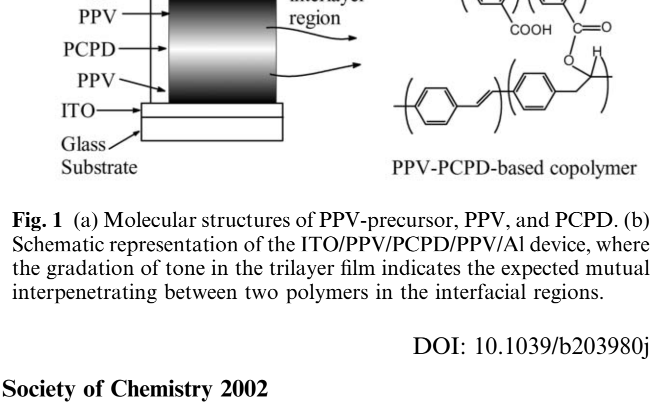

Fig. 1 (a) Molecular structures of PPV-precursor, PPV, and PCPD. (b) Schematic representation of the ITO/PPV/PCPD/PPV/Al device, where the gradation of tone in the trilayer film indicates the expected mutual interpenetrating between two polymers in the interfacial regions.

DOI: 10.1039/b203980j

of 1.75 was synthesized by the Chaturvedi method.[12] The prepared PCPD was only soluble in basic solvents such as pyridine and quinoline.

Neat PPV film was prepared by spin-coating the PXT aqueous solution ($\sim$0.25 wt%) onto an indium tin-oxide (ITO)-coated glass plate (20 Ω square^{-1}, Merck Co.) followed by heat treatment at 180 °C for 2 h (under vacuum $<10^{-5}$ Torr). Neat PCPD film was prepared by spin-coating its pyridine solution ($\sim$15 mg ml^{-1}) onto an ITO-coated glass plate and the pyridine solvent was removed at 180 °C under high vacuum. The PPV/PCPD/PPV trilayer film was fabricated by the following procedure. At first, the PXT aqueous solution was spin-coated onto an ITO glass substrate. After drying, the PCPD pyridine solution was spin-coated on the top and then the third layer of PXT was applied. The PXT/PCPD/PXT trilayer film was then heat-treated under vacuum ($<10^{-5}$ Torr) at 180 °C for 2 h to give a final PPV/PCPD/PPV configuration. After heat treatment, the trilayer film appeared to be homogeneous and transparent. The individual layer thickness of the PPV/PCPD/PPV trilayer film sample was controlled at $\sim$25, 50, and 25 nm, respectively; measured using a surface profilometer (Dektek Co., Model 3030). Neat PPV and PCPD film samples were also prepared in a thickness of 100 $\pm$ 10 nm for comparison.

The PLED devices used in this study typically consist of an ITO on a glass substrate acting as a hole-injecting electrode, a polymer film, and an evaporated Al metal acting as an electron-injecting electrode. Evaporation of the Al metal electrode was performed by using a thermal evaporator (JEOL Co, Model JEE-4C). The coated Al electrode was controlled at a thickness of 1500–2000 Å. The active areas of each device for emission were 5 mm^2.

Characterization

Infrared spectra of polymer films (removed from the coated glass substrates) were recorded on a Jasco 300E model FTIR spectrometer. The ultraviolet/visible (UV/vis) absorption spectra were recorded on a Jasco-555 model spectrometer. PL and photoluminescence excitation (PLE) spectra of the films were recorded on a Jasco FR-777 spectrofluorometer. The current-voltage (I-V) characteristics of the devices were measured by a Keithley 2400 model electrometer, where the concurrent EL intensities were recorded by using a calibrated photometer (International Light, Inc., model IL1400A). The external quantum efficiency was measured using a calibrated integrating sphere. The EL spectra of devices were recorded on a Jasco FR-777 spectrofluorometer. Time-resolved fluorescence of the specimens in a closed cycle cryostat under vacuum ($<10^{-5}$ Torr) at room temperature was recorded by a time-correlated single photon counting apparatus with a time resolution of $\sim$80 ps. The excitation was from the triplet of Ti : Sapphire laser at a wavelength of 290 nm. The excitation power was less than 1 mW. Cyclic voltammograms of polymer films coated on platinum (Pt) substrate were recorded against a Ag/AgCl reference electrode at a scanning speed of 10 mV s^{-1}, using a conventional 3-electrode cell in an acetonitrile–0.1 M tetrabutylammonium tetrafluoroborate solution. A platinum plate was used as a counter electrode. Each measurement was calibrated with the internal standard ferrocene/ferrocenium (Fc/Fc$^+$), whose potential was measured as 0.47 V against a Ag/AgCl reference electrode.

Results and discussion

Fig. 2 shows the infrared spectra of PPV, PCPD, and PPV/PCPD/PPV films respectively. The chemical reactions between PPV and PCPD in the trilayer film to form the C–O–C linkages were resolved by the shift of asymmetrical and symmetrical C–O stretching vibrations of PCPD from 1228 to 1237 cm^{-1}. In addition, the band at 965 cm^{-1} contributed by the bending vibration of the *trans*-vinylene C–H out of plane mode of PPV was shifted to a lower frequency ($\sim$959 cm^{-1}). Similar shifting was also reported for the PPV chains with shorter conjugated length.[13,14]

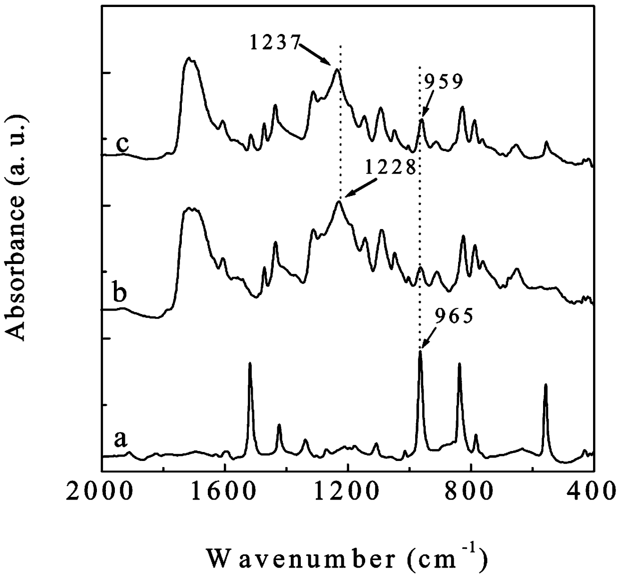

Fig. 2 Infrared spectra of films of (a) PPV, (b) PCPD, and (c) PPV/PCPD/PPV.

The absorption and PL spectra of PPV, PCPD, and PPV/PCPD/PPV are shown in Fig. 3. The absorption of the trilayer configuration is approximately the sum of those of the individual layers. However, the bandgap (E_g) estimated from the onset of absorption of the trilayer film (2.40 eV) is slightly larger than that of the neat PPV (2.36 eV). The PL spectrum of the trilayer film at 290 nm excitation is basically similar to that of PPV but with much higher intensity. It should be noted that no emission from the PCPD layer was observed, strongly suggesting that an energy transfer from PCPD toward PPV contributed to the strong emission of PPV.

The energy transfer phenomenon was further investigated by photoluminescent excitation (PLE) spectroscopy as shown in Fig. 4. For the trilayer film the PLE (in response to the 540 nm emission) is the sum of the individual PLEs, indicating that the energy absorbed by the PPV and PCPD in excitation both contribute to the emission of PPV. Since the energy transfer efficiency is dependent on the distance between

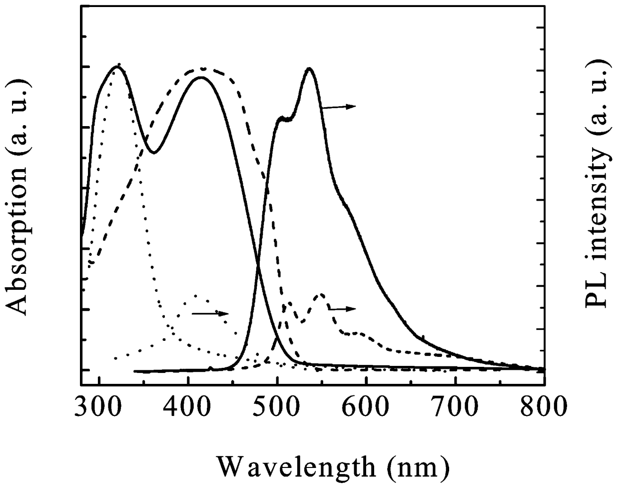

Fig. 3 Optical absorption spectra and PL spectra (λ_{exc} = 290 nm) of PPV (dashed line), PCPD (dotted line), and PPV/PCPD/PPV films (solid line).

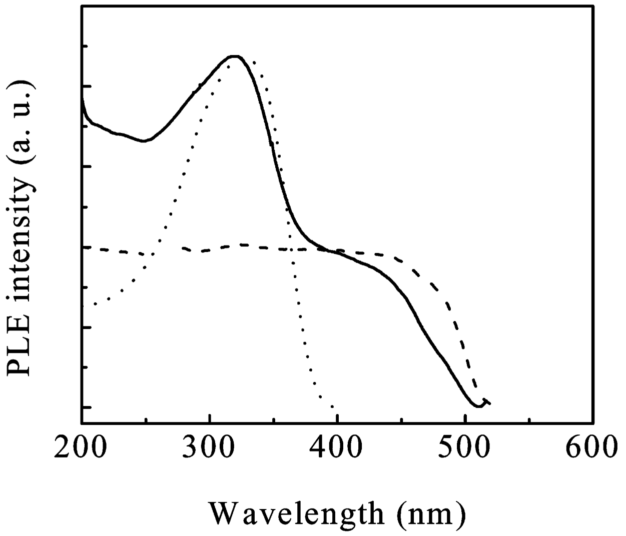

Fig. 4 PLE spectra of PPV (λ_{em} = 550 nm, dashed line), PCPD (λ_{em} = 420 nm, dotted line), and PPV/PCPD/PPV films (λ_{em} = 540 nm, solid line). Note that the spectra have arbitrary units and the curves have been offset for clarity.

donor and acceptor,[15,16] we believed that the interfaces where the polymer chains of PPV and PCPD were chemically-interlocked provided a specific region for the energy transfer. The energy transfer efficiency from PCPD donor to PPV acceptor in the trilayer film was close to 100% because we did not observe any PCPD emission at 420 nm in the PL spectrum. However, the possibility that PPV layers may absorb the PCPD emission in bulk region and subsequently re-emit should not be ruled out.

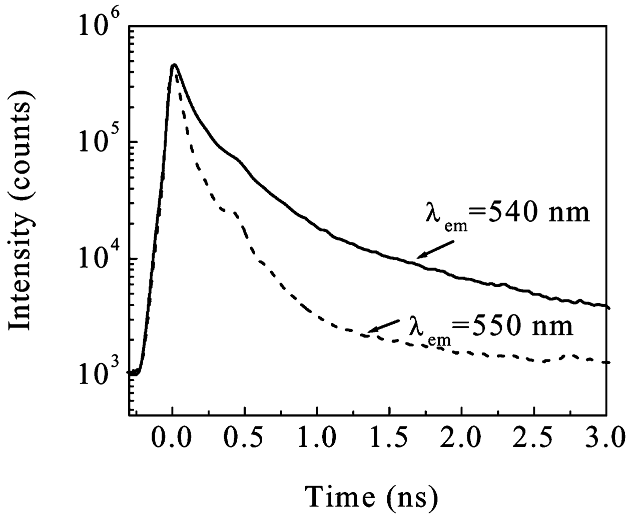

Fig. 5 Time-resolved PL of PPV (dashed line) and PPV/PCPD/PPV (solid line) at a pump wavelength of 290 nm, collected at 0–1 transition bands (as indicated by λ_{em}) of PPV, respectively. The curves were normalized to the same peak intensity.

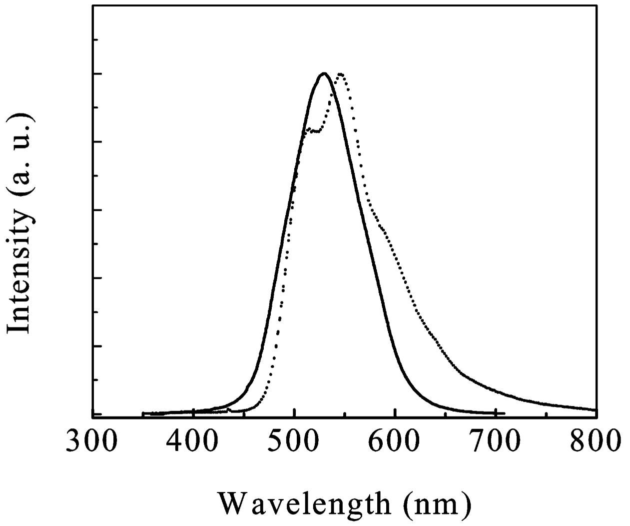

Fig. 6 EL spectrum (solid line) of the ITO/PPV/PCPD/PPV/Al device along with the PL spectrum (dotted line) of the PPV/PCPD/PPV film (at λ_{em} = 290 nm) for comparison.

Fig. 5 shows the picosecond time-resolved PL decay profiles of neat PPV and PPV/PCPD/PPV films, pumped by 290 nm pulses at room temperature. The decay dynamics were monitored at the maximum emission wavelength. The decay profiles show that the decay cannot be described with exponential decays, similar to the previous reports on PPV in the solid state.[17–22] For such non-exponential decays, it is not straightforward to determine the lifetime of the decay. For comparison of the PL decay in different samples, the lifetime may be considered to be the average time period a chromophore spends in the excited state. Thus, the average lifetime $\langle\tau\rangle$ determined from the area under the decay curve is given by[23]

$$\langle\tau\rangle = \frac{\int_0^\infty tI(t)\mathrm{d}t}{\int_0^\infty I(t)\mathrm{d}t} \qquad (1)$$

where $I(t)$ is the PL intensity at time t following excitation. The average lifetime of PPV emission in the trilayer film is calculated as 414 ps, much longer than that of the PPV single layer (249 ps), indicating that the energy transfer from PCPD to PPV occurred during the time-resolved PL decay. A longer lifetime (484 ps) of PPV emission in the PPV/PCPD bilayer film has also been reported.[7] However, if PXT was transformed to PPV by heat treatment before the PCPD layer was applied in preparation of the PPV/PCPD film, the measured lifetime was shorter and inconsistent if detectable.[8]

EL spectrum of the ITO/PPV/PCPD/PPV/Al device was shown in Fig. 6. Compared to its PL spectrum, the EL spectrum has only one emission peak at 530 nm, close to the PL peak with the highest emission energy. A similar phenomenon has been found for the EL spectra of PPV blending with poly(*N*-vinylpyrrolidone) (PVP), which is a non-conjugated polymer and only provided the dilution effect on PPV in polyblends.[11] Recent arguments on PL and EL spectra of poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) in solution and in solid films indicated that the peak with higher emission energy is contributed by the single-chain or intrachain emission, whereas that with lower emission energy is associated with the aggregated state of polymer chains.[24–29] Thus, it is implied that multi emission peaks found in the PL spectrum of PPV/PCPD/PPV film as shown in Fig. 6 were contributed by both the intrachain and interchain emissions of PPV, whereas the single peak found in the EL spectrum was contributed primarily by the intrachain emission.

Fig. 7 shows the voltage dependence of current density and radiance for ITO/PPV/Al and ITO/PPV/PCPD/PPV/Al devices. Their radiance-current density characteristics are shown in Fig. 8. The turn-on voltage (V_{on}) of the trilayer film device ($\sim$14 V) is larger than that of the neat PPV ($\sim$4 V). In the low current density region, the EL intensity of the trilayer film device is lower than that of the neat PPV. However, in the high current density region, the EL intensity of the trilayer film device became stronger with increasing bias, whereas that of the neat PPV leveled off at rather low radiance. Surprisingly, the EL light output of the trilayer is about 500 times that of the single PPV layer under the same current

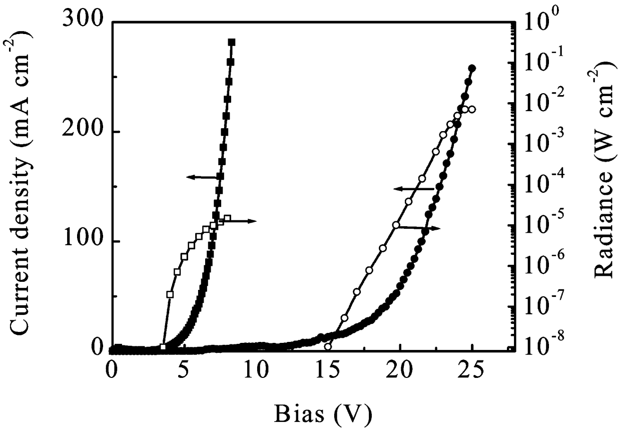

Fig. 7 Current density-voltage (closed symbols) and radiance-voltage (open symbols) characteristics of ITO/PPV/Al (squares) and ITO/PPV/PCPD/PPV/Al (circles) devices.

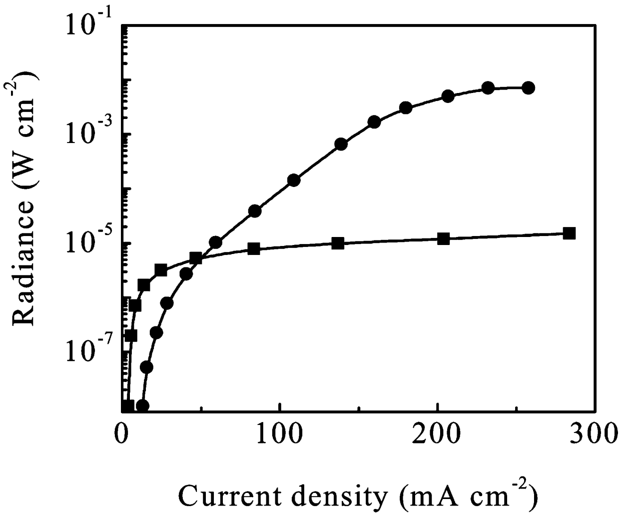

Fig. 8 Radiance-current density characteristics of the ITO/PPV/Al (squares) and ITO/PPV/PCPD/PPV/Al (circles) devices.

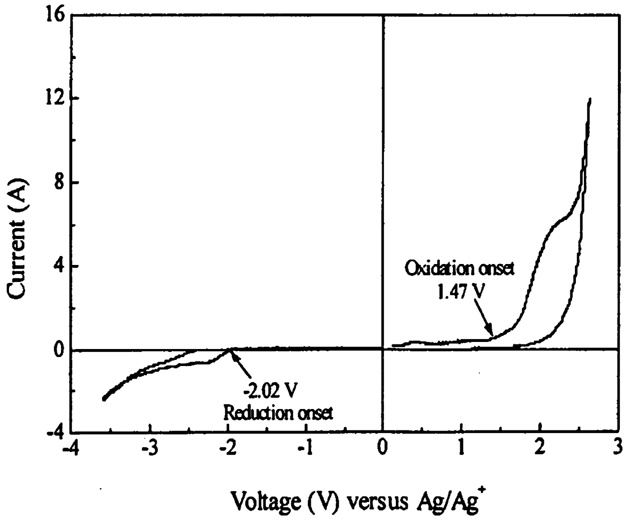

Fig. 9 Cyclic voltammogram of PCPD film coated on Pt in an acetonitrile–0.1 M tetrabutylammonium tetrafluoroborate solution.

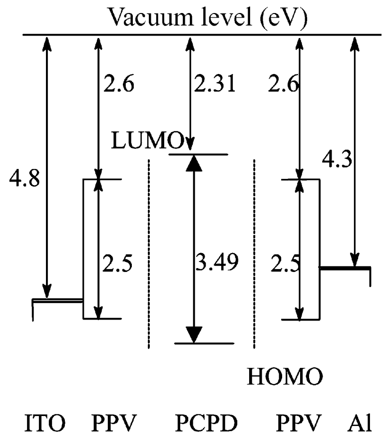

Fig. 10 Energy band diagram of the ITO/PPV/PCPD/PPV/Al device. The dashed lines indicate the undefined interfacial regions.

density of 280 mA cm^{-2} but different applied bias. The maximum external EL quantum efficiency (photons/electron) of the trilayer film device is 1.3% (at 24 V), about 16 times that of the PPV/PCPD film device (8.3 × 10^{-2}% at 9.5 V)[9] and about 16 × 16 = 256 times that of the conventional PPV device (5.3 × 10^{-3}% at 5.5 V). The reason behind this high EL emission for the trilayer film device is not clear. However, it might be attributed to the higher energy bandgap of the PCPD layer compared to the PPV, trapping the holes and electrons in the chemically-interlocked interfacial regions that facilitate the formation of excitons *in situ* and energy transfer from PCPD to PPV.

The cyclic voltammogram of PCPD against a Ag/Ag^{+} reference is shown in Fig. 9. The onset potentials of oxidation (E_{ox} = 1.47 V) and reduction (E_{red} = −2.02 V) can be used to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of PCPD.[30] Because the reported energy level of ferrocence (Fc) was −4.8 eV below the vacuum level[31] and its measured oxidation potential (Fc/Fc^{+}) against Ag/Ag^{+} reference was 0.47 V, we estimated the $E_{\mathrm{HOMO\ of\ PCPD}}$ = 5.8 eV and $E_{\mathrm{LUMO\ of\ PCPD}}$ = 2.31 eV. Similarly, the HOMO and LUMO energy levels of PPV were estimated as 5.1 and 2.6 eV, respectively. Thus, the energy band diagram of the trilayer film device was schematically shown in Fig. 10. The work functions of ITO and Al were obtained from the literature.[32] Accordingly, the insertion of the PCPD layer was believed to lead to electron-hole combinations, being concentrated in the interfacial regions due to the energy barriers. Because of chemical interlocking of the two polymers, PPV chains were surrounded by the PCPD chains in the interfacial regions. This explained why the EL spectrum of trilayer films showed the intrachain emission from PPV (see Fig. 6). As a result, those of excitons formed in the PCPD polymer chains had more chance to undergo the energy transfer to PPV and those of excitons in the PPV polymer chains have less chance to be quenched. We were also surprised to find out that the maximum external EL quantum efficiency of the PPV/PCPD/PPV film device is about 16 times that of the PPV/PCPD device and about 16 × 16 = 256 times that of the conventional PPV device. Since double interfaces in the trilayer film created double energy barriers, it implied that the number of excitons formed in the interfaces was increased exponentially with the energy barrier. However, before jumping to conclusions, further experimental data and theoretical studies were needed to interpret this phenomenon.

Conclusions

The interfaces in our designed PPV/PCPD/PPV film, where the polymer chains were chemically-interlocked, provided a specific region for the energy transfer from PCPD to PPV that increased the PL and EL efficiencies of PPV. The single emission peak found in the EL spectrum was contributed primarily by the intrachain emission from the interfacial regions, in which the excitons formed in the PCPD polymer chains had more chance to undergo the energy transfer to PPV and those formed in the PPV chains had less chance to be quenched. The maximum EL efficiency of the trilayer film was ~16 times that of the PPV/PCPD film and ~16 × 16 times that of the neat PPV.

Acknowledgement

The authors would like to acknowledge the financial support of the National Science Council in Taiwan, Republic of China, through Grant NSC 87-2216-E-002-01. We also thank Professor W. S. Fann and Dr. J. H. Hsu, Institute of Atomic and Molecular Sciences, Academia Sinica in Taiwan, for the technical assistance to the time-resolved photoluminescent measurements.

References

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539.
2 R. Gupta, M. Stevenson, A. Dogariu, M. D. McGehee, J. Y. Park, V. Srdanov, A. J. Heeger and H. Wang, *Appl. Phys. Lett.*, 1998, **73**, 24.
3 S. Tasch, E. J. W. List, C. Hochfilzer, H. Leising, P. Schlichting, U. Rohr, Y. Geerts, U. Scherf and K. Müllen, *Phys. Rev. B*, 1997, **56**, 4479.
4 I. N. Kang, D. H. Hwang, H. K. Shim, T. Zyung and J. J. Kim, *Macromolecules*, 1996, **29**, 165.
5 J. I. Lee, I. N. Kang, D. H. Hwang and H. K. Shim, *Chem. Mater.*, 1996, **8**, 1925.
6 J. Liu, Y. Shi and Y. Yang, *Appl. Phys. Lett.*, 2001, **79**, 578.
7 H. L. Cheng and K. F. Lin, *Synth. Met.*, 2001, **122**, 387.
8 H. L. Cheng, *Processing, Structure and Optoelectronic Properties of Poly(p-phenylenevinylene) and Its Blended Systems*, PhD Thesis, National Taiwan University, 2000.
9 R. A. Wessling, *J. Polym. Sci., Polym. Symp.*, 1985, **72**, 55.
10 R. W. Lenz, C. C. Han, J. Stenger-Smith and F. E. Karasz, *J. Polym. Sci., Polym. Chem. Ed.*, 1988, **26**, 3241.
11 K. F. Lin, L. K. Chang and H. L. Cheng, *Morphology and Luminescence Properties of Poly(phenylenevinylene) and Poly(*N*-vinylpyrrolidone) Polyblends*, in *Field Responsive Polymers*, ACS Symposium Series, Vol. 726, ed. J. Simpson and I. Khan, American Chemical Society, Washington, DC 1999, p. 71.
12 V. Chaturvedi, S. Tanaka and K. Kaseriyama, *Macromolecules*, 1993, **25**, 2607.
13 A. Sakamoto, Y. Furukawa and M. Tasumi, *J. Phys. Chem.*, 1992, **96**, 1490.
14 H. L. Cheng and K. F. Lin, *J. Polym. Res.*, 1999, **6**, 123.
15 T. Förster, *Discuss. Faraday Soc.*, 1959, **27**, 7.
16 D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836.
17 I. D. W. Samuel, B. Crystall, G. Rumbles, P. L. Burn, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1993, **213**, 472.
18 I. D. W. Samuel, B. Crystall, G. Rumbles, P. L. Burn, A. B. Holmes and R. H. Friend, *Synth. Met.*, 1993, **54**, 281.
19 N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Philips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1995, **241**, 89.
20 L. Smilowitz, A. Hays, A. J. Heeger, G. Wang and J. E. Bowers, *J. Chem. Phys.*, 1993, **98**, 6504.
21 U. Lemmer, R. F. Mahet, Y. Wada, A. Greiner, H. Bässler and E. O. Göbel, *Appl. Phys. Lett.*, 1993, **62**, 2827.
22 M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin and T. M. Miller, *Phys. Rev. Lett.*, 1994, **73**, 744.
23 J. R. Lakowicz, *Principle of Fluorescence Spectroscopy*, Plenum Press, New York, 1983, p. 52. It should be noted that the time distribution of the pulse was ignored.
24 T. Q. Nguyen, V. Doan and B. J. Schwartz, *J. Chem. Phys.*, 1999, **110**, 4068.
25 T. Q. Nguyen, I. B. Martini, J. Liu and B. J. Schwartz, *J. Phys. Chem. B*, 2000, **104**, 237.
26 Y. Shi, J. Liu and Y. Yang, *J. Appl. Phys.*, 2000, **87**, 4254.
27 R. Chang, J. H. Hsu, W. S. Fann, J. Yu, S. H. Lin, Y. Z. Lee and S. A. Chen, *Chem. Phys. Lett.*, 2000, **317**, 153.
28 C. J. Collison, L. J. Rotherberg, V. Treemaneekarn and Y. Li, *Macromolecules*, 2001, **34**, 2346.
29 C. J. Collison, V. Treemaneekarn, W. J. Oldham, Jr., J. H. Hsu and L. J. Rotherberg, *Synth. Met.*, 2001, **119**, 515.
30 Y. Li, Y. Cao, J. Gao, D. Wang, G. Yu and A. J. Heeger, *Synth. Met.*, 1999, **99**, 243.
31 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551.
32 I. D. Parker, *J. Appl. Phys.*, 1994, **75**, 1656.