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## An efficient electron-transporting polymer for light-emitting diodes

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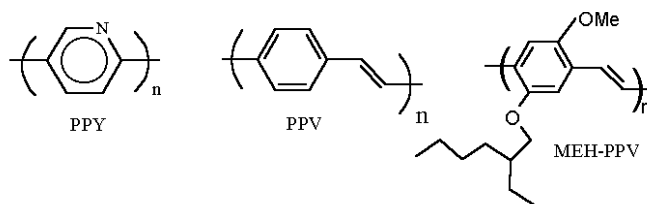
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**Abstract.** The efficient operation of polymer light-emitting diodes (LEDs) requires balanced injection and transport of electrons and holes. This has stimulated much research into suitable electron-injecting and transporting materials. We report the use of polypyridine as an efficient electron-transporting polymer. We have achieved much-improved LED performance by incorporating polypyridine as an electron-transporting layer in a poly(*p*-phenylene vinylene) (PPV) LED and optimizing layer thicknesses to balance transport of electrons and holes. The external quantum efficiency of these LEDs is 0.25%, 60 times greater than similar devices without the electron-transporting layer.

### 1. Introduction

The discovery that semiconducting polymers can be used as the active layer in light-emitting diodes (LEDs) [1] has stimulated great interest in the physics of these materials and offers enormous potential for making highly visible flat large area colour displays. Many groups are working to develop new methods and materials to make brighter, more efficient and more stable devices. This has led to a search for improvements in both the luminescent materials used and the contacts which inject charge into the device. We have studied poly(2,5-pyridinediyl) (PPY) as an electron-transporting polymer in bilayer polymeric LEDs in an effort to address some of these issues. These bilayer LEDs show improved efficiencies whilst using air stable electrodes. The polymers used in this study are poly(*p*-phenylene vinylene) (PPV), poly(2,5-pyridinediyl) (PPY) and poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV). The chemical structure of these polymers is shown in figure 1. PPV exhibits green luminescence and is the most widely studied luminescent polymer. MEH-PPV is a soluble derivative of PPV which has orange luminescence and has been widely studied as an emissive layer [2–4]. PPY is a nitrogen containing luminescent polymer which has been studied as the emissive layer in polymer LEDs [5, 6] and has also given intriguing a.c. operation [7], but the efficiency of these devices is very low. Our work differs from previous work in two ways. Firstly, we are using PPY as an electron-transporting layer and not as an emissive layer [5, 6]. Secondly, the high photoluminescence quantum yield shown by our PPY suggests that refinements we have made to the synthesis have resulted in a polymer with higher purity. An attractive feature of PPY is that it is very resistant to both photo- and electro-chemical oxidation [8, 9].

The operation of organic LEDs involves the injection of opposite charges by electrodes, transport of charge through the device and capture of opposite charges to form an exciton



**Figure 1.** Chemical structure of the polymers studied.

which, if singlet, can emit light. Charge injection is achieved by the use of two contact materials, one to inject holes, the other to inject electrons into the polymer. Indium tin oxide (ITO) is commonly used as a hole-injecting material as it is reasonably transparent in the visible region of the spectrum and has a high work function. It presents a low barrier to hole injection into the highest occupied molecular orbital of the polymer [3]. The barrier to electron injection into the lowest unoccupied molecular orbital can be reduced through use of a low work function metal [2] or a high electron affinity polymer [10]. Low work function metals such as magnesium and calcium have been demonstrated to increase the efficiency of PPV devices, but these metals are very reactive and the devices must be encapsulated or operated in vacuum. The use of charge transport layers has led to improved performance in organic LEDs with small molecules [11–15]. There is a challenge to find suitable materials for polymer electron-transporting layers. The advantage would be polymer processing flexibility with charge transport improvements. There have been studies of polymeric electron-transporting materials [6, 10, 16–19], but there is much room for improvement. Electron transport layers can present a reduced barrier to electron injection as well as improving charge transport. This can enable air stable electrodes, such as aluminium, to be used to produce efficient devices instead of reactive metals such as calcium.

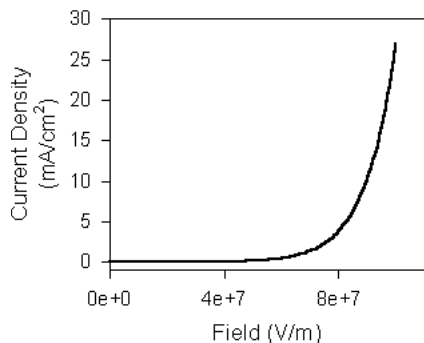
## 2. Experiment

We have investigated bilayer polymer LEDs containing PPY as an electron transport layer, with PPV or MEH-PPV as the hole-transporting and emissive layer. PPV films were prepared by spinning a tetrahydrothiophenium (THT) leaving group precursor polymer onto a quartz or ITO-coated glass substrate followed by conversion to PPV by heating in vacuum for 10 hours at 250 °C. The PPY in our study was prepared by dehalogenation polycondensation of 2,5-dibromopyridine, following a modified Yamamoto route [8]. The spinning solvents used were methanol (for PPV precursor), chlorobenzene (for MEH-PPV) and formic acid (for PPY). PPY and MEH-PPV films were prepared by spin-coating onto substrates directly from solution. The photoluminescence quantum yield (PLQY) of spin-coated films of each of the polymers was measured using an integrating sphere to collect the light emitted in all directions as explained by Greenham *et al* [20]. The excitation wavelength was 370 nm for PPY, 488 nm for PPV and 514 nm for MEH-PPV.

Polymer LEDs were fabricated by spin-coating the polymer solutions onto ITO-coated glass substrates. A convenient feature of PPY is that, in contrast to most other conjugated polymers, it is soluble in formic acid. We were therefore able to prepare bilayer structures by spinning PPY directly onto PPV or MEH-PPV without dissolving these layers. The LED structure, shown in figure 2, was then completed by evaporation of electrodes. Single layer devices were made for comparison. Aluminium contacts were used for the bilayer



**Figure 2.** Structure of single and bilayer polymer diodes. The left figure shows the structure of a single layer diode, the polymer layer consisting of PPV, MEH-PPV or PPY, fabricated with aluminium or calcium electrodes. The right panel shows the structure of a bilayer diode.



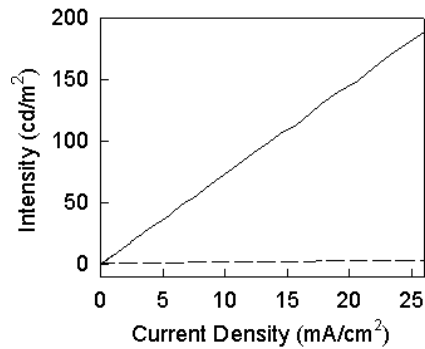
**Figure 3.** Current density–field characteristics of a bilayer PPV/PPY diode.

devices and for some single layer devices. Calcium contacts were used on some single layer devices, with an aluminium covering layer to reduce oxidation of the calcium. The metal contacts defined an LED of area  $2 \text{ mm}^2$ . Current–voltage and current–light output measurements of the LEDs were performed simultaneously in vacuum. These data are used to deduce the external quantum efficiency (EQE), which is defined as the number of photons emitted by the device divided by the number of electrons passing through it. The light output was measured in the forward direction and the efficiency deduced assuming Lambertian emission, following Greenham *et al* [21]. Electroluminescence spectra were measured using a spectrograph and diode array or CCD.

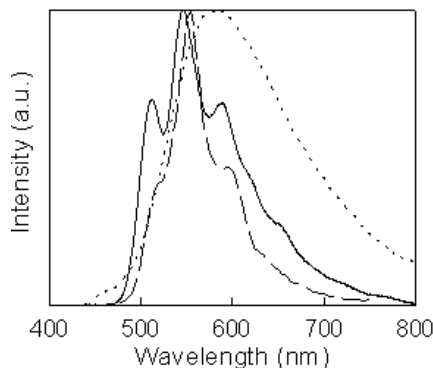
### 3. Results

The photoluminescence quantum yield values of the polymers were measured and found to be  $30 \pm 3\%$  for PPY,  $24 \pm 2\%$  for PPV and  $15 \pm 2\%$  for MEH-PPV. The PLQY of 30% for polypyridine is much higher than the value of 7% recently reported [22]. This indicates that the PPY in this study is of good quality and substantially free of impurities which would quench the luminescence. FTIR studies of PPY films spun onto silicon substrates detect no residual formate, consistent with measurements by Yamamoto *et al* [8].

The performance of a bilayer diode with aluminium contacts was compared with single layer diodes with calcium and/or aluminium contacts. The current through the devices, both single and bilayer, showed characteristic diode field dependence. The current density–field curve for a bilayer diode is shown in figure 3. The light output, in candela per square metre, as a function of current density for a bilayer diode is shown in figure 4 and compared with the results from a single layer PPV diode with aluminium contacts. The EQE of the bilayer device shown is calculated to be 0.25%, and the turn on field for light emission is  $0.7 \text{ MV cm}^{-1}$ . The EQE of the single layer PPV diode is 0.004%. We have



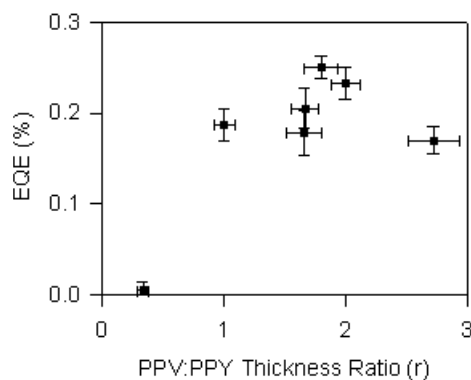
**Figure 4.** Intensity–current density characteristics of a bilayer diode (full curve) and a single layer PPV diode (broken curve), with aluminium contacts.



**Figure 5.** Electroluminescence spectra of a bilayer diode (full curve) and single layer PPV (dashed curve) and PPY (dotted curve) diodes.

achieved brightnesses in excess of  $900 \text{ cd m}^{-2}$  for our bilayer devices in d.c. operation. Much higher brightnesses should be possible in pulsed operation. The electroluminescence spectra of a bilayer diode, and PPV and PPY single layer diodes are shown in figure 5. The electroluminescence spectra from the single layer PPV and PPY devices are very different. The PPV emission spectrum peaks at 550 nm and has two strong vibronic features, whereas the PPY emission spectrum is broad and featureless, peaking at 590 nm. The emission from the bilayer diode is similar to that of the single layer PPV diode, peaking at approximately 550 nm with strong vibronic features, suggesting emission is predominantly from the PPV layer. Further insight into device operation is gained when studying devices made with a range of PPV:PPY layer thickness ratios. The efficiency of bilayer PPV/PPY devices is shown as a function of PPV:PPY layer thickness ratio ( $r$ ) in figure 6. The maximum EQE of the bilayer devices is 0.25% for a thickness ratio  $r = 1.8$ . The efficiency decreases for thickness ratios higher and lower than 1.8. A summary of device structures and efficiencies is shown in table 1.

Bilayer devices with MEH-PPV as the emissive and hole-transporting layer were fabricated and demonstrated improved efficiency with a PPY electron transport layer. Single layer MEH-PPV devices with aluminium contacts had an EQE of 0.01%, whereas bilayer MEH-PPV/PPY devices with aluminium contacts had an EQE of 0.04%.



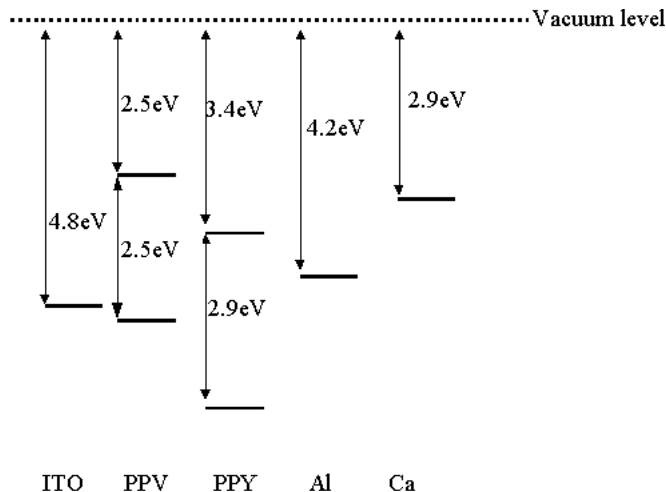
**Figure 6.** External quantum efficiency (EQE) as a function of PPV:PPY layer thickness ratio ( $r$ ).

**Table 1.** Summary of diode structures and efficiencies. The first five rows show data of bilayer PPV/PPY diodes of various thickness ratios. The subsequent three rows show data of single layer PPV or PPY diodes. The final rows compare bilayer MEH-PPV/PPY diodes with a single layer MEH-PPV diode.

Device structure	Thickness ratio $r$	Total thickness (nm)	EQE (%)
ITO/PPV/PPY/Al	0.3	160	0.004
ITO/PPV/PPY/Al	1.0	120	0.19
ITO/PPV/PPY/Al	1.7	160	0.21
ITO/PPV/PPY/Al	1.8	135	0.25
ITO/PPV/PPY/Al	2.7	165	0.17
ITO/PPY/Al	n/a	110	0.002
ITO/PPV/Al	n/a	140	0.004
ITO/PPV/Ca/Al	n/a	120	0.01
ITO/MEH-PPV/PPY/Al	1.0	250	0.04
ITO/MEH-PPV/PPY/Al	2.9	120	0.03
ITO/MEH-PPV/Al	n/a	110	0.01

#### 4. Discussion

As previously mentioned, several groups are working to create new electron-transporting polymers [6, 16–19]. The Sheffield group have considered design criteria for electron-transporting molecules and have identified a range of suitable functional groups. They have demonstrated the use of poly(2,6-pyridine vinylene-co-2,5-diheptoxy-*p*-phenylene vinylene) (PPyV-co-DHepOPV) [18], although efficiencies are not reported. They have also demonstrated the use of poly(*p*-phenylene-2,3'-bis(3,2'-diphenyl) quinoxaline-7-7'-diyl), as an electron-transporting layer with poly(2,5-dialkoxy-*p*-phenylene vinylene) as the hole-transporting and emissive layer. Utilizing aluminium and gold electrodes, this arrangement produces diodes with an efficiency of 0.35%, a factor of ten higher than comparable single layer devices [17]. Yamamoto *et al* [6] have used vacuum deposited PPY, poly(4,4'-disubstituted-2,2'-bithiazole-5,5'-diyl) and poly(1-10-phenanthroline-3,8-diyl) as electron-transporting and emissive layers with hole-transporting polythiophene, although no efficiencies are reported. Pei and Yang [16] have shown improved efficiencies when using 1,3,4-oxadiazole-containing polymers as electron-transporting materials with aluminium



**Figure 7.** Energy levels of the polymers and contacts.

and ITO as electrodes. They show an increase in efficiency of a factor of 40 and a factor of ten over single layer diodes with MEH-PPV and poly(2,5-bis(cholestanoxo)-1,4-phenylene vinylene) (BCHA-PPV), producing diodes with efficiencies of 0.08% and 0.30% respectively. Baigent *et al* [19] have fabricated bilayer diodes using cyano-derivatives of PPV as the emitting and electron-transporting layer, and PPV as a hole-transporting layer. Efficiencies of up to 2.5% have been reported, although there have been stability concerns. PPY has a wider band gap and therefore it should be possible to use PPY with a broader range of polymers.

The efficiency improvement in our polymer diodes, upon addition of a PPY layer, is encouraging and is similar to the best efficiency improvements in the references listed above. An added advantage of PPY is its resistance to oxidation. The efficiency of the bilayer device is 60 times higher than a single layer PPV device with aluminium contacts, 120 times higher than a single layer PPY diode with aluminium contacts and a factor of 20 more efficient than a single layer PPV device with calcium contacts. These improvements illustrate the value of multilayer device structures. Varying the layer thickness ratio provides insight into the operation of our bilayer LEDs and suggests that improvements in efficiency can be realized when balanced electron and hole injection is achieved. As shown in figure 6, the efficiency of the bilayer devices depends on layer thickness ratio and deviation from our optimum ratio of 1.8 produces devices with reduced efficiency. The small variations in efficiency around the ratio of 1.8 could be attributed to the variation in the overall thickness of the diodes, although we believe that larger variations are caused by the variation of the PPV:PPY thickness ratio. We consider that changing the thickness ratio,  $r$ , upsets the balance of charge injection and transport, moves the region where positive and negative charges meet in the device, and affects the amount of trapping of charge that occurs. In a single layer device the position of the region of light emission will be defined by the relative mobilities of positive and negative polarons in a single material, but in bilayer devices the situation is complicated by the presence of the heterojunction. There is a large barrier to hole injection from PPV [23] to PPY [24], and a smaller barrier to electron injection from PPY to PPV as shown in figure 7. This explains why light emission is seen mainly or entirely from the PPV layer. It also explains the low efficiency of the device with thickness

ratio  $r = 0.33$ : the holes are largely confined to the PPV layer and electrons tend to trap as they traverse the relatively large distance through the PPY layer from the aluminium contact. An additional way in which the efficient electron-transporting layer may benefit LED performance is by moving the emissive region away from the metal contact which could otherwise quench luminescence either directly or by interference effects.

The most exciting aspect of this work is that the use of a PPY electron-transporting layer should improve the performance of polymer LEDs made from a wide range of light-emitting polymers. The efficiency of MEH-PPV LEDs is improved by a factor of four by making bilayer LEDs incorporating a PPY electron-transporting layer. There is also an optimal thickness ratio which produces maximum efficiency. The increase in efficiency is not as large as for PPV, which may be, at least in part, accounted for by the difference in the electron affinity of the polymers. The barrier to electron injection is smaller in MEH-PPV [3] than PPV [23] and hence the improvement in electron injection will not be as significant.

## 5. Conclusion

In conclusion, we have demonstrated that PPY is an efficient electron-transporting polymer giving much improved performance in polymer light-emitting diodes. There is an improvement in efficiency of a factor of 60 when PPY is used as an electron-transport layer and the layer thicknesses are optimized to balance charge transport in a bilayer device with aluminium contacts. We have also demonstrated an improved efficiency with MEH-PPV and it should be possible to use PPY as an electron-transporting polymer with a wide range of luminescent polymers.

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