

A Triazole containing co-polymer for use as an Electron Transport Material in Multilayer LEDs

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ABSTRACT

We report investigations into a poly(1,20-(10,13-didecyl)distyrylbenzene-co-1,2-[4-(p-ethylphenyl)]triazole) (TRIDSB) electron transport material and its incorporation into single and multilayer LEDs. Multilayer devices have been investigated with poly(p-phenylenevinylene) (PPV) and poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) as hole transport layers (HTLs). The incorporation of the polymer into an ITO/PPV/TRIDSB/Al LED facilitates electron injection into the hole transporting emissive layer and results in a ten fold increase in the external quantum efficiency for electroluminescence (EL) of the PPV layer from 0.008% to 0.08-0.1%. In an ITO/I-MEHPPV/TRIDSB/Al device the corresponding increase in the quantum efficiency for EL from the I-MEHPPV is fifty fold, from 0.002% to between 0.06-0.11%. The polymer has been shown to be thermally stable with no glass transition temperature or melting point detected within the range 25-250°C.

Keywords: TRIDSB, PPV, I-MEHPPV, electron transport material, EL, multi layer LEDs.

INTRODUCTION

Electron transport materials are generally prepared by the incorporation of electronegative moieties either into the polymer backbone or as pendant groups¹. An example of the latter is CN-PPV², wherein the attachment of electron withdrawing cyano groups onto the vinylene double bond increases the electron affinity of the polymer. This facilitates improved electron injection and reduces the effect of electron traps (such as absorbed oxygen) which are believed to be present in most conjugated polymers.

The most widely used electron transporting materials are low molecular weight 1,3,4-oxadiazoles and 1,2,4-triazoles³⁻⁷. One of the inherent problems with such materials is that although they may be vacuum deposited, as a consequence of their low glass transition temperatures they have a strong tendency to recrystallise. As such, device stability has been an important issue particularly under high driving voltages and associated electric fields. 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) is a good example of a widely used electron transport material that suffers from crystallisation in thin film form⁵. It is often dispersed in an inert polymeric matrix such as poly(methyl methacrylate), but this dilution of the active material leads to higher driving voltages and reduced conductivities. Another well characterised electron transport material is 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ)⁶. More recently, research has been carried out on poly(methacrylates) bearing PBD and derivatives as pendant groups⁸, or incorporation of segments of PBD onto a polymeric main chain⁹, to try to increase stability. We have synthesised a thermally stable electron transport layer which upon incorporation into a multilayer device structure results in a significant improvement of the device efficiency.

RESULTS & DISCUSSION

We have synthesised a poly{1,20-(10,13-didecyl)distyrylbenzene-co-1,2-[4-(p-ethylphenyl)]triazole} (TRIDSB), (fig.1). The 1,2-[4-(p-ethylphenyl)] triazole unit results in significant steric crowding, forcing the chain out of a planar conformation and reducing the effective conjugation. Differential Scanning Calorimetry measurements (DSC) have been performed on the polymer at a heating rate of 20°C per minute and no glass transition temperature has been detected through the range 25-250°C. No melting point has been detected either. This confirms that the TRIDSB is thermally stable and will not re-crystallise upon device operation. Strukelj et al reported glass transition temperatures of between 224-277°C for a family of poly (aryl ether pyridyltriazine)s¹⁰ and of between 125-190°C¹¹ for a family of triazole containing polymers.

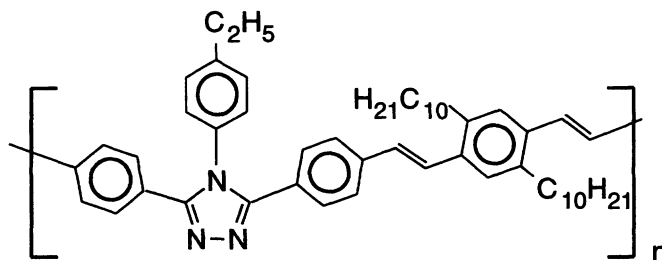


Fig.1 Chemical structure of poly(1,20-(10,13-didecyl)distyrylbenzene-co-1,2-[4-(p-ethylphenyl)]triazole) (TRIDSB).

The solid state optical absorption and emission spectra for TRIDSB are shown in fig.2. The optical absorption and photoluminescence (PL) spectra in chloroform solution are also shown. The absorption spectrum in thin films peaks at 3.3 eV. The emission from a thin film of TRIDSB is blue-green with a peak in the PL spectrum at 2.55 eV and a peak in the EL spectrum at 2.5 eV. TRIDSB has a solid state PL quantum efficiency (as measured within a fully calibrated integrating sphere) of 33% which compares favourably with standard PPV. The peak in the PL spectrum in solution is blue shifted by 0.11 eV with respect to that of the thin film. The peak absorption in chloroform solution is only shifted by 0.01 eV.

TRIDSB was incorporated into both single and double layer device structures. A single layer structure consists of the polymer sandwiched between an ITO/glass anode and an Aluminium cathode. TRIDSB was spin coated from a 1% concentration by weight chloroform solution onto ITO/glass. This gave a polymer layer thickness of 50 nm. Electrodes were then deposited under high vacuum conditions ($<10^{-6}$ mbar). The single layer electrical characteristic is shown in fig.3. It exhibits a threshold field for a current density of 5 mA/cm² of 1.8 MV/cm. When compared to that of an ITO/PPV/Al device of 0.8 MV/cm it is clear that this represents a large threshold field. In an ITO/polymer/Al device charge injection is often the limiting factor to the efficiency of wide band gap materials. It is believed that this large threshold field is indicative of a large barrier to electron injection into the polymer film at the cathode. To investigate the transport properties of TRIDSB gold was substituted for aluminium as the cathode. The workfunction of gold ($\Phi=5.2$ eV) is 1eV larger than that of aluminium ($\Phi=4.2$ eV) and thus the barrier to electron injection rises substantially. The current density drawn through the device at a fixed field strength dropped markedly. The threshold field for the ITO/TRIDSB/Au device has increased with respect to that of the ITO/TRIDSB/Al device by 1.5 MV/cm to 3.3 MV/cm for a current density of 5 mA/cm². This large increase in the threshold field is interpreted as being a direct result of the increased barrier for electron injection into the polymer. It is thus deduced that electrons are the majority charge carrier. The external quantum efficiency for EL from the two device structures was comparable (0.021% with Al compared to 0.0146% with Au). If holes constituted the majority carrier flow then a larger drop in the quantum efficiency would be expected when switching from aluminium to gold as there would be a lower injection probability and hence smaller population density of electrons injected at a fixed field strength, resulting in a greater fraction of holes passing straight through the device avoiding coulomb capture with the electrons.

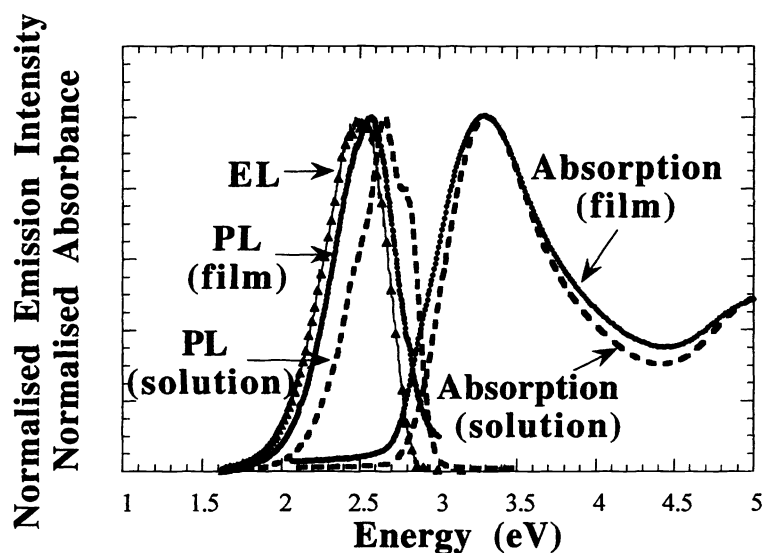


Fig.2 Room temperature optical absorption and photoluminescence spectra of TRIDSB in solid state and solution. The electroluminescence spectrum is also shown.

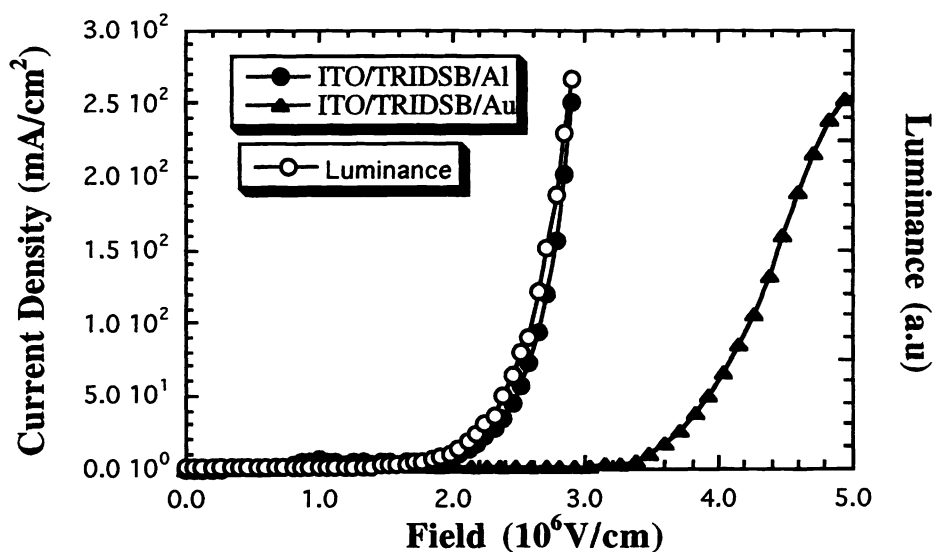


Fig. 3 The electrical characteristic for an ITO/TRIDSB/Al and an ITO/TRIDSB/Au device. Luminance data points are shown for the ITO/TRIDSB/Al device.

Multilayer polymer LEDs have also been investigated with TRIDSB as an electron transport layer (ETL). A multilayer device utilises separate transport layers for optimisation of the injection and transport of each carrier type with a hole transport layer (HTL) next to the anode and an ETL next to the cathode. The internal field is redefined owing to the energy level offsets at the polymer/polymer interface and charge confinement at this heterojunction leads to an improvement

in the injection and transport of both carriers and helps to ensure that the exciton recombination zone is not situated at or near to the electrodes.

Multilayer devices were fabricated with PPV as the HTL and TRIDSB as the ETL. A tetrahydrothiophenium chloride precursor to PPV was spin coated onto the ITO/glass from a methanol solution and then thermally converted at 250°C for 10 hours under dynamic vacuum conditions (10^{-6} mbar). The resulting polymer layer was insoluble in chloroform and had a thickness of between 40-50 nm. TRIDSB was then spin coated on top and electrodes were deposited as before. The best results were obtained with a thin TRIDSB electron injection layer of thickness 20 nm. The HTL is the emissive layer. Peak external quantum efficiencies of 0.1% were obtained in this configuration corresponding to a ten fold increase in efficiency with respect to the single layer ITO/PPV/Al devices. The electrical characteristic of the single and double layer devices are shown in fig.4. The threshold field for a current density of 5 mA/cm² is 1.1 MV/cm, significantly reduced from that of the single layer ITO/TRIDSB/Al device. Peak luminances of 250 cd/m² were obtained at current densities of 100 mA/cm².

Multilayer devices were also investigated using an insoluble MEHPPV (I-MEHPPV) derived from a chloro precursor route to MEHPPV¹² as the HTL. The precursor I-MEHPPV was spin coated on to ITO/glass and then thermally converted under identical conditions to the precursor to PPV. Electrodes were deposited as before. The resulting I-MEHPPV was insoluble in chloroform. The threshold field for the double layer device is 0.95 MV/cm. The best results were obtained with I-MEHPPV/ TRIDSB layer thicknesses of 20/50 nm. I-MEHPPV was the emissive layer in these devices. Peak external quantum efficiencies of 0.11% were recorded at a current density of 100 mA/cm². This corresponds to a fifty fold increase in the efficiency of EL from the I-MEHPPV layer with respect to that of the single layer ITO/I-MEHPPV/Al devices. This approaches the external quantum efficiency obtained in an ITO/MEHPPV/Ca device which is typically about 0.25%¹³. This demonstrates that the TRIDSB works efficiently as an electron transport layer and facilitates improved electron injection into the emissive polymer layer. The use of this ETL in a multilayer device then allows aluminium to be utilised as a cathode whilst achieving efficiencies comparable to those obtained in a single layer device with a calcium electrode. Yang and Pei¹³ reported similar results with an efficiency of 0.08% from a multilayer device obtained using an oxadiazole-containing polymer (PPOPH) as an electron transport layer in an ITO/ Σ -MEHPPV/PPOPH/Al device.

The results from the incorporation of the TRIDSB into multilayer devices taken in conjunction with literature data for other triazole containing materials leads to the conclusion that TRIDSB has an ionisation potential in the region of 5.8 eV. The low molecular weight small molecule 3-(4-biphenyl)-5-(4-t-butylphenyl)-4-(4-ethyl-phenyl)-1,2,4-triazole (pEtTAZ) has an ionisation potential of 5.8 eV⁶. The proposed energy level diagram is illustrated in fig.6. The striped area (± 0.2 eV) is due to the uncertainty in the value of the ionisation potential for TRIDSB. In both multi layer devices the HTL was the emissive layer and for both, a significant drop in the current density drawn and a rise in the luminance values were observed compared to the single layer ITO/HTL/Al devices. This fits with a picture wherein the barrier to holes at the polymer/polymer heterojunction is larger than that to electrons. This would then result in a confinement of positive space charge at this interface which would facilitate improved injection and transport of electrons from the opposite electrode into the device. This would both limit the current flow and increase the efficiency of exciton formation, resulting in the large increase in external quantum efficiency observed for EL.

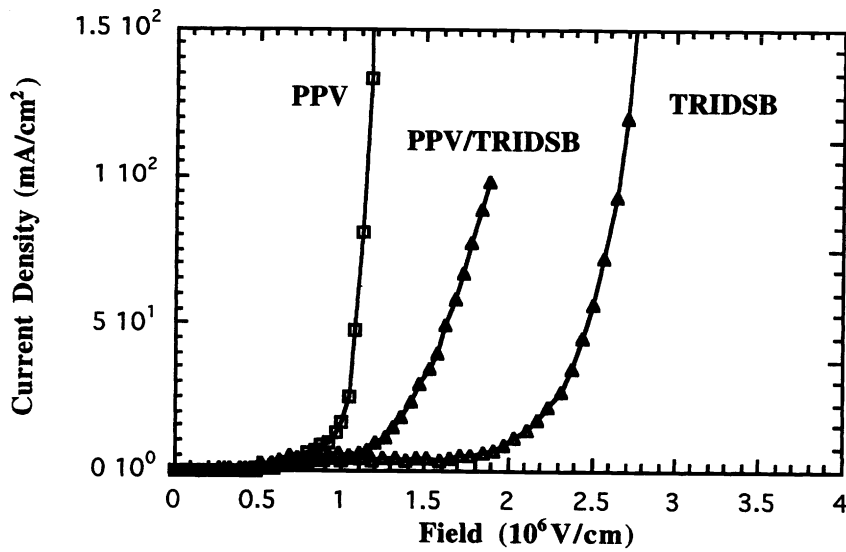


Fig.4 The electrical characteristics for both single and double layer devices with PPV

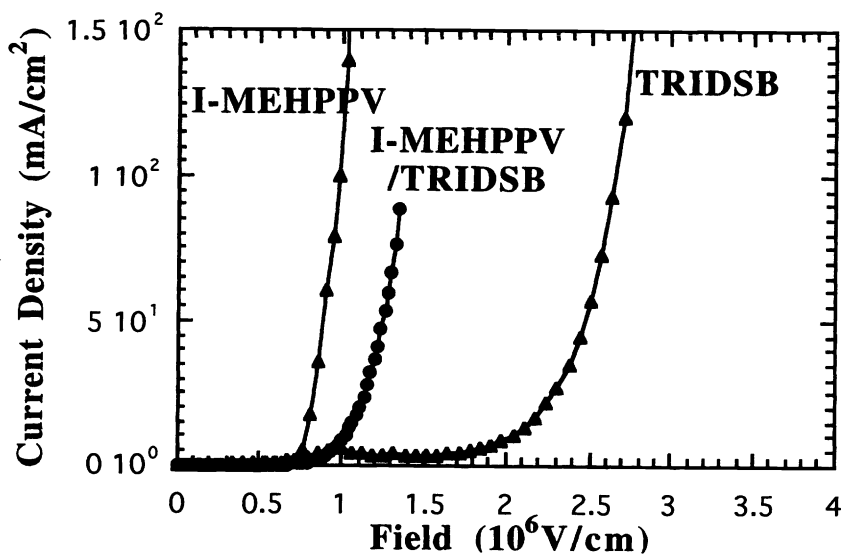


Fig.5 The electrical characteristic for both the single and double layer devices with I-MEHPPV

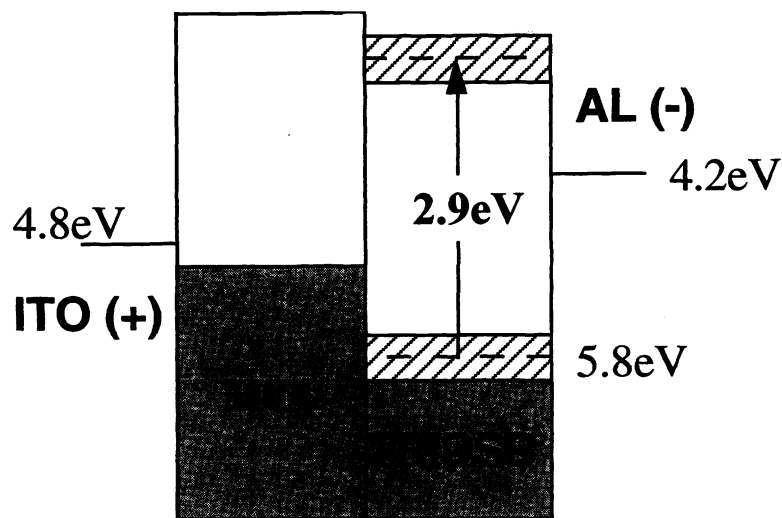


Fig.6 The proposed energy level diagram for an ITO/HTL/TRIDSB/Al device structure

CONCLUSIONS

We have synthesised a triazole containing co-polymer (TRIDSB) and characterised it as an electron transport layer in multilayer LEDs. It has been shown to enhance the external quantum efficiency of the emissive HTL by ten fold in an ITO/PPV/TRIDSB/Al device to 0.08% and by fifty fold in an ITO/I-MEHPPV/TRIDSB/Al device to 0.11%. Efficient electron injection has been reported and the two layer device with an aluminium cathode is comparable to single layer MEHPPV devices with calcium cathodes. TRIDSB has also been shown to be thermally stable with no evidence for a melting point or glass transition temperature across the range 25-250°C.

ACKNOWLEDGEMENTS

This work was supported by the Engineering and Physical Sciences Research Council (EPSRC, UK) via an Electronic Materials for Displays Initiative grant "Approaches to Efficient Blue Light-Emitting Polymers". DDCB thanks the Royal Society for the Amersham International Senior Research fellowship. We thank Andreas Bleyer and Diarmuid O'Brien for helpful discussions.

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