Investigation of poly(2-methoxy-5-(2'-ethylhexyloxy) -1,4-phenylenevinylene) prepared via a chloro precursor route

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ABSTRACT

We report the characterisation of an insoluble MEHPPV (I-MEHPPV) prepared via a chloro precursor route. Optical absorption and emission spectra are discussed with reference to those of the common soluble variant. PL quantum efficiencies are also reported. Results obtained for single ITO/I-MEHPPV/Al and double layer ITO/I-MEHPPV/electron transport layer (ETL)/Al LED structures are discussed. Peak luminances of 800cd/m^2 are found for the multilayer device and a peak EL external quantum efficiency of 0.11% (power conversion efficiency of 1.5×10^{-5}W/W) is obtained.

Keywords: I-MEHPPV, precursor route, EL, LED, quantum efficiency, power conversion efficiency.

INTRODUCTION

Traditionally MEHPPV has been synthesised to be a polymer that is soluble in its conjugated form[1](Σ-MEHPPV). MEHPPV has been shown to preferentially transport holes. In this paper we present the optical and electrical characterisation of an insoluble form of MEHPPV (I-MEHPPV) and its incorporation into multilayer polymer LEDs. The insolubility of the I-MEHPPV layer in common organic solvents lends itself to applications within multilayer device heterostructures since subsequent layers may be spin coated on top without dissolving the I-MEHPPV film.

RESULTS & DISCUSSION

The synthetic route to precursor I-MEHPPV is described elsewhere[2]. The chloro precursor to I-MEHPPV was spin coated from a tetrahydrofuran solution. The full conversion of the polymer was then achieved by heating to 250°C for 10 hours under dynamic vacuum conditions (10^{-6}mbar), see fig. 1. The resulting polymer is insoluble in a range of common organic solvents (chloroform, tetrahydrofuran, ether, toluene, cyclohexane, methanol, acetone, dimethylsulfoxide, N,N-dimethylacetamide and 90% formic acid)[2]. This was confirmed by comparing the UV/visible absorption spectra of a film before and after standing the film in the solvent. No change in absorbance was observed and there was no colouration of the solvent.
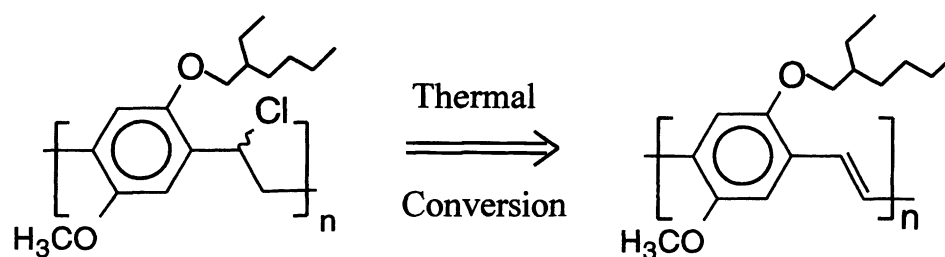
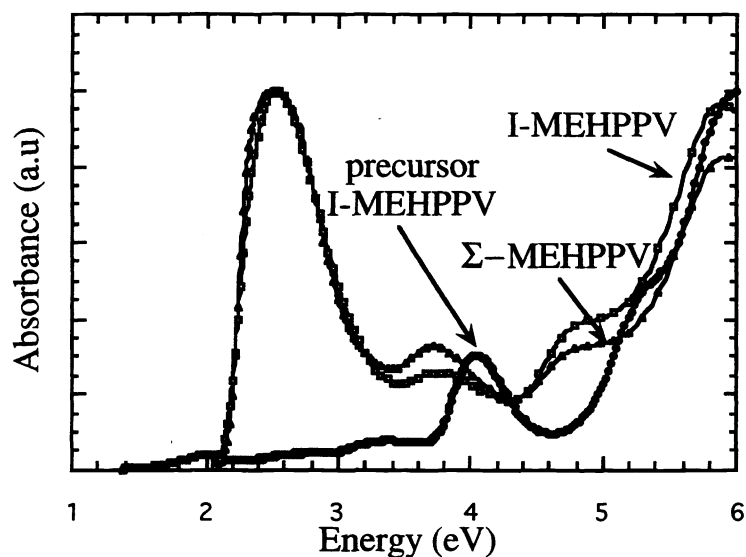Fig.1. The structure of the precursor and fully converted I-MEHPPV

Fig.2 The solid state optical absorption spectra for precursor I-MEHPPV, Σ-MEHPPV and I-MEHPPV.

The solid state optical absorption spectra of both the precursor I-MEHPPV and the conjugated polymer I-MEHPPV are shown in fig.2. Also shown for comparison is the spectrum for Σ-MEHPPV. The precursor absorption spectrum shows features at 3.35 eV, 4.03 eV, 5.31 eV and a peak unresolved beyond 6 eV. Upon conversion a strong absorption peak appears at 2.52eV which corresponds to the $\pi-\pi^*$ transition of the most delocalised π electrons. There are three further features visible in the absorption spectrum at 3.75 eV, 4.8 eV and 5.87 eV corresponding to transitions to additional excited states. The absorption spectrum of Σ-MEHPPV, as prepared by the traditional route, exhibits the same four prominent peaks with the main absorption peak occurring at 2.51 eV and the other features at 3.71 eV, 4.77 eV and 5.96 eV. This is important as it shows that the two routes give materials which have essentially the same optical properties.

The room temperature solid state electroluminescence and photoluminescence spectra are shown in fig.3. The onset for photoluminescence is at 2.34 eV, with a peak at 2.1 eV and a vibronic shoulder at 1.97 eV. The PL spectrum has a FWHM of ≈ 0.33 eV. The onset for electroluminescence is at 2.34 eV, with a peak at 2.12 eV and a vibronic structure at 1.98 eV. The EL spectrum has a FWHM of 0.33 eV. In comparison, Σ-MEHPPV prepared by the conventional route has a PL emission peak in the solid state at 2.11 eV with a FWHM of 0.25eV[3].
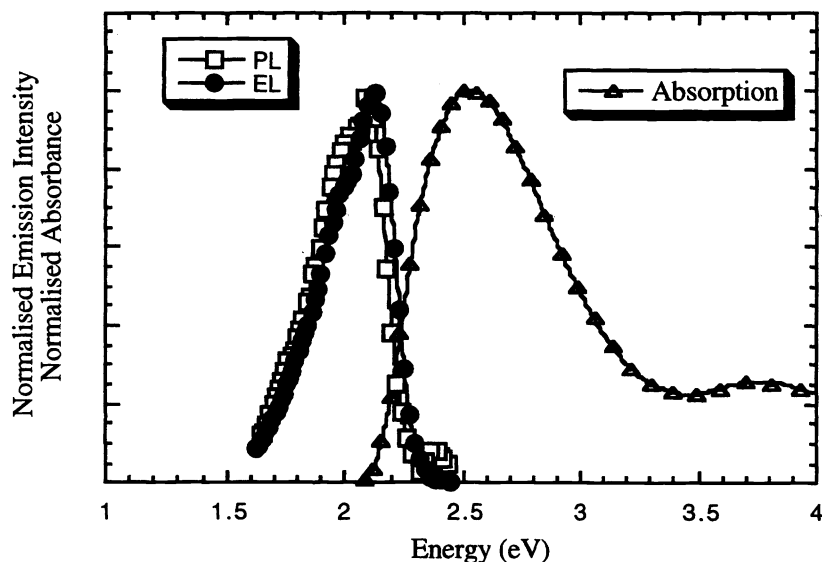
Fig.3 The solid state optical absorption and emission spectra for I-MEHPPV

The quantum efficiency for photoluminescence in the solid state is 13%, as measured using a fully calibrated integrating sphere flushed with nitrogen to avoid photo-oxidation of the polymer film. Greenham et al quote very similar values of between 10-15% for the PL efficiency of the solution processible thin film Σ-MEHPPV[4], with the variation therein attributed to sample storage time in ambient air; the older the sample, the worse the efficiency. They observed a 5 fold reduction in the efficiency over the timescale of a week. The samples measured here were at most a few hours old.

Current-voltage measurements were carried out on the polymer by incorporating it between ITO and aluminium electrodes. Precursor I-MEHPPV was spin coated from a tetrahydrofuran solution onto ITO/glass and then thermally converted at 250°C for 10 hours, under dynamic vacuum conditions (10^{-6}mbar). Aluminium electrodes were then deposited ($<10^{-6}$mbar). Multi layer LEDs were fabricated in the same manner but with an electron transport layer (ETL) deposited between the polymer and the cathode. In this way each layer may be optimised to the injection and transport of a single carrier, resulting in a more balanced bipolar device current, which in turn should improve the quantum yield of the LED.

The single layer electrical characteristic of an ITO/I-MEHPPV/Al device is shown in fig.4. The film thickness was 50 nm. The threshold field for a current density of 5 mA/cm^2 is 0.75 MV/cm, compared to that of 0.8 MV/cm for an ITO/PPV/Al device. The EL yield is poor in a single layer device with peak luminances of 10 cd/m^2 at current densities of 22 mA/cm^2. This corresponds to an external quantum efficiency for EL of 0.002%. This is essentially identical to published efficiencies for Σ-MEHPPV within the same device configuration[5].
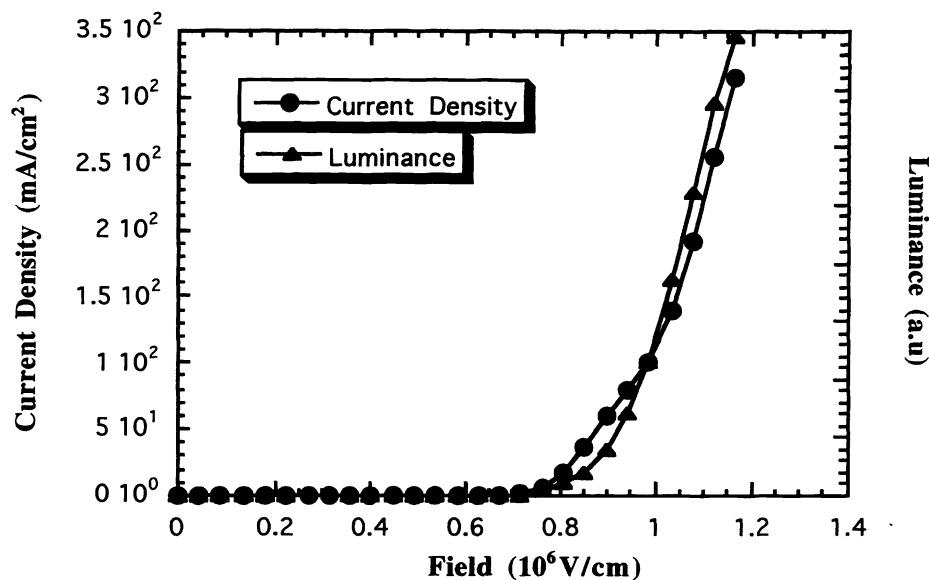
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Fig.4 The electrical characteristic for an ITO/I-MEHPPV/Al device. The luminance vs field curve is also shown.

Multilayer devices incorporating an ETL between the I-MEHPPV and the electron injecting contact were investigated. This should improve the injection and transport of electrons within the LED which is expected to significantly boost the external quantum efficiency for EL. The first ETL used was a triazole containing co-polymer, namely TRIDSB[6], see fig.5. TRIDSB was spin coated on top of the I-MEHPPV from a chloroform solution. Aluminium electrodes were then deposited as before.
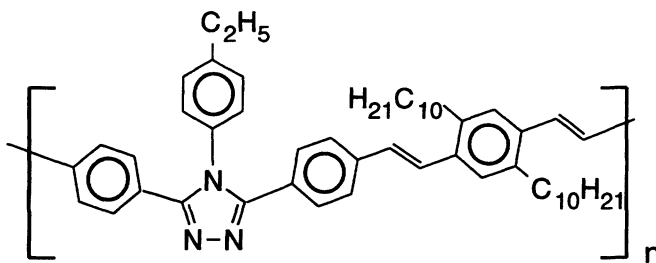

Fig. 5 The structure of a poly(1,20-(10,13-didecyl)distyrylbenzene-co-1,2-[4-(p-ethylphenyl)]triazole) (TRIDSB)

The electrical characteristic of the single layer ITO/I-MEHPPV/Al and double layer ITO/I-MEHPPV/TRIDSB/Al devices under forward bias are shown in fig.6. The threshold field of the two layer device is at 0.9 MV/cm. I-MEHPPV is the emissive layer in the two layer devices. Peak external quantum efficiencies of 0.11% have been achieved at current densities of 100 mA/cm^2. Peak absolute luminances of 800 cd/m^2 were recorded at current densities of 600 mA/cm^2. Polymer layer thicknesses for I-MEHPPV/TRIDSB were 20/50 nm.
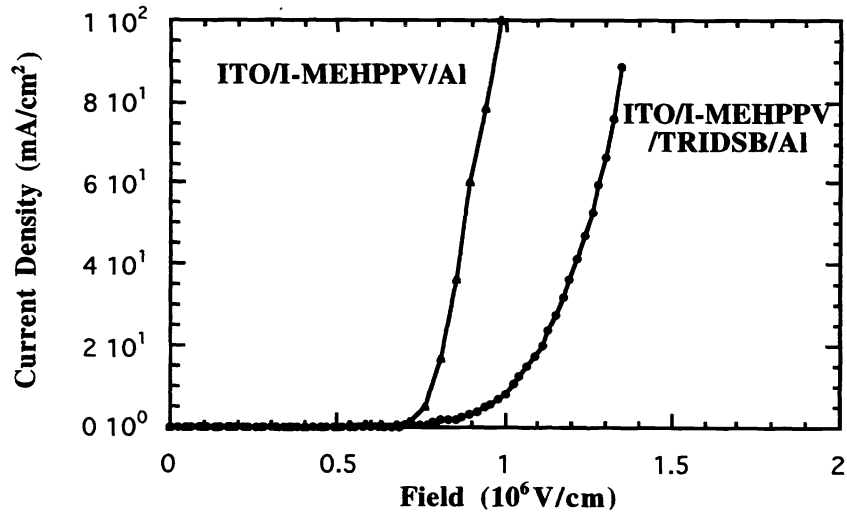
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Fig.6 The electrical characteristic for both an ITO/I-MEHPPV/Al and an ITO/I-MEHPPV/TRIDSB/Al device.

Multilayer device structures were also investigated using another ETL, a poly(p-phenylene-2,3'-bis(3,2'diphenyl) quinoxaline-7-7'-diyl) (PPQ)[7].
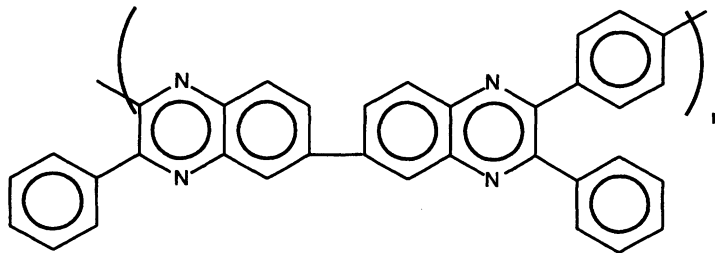

Fig. 7 The structure of non-ether poly(p-phenylene-2,3'-bis(3,2'diphenyl) quinoxaline-7-7'-diyl) (PPQ)

PPQ was spin coated from a tetrachloroethane:chloroform 1:1 solution. The electrical characteristic of the single and double layer device are shown in fig.8. The ITO/I-MEHPPV/PPQ/Al characteristic shows a threshold field for a current density of 5 mA/cm^2 of 1.27 MV/cm. In these double layer devices a peak external quantum efficiency for EL from the I-MEHPPV layer of 0.004% was achieved at a current density of 110 mA/cm^2. One explanation for the lower efficiencies in the double layer devices when using PPQ instead of TRIDSB is that the barrier to electron injection from the PPQ to the I-MEHPPV is expected to be between 0.4-0.6eV larger than that from the TRIDSB to the I-MEHPPV. Electron injection into the emissive layer may then be the limiting factor in the performance of the ITO/I-MEHPPV/PPQ/Al devices. A peak power efficiency of 6.3x10^{-6} W/W was achieved in this configuration at 13V. Polymer layer thicknesses for I-MEHPPV/PPQ were 20:50 nm.
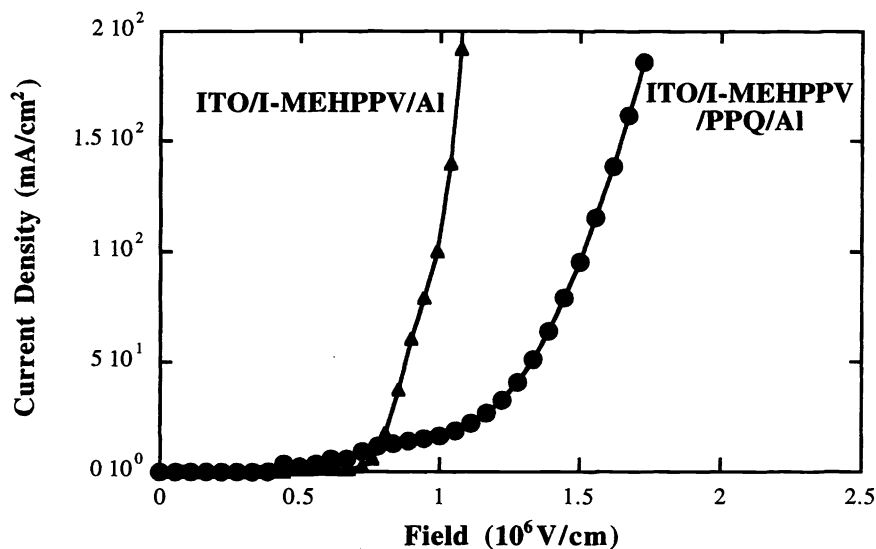
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Fig.9.The electrical characteristic for both an ITO/I-MEHPPV/Al and an ITO/I-MEHPPV/PPQ/Al device.

CONCLUSIONS

Analysis of the solid state absorption and emission spectra of I-MEHPPV prepared via the precursor route coupled with results on the incorporation of the polymer as the active emissive layer in LEDs suggests that I-MEHPPV is essentially identical in terms of device physics and photophysics to the standard Σ-MEHPPV but with the advantage that multilayer devices can be easily prepared.

Double layer heterostructures were investigated using an ITO/I-MEHPPV/ETL/Al device configuration with I-MEHPPV as the emissive layer. Using a triazole containing polymer as ETL, a peak external EL quantum efficiency of 0.11% was obtained at a current density of 100 mA/cm^2, and at an applied bias of 16V corresponding to a power efficiency of 1.5x10^{-5} W/W.

ACKNOWLEDGEMENTS

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