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BLUE-SHIFTED ELECTROLUMINESCENCE FROM A STABLE PRECURSOR TO POLY(*P*-PHENYLENE VINYLENE)

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Abstract A partially conjugated polymer precursor to poly(*p*-phenylene vinylene) (PPV) is used to produce stable electroluminescence with enhanced efficiency over PPV in a simple device configuration with a blue-shift in both the electroluminescence and photoluminescence emission spectra.

INTRODUCTION

Injection electroluminescent devices fabricated from conjugated organic material are being considered for use in large area display applications. Conjugated molecular materials are suitable in that they display strong fluorescence in the solid state and by careful synthetic manipulation there is the potential for full colour displays. Early work on single crystals such as anthracene¹, naphthalene² and pyrene³ was hampered by the large drive voltages required to produce electric fields high enough to promote bipolar charge injection.⁴ The advent of vacuum-deposition of thin films of such materials⁴ and the inclusion and evaporation of associated charge transport layers⁵ has given rise to the potential for manufacture of large area devices with low drive voltages and emission intensities suitable for practical applications. However the lifetimes of these devices are short due to the instability of the amorphous molecular films against recrystallisation.

Spin-coating of thin polymeric films represents a rival technology because, although polymeric conjugated materials do not display as strong fluorescence as molecular equivalents, polymeric films do display long-term stability against morphological

changes. We first reported on the use of a conjugated polymer, PPV⁶, for the manufacture of electroluminescent polymer diodes (ELPD). This phenomenon has also been seen in poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene-vinylene).⁷ Here we report on the extension of electroluminescence to a partially conjugated polymer.

EXPERIMENTAL

The polymer used in this study was produced from a methoxy-leaving group precursor polymer to PPV.^{8,9} ITO-coated substrates were thoroughly cleaned by ultrasonic treatment in acetone and then 2-propanol. The precursor polymer was spin-coated onto the substrate to give a film thickness of about 800 Å. The samples were then thermally treated at 300 °C for 12 hours in a vacuum of 10⁻⁵ torr. Aluminium top contacts were vacuum-deposited to define active areas of 0.1 cm².

Ultraviolet/Visible absorption measurements were made using a Perkin Elmer Lambda 9 Spectrometer and infrared spectra were made using a Nicolet 55XB FTIR Spectrometer on polymer samples spin-coated onto wide-field spectroil substrates and KBr substrates respectively. The samples for material characterisation were converted in parallel with the ELPDs.

For ELPD analysis, a positive potential was applied to the ITO with a Keithley 230 Voltage source and currents were monitored with a Keithley 195A multimeter. Electroluminescence (EL) and Photoluminescence (PL) emission were observed through the ITO substrate. Integrated light output was monitored with a large area silicon photodiode in photoamperic mode, measuring the photocurrent as a voltage across a 1MΩ resistor. Spectrally resolved EL and PL measurements were made using a Coderg PH1 double monochromator and a Hamamatsu R943-02 photomultiplier tube. Optical excitation for the PL measurement was supplied from the multi-line UV output of an argon-ion laser. Capacitance measurements were made using a Hewlett-Packard 4192A LF impedance analyser.

RESULTS AND DISCUSSION

To fully convert thin films of MeO-leaving group precursor polymer to PPV into fully conjugated PPV, samples need heating at 220 °C in the presence of an acid catalyst.^{8,9} We have thermally treated the material so that we have produced a partially conjugated polymer as evidenced from IR and UV spectroscopy. The FTIR data show a decrease in

the 1097 cm^{-1} peak characteristic of the MeO-leaving group stretch and there are increases at 965 cm^{-1} and 3024 cm^{-1} assigned as *trans*-vinylene CH bends and stretches respectively. The UV/visible absorption spectra reveal that the elimination process does not go to completion. Absorption oscillator strength starts to shift from the major absorption band near 6 eV (the π - π^* gap of the benzene ring) to the absorption band near 3 eV (the π - π^* gap of the conjugated phenylene-vinylene linkages) but it in no way approaches parity as is the case for the fully conjugated material (Figure 1). Moreover the absorption features near 3 eV are at higher energy than for PPV, as has been observed in oligomers of PPV.^{10,11} Further the clear peaks at 2.93 eV, 3.13 eV, 3.33 eV and 3.63 eV, 3.80 eV, 4.00 eV cannot all be attributed to the absorptions of different length oligomers and is due in part to phonon structure on the absorption edge and is indicative of significant electron-phonon coupling of the involved electrons. Thus it is clear that the absorption features are due to the development of short conjugated sequences in amongst an unconjugated polymer backbone.

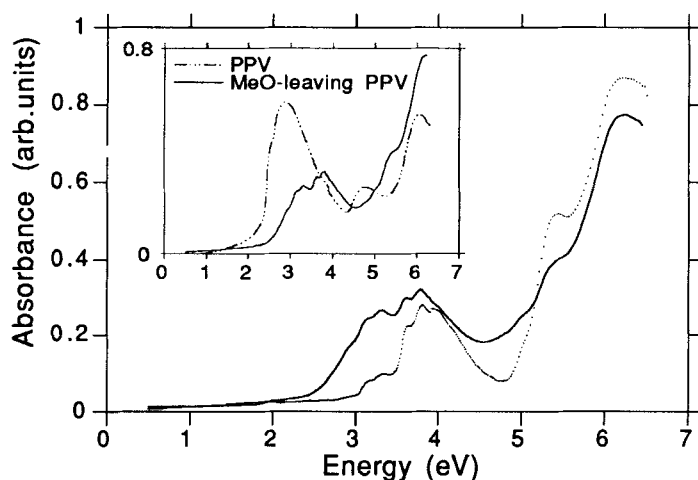


FIGURE 1 UV/Visible Absorption Spectra of the methoxy-leaving group precursor (dots) and the material after 12 hours conversion at 300 °C (line) (The insert shows the absorption spectrum of PPV in comparison with the partially conjugated material)

The absorption spectrum of the precursor shows that it is not fully saturated. If we attribute the higher energy set of three peaks to phonon structure on the absorption edge of the smallest possible conjugated sequence of two phenyl rings joined by one vinyl link, $n=2$, then the lower energy set of three peaks in the thermally converted material must be due to a sequence of units with $n=3$ at least. It is observed that during the thermal conversion the lower energy peaks develop at a faster rate than the high energy peaks and

we conclude that the polymer used in this study has a range of at least two different lengths of conjugated sequences ($n=2$ and $n=3$).

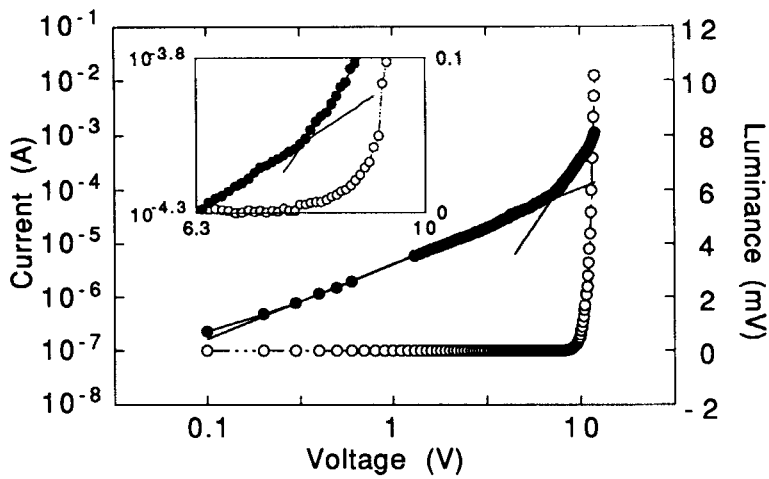


FIGURE 2 A typical current (solid)-luminance (open)-voltage characteristic for an ELPD (the insert is an enlargement at the threshold of electroluminescence). The gradients of the two regimes of the log-log current-voltage plot are 1.4 and 5.1.

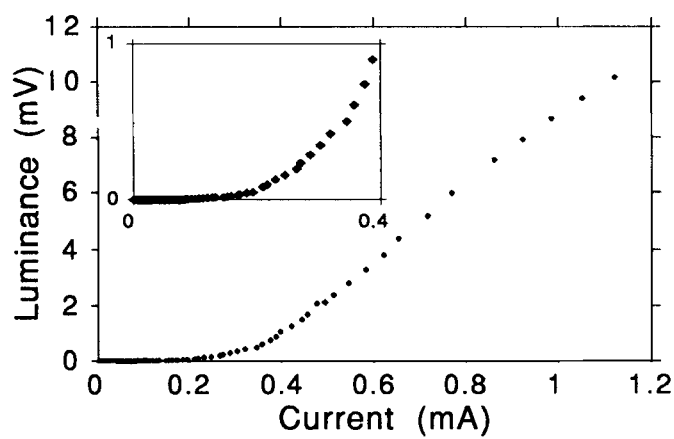


FIGURE 3 EL emission against current (the insert is an enlargement of the low current regime).

The current-voltage-luminance characteristics of devices show that the current injection has two distinct phases with a knee in the current-voltage curve at about 8.8 V (Figure 2). At this point electroluminescence is first detected. This represents the transition from

monopolar injection to bipolar injection and evidence that the mechanism for EL is double-injection recombination. The correspondance between the EL and PL spectra confirm this (Figure 4) (PL being unambiguously attributed to the decay of a single exciton).⁶ The quantum efficiency of the ELPD is 2×10^{-4} , a factor of two better than for PPV in an identical device configuration. This may be attributed to the significantly stronger fluorescence of the partially conjugated material over fully conjugated material.¹²

The luminance-current characteristics in the low current regime show appreciable quadratic nature (Figure 3). This phenomenon is well known in injection EL and is attributed to triplet-triplet annihilation delayed EL.¹³ The high current regime is sublinear and we attribute this to the linear response of prompt singlet formation EL in the high current regime¹³ combined with an overall signal decay due to an effect such as thermal heating or space-charge build-up.

The EL and PL emission spectra at room temperature of the partially conjugated material are significantly blue shifted with respect to the corresponding spectra for PPV (Figure 4). From comparison with PL from oligomeric material¹⁰, the emission spectrum appears to arise from conjugated sequences of length $n=3$, confirming our analysis of the UV/Visible absorption spectra. The sharp vibronic structure is indicative of there being one conjugation length being the preferred emission centre.

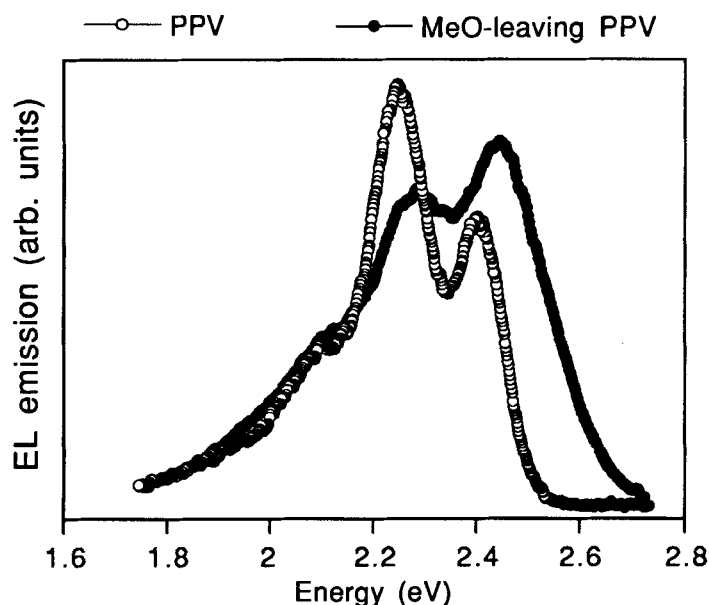


FIGURE 4 The electroluminescence spectra of PPV (open circles) and the partially conjugated material (solid circles) recorded at room temperature.

The ELPDs were stable over a timescale of several weeks and could be run for several hours continuously in air. The sample decay mechanism was primarily that of oxidation of the aluminium top contact, subsequently impairing electron injection efficiency and decreasing the active device area as observed by a decrease in device capacitance.

CONCLUSIONS

EL has been observed in a polymer consisting of conjugated and unconjugated sequences. The emission was blue-shifted with respect to fully conjugated PPV and has an enhanced quantum efficiency over it in these simple structures. The very stable form of the polymer offers considerable opportunities for development of full-colour displays.

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