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Synthetic Metals 71 (1995) 2193–2194

SYNTHETIC METALS

Stable Poly(Para-Phenylene)s and their Application in Organic Light Emitting Devices

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Abstract

Organic materials like oligophenyls, poly(para-phenylene) (PPP), and some derivatives (ladder polymers) are used as the active layer of light emitting diodes (LEDs). The electrical characteristics of these devices depend on the band structure of the organic layer as well as on the electrode materials. The optical and electrical LED performance is discussed with regard to the electronic structure of the stratified device arrangement.

Introduction

Conjugated polymers with high photoluminescence quantum yields are now investigated worldwide searching for efficient active layers for LEDs. Both band-based models and exciton based models have been proposed to explain recent measurements of I-V-characteristics [1,2]. The polymeric equivalent to the inorganic Schottky diode is formed when charge carriers of both polarity are injected into the polymer layer via suitable electrodes. Light emission is explained in terms of radiative recombination of singlet polaron excitons [3]. To achieve high efficient light generation, the device requires high quantum yield in photoluminescence of the polymer layer as well as balanced carrier injection. Tsutsui and Saito [4] propose the following simple formula for the efficiency of the LED:

$$\eta_{\phi} = \gamma\, \eta_F\, \eta_r$$

η_{ϕ} is the electroluminescence efficiency, γ is the charge injection factor, η_F is the fluorescence quantum yield, and η_r is the efficiency of singlet exciton formation and includes the mobility of the charge carriers. We have shown that poly(para-phenylene) and its derivatives are suitable materials for blue LEDs [5]. The emission colour can be tuned by chemical means [6] and high η_F-values of up to 30% are reported for these films [7]. The band structures of the polymers are currently under investigation [8], therefore we choose the well known hexaphenyl oligomer [9] as a model compound to evaluate the influence of different electrode materials on the device characteristics.

Experimental

Patterned indium tin oxide (ITO) layers on glass substrates act as the high work function hole injecting contact. The active material is deposited onto these substrates by spin coating (polymers) under ambient conditions or vacuum deposition below 10^{-6} mbar (oligomer). Figure 1 shows the chemical structure of the different derivatives used in LED preparation. Aluminium electrodes are evaporated onto the organic layers. For details concerning the characterization see ref [6].

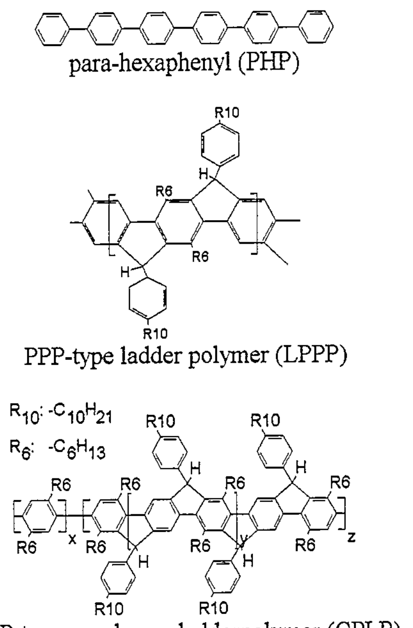

Figure 1. Chemical structure of PHP, LPPP, and CPLP [10,11].

Results and Discussion

The photo- and electroluminescence spectra of the different organic layers are depicted in figure 2. In the ground state the phenyl rings of the PHP are tilted against each other [12]. The bridging of the phenyl rings in the LPPP forces the PPP backbone into a planarized structure and hence lowers the band gap [8]. The initial electroluminescence and photoluminescence spectra of the LPPP are similar. The red shift observed in the electroluminescence emission of this polymer is ascribed to excimer formation and is also measured in the photoluminescence emission of aged films. In the case of the copolymer ladderpolymer the spontaneous radiative emission is favoured although we observe some contribution due to excimer formation around 600 nm. In the case of PHP the electroluminescence and photoluminescence spectra match perfectly.

Table 1
PPP-derivatives used as the active layers in LEDs. The band gap Eg and the effective conjugation length presented by the number of phenyl rings is determined from the absorption spectra [6]. λmax describes the position of the dominant peak of the electroluminescence emission.

Material	n (phenyl)	Eg [eV]	λmax [nm]
LPPP	9.4	2.7	599
CPLP	8.1	2.7	449
PHP	6.0	3.1	423

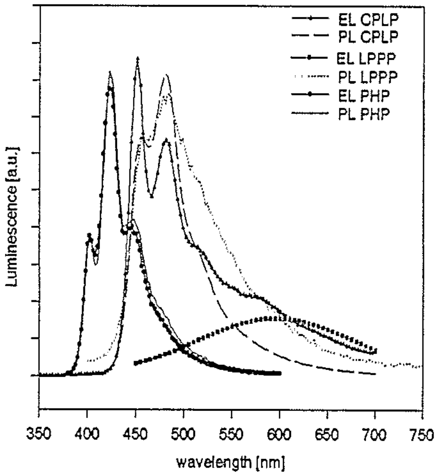

Figure 2. Electroluminescence (EL) and photoluminescence (PL) spectra of the PPP-derivatives.

Figure 3 depicts the absolute values of the HOMO and LUMO of the PHP. Chemical modifications of the electronic structure shift the absolute position of the band edges of the polymer only slightly [13]. The CPLP contains spacer segments of 2,5-alkyl-substituted phenylrings leading to an increase in the band gap for these segments. Compared to the LPPP this "quantum well" structure leads to an exciton confinement and enhances both electroluminescence and photoluminescence quantum yield [7].

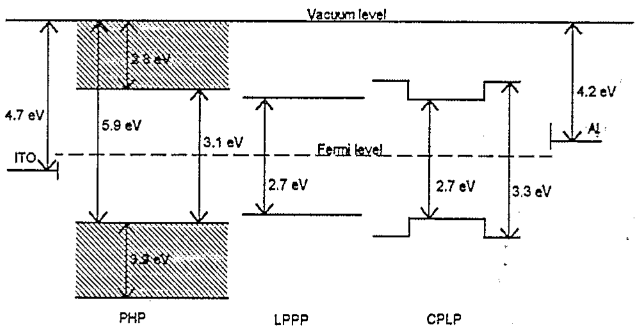

Figure 3. Electronic structure schemes of the devices

All our devices show field dependent I-V-behaviour indicating that a tunnel process governs the carrier injection [1]. The turn on field strength for these ITO/polymer/Al devices is in the order of 10^6 V/cm. Rectification ratios in excess of 100 are achieved with this device structure. Both electrical characteristics and electroluminescence efficiency can be enhanced by modifying the electrode materials. A thin platinum layer on the ITO increases the rectification ratio of the Al devices by a factor of 20 while the turn on voltage is unaffected.

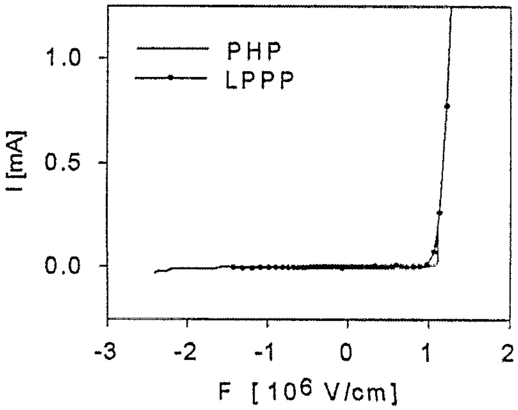

Figure 4. I-V-characteristics of ITO/LPPP (or PHP)/Al-LEDs

Conclusion

We have shown electroluminescence emission from single layer LEDs with para-hexaphenyl and PPP type derivatives as the active layers. The emission colours ranges from blue to yellow. The diode behaviour can be improved by hetero structured devices.

Acknowledgement

We thank U.Scherf from the MPI für Polymerforschung, Mainz, Germany for the synthesis of the ladderpolymer derivatives, G.Froyer and L.Athouel from the Institut Universitaire de Technologie, Nantes, France for the synthesis of highly pure PHP.
The financial support of the Volkswagen-Stiftung is gratefully acknowledged.

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