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EXCITATION ENERGY TRANSFER IN SEGMENTED LADDER-TYPE  
POLY (PARA-PHENYLENE) BLUE LIGHT EMITTING DIODES

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Light emitting diodes were fabricated in ITO/polymer/metal layer structure using Al as metal electrodes and a derivate of poly(para phenylene) (PPP) as the active layer. This novel polymer is a ladder-type PPP, segmented by a copolymer for enhanced quantum efficiency and soluble due to its side-groups. Bright blue emission, high quantum efficiency and easy processing make copolymers of this type promising materials for technical optoelectronic device applications. We present results on electroluminescence, absorbance and photoluminescence and discuss polymer properties as well as possible recombination processes. We observe the formation of excimer like states under the influence of an electric field and their radiative recombination giving electroluminescence emission in the wavelength region of about 580 nm.

Keywords: electroluminescence, energy-transfer, poly(para-phenylene).

## 1. INTRODUCTION

BESIDES inorganic semiconducting materials which are widely used in industrial applications, in recent years organic semiconductors became an important subject of investigation. Especially conjugated polymers have been used in fabricating light-emitting diodes (LED). Since the first realisation of such a device [1] a major direction of research was to move the emission colour towards the blue side of the optical spectrum. The aims are to produce red, green and blue LED dots or to tune the emission colour via voltage control [1a] and to obtain sufficient device lifetime for flat screen application.

Due to its bandgap of approximately 2.7 eV the nonsoluble poly(para phenylene) (PPP) has been demonstrated to be a good candidate for blue LEDs [2, 3]. Scherf and Müllen [4] synthesised a planarized ladder-type PPP (LPPP), which is soluble due to alkyl

side groups. We have already demonstrated that efficient LEDs with different emission colours can be fabricated with this type of soluble PPP [5]. Recently this polymer was improved further by synthesising a statistical ABA triblock copolymer [6]. This quantum well-like structure leads to a stabilisation of singlet excitons in the potential of the ladder-type B sequences of the polymer chain. The result is an enhanced photoluminescence quantum efficiency [7] of the blue fluorescence both in solution and in films.

We report results of spectroscopic studies of so called segmented ladder-type PPP (SLPPP) and optical properties of LEDs with SLPPP as the active layer.

## 2. EXPERIMENTAL

Details of the synthesis of SLPPP can be found in [7]. LEDs were fabricated as a typical electrode/polymer/electrode sandwich structure. We used indium tin

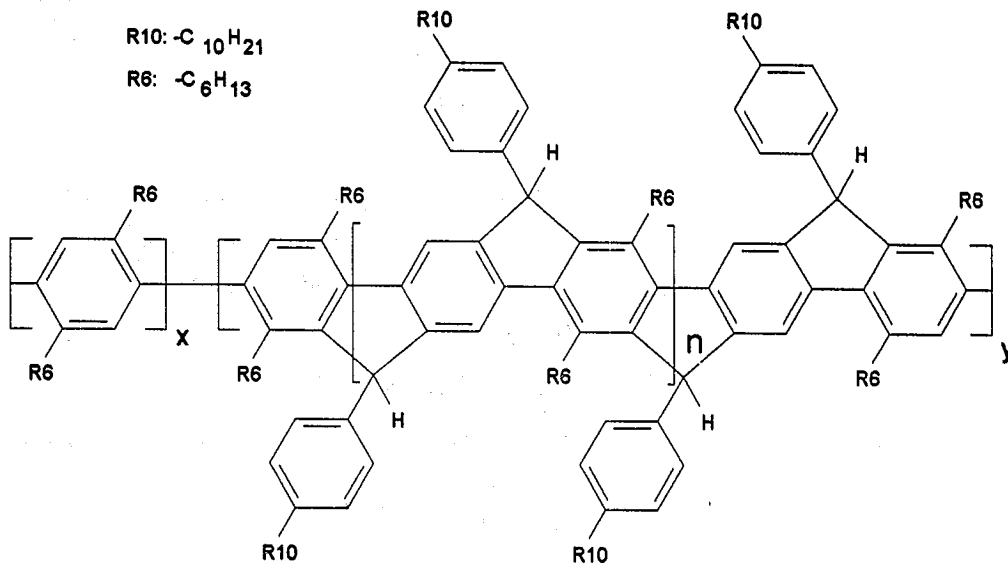


Fig. 1. Chemical structure of the segmented ladder-type poly(para phenylene).

oxide (ITO) coated glass as substrates. The ITO-layer was structured via a photolithographic process. Then the polymer, dissolved in toluene was spun onto the substrate. We achieved high quality films with thicknesses varying from 60–300 nm depending on the concentration of the solution and on the frequency of the spincoater. Finally an aluminium electrode was deposited onto the device by thermal evaporation in high vacuum.

We used a Perkin-Elmer  $\lambda$ -9 UV-VIS-NIR spectrometer for recording of UV/VIS absorbance spectra and a Jobin Yvon monochromator with a Hamamatsu photomultiplier for photoluminescence spectra. Electroluminescence spectra were recorded either by photon counting or by a Princeton Applied Research multichannel analyser.

### 3. RESULTS AND DISCUSSION

#### 3.1. Polymer properties

Figure 1 shows the chemical structure of the SLPPP polymers. The length of the ladder-type part of the molecule varies statistically ( $n \leq 10$ ). We used two different modifications, which are distinguished by their different average ratios  $x/y$  of co- and ladder polymer segments: 0.5/0.5 (abbreviated 55) and 0.6/0.4 (64). Their general behaviour (e.g. emission colour, resistivity,  $I/V$ -characteristics shape of LED devices) is very similar but shows some characteristic differences in absorption and emission spectra.

As can be seen in Fig. 2 the absorption spectra (1) of both SLPPP 55 and 64 are well structured, the three maxima close to the band edge (373/394/418 nm)

are separated by 0.177 eV. The photoluminescence emission spectra (2) reflect this structure; the interval between the two major maxima (450/480 nm) and the minor one at 515 nm is 0.173 eV. This vibronic splitting is attributed to the C–C ring stretching  $A_g$ -modes which are observed in Raman spectra of PPP type polymers and oligomers [8, 9]. The slightly different shapes of the polymers 55 and 64 in absorption and emission spectra are due to a nonidentical sequence length distribution function of these statistical copolymers.

For a determination of the bandgap we modelled

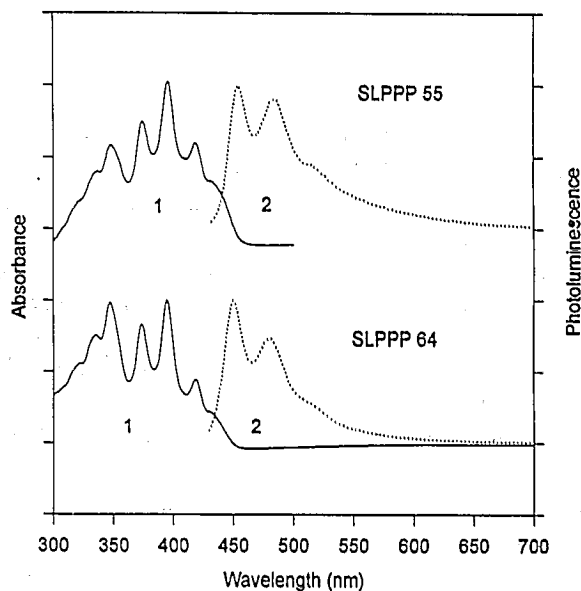


Fig. 2. Absorbance (1) and photoluminescence (2) of SLPPP 55 and 64.

the absorption spectra with a series of oligomer absorption contributions (five Gaussian peaks). The peak of lowest energy is located at 434 nm. This we identify as the 0-0 transition maximum. From that we calculate the width of the bandgap  $E_g = 2.84$  eV. The position of the first emission maximum at 450 nm is well outside the absorption onset. Self-absorption might only steepen the onset of emission but will not alter the position of the maximum itself. The Stokes shift is therefore 0.1 eV which is quite small compared to PPP [2] but shows – as does LPPP – the little ability of SLPPP to relax the distortion of its chain in the picture of singlet excitons. In the model of polaron-excitons their energetic levels are just 0.05 eV apart from the edges of the valence and conduction bands.

For determining the absorption coefficient  $\alpha$  of the polymer we used the Fabry-Perot fringes in the NIR region of the reflection spectrum which occur due to multiple reflections in transparent films. Straight forward multiple beam interference theory gives the thickness of a plane parallel film layer. For the calculations we used the refraction index  $n = 1.6$  determined from long LPPP (42 monomer units) [10]. From the absorption spectrum we derived the absorption coefficient  $\alpha(395 \text{ nm}) = 5.98 \times 10^4 \text{ cm}^{-1}$ . With this knowledge we are able to determine the thickness of the polymer films in our LEDs by simple absorption measurements prior to deposition of the top metal electrode.

### 3.2. Electroluminescence

Intense blue photoluminescence with two peaks at 450 nm and 480 nm and an overall emission linewidth of about 50 nm is a characteristic of SLPPP. Figure 3 compares electroluminescence (EL) and photoluminescence (PhL) of both SLPPP 55 and 64.

In the high energy region we obtain an acceptable agreement between EL and PhL. We therefore assume the same paths of radiative recombination for both EL and PhL in this part of the spectra, which is usually observed in conjugated polymer LEDs [11, 12].

In the lower energy region EL shows an enhanced intensity compared to the PhL. We propose fission of singlet-excitons due to the applied electric field to be the generating process. Kersting *et al.* [13] showed a considerable decrease of the entire emission spectrum when applying an electric field in excess of  $2 \times 10^8 \text{ Vm}^{-1}$  to poly(phenylphenylvinylene) samples. If fission of a part of the excitons, which would recombine radiatively under zero field conditions, takes place one expects generation of free charge carriers. It should not play a too important role in the following process if a part of the positive carriers are trapped at defect sites because in polymer devices, injecting positive carriers into the active layer was never as much problem as injecting electrons [11] and thus the carrier concentration of positive carriers is always higher than that of the negative ones. Therefore we focus on the gained free negative carriers which can stay free, combine to singlet excitons which may recombine radiatively afterwards, or are also trapped at defect sites. Modelling the spectra in Fig. 3 with a series of three Gaussian peaks shows that the additional light intensity in the red is due to a peak around 576 nm. This is a 0.6 eV energy drop compared to the 0-0 peak and therefore excitons are ruled out.

LPPP [14] and several other molecular crystals and polymers [15, 16] show PhL emission due to excimer generation. Especially LPPP films show a broad PhL maximum between 520 nm and 650 nm, whereas no peak is observed for LPPP in solution. This we regard as a strong hint for excimer generation since the average distance between the polymer molecules is crucial for this effect. Moreover the effect should increase when one goes from solvents to solid state films. This is also consistent with the stronger EL and PhL emission of SLPPP 55 in that energetic region. Comparison of LPPP and SLPPP shows that excimer generation is a property of the ladder segments of the molecule. SLPPP 55 with its higher content should therefore show the stronger emission and this is what we observe in Fig. 3.

SLPPP 55 films show a PhL quantum efficiency of

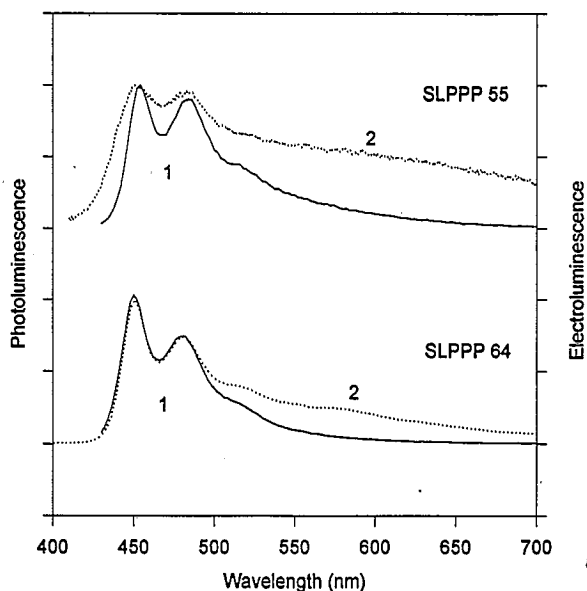


Fig. 3. Photoluminescence (1) and electroluminescence (2) of SLPPP 55 and 64. The enhanced signal/noise ratio of SLPPP 55 (2) is due to the use of a multichannel detection in opposition to photon-counting for SLPPP 64 (2).

21%. The quantum well like structure of the molecule separates effectively excited states on the chain thus reducing the probability of nonradiative recombination. Taking into account the device geometry [17] we estimate a total external quantum efficiency in excess of 0.4% of EL for our A1 devices at room temperature. A detailed discussion of the total quantum efficiency will be published elsewhere.

#### 4. CONCLUSIONS

Light emitting diodes were fabricated in an ITO/polymer/metal layer structure using A1 as metal electrodes and a novel derivate of poly(para phenylene) (PPP) as the active layer. It is a soluble ladder-type PPP segmented by a copolymer, the polymeric version of a quantum well structure.

We observed bluish electroluminescence emission around 460 nm. Compared to photoluminescence spectra an enhanced emission in the red region of the spectrum was detected, which we explain by the generation of excimer-like centres due to fission of singlet excitons in the electric field. Optimising this process would offer the possibility to tune the emission colour of the devices by varying the voltage.

The quantum efficiency of photoluminescence is as high as 21% in the solid state. The electroluminescence quantum efficiency is in excess of 0.4% for our devices with air stable electrodes.

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