Polarized electroluminescence from rubbing-aligned poly(p-phenylenevinylene)

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Polarized electroluminescence from rubbing-aligned poly(*p*-phenylenevinylene)

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Abstract

In this paper the rubbing-alignment of a poly(*p*-phenylenevinylene) (PPV) precusor polymer is described. Highly oriented films have been prepared leading to a dichroic ratio of 18 for photoluminescence corresponding to an order-parameter $S_{PL} = (PL_{\parallel} - PL_{\perp})/(PL_{\parallel} + PL_{\perp})$ of 0.9. Two-layer LEDs with the configuration ITO/PPV/Poly(phenylquinoxaline) (PPQ)/Al that have been fabricated show dichroic ratios for electroluminescence ($EL_{\parallel}/EL_{\perp}$) of 12 and a maximum brightness of 200 cd/m^2.

Keywords: Electroluminescence; Polarization; Poly(*p*-phenylenevinylene); Rubbing alignment

1. Introduction

Organic light emitting diodes (OLEDs) currently attract a lot of interest as a new display technology competing with the well-established LCDs [1,2].

A number of optical applications require polarized light. So for backlighting of LCD — displays light from a glow — discharge lamp is passed through a set of polarizers in the back and in the front of the active LCD-layer. A polarizer usually absorbs 50% of the light, which leads to an increased power consumption and is undesirable for use in portable computers and mobile phones.

Generally low molar mass chromophores or polymers in OLEDs are randomly distributed and have no preferential orientation. Alignment of such small molecules and polymers with a large anisotropy of the optical dipole moment is an attractive feature since it can directly lead to OLEDs emitting polarized light. This represents a promising application for backlighting in LCD displays.

Several methods for the orientation process like stretch alignment [3], epitaxial evaporation of rod-like emitters [4,5], the use of liquid crystalline polymers and low molar mass materials [6–8] and LB-films [9,10] have already been described. Hamaguchi et al. reported on polarized EL from rubbing-aligned liquid crystalline dialkoxy–PPV derivatives with dichroic ratios of 4.5 (UV/VIS) and 5.3 (photoluminescence) [11–13].

In this paper we present a simple and effective method for the rubbing alignment of segmented precursor PPV.

2. Experimental

For our experiments (Scheme 1), we used a chlorine polyelectrolyte precursor **1** which was synthesized similar to the procedure described in Ref. [14]. The polymerization of the chlorine salt was carried out with an excess of lithium hydroxide and, after polymerization, the solution of the precursor polymer was neutralized with acetic acid. The precursor polymer contains acetate side groups that partially remain in the polymer during the thermal elimination (argon, 165°C, 3 h). This leads to a segmented poly(*p*-phenylenevinylene) **2** with improved photoluminescence and electroluminescence (EL) quantum efficiency [15]. A similar route starting from a precursor polymer with bromine counterions was described by Carter et al. [16].

Thin films from the precusor polymer **1** were prepared by doctor-blade technique.

Since the orientation of polymers requires a uniaxial alignment of polymer chains, which is unfavourable for entropic reasons, stiff segments like conjugated pheny-

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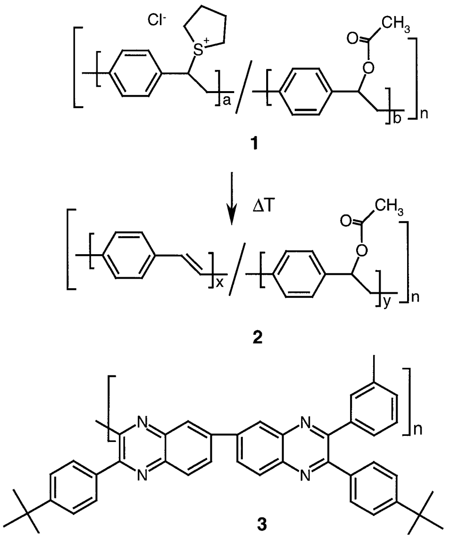

Scheme 1. Thermal conversion of polyelectrolyte precursor **1** into acetoxy-substituted PPV **2**; *t*-Bu-poly(phenylquinoxaline) *t*-Bu-PPQ **3**.

lenevinylene units were supposed to be ideal for this purpose. On the other hand, for an orientation of photoluminescent segments to occur, there is a demand for a minimum fluidity in the polymer film, so that chain segments can reorient. During elimination, the mechanically soft precursor film is converted into a tough polymer (for mechanistic details of the elimination reaction see Ref. [17]). Preliminary experiments showed that the precursor film seemed not to be ideal for the rubbing-alignment process whereas fully converted PPV did not lead to a maximum orientation. Optimum conditions were found by rubbing partially eliminated PPV several times with a piece of lint free paper.

3. Characterization

The orientation of the rubbed films was measured by UV–VIS spectroscopy using a Glan–Thompson polarizer and with a commercial sheet polarizer for photoluminescence measurements.

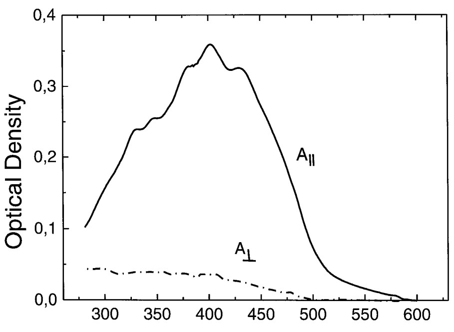

Fig. 1. Absorption parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the rubbing direction of the PPV film.

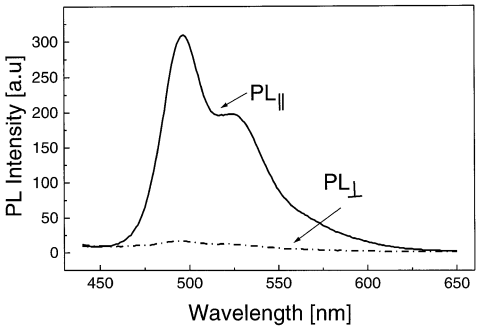

Fig. 2. Polarized photoluminescence of a 40-nm thick rubbed PPV film.

Fig. 1 shows the absorption spectra of a 40-nm thick, rubbed PPV film **2** after elimination (in the following, **2** is refered to as PPV).

The absorption parallel to the rubbing direction ($A_{\parallel}$) is about 10 times larger than perpendicular to the rubbing direction ($A_{\perp}$), showing a remarkable orientation of the optical dipole moment axis of the polymer chain with an in-plane order parameter $S_{\mathrm{UV}} = (A_{\parallel} - A_{\perp})/(A_{\parallel} + A_{\perp})$ of 0.82 (Fig. 1).

Like in the case of EL (Fig. 5) the absorption $A_{\parallel}$ is slightly red-shifted compared to the absorption $A_{\perp}$. The maximum of the ratio ($A_{\parallel}/A_{\perp}$) is located in the low-energy absorption range of the spectrum. Anisotropic alignment of polymer segments becomes probably more efficient for longer, stiff, conjugated phenylenevinylene segments. An analogous redshift of $A_{\parallel}$ was also observed in oriented poly(*p*-phenylenes) [10].

A convenient method to measure the orientation of thin films is photoluminescence spectroscopy. Fig. 2 shows the photoluminescence spectrum of a 40-nm thick rubbed PPV film. A polarization ratio ($\mathrm{PL}_{\parallel}/\mathrm{PL}_{\perp}$) of 18 is obtained which corresponds to an order parameter $S_{\mathrm{PL}} = (\mathrm{PL}_{\parallel} - \mathrm{PL}_{\perp})/(\mathrm{PL}_{\parallel} + \mathrm{PL}_{\perp})$ of 0.90.

4. Polarized emission from OLEDs

In a second step we made polarized OLEDs with oriented PPV layers. In order to prevent electrical breakdown

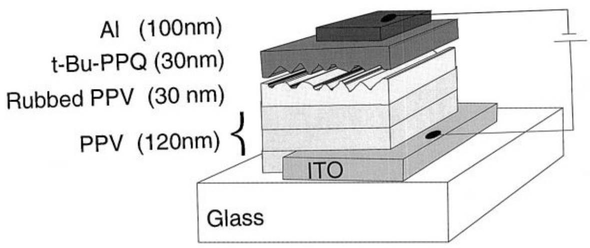

Fig. 3. Device architecture of the two-layer device with rubbed PPV.

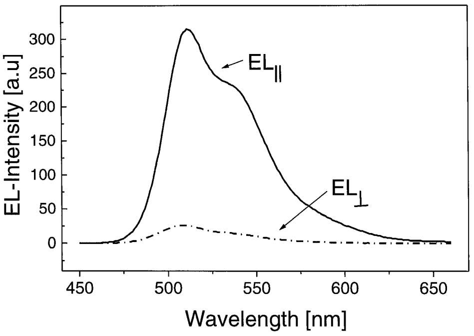

Fig. 4. Polarized electroluminescence from a two-layer OLED with the configuration ITO/PPV(150 nm)/*t*-Bu-PPQ(30 nm)/Al.

by mechanical destruction of the thin films during rubbing, we made multilayer LEDs. First, a 120-nm thick PPV layer was prepared on top of ITO-glass followed by a second PPV layer (30 nm) which was subjected to the rubbing process described before. The PPV was covered with a 30-nm thick poly(phenylquinoxaline) **3** electron transport layer [18] and an aluminum top electrode (Fig. 3).

Fig. 4 shows the polarized EL spectra from this LED. The polarization anisotropy ($EL_{\|}/EL_{\perp}$) is 12 (at 511 nm) corresponding to an order parameter $S_{EL} = (EL_{\|} - EL_{\perp})/(EL_{\|} + EL_{\perp})$ of 0.85. Again, a slight redshift is observed for the emission parallel to the rubbing direction compared to that perpendicular (Fig. 5).

The shift of the emission peak from 498 nm (PL) to 511 nm (EL) may be attributed to Charge–Transfer interactions between the electron donor PPV and the electron accepting PPQ as well as cavity effects.

The *I–V* and brightness–voltage characteristics of the polarized PPV–LED are shown in Fig. 6. A maximum brightness of 200 cd/m^2 is obtained in these LEDs at 20 V.

During the mechanical treatment of the precursor PPV, scratches, which can be visualized by electron- and AFM-microscopy, are formed (Fig. 7). These scratches lead to leakage currents which up to now limit the lifetime of our devices. Alternative methods for the orientation of precursor PPV, which minimize the mechanical destruction, are currently under investigation and will be reported.

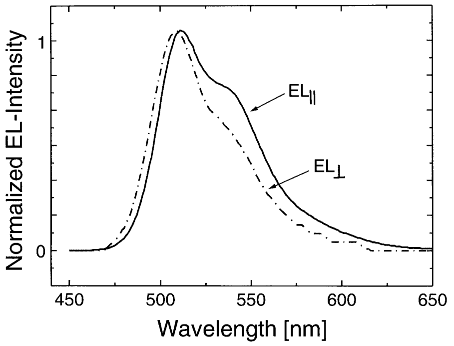

Fig. 5. Redshift of the emission parallel to the rubbing direction $EL_{\|}$ relative to the emission perpendicular $EL_{\perp}$.

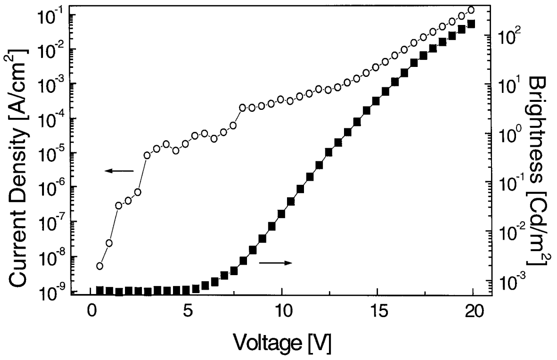

Fig. 6. I–V characteristics and brightness of the ITO/PPV/rubbed-PPV/*t*-Bu-PPQ/Al device.

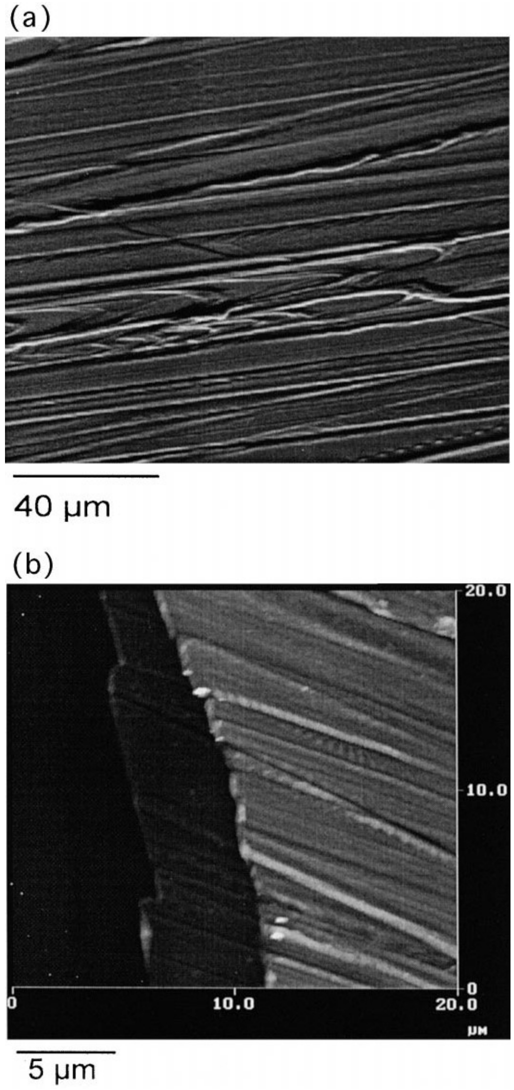

Fig. 7. (a,b) SEM (left) and AFM (right; tapping mode) images of a rubbed layer of PPV (30 nm) on glass/ITO/PPV (120 nm) substrate (the dark area on the left side of the AFM-image is the glass substrate).

5. Conclusion

We have demonstrated the manufacturing of uniaxially oriented PPV-films for polarized EL applications by simply rubbing films of a partially eliminated PPV precursor polymer. A large dichroic ratio of 18 for photoluminescence was obtained. The macroscopic order parameters are in the range of 0.8–0.9. Polarized EL was obtained from two-layer PPV LEDs with a dichroic ratio for EL ($EL_{\parallel}/EL_{\perp}$) of 12 and a maximum brightness of 200 cd/m^2.

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