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Polarized Electroluminescence from Rubbing-Aligned Poly(*p*-phenylenevinylene)**

By Markus Jandke, Peter Strohmriegl,* Jürgen Gmeiner, Wolfgang Brütting, and Markus Schwoerer

A number of optical devices such as liquid crystal displays (LCDs) require polarized light. In such displays linearly polarized light is usually made from unpolarized light emitted by a glow-discharge lamp by means of a sheet polarizer in the back of the active LCD layer. However, 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.

Organic light-emitting diodes (OLEDs) are an alternative light source and they have been extensively developed over the last decade. Currently they attract a lot of interest as a new display technology,^[1–5] as the use of organic materials in OLEDs offers the possibility of polarized emission. 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 leads directly to OLEDs emitting polarized light.

Several polarized OLEDs based on different orientation mechanisms have already been described. For low molar

mass materials epitaxial evaporation of rod-like emitters,^[6,7] and Langmuir–Blodgett films^[8,9] have been used. For polymers, stretch alignment^[10] turned out to be a suitable method for polarized OLEDs.

Liquid crystallinity is known to provide quick access to one- or two-dimensional orientation of chromophores. Thermotropic liquid crystals, including both low molar mass materials and polymers with smectic phases, have been used in electroluminescence (EL) devices.^[11–13] A stabilization of the LC state was accomplished either by device operation at elevated temperatures or by quenching the LC state of the polymer into a glass. Grell et al. used a main-chain liquid-crystalline polymer, poly(9,9-di-*n*-octyl-2,7-fluorene), which was reported to show excellent hole-transport mobility, to demonstrate polarized electroluminescence.^[14,15] The highest dichroic ratios for polarized electroluminescence ($EL_{\parallel}/EL_{\perp} = 15$) were recently reported for poly(9,9-di-(2-ethylhexyl)-2,7-fluorene).^[16]

From a technological point of view a rather interesting technique for the preparation of polarized OLEDs is rubbing alignment of polymers. Hamaguchi and Yoshino reported on polarized EL from rubbing-aligned liquid-crystalline poly(2,5-di-nonyloxy-1,4-phenylenevinylene)^[17–19] whereby a dichroic ratio of 5.3 for photoluminescence was demonstrated. The corresponding ratio of polarized EL was 1.6. To what extent these anisotropies originate from the LC phase of the polymer used is not clear since similar results were obtained from non-liquid-crystalline poly(2,5-dialkoxy-1,4-phenylenevinylens) and poly(3-alkyl-thiophenes).^[19]

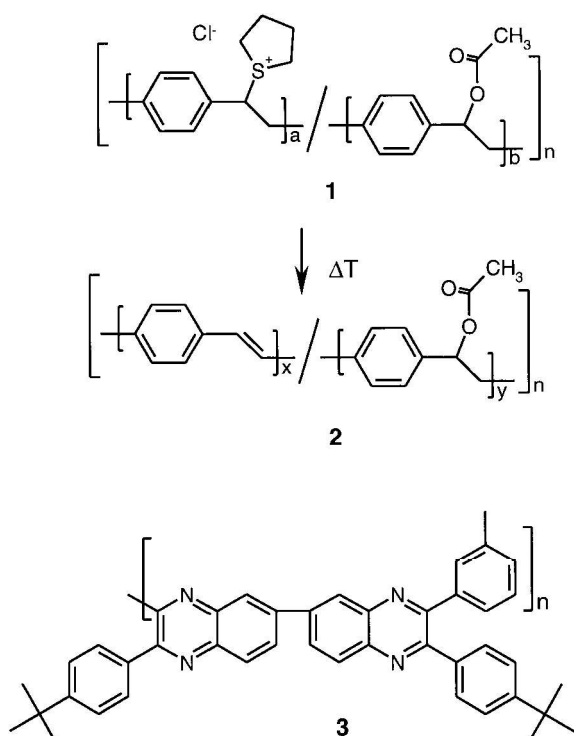
In this paper we present a simple and effective method utilizing rubbing alignment of segmented precursor poly(*p*-phenylenevinylene) (PPV) for the preparation of two-layer LEDs showing high dichroic ratios of linearly polarized electroluminescence.

For our experiments we used the chlorine polyelectrolyte precursor **1** (see Scheme 1), which was synthesized according to a procedure described in the literature.^[20] 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, which partially remain in the polymer during thermal elimination. This leads to a segmented PPV **2** with an improved photoluminescence and electroluminescence quantum efficiency (see Scheme 1).^[21] The fully converted segmented PPV **2** is referred to as PPV. A similar route starting from a precursor polymer with bromine counterions was described by Carter et al.^[22] Thin films from the precursor polymer **1** were prepared on glass or indium tin oxide (ITO) substrates by the doctor-blade technique.^[20]

Since the orientation of polymers requires a uniaxial alignment of polymer chains, which is unfavorable for entropic reasons, stiff segments such as conjugated phenylenevinylene units were believed to be ideal for this purpose. On the other hand, for an orientation of the photoluminescent segments to occur there is a minimum

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

demand for fluidity in the polymer film, so that chain segments can reorient. During elimination the mechanically soft precursor film is converted into a tough polymer (the mechanistic details of the elimination reaction can be found in the literature^[23]). Preliminary experiments showed that the precursor film appeared not to be ideal for the rubbing-alignment process due to the softness of the layer. On the other hand fully converted PPV did not fully orientate. Dichroic ratios, $PL_{\parallel}/PL_{\perp}$, of approximately four were obtained in preliminary experiments. Optimum conditions were found by rubbing partially eliminated PPV several times with a piece of lint-free paper.

The orientation of the rubbed PPV films was measured by UV-vis and photoluminescence spectroscopy. Figure 1 shows the absorption and photoluminescence spectra of a 40 nm thick, rubbed film of PPV **2** after elimination.

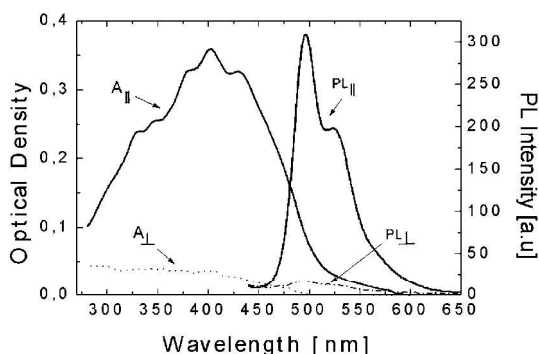


Fig. 1. Absorption and photoluminescence of a 40 nm thick rubbed PPV (**2**) film parallel (A_{\parallel} , PL_{\parallel}) and perpendicular (A_{\perp} , PL_{\perp}) to the rubbing direction.

The absorption parallel to the rubbing direction (A_{\parallel}) is about 10 times larger than that perpendicular to the rubbing direction (A_{\perp}), showing a remarkable orientation of the optical dipole moment axis of the polymer chain. The in-plane order parameter, $S_{UV} = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + A_{\perp})$, at the absorption maximum (404 nm) was calculated to be 0.82. As in the case of EL, 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 the polymer segments probably becomes more efficient for longer, stiff, conjugated phenylenevinylene segments.

A convenient method for measuring the orientation of thin films is photoluminescence spectroscopy. The photoluminescence spectra of a 40 nm thick rubbed film are given for polarizations parallel (PL_{\parallel}) and perpendicular (PL_{\perp}) to the rubbing direction (Fig. 1, right side). A polarization ratio ($PL_{\parallel}/PL_{\perp}$) of 18 is obtained at the fluorescence maximum (497 nm), which corresponds to an order parameter S_{PL} of 0.90.

In a second step we made polarized OLEDs with oriented PPV layers. In order to prevent electrical breakdown 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 above. The PPV was covered with a 30 nm thick poly(phenylquinoxaline) (**3**, see Scheme 1) electron transport layer^[24] and an aluminum top electrode (Fig. 2).

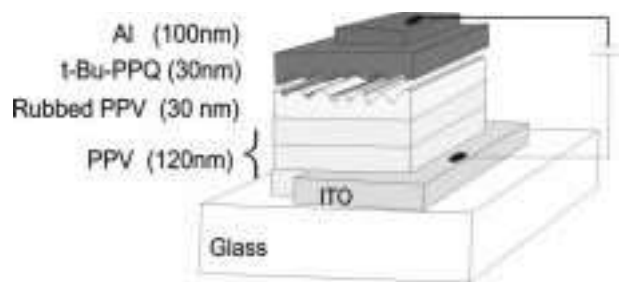


Fig. 2. Structure of the two-layer device with rubbed PPV.

Figure 3a shows the polarized electroluminescence spectra from this LED. The polarization anisotropy ($EL_{\parallel}/EL_{\perp}$) is 12 (at 511 nm), corresponding to an order parameter S_{EL} of 0.85. 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 poly(phenylquinoxaline) as well as cavity effects.

The current-voltage and brightness-voltage characteristics of the polarized PPV LED are shown in Figure 3b. A maximum brightness of 200 cd/m^2 is measured in these LEDs at 20 V.

During the mechanical treatment of the precursor PPV, scratches are formed that can be recorded by scanning electron microscopy (SEM) and atomic force microscopy (AFM, Fig. 4a and b). These scratches lead to leakage cur-

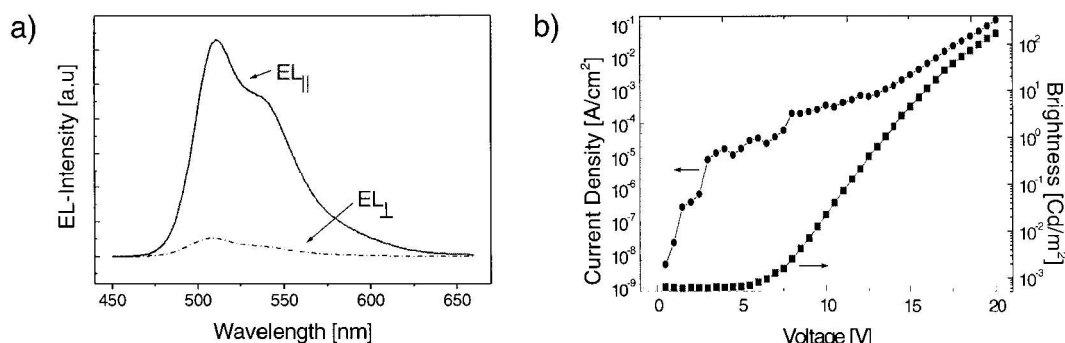


Fig. 3. a) Polarized electroluminescence from a two-layer OLED with the configuration ITO/PPV (120 nm)/rubbed PPV (30 nm)/tBu-PPQ (30 nm)/Al. b) I - V characteristics and brightness of the device.

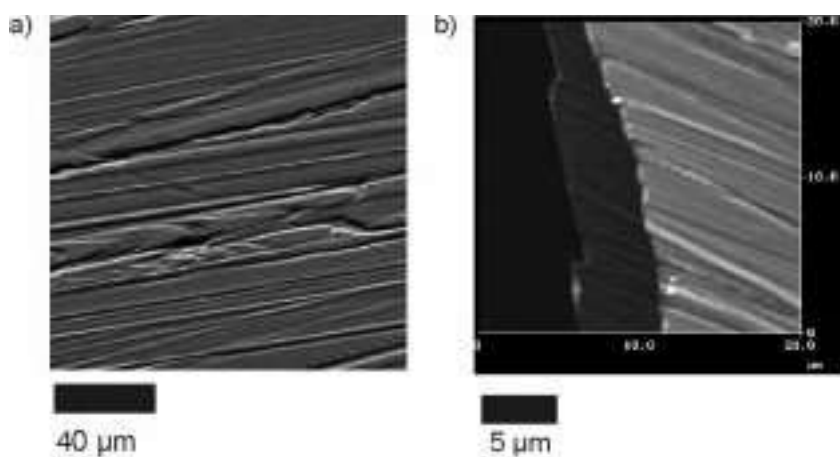


Fig. 4. SEM micrograph (a) and AFM image (b) of the rubbed PPV layer (30 nm) on glass/ITO/PPV(120nm). The dark area on the left side of the AFM image is the glass substrate.

rents, which, up to now, limit the lifetime of the devices. Alternative methods for the orientation of precursor PPV that minimize the mechanical destruction are currently under investigation.

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

Experimental

Films from the precursor polymer **1** were cast from an acetone/methanol solution (0.1 wt.-%) onto a glass or ITO substrate via doctor blading [20]. The precursor film was then transferred to a hot stage for pre-elimination (180 °C/20 s) and subsequently uniaxially rubbed 10 times with a piece of lint-free paper. The final elimination to the segmented PPV **2** was carried out in argon atmosphere at 165 °C for 3 h.

UV-vis polarized absorption spectra of 40–50 nm thick films on quartz substrates were measured with a Hitachi U-3000 spectrometer. A Glan-Thompson polarizer was used for the polarization of the incident beam parallel and perpendicular to the rubbing direction. Baseline corrections were carried out for each polarization direction.

Photoluminescence spectra were recorded using a Shimadzu RF-PC-5301 spectrofluorophotometer with a linear sheet polarizer between the sample and the detection system. The polymer film (30–40 nm, on glass substrate) was excited with non-polarized light ($\lambda_{\text{ex}} = 420 \text{ nm}$).

For OLEDs a 120 nm PPV layer was coated onto ITO glass, followed by an additional 30 nm PPV layer, which was subjected to rubbing alignment. The PPV was covered with 30 nm of poly(4-*tert*-butylphenylquinoxaline) (tBu-PPQ) **3**, which was spin-coated from chloroform solution. Finally an aluminum cathode was evaporated on top of the ET layer at a pressure of 10^{-6} mbar. Current–voltage characteristics were recorded with a Keithley 236 source-measure unit working in a glove box. Spectral emission was determined using a Shimadzu RF-PC 5301 spectrofluorophotometer, at a driving voltage of 15 V. A sheet polarizer was used to measure the electroluminescence intensities parallel and perpendicular to the rubbing direction.

Optical characterization of the rubbed films was carried out using atomic force microscopy (DI Instruments 3000, tapping mode) and scanning electron microscopy (JEOL 840A).

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