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# Highly polarized polymer light-emitting diodes utilizing friction-transferred poly(9,9-dioctylfluorene) thin films

Masahiro Misaki and Yasukiyo Ueda<sup>a)</sup>

*Graduate School of Science and Technology, Kobe University, 1-1 Rokko, Nada, Kobe 657-8501, Japan*

Shuichi Nagamatsu, Masayuki Chikamatsu, Yuji Yoshida,

Nobutaka Tanigaki, and Kiyoshi Yase

*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST),*

*Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan*

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Polarized polymer light-emitting diodes (PLEDs) have been constructed utilizing friction-transferred poly(9,9-dioctylfluorene) (PFO) thin films. The friction transfer technique allows oriented PFO to be deposited directly onto an indium tin oxide anode without an alignment layer such as polyimide. Polarized absorption and photoluminescence spectra revealed that the polymer backbones are highly aligned in the friction direction. We fabricated PLEDs consisting of friction-transferred PFO as an emissive layer, vacuum-deposited bathocuproine as an electron transport and hole-blocking layer, and a vacuum-deposited LiF/Al cathode. Highly polarized blue emission with an integrated polarization ratio of 31 and a luminance of up to 300 cd/m<sup>2</sup> was observed from the PLEDs. © 2005 American Institute of Physics. [DOI: 10.1063/1.2142082]

Considerable progress in the field of polymer light-emitting diodes (PLEDs) has been made since the report of Burroughes *et al.*<sup>1</sup> Most of the work carried out on PLEDs has involved unpolarized light emission. On the other hand, PLEDs consisting of an aligned emissive layer are expected to exhibit polarized emission,<sup>2</sup> because the intrinsic characteristic of conjugated polymers originates from the electrons delocalized along the polymer backbone (main chain). The development of polarized PLEDs is important for their application to liquid crystal display (LCD) backlights: if polarized light is employed as a backlight, the backlight's power efficiency is markedly improved since a polarizer is not necessary. For the most efficient use of such LCD backlights, typically, electroluminescence (EL) polarization ratios of 30–40 are required.

Most polarized PLEDs have aligned liquid crystalline (LC) polymers deposited on a rubbed alignment layer.<sup>3</sup> One very attractive class of such LC polymers is polyfluorene (PF) for the following reasons. PF has emerged as an attractive material for PLEDs and can be well aligned on a rubbed polyimide layer in the thermotropic LC state.<sup>4</sup> Once suitable LC polymers have been identified, the main issue to be addressed is the choice of alignment layer. In general, the alignment layer is positioned between an electrode and an active semiconducting layer, which causes some problems in terms of device performance. In particular, standard polyimide is a good electrical insulator, leading to poor device performance when it is used for the alignment layer. Improvement in device performance has been achieved by increasing the conductivity of the alignment layer.<sup>5–9</sup> For example, Grell *et al.* have reported on an alignment layer consisting of polyimide filled with a starburst-type amine, to allow sufficient hole transport through the alignment layer.<sup>5,6</sup> Recently, device performance has been considerably improved using rubbed poly(*p*-phenylenevinylene) (PPV) (Refs. 6 and 7) or

poly(3,4-diethylenedioxythiophene) (Refs. 8 and 9) as alignment layers. However, certain drawbacks of these methods arise from the mechanical damage of the alignment layers and the induction of electrostatic charge. Therefore, several attempts to remove mechanical rubbing process have been made.<sup>10–13</sup> Although new techniques utilizing a noncontact photoalignment layer<sup>10–12</sup> or a top-down alignment approach<sup>13</sup> are proposed, the device performance, EL polarization ratio in particular, is not as high as that obtained from a mechanically rubbed layer.

A friction-transfer technique offers a way for direct preparation of an oriented polymer layer without an underlying alignment layer, thus avoiding the disadvantages of the alignment technique described earlier. The formation of highly oriented poly(tetrafluoroethylene) (PTFE) films by the friction-transfer technique of Tabor *et al.* has been well known since 1964.<sup>14</sup> When PTFE is squeezed and drawn against a clean surface of metal or glass, a highly oriented PTFE film remains on the surface. Moreover, Wittmann and Smith reported that friction-transferred PTFE films induce the orientation of a variety of crystalline and liquid crystalline materials, including polymers, monomers and small organic and inorganic molecules.<sup>15</sup> Chen *et al.* reported polarized PLEDs utilizing oriented PPV thin films on the friction-transferred PTFE substrate.<sup>16</sup> We have applied the friction-transfer technique to direct preparation of oriented films of various conjugated polymers, such as polysilane, poly(*p*-phenylene), poly(*p*-phenylenevinylene), poly(alkylthiophene), and their derivatives.<sup>17–20</sup> Recently, we have succeeded in preparing highly oriented films of thermotropic LC polymer, poly(9,9-dioctylfluorene) (PFO) by this technique, and found that subsequent thermal treatments of the friction-transferred PFO films are specifically effective for the improvement of molecular orientation and surface morphology.<sup>21</sup>

In this study, we fabricate highly polarized blue-emitting PLEDs utilizing a friction-transferred PFO thin film. The friction-transfer technique allows the emissive oriented poly-

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: yueda@kobe-u.ac.jp

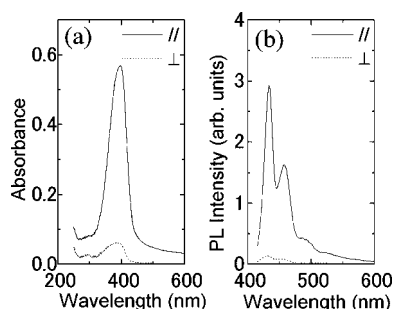


FIG. 1. Polarized absorption (a) and PL spectra (b) for oriented PFO films by a friction-transfer technique with subsequent thermal treatments. The spectra were measured for lights polarized parallel ( $\parallel$ , solid line) and perpendicular ( $\perp$ , dashed line) to the friction direction. For PL spectra, the excitation wavelength was 390 nm.

mer to be deposited directly onto an indium tin oxide (ITO) anode substrate, avoiding the alignment layer between the electrode and emissive layer thus leading to improved device performance.

The PFO used here was purchased from American Dye Source, Inc. (catalog No. ADS129BE). Differential scanning calorimetry (Perkin Elmer Instruments) scans showed a crystallization peak at approximately 80–90 °C and a melting endothermal peak at approximately 160 °C at a heating/cooling rate of 20 °C/min. Above this temperature, PFO shows a birefringent nematic LC melt and becomes isotropic at approximately 270–280 °C.<sup>4</sup> The PFO powder was compressed into a pellet under a pressure of 400 kgf/cm<sup>2</sup>. The thin films of PFO were prepared by the friction-transfer technique.<sup>21</sup> The friction-transfer process was carried out by squeezing and drawing the pellet directly on a quartz substrate or an ITO substrate maintained at approximately 100 °C. The applied load for squeezing was 30 kgf/cm<sup>2</sup>, and the drawing speed was 0.5 m/min. The thickness of the resulting films was approximately 50 nm, which was determined by a surface profile tracer (Tencor Instruments). The friction-transferred films were thermally annealed in the nematic LC phase at 180 °C for half an hour under an inert nitrogen atmosphere. Nematic glass films were prepared by placing the sample from the hot stage onto a metallic surface at room temperature. Note that subsequent thermal annealing is necessary to obtain films with a very smooth topography<sup>21</sup> and this opens the way to the realization of polarized PLEDs. The mechanism of reorientation has been discussed in detail in our previous report.<sup>21</sup> In this letter, we call the nematic glass films “friction-transferred films.”

Samples for optical measurements were prepared on quartz substrates. An ultraviolet-visible absorption spectrometer (Shimadzu MPS2000) and a fluorescence spectrometer (JASCO FP777) with Glan-Thompson prisms were used to investigate the degree of molecular alignment in the films. Samples for polarized PLEDs were prepared on ITO substrates. The device structure and fabrication procedures are described in the results and discussion. The brightness of the device was measured using a luminance meter (Topcon BM-9) and current-voltage characteristics were measured with an electrometer (Keithley 2400 source/measure unit). The polarization of light emitted from the PLEDs was analyzed using a Glan-Thompson prism. The light was then collected with a glass fiber, dispersed in a spectrograph, and detected with a charge coupled device camera (Roper Scien-

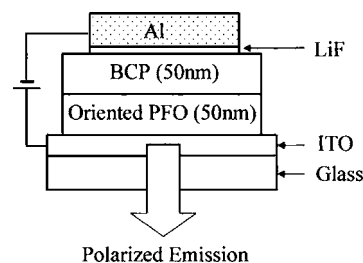


FIG. 2. Structure of polarized PLED.

tific, Inc.). All measurements were performed at room temperature in air without sample encapsulation.

Figure 1(a) shows the polarized absorption spectra of the friction-transferred PFO films. The spectra showed different profiles between the polarization directions parallel and perpendicular to the friction direction. In the absorption spectrum with the parallel polarization ( $A_{\parallel}$ ), a maximum peak was observed at 397 nm, which was associated with delocalized  $\pi$ - $\pi^*$  transitions on fluorene backbones. In the absorption spectrum with the perpendicular polarization ( $A_{\perp}$ ), however, this peak was sufficiently suppressed. The dichroic ratio in absorption ( $A_{\parallel}/A_{\perp}$ ) was estimated to be approximately 10 for the peak at 397 nm. This result indicates that the friction-transferred PFO forms an excellent uniaxial alignment of the polymer backbone in the films.

Figure 1(b) shows the polarized photoluminescence (PL) spectra of the films. The spectra also showed different profiles between the polarization directions parallel and perpendicular to the friction direction. The PL spectrum with the parallel polarization ( $PL_{\parallel}$ ) showed a strong emission having a vibronic structure with peaks at 434 (0-0), 458 (0-1), and approximately 490 nm (0-2) with a shoulder at approximately 530 nm. On the contrary, the PL spectrum with the perpendicular polarization ( $PL_{\perp}$ ) showed a very weak emission. The dichroic ratios in ( $PL_{\parallel}/PL_{\perp}$ ) were estimated to be approximately 23 at 434 nm, 21 at 458 nm, and 16 at 494 nm. Thus, the polarized PL spectra showed a large dichroism due to an excellent uniaxial alignment of the polymer backbone. The highly oriented structure in the friction-transferred PFO films has been confirmed by transmission electron microscopy analysis in our previous study.<sup>21</sup>

We constructed polarized PLEDs utilizing friction-transferred films as emissive layers. The device structure is

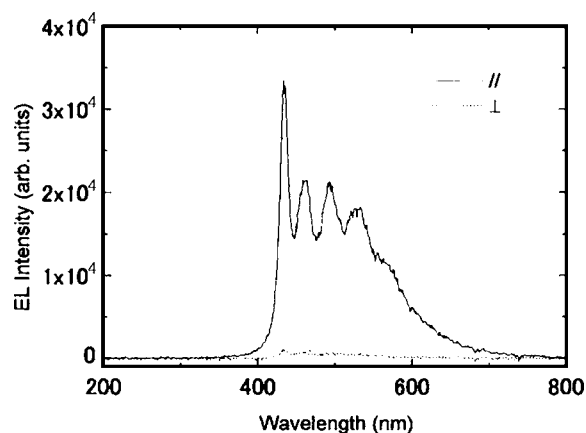


FIG. 3. Polarized EL spectra for the devices. Spectra are shown for lights emitted parallel ( $\parallel$ , solid line) and perpendicular ( $\perp$ , dashed line) to the friction direction.

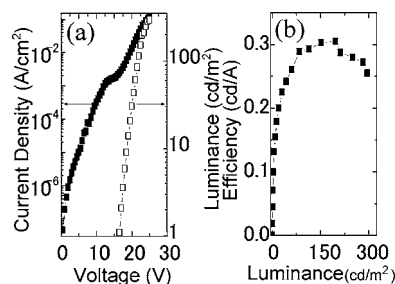


FIG. 4. Current-brightness-voltage (a) and efficiency-luminance (b) characteristics of polarized PLED.

shown in Fig. 2. An oriented PFO as an emissive layer was prepared on an ITO substrate. After that, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine or BCP) as an electron transport and hole-blocking layer was deposited on the PFO film. The thickness of the BCP layer was 50 nm. Finally, 1-nm-thick LiF and 60-nm-thick Al as a cathode were deposited through a shadow mask.

We clearly observed blue emission from the side of the ITO substrate under applied voltage. Figure 3 shows the polarized EL spectra of the device. The spectra showed different profiles between the polarization directions parallel and perpendicular to the friction direction. The EL spectrum with the parallel polarization ( $EL_{\parallel}$ ) showed a strong emission having a well-resolved vibronic structure with peaks at 434, 458, 494, and 533 nm. Although the peak positions in the EL spectrum were the same as those in the PL spectrum, an additional broad emission at approximately 535 nm (well-known as green emission)<sup>22</sup> was observed in the EL spectrum. We consider that this green emission is attributed to enhanced interchain excimer formation under device working.<sup>23</sup> On the contrary, the EL spectrum with the perpendicular polarization ( $EL_{\perp}$ ) showed a very weak emission. The dichroic ratios in EL ( $EL_{\parallel}/EL_{\perp}$ ) were estimated to be approximately 33 at 434 nm, 28 at 458 nm, and 29 at 494 nm. The dichroic ratio of the integrated intensity of the parallel-polarized EL spectra to that of the perpendicular-polarized EL spectra (integrated  $EL_{\parallel}/EL_{\perp}$ ) was estimated to be approximately 31. The ratio is significantly higher than that previously reported by Whitehead *et al.* for PLEDs utilizing a rubbed PPV alignment layer.<sup>7</sup> In addition, their devices have a disadvantage in that there is a loss of emission caused by absorption of the PPV layer. In our devices, such an absorption filter effect was not observed because no alignment layer was positioned between the transparent electrode and the emissive layer.

Figure 4(a) shows the current-brightness-voltage characteristics of the device without polarization analysis. The turn-on voltage (the bias required to give a luminance of 1 cd/m²) of the device was 16.5 V. The device reached a brightness of 300 cd/m² at 25 V. Figure 4(b) shows the efficiency-luminance characteristics of the device. The efficiency increases with luminance and becomes 0.3 cd/A at 100 cd/m². The high efficiency is maintained up to 300 cd/m². The efficiency of our device is approximately 2.5 times higher than that of the device utilizing a rubbed PPV alignment layer (0.12 cd/A).<sup>7</sup> Thus, an improvement in de-

vice performance, i.e., not only EL polarization ratio but also efficiency, was realized using the friction-transfer technique. The optimization of the device structure is currently under way for further improving the device performance.

In conclusion, we have demonstrated highly polarized blue-emitting PLEDs utilizing friction-transferred PFO thin films. The friction-transfer technique offered a way of directly preparing an oriented polymer layer without an alignment layer, leading to improved device performance. In particular, we obtained an EL polarization ratio of more than 30 and a luminance of up to 300 cd/m². These values are sufficient for the application of these PLEDs to LCD backlights. The friction-transfer technique has significant potential for application to various electronic and optoelectronic devices that have highly anisotropic properties.

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