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Highly efficient polarized polymer light-emitting diodes utilizing oriented films of β -phase poly(9,9-dioctylfluorene)

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Uniaxially oriented films of β -phase poly(9,9-dioctylfluorene) (PFO) were realized by a friction-transfer technique followed by thermal annealing and vapor treatments. Absorption and photoluminescence (PL) spectra show the characteristics of β -phase: an additional absorption peak at 433 nm and redshifted PL peaks compared with those of the usual nematic (N) phase. We fabricated polarized polymer light-emitting diodes utilizing oriented films of β -phase PFO. Highly polarized β -phase emission with an integrated polarization ratio of 51 was observed from the devices. The efficiency of the devices based on β -phase reached 2.0 cd/A, which is two times higher than that based on N-phase. © 2008 American Institute of Physics.

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Considerable progress in the field of polymer light-emitting diodes (PLEDs) has been made since the report of Burroughes *et al.*¹ Most of the work carried out on PLEDs has involved unpolarized light emission. On the other hand, PLEDs consisting of an uniaxially oriented emissive layer are expected to exhibit linearly polarized emission, because the intrinsic characteristic of conjugated polymers originates from the electrons delocalized along the polymer backbone. Polarized PLEDs are potentially useful as an efficient light source for liquid-crystal displays (LCD) backlights and for various optical devices.²

In most cases, an aligned active semiconducting layer is achieved by depositing liquid crystalline (LC) polymer onto a rubbed alignment layer.³ The rubbed alignment layer is usually positioned between an electrode and an active semiconducting layer, which causes some problems in terms of device performance. For example, polyimide is normally 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.⁴⁻⁶ However, certain drawbacks of these methods arise from the mechanical damage of the alignment layers and the induction of electrostatic charge. Although many techniques utilizing a noncontact photoalignment layer⁷⁻⁹ or a top-down alignment approach¹⁰ are proposed, the device performance, 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 above.¹¹ We have succeeded in preparing highly oriented films of thermotropic LC polymer, poly(9,9-dioctylfluorene) (PFO) by this technique,¹² and fabricated highly polarized blue-emitting PLEDs utilizing

friction-transferred PFO films.¹³ However, the conformation of PFO was in all cases nematic glass (N) phase.

The PFO forms three different polymer conformations in solid state at room temperature (RT), which are called N, α , and β phases.¹⁴ The PFO films with different phases are obtained depending on the cooling rate from 190 °C (nematic LC state) to RT; rapid quenching and slow cooling result in N-phase and α -phase, respectively. Generation of the β -phase usually requires additional treatments, such as cooling to -196 °C and reheating to RT or exposure to certain solvent vapor.¹⁵ It is well known that the β -phase PFO forms the most planar conformation and has significant photophysical differences with N-phase and α -phase PFO.¹⁶ However, device applications of oriented films of β -phase PFO have not been reported.¹⁷⁻¹⁹

In this study, oriented films of β -phase PFO have been prepared by the friction-transfer technique followed by thermal annealing and vapor treatments. We have fabricated polarized PLEDs utilizing oriented films of β -phase PFO and improved the device performance up to 2.0 cd/A with the polarization ratio larger than 50, which is the best record in polarized blue PLEDs.

The PFO used in this paper was purchased from American Dye Source, Inc. (cat. No. ADS129BE). Since our experimental setup and the friction-transfer technique were previously described in detail,¹³ only a brief outline is presented here. The friction-transferred PFO films were annealed in a nitrogen atmosphere at 190 °C for 15 min and quenched from 190 °C to RT, resulting in oriented films of N-phase PFO. Then, the films were exposed to saturated toluene vapor to obtain oriented films of β -phase PFO.

Figure 1(a) shows the polarized absorption spectra of the films treated with toluene vapor for 20 h, where A_{\parallel}^{β} and A_{\perp}^{β} are the absorption spectra for the light polarized parallel and perpendicular, respectively, to the friction direction. The absorption spectrum before vapor treatments (A^N) is also shown in Fig. 1(a). For A_{\parallel}^{β} , the maximum peak was observed at approximately 400 nm, which was associated with delo-

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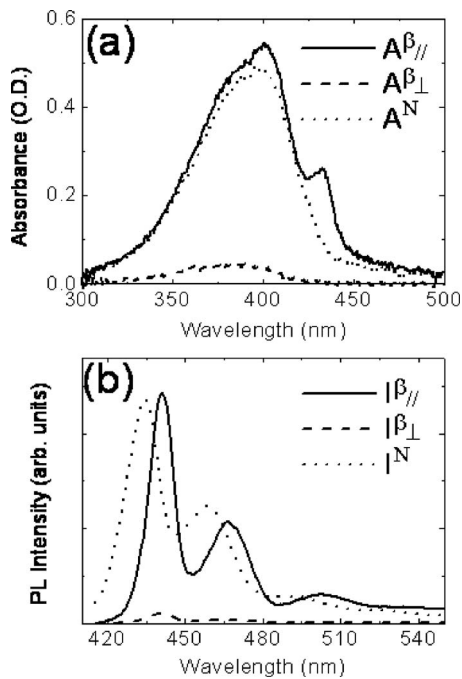


FIG. 1. (a) Polarized absorption spectra of the oriented film of β -phase PFO. A_{\parallel}^{β} and A_{\perp}^{β} are the absorption spectra for the light polarized parallel and perpendicular, respectively, to the friction direction. The absorption spectrum before vapor treatments, A^N , is also shown. (b) Polarized PL spectra of the oriented β -phase PFO film. I_{\parallel}^{β} and I_{\perp}^{β} are the parallel and perpendicular components with respect to the friction direction, respectively. The PL spectrum before vapor treatments I^N is also shown. All profiles were recorded upon excitation at 390 nm and intensities of I_{\parallel}^{β} and I^N were normalized by each maximum.

calized π - π^* transitions on fluorene backbones. Moreover, A_{\parallel}^{β} exhibited a conspicuous peaks at 433 nm that is a characteristic feature of the existence of β -PFO chains.¹⁴ For A_{\perp}^{β} , however, these peaks were sufficiently suppressed. The dichroic ratio in absorption ($A_{\parallel}^{\beta}/A_{\perp}^{\beta}$) was estimated to be 16 and 45 for the peak at 400 and 433 nm, respectively. This implies that the β -PFO chains were highly aligned parallel to the friction direction. In this paper, we call the films that contain fraction of oriented β -phase PFO chains “oriented films of β -phase PFO.”

The in-plane anisotropy of the films can be also determined from the polarized PL spectra. Figure 1(b) shows the corresponding polarized PL spectra of oriented films of β -phase PFO, where I_{\parallel}^{β} and I_{\perp}^{β} are the parallel and perpendicular components with respect to friction direction, respectively. The PL spectrum before the vapor treatment (I^N) is also shown in Fig. 1(b). I_{\parallel}^{β} exhibited redshifted emission compared with I^N , having a vibronic structure with peaks at 441 (0-0), 466 (0-1), and approximately 500 nm (0-2), which are corresponded with previously reported β -phase emission.¹⁴ These peak shifts indicate increased effective conjugation length along the friction direction. On the other hand, I_{\perp}^{β} showed much smaller emission. The dichroic ratios in PL ($I_{\parallel}^{\beta}/I_{\perp}^{\beta}$) were estimated to be 22 at 441 nm, 28 at 466 nm, and 18 at 503 nm, indicating that β -phase PFO chains are highly aligned parallel to the friction directions.

To investigate the effect of β -phase on the efficiency of devices, we constructed the polarized PLEDs utilizing the oriented film of β -phase PFO as an emissive layer. The oriented layer of β -phase PFO (~ 50 nm thick) was formed on patterned indium tin oxide substrate with poly(3,4-

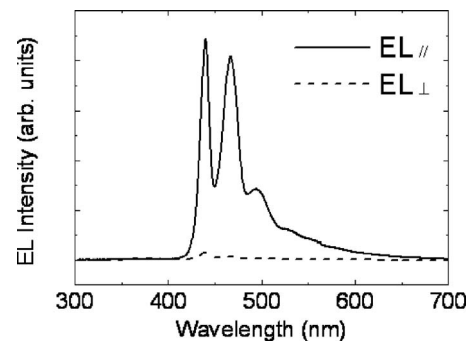


FIG. 2. Polarized EL spectra of the polarized PLED utilizing the oriented film of β -phase PFO. EL_{\parallel} and EL_{\perp} are the EL intensities parallel and perpendicular to the friction direction, respectively.

ethylenedioxythiophene) and polystyrene sulfonic acid layer (~ 50 nm thick). Then, 1,3,5-tris(phenyl-2-benzimidazolyl)benzene as electron transport and hole-blocking layer (~ 40 nm thick) was vacuum-deposited on the oriented layer of β -phase PFO. Finally, 0.5-nm-thick LiF and 60-nm-thick Al as cathodes were deposited through a shadow mask. The devices were encapsulated in a nitrogen glovebox.

Figure 2 shows the polarized electroluminescence (EL) spectra of the device taken under a constant current density of 125 mA/cm². The polarized EL spectra parallel to the friction direction (EL_{\parallel}) showed strong emission having a well-resolved vibronic structure with peaks at 440 (0-0), 466 (0-1), and 496 nm (0-2). The spectral feature of EL_{\parallel} , attributed to the emission from the β -phase portion of the film, is almost the same as that of PL [see Fig. 1(b)]. On the contrary, the polarized EL spectra perpendicular to the friction direction (EL_{\perp}) showed extremely weak emission. The emission polarization ratio, $R_{EL} = EL_{\parallel}/EL_{\perp}$, were estimated to be 33 at 440 nm, 53 at 466 nm, and 36 at 496 nm. For the estimation, we measured third run of EL_{\parallel} after second run of EL_{\perp} and took average of first and third run of EL_{\parallel} . The ratio of the integrated intensity of the EL_{\parallel} to that of the EL_{\perp} (integrated R_{EL}) was estimated to be 51, which is higher than that of the oriented N-devices (45). We assume that this increased R_{EL} is attributed to the more planar and extended molecular conformation of β -phase which has larger transition dipole moment than that of N-phase.

Figure 3(a) shows the current-luminance-voltage characteristics of the polarized PLED utilizing the oriented film of β -phase PFO (hereafter described as the oriented β -device). The turn-on voltage (at 1 cd/m²) was 4.3 V, and the luminance reached approximately 8000 cd/m² at 10.5 V. At the luminance of 1000 cd/m², the voltage and current density were 7.1 V and 54 mA/cm², respectively. For comparison, the current-luminance-voltage characteristics of the polarized PLED utilizing the oriented film of N-phase PFO (hereafter described as the oriented N-device) is shown in Fig. 3(b). The voltage and current density at the luminance of 1000 cd/m² were 7.6 V and 103 mA/cm², respectively.

The corresponding efficiency-luminance characteristics of these devices are shown in Fig. 4. For the oriented β -device, the efficiency increases with increasing luminance, reaching a maximum of 2.0 cd/A at 100 cd/m², and then gradually decreased. In our results, the efficiency of the oriented β -device was approximately two times higher than that of the oriented N-device. Recently, Lu *et al.* reported that

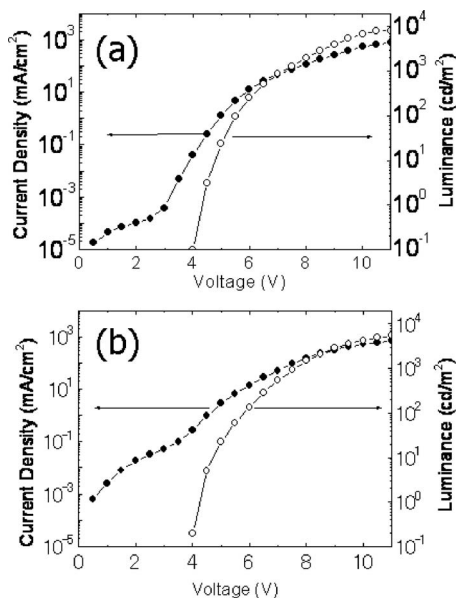


FIG. 3. Current-luminance-voltage characteristics of the polarized PLED utilizing the oriented film of β -phase (a) and N-phase (b) PFO.

PLEDs utilizing nonoriented films of β -phase PFO, prepared by dipping a spin-coated PFO film into a mixture of good and poor solvents, shows a dramatically enhanced efficiency of 3.85 cd/A, relative to that without such treatment (1.26 cd/A).¹⁷ They concluded that such a high efficiency results from the special functionalities of the β -phase: electron-trapping and promoted hole mobility. Therefore, we assume that the observed high efficiency results from more efficient charge recombination in oriented β -devices, though

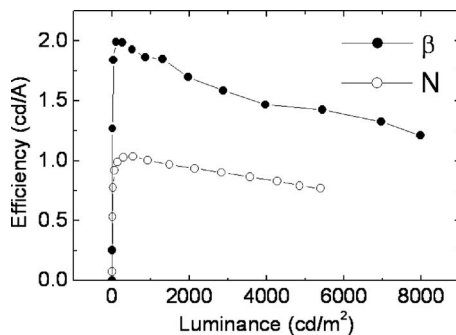


FIG. 4. Efficiency-luminance characteristics of the polarized PLED utilizing the oriented film of β -phase and N-phase PFO.

the influence of molecular orientation may also contribute the efficiency improvement. Further studies are currently under way to clear up the effects of the molecular orientation on the efficiency.

In conclusion, oriented films of β -phase PFO have been formed by the friction transfer technique followed by thermal annealing and vapor treatments. We have constructed polarized PLEDs utilizing the oriented films of β -phase PFO and showed the importance of controlling the conformation of PFO to its device performance. The performance of the oriented β -devices is the best record in polarized blue PLEDs and sufficient for the application to LCD backlights.

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