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Birefringence-dependent linearly-polarized emission in a liquid crystalline organic light emitting polymer

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Abstract: We investigated the linearly polarized emission of uniformly aligned poly(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thia-diazol-4,8-diyl) (F8BT) with a liquid crystalline phase on a rubbed alignment layer. The polarization ratio, defined by the ratio of luminous intensities polarized parallel and perpendicular to the rubbed direction, gradually decreased with increasing thickness of the F8BT film. In the photoluminescence (PL) process, the polarized light is emitted throughout the whole F8BT film, while in the electroluminescence (EL) process, the polarized light is emitted at a certain region within the F8BT film. The thickness-dependent polarization ratios in both PL and EL processes were successfully described based on a simple model wherein the mean optical birefringence was expressed as a function of the thickness of the F8BT film.

OCIS codes: (230.3670) Light-emitting diodes; (250.3680) Light-emitting polymers; (160.3710) Liquid crystals.

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1. Introduction

The control of orientational ordering in conjugated, semiconducting polymer has been of interest as a means for improving the performance of many optoelectronic applications such as photovoltaic cells, light-emitting diodes, and field effect transistor [1–3]. In addition, the anisotropic optical properties such as birefringence have been correlated to dipole orientations of electroluminescence (EL) conjugated polymers, and these properties affect the efficiency of the organic light emitting diode [4]. Surface-induced alignment techniques such as stretched alignment [5,6], rubbed alignment [7–10], Langmur-Blodgett deposition [11] and photoalignment [12] have were proposed to obtain a high anisotropy and the associated high ordering of the EL conjugated polymer. Liquid crystalline (LC) conjugated polymers have been widely used due to their self-orientational ordering, which is achieved via rubbing methods in conventional LCs. These LC conjugated polymers on a rubbed alignment layer sometimes acts as a hole injection/transport layer, and a high polarization ratio ($I_{\parallel}/I_{\perp}$) was observed [7–10]. This ratio is defined as the ratio of luminous intensities of parallel ($I_{\parallel}$) and perpendicularly ($I_{\perp}$) polarized components relative to the rubbed direction. Based on such reports, the polarization ratio was strongly governed by thermal annealing condition, the anchoring strength of the alignment layer, or the molecular weight [8–10,13]. However, such studies have just focused on the phenomenologically dipole ordering of EL conjugated polymers. The EL and PL polarization ratios associated with the order parameter of the EL conjugated polymers have not been theoretically discussed yet.

In this work, we investigated a birefringence-dependent linearly polarized emission of poly(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo [2,1,3]thia-diazol-4,8-diyl) (F8BT) with an LC phase. The optical birefringence directly corresponds to the macroscopic order parameter. To vary the birefringence of the F8BT, the thickness of the F8BT on a rubbed alignment layer was controlled by manipulating the concentration of the F8BT in a toluene solvent. We also introduced a simple model based on the mean optical birefringence of the planar wall-adjacent LC layers [14] to describe the resulting order parameter in terms of the thickness of the F8BT film. Such a model can account for the thickness-dependent polarization ratios in the photoluminescence (PL) process (emitted throughout the whole F8BT film) and the EL process (emitted at a certain region within the F8BT film). Also, the fitting values matched those of the previously reported literature.

2. Experiments

Organic light-emitting diodes (OLEDs) emitting partially linearly-polarized light were fabricated with a LC light emitting polymer and an alignment layer for the LC as shown in Fig. 1. Poly(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo [2,1,3]thia-diazol-4,8-diyl) (F8BT from American Dye Source) was used as the light emitting polymer. To promote the uniformly planar alignment of the F8BT at its LC phase, a polyimide-type (PI) alignment layer of AL22620 (from JSR) was coated on an indium-tin-oxide (ITO) substrate. The layer was rubbed with a cotton roller after imidization of the alignment layer (soft baking at 100 °C for 10 min and hard baking at 210 °C for 60 min) [10]. The thickness of the PI alignment layer was at most 20 nm, and it was kept thin to mitigate the burden of poor hole transportation. The F8BT was dissolved in toluene and was spin-coated onto the rubbed PI layer followed by thermal annealing at 270 °C for 3 min to produce a nematically ordered

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F8BT film [10,13]. The thickness of the F8BT film was varied from about 20 nm to about 400 nm for PL samples and from about 30 nm to about 270 nm for EL samples by controlling the concentration of the F8BT dissolved in toluene. The thermally annealed samples were cooled down, and Ca and Al layers (as a cathode) were sequentially deposited by thermal evaporation for EL samples, as shown in Fig. 1. The thicknesses of the Ca and Al were 20 and 70 nm, respectively. All fabrication processes were carried out in a glove box filled with nitrogen gas to mitigate the device degradation.

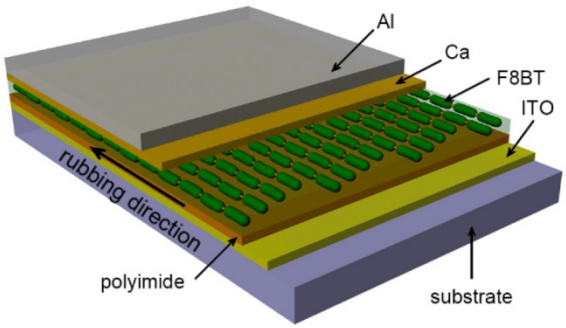

Fig. 1. Schematic diagram of the linearly polarized light emitting device proposed here.

The optical retardation of the F8BT film was measured with a He-Ne laser (632.8 nm), a photoelastic modulator (PEM90 from Hinds Instruments), and a lock-in amplifier (SR830 from Stanford Research System) [15]. A fiber optic spectrometer (USB-2000 from Ocean Optics) and a polarizing microscope (E600W POL from Nikon) with frame-grabbing system (SDC-450 from Samsung) were used for measuring the luminescence spectrum and observing the microscopic images, respectively.

3. Results and Discussion

The polarization ratio of the light emitting polymer with the LC phase can be increased via uniform alignment of the conjugated polymer. That is, higher order parameters exhibit higher polarization ratios. The orientational ordering of the LC molecules bound to solid walls (such as the alignment layer) becomes a function of distance from the solid wall to the bulk of the LC, which has been numerically evaluated by Sheng [16]. Numerical analysis based on the Landau-de Gennes theory [17] show that the order parameter in the bulk of the LC gradually decreased with increasing distance from the alignment layer [16]. Although it is difficult to measure the order parameter experimentally, the effective optical birefringence (Δn_{eff}) is directly associated with the order parameter. To describe the asymptotic relationship between the effective optical birefringence and the thickness of the LC emitting polymer film, we introduced the mean optical birefringence of the planar wall-adjacent layers to preserve the nematic ordering [14]. In this type of model, the effective optical birefringence is inversely proportional to the thickness preserving nematic ordering as follows:

$$\Delta n_{eff} = \Delta n_{\infty}\left(1+\frac{d_c}{d-d_0}\right), \tag{1}$$

where Δn_{∞} implies the optical birefringence at infinity, and d_c represents the critical thickness, which is related to the surface anchoring strength and the LC elasticity [14]. The effective optical birefringence was calculated from the retardation of the F8BT film. In Fig. 2, the experimental data of the effective optical birefringence (open circles) were fitted by Eq. (1). The fitted values of Δn_{∞}, d_c, and d_0 were evaluated to be 0.41, 22.05 nm, and −17.05 nm, respectively. Here, the measured retardation, $\Gamma = 2\pi d\Delta n_{eff}/\lambda$, (open squares) is shown in the inset. The saturated optical birefringence of a sufficiently thick F8BT film (at infinite

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thickness) was estimated to be about 0.41 at 632.8 nm [18]. It should be noted that the effective optical birefringence at the EL peak (about 540 nm) should increase due to the dispersion.

The polarization ratio ($I_{\parallel}/I_{\perp}$) (where wavelength is 540 nm) was evaluated from the two luminescence spectra of the F8BT using polarizers parallel and perpendicular to the rubbed direction, as shown in Fig. 3(a). The polarization ratio (R_p) in the conjugated polymer in terms of an order parameter S is written as $R_p = (1 + 2S)/(1–S)$ [19], and the order parameter is directly associated with the effective optical birefringence in Eq. (1). The polarized light in the PL process was emitted throughout the whole F8BT film, where the order parameter varied based on the emitting position in the F8BT film. Therefore, the order parameter contribution to the polarization ratio should be averaged through the total F8BT film. We assume that the thickness-dependent order parameter $S(d)$ was proportional to the effective optical birefringence in Eq. (1), $S(d) = a + b/(d - d_0)$, where a and b are fitting constants. The resulting order parameter (S_{PL}) contribution to the polarization ratio is given as $S_{PL} = a' + [b' \ln(d - d_0)]/d$ by integrating $S(d)$ over the thickness. Finally, the PL polarization ratio R_{PL} is expressed as

$$R_{PL} = \frac{1+2S_{PL}}{1-S_{PL}} = \frac{Ad + 2\ln(d-d_0)}{Bd - \ln(d-d_0)}. \tag{2}$$

Here, A and B are fitting constants and $d_0 = -17.05$ nm, which is determined from the fitting results in Fig. 2. In Fig. 3(b), the experimental data of the PL polarization ratio (open circles) were fitted using Eq. (2), and the fitted values of A and B were determined to be 2.54 and 0.20, respectively. It should be noted that the proportionality between the order parameter and the optical birefringence is not guaranteed to be in an extremely ordered region, i.e., in the region with a negative denominator in Eq. (2). The corresponding lower limit thickness was estimated to be about 17 nm. The saturated R_{PL} of a sufficiently thick F8BT film (at infinite thickness) was estimated to be about $A/B = 12.7$.

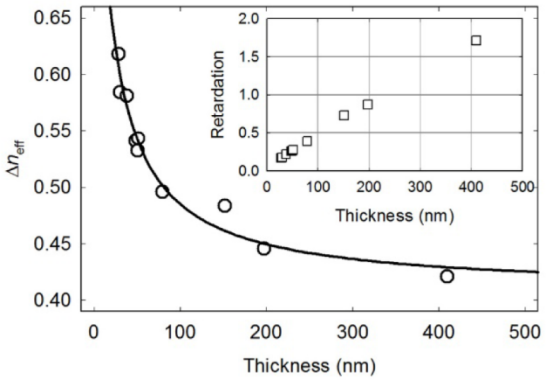

Fig. 2. The effective optical birefringence (Δn_{eff}) and measured optical retardation (inset) of the F8BT film as a function of thickness. The solid curve depicts the least square fit to Eq. (1).

Combining two results in Figs. 2 and 3, we investigated the relationship between the PL polarization ratio and the optical birefringence, i.e., the order parameter. As mentioned above, since the order parameter is proportional to the optical birefringence in a certain region, Eq. (2) was simply modified in terms of the optical birefringence Δn_{eff} as

$$R_{PL} = \frac{C + 2\Delta n_{eff}}{D - \Delta n_{eff}}, \tag{3}$$

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where C and D are fitting constants. The inset in Fig. 3(b) shows the PL polarization ratio as a function of the optical birefringence. The experimental data of the polarization ratio (open squares) were fitted using Eq. (3), and the fitted values of C and D were determined to be 2.75 and 0.71, respectively. It should be note that our assumption about the proportionality between the order parameter and the birefringence is valid where $\Delta n_{eff} < 0.71$, which corresponds to thicknesses larger than about 15 nm from Eq. (1). In addition, the lower limit thickness assumption must be met to ensure the validity of Eq. (2).

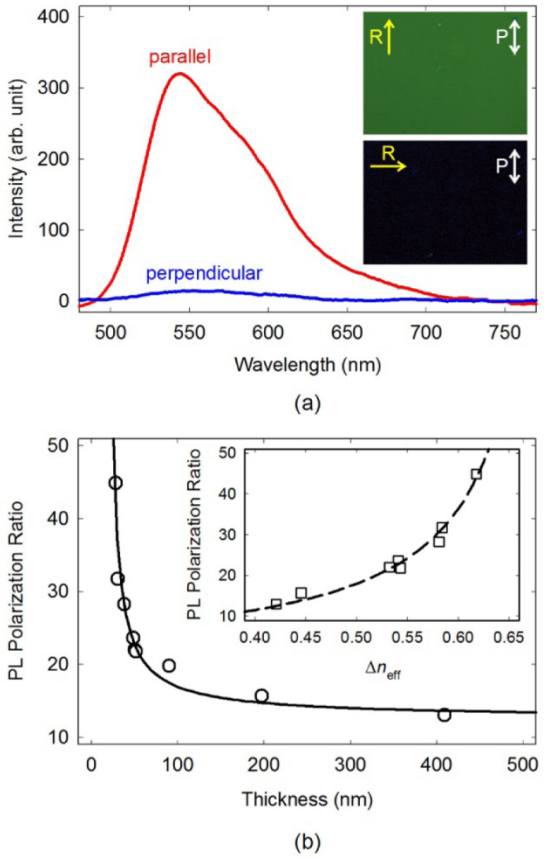

Fig. 3. (a) The PL spectra and the corresponding images (inset images) of the 60 nm thick F8BT film on a rubbed alignment layer under polarizers that are parallel (red solid curve) and perpendicular (blue solid curve) to the rubbing direction. The arrows "R" and "P" represent the rubbing direction of the alignment layer and the direction of the polarizer, respectively. (b) The PL polarization ratios of the F8BT film as a function of thickness and effective optical birefringence (inset). The solid curve and the dashed curve depict the least square fits to Eqs. (2) and (3), respectively.

The EL intensity and the EL polarization ratio R_{EL} were investigated in the polarized EL process. Unlike the PL process, the polarized light in the EL process is emitted at a certain region within the F8BT film, and thus we did not need to integrate the order parameter over the whole F8BT film in Eq. (2). Using Eq. (1), the EL polarization ratio R_{EL} is expressed as,

$$R_{EL} = \frac{A'd + 2\alpha}{B'd - \alpha}, \tag{4}$$

where A', B', and are α fitting constants. In Fig. 4, the experimental data of the EL polarization ratio (open circles) were fitted using Eq. (4), and the fitted values of A', B', and

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are α were determined to be 15.42, 0.60, and 7.62, respectively. The saturated R_{EL} of a sufficiently thick F8BT film (at infinite thickness) was estimated to be about $A'/B' = 25.7$, which is greater than the saturated R_{PL} since the polarized light in the PL process is integrated over the whole F8BT film, which gradually reduced the order parameter. Like the PL polarization ratio, our assumption about the proportionality between the order parameter and the birefringence was valid where $d > \alpha/B' \approx 12.7$ nm, which is slightly smaller than that in the PL process. This was attributed to the fact that the light emitting position in the EL process was in the inner layer of the F8BT film.

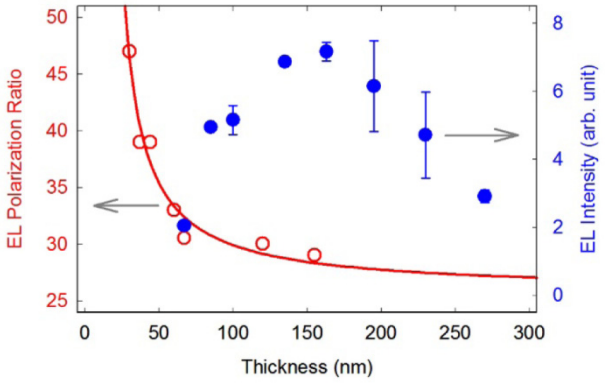

Fig. 4. The EL polarization ratio and the EL intensity of the F8BT-based OLEDs as a function of thickness. The solid curve depicts the least square fits to Eq. (4).

In the conventional OLED, a metal cathode acts as a reflector, and thus the EL intensity varies with the thickness of the emitting layer due to interference from the half-cavity effect. When the effective optical length matched to the half wavelength (resonance condition), the EL intensity was maximized [4,20]. The ordinary (n_o) and extraordinary (n_e) refractive indices of the F8BT were measured to be 1.59 and 2.26 at 540 nm [18]. The average refractive index is estimated to be $(n_e + 2\ n_o)/3$ regardless of degree of its anisotropy. The resulting average refractive index and the resonance thickness at 540 nm were estimated to be 1.81 and 149 nm, respectively. As shown in Fig. 4, the EL intensity (solid circles) exhibited maximum value at a thickness of around 150 nm.

4. Conclusion

We analyzed the thickness-dependent PL and EL polarization ratios of F8BT having a LC phase on the rubbed alignment layer. The order parameter was described in terms of the thickness of the F8BT film based on the mean optical birefringence of the planar wall-adjacent layers, which preserved nematic ordering. In the PL process, the order parameter was modified by integrating over the thickness to reflect the averaged emission since the polarized light was emitted through the whole F8BT film. The PL polarization ratio was determined using the modified order parameter. In the EL process, the EL polarization ratio was directly evaluated with the order parameter since the polarized light was emitted at a certain region within the F8BT film. All theoretical simulations of the effective birefringence and the PL and EL polarization ratios coincided with our experimental results, and the fitting values matched previously reported literatures. From our results, the governing mechanism of the PL and EL polarization ratio is theoretically investigated based on the nematic ordering.

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