



The Orientation and Photophysical Properties of Polyfluorene-based Conjugated Polymers in Ultrahigh Molecular Weight Polyethylene Films

Ben Qiao He

Tianjin Key Laboratory of Fiber Modification and Functional Fiber
School of Materials and Chemical Engineering, Tianjin Polytechnic University
Tianjin-300160, China

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ABSTRACT

The highly oriented light-emitting films of polyfluorene-based conjugated polymers blended with ultrahigh molecular weight polyethylene (U-PE) are prepared by using a tensile deformation technique. The high dichroic ratios of blue light (58 in photoluminescence (PL)) from the poly(9,9-dioctylfluorene) (PFO)/U-PE blending film and of green light (36 in PL) from the poly(9,9-dioctylfluorene) containing one fluorenone unit (PFF)/PFO/U-PE blending film are obtained. In the PFO/U-PE blending film, the variation of the photophysical properties of the blending films with the drawing ratio is discussed in detail which suggests that the conjugated polymer chains are forced to a highly dispersed and oriented condition in the oriented PE matrix. The green band (g-band) of the blending film containing PFF is also studied and found in such a highly oriented condition, and a set of new evidence was obtained demonstrating the keto-defect origin of g-band.

Key Words:

conjugation;
polarization;
orientation;
blending;
photoluminescence.

INTRODUCTION

There is an increasing interest in rod-like conjugated polymers because of their utility in light-emitting devices, lasers, thin film transistors, and polarizers. Due to the need of thinner and flexible liquid crystal displays (LCDs) many research works have been focused on the electroluminescence (EL)

properties of conjugated polymers [1,2] because of their potential applications as the backlight for LCDs. Recently, the polarized photoluminescence (PL) properties of the oriented conjugated polymers have also received considerable attention. It has been found that an anisotropic luminescent film can

(*) To whom correspondence to be addressed.
E-mail: he bq2008@gmail.com

combine polarization of light with bright colour emission and thus, replace both the polarizer (analyzer) and the colour filter used in current LCDs [3].

The tensile deformation of host-guest systems is a very useful technique to prepare high performance PL polarizer. Hagler et al. have adopted this method to align (poly (2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene-vinylene)) (MEH-PPV) in polyethylene (PE) film and obtained green PL polarizer with a PL dichroic ratio in excess of 60 [4,5]. Weder et al. have used a similar technique to orient poly (*p*-phenylene-ethynylene) (PPE) and found a PL dichroic ratio of 72 [6]. Miller et al. have studied the orientation of poly(9,9-dioctylfluorene)(PFO) using this technique and a dichroism of 7:1 in PL and absorbance were obtained at a high drawing ratio of 50 [7]. The cause of low dichroism obtained may be due to a very high concentration of PFO (15 wt%) in PE. Then, the higher dichroic ratio of PFO was obtained at a lower concentration of PFO [8]. During the drawing, the conjugated polymer chains are forced to disperse and orient in host polymer [9] which results in the variations of both the interaction of the conjugated polymer chains and photophysical behaviour. Therefore, the tensile deformation technique is not only a good means of orienting conjugated polymers, but also a wise choice of studying the photophysical behaviours of conjugated polymers in different aggregated states.

PFO has emerged as an attractive blue-light emitting material for light emitting diodes owing to its pure blue emission, efficient electroluminescence coupled with a high charge-carrier mobility, and good processability. It is also a good candidate to prepare blue PL polarizer due to its rod-like shape polymer. However, an undesired long wavelength emission in the region of 490-550 nm [10-13] i.e., green emission (g-band) is observed in the PFO spectra after ultraviolet light exposure, heating in air, or passage of current. It has been believed that the g-band is related to the production of fluorenone in polyfluorene chains and mainly ascribed to fluorenone defect [14-17] or fluorenone-based excimer [18] which is truly an ongoing debating topic [19]. Therefore, many methods including model polymers [20-22] i.e., copolymers of fluorenone and fluorene mainly in solution have been used to clarify the initial origin of the g-band. Due to the advantages of tensile deformation

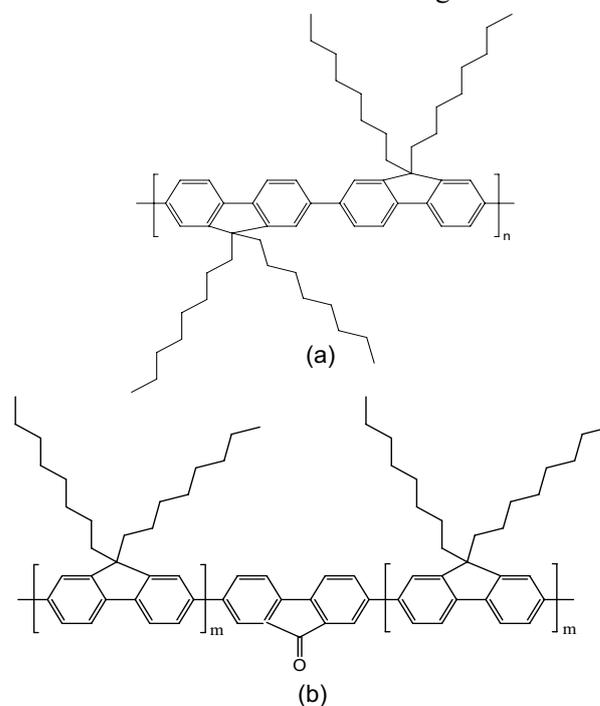
mentioned above, it will be a novel method to study the origin of g-band from treated PFO using a model polymer.

In this work, the tensile deformation technique was used to prepare the oriented blending films: PFO/ultrahigh molecular weight polyethylene (U-PE), poly (9,9-dioctylfluorene) containing one fluorenone unit (PFF)/U-PE, and PFF/PFO/U-PE. The photophysical properties of PFO and PFF in the oriented films were discussed. Especially, the origin of g-band in such highly oriented samples was investigated by using the model polymer PFF.

EXPERIMENTAL

Materials and Method

PFO and PFF were synthesized by using Suzuki polycondensation [23,24]. Their structures are shown in Scheme I. The number-average molecular weight (M_n) of the conjugated polymers was determined by gel permeation chromatography (GPC) calibrated with polystyrene standard. The (M_n)s of PFO and PFF are 9000 and 8000, respectively. There is only one fluorenone unit in a PFF chain according to the synthetic route [24]. The ratio of fluorenone unit to fluorene unit in PFF is around 1:20 according to the feeding



Scheme I. The chemical structures of: (a) PFO and (b) PFF.

ratio. U-PE was purchased from Beijing Chemical Co., China (M-II, the viscosity-average molecular weight (M_{η}) of 2,000,000-3,000,000) which is used due to its high percentage elongation.

A desired amount of PFO/xylene solution was added into a boiling solution of 1 wt% U-PE/xylene. The PFO/U-PE/xylene solution was refluxed for 10 min to dissolve completely. The boiling solution was then poured into a Petri dish with a diameter of 9 cm where it formed a gel upon cooling and was dried under ambient conditions for more than two days.

All the blending films obtained had a homogeneous thickness of about 60 μm . To fabricate the oriented films, the resulting PFO/U-PE films were mounted on a lab-made clamp and heated in a vacuum stove at the temperature below the melting point of U-PE and above the T_g of PFO at the range of 90-100°C for 15 min and then were drawn at this temperature.

The same processing and drawing methods were used to prepare the PFF/PFO/U-PE and the PFF/U-PE films. Drawing ratio (D_R) was calculated from the displacement of distance marks printed on the film prior to drawing. The anisotropic photophysical properties of the oriented films were studied by UV-vis absorption and steady state PL spectroscopy methods at room temperature. The polarized absorption spectra were recorded with a UV-vis spectrophotometer (Shimadzu, UV-1601PC) fitted with a Glan-Thomson polarizer on a rotational stage just before the sample. All absorption spectra were corrected with pure U-PE films of the comparable drawing ratio and thickness as the background.

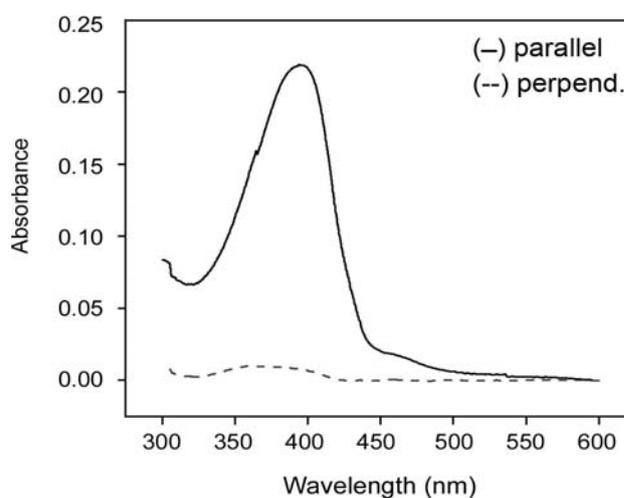
The polarized PL spectra were recorded with a fluorescence photometer (Varian, Cary Eclipse, FLR025) using a Glan-Thomson polarizer on the detector side. For the photophysical experiments, the blending films were sandwiched between two quartz slides which prior to that had been coated with silicon oil on the sides contacting with the blending film in order to minimize light scattering at the film surfaces. In order to quantify the anisotropic optical characteristics of the oriented films, the dichroic ratios were defined and determined for emission (DR_E) and absorption (DR_A) as the ratios between the related spectra measured with the polarizations parallel and perpendicular to the drawing direction, respectively.

The dichroic ratio was calculated from maximum spectral intensity.

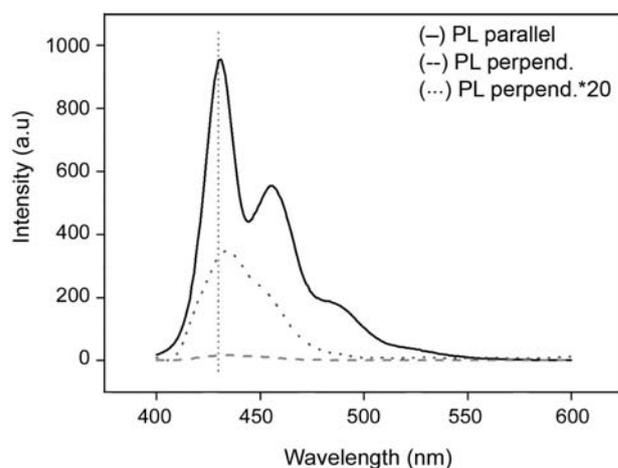
RESULTS AND DISCUSSION

Orientation of the PFO/U-PE Blending Films

The absorption spectra for an oriented (drawing ratio 70) 1 wt% PFO/U-PE film are shown in Figure 1a for polarizations both parallel and perpendicular to the drawing axis. In the parallel polarization, a major absorption maximum is observed at 396 nm which is assigned to the delocalized π - π^* transition of polyflu-



(a)



(b)

Figure 1. The spectra of: (a) polarized absorption and (b) polarized PL for 1 wt% PFO/U-PE film at drawing ratio =70 (the dot line shows the spectrum at a magnification of 20 recorded perpendicular to the drawing direction).

orene backbone. In the perpendicular polarization, however, this peak is nearly suppressed. Thus, the film shows very strong dichroism ($DR_A=24$) which is in excess to the results reported on oriented PFO indicating that polymer backbones in the film are highly aligned parallel to the drawing direction. The macroscopic order parameter (S) is calculated from the absorption spectra using eqn (1) [25] and it turns out to be $S=0.92$ which indicates a very high degree of orientation.

$$S = (DR_A - 1) / (DR_A + 1) \quad (1)$$

Figure 1b shows the polarized PL spectra of the same PFO/U-PE sample. The PL spectrum of the parallel polarization shows a well-resolved vibronic structure with peaks at 430, 455, and 488 nm assigned to the 0-0, 0-1, and 0-2 transitions, respectively and the 0-0 transition being the most intense one. On the other hand, in the spectrum of the perpendicular polarization these peaks are nearly suppressed. The peaks in the perpendicular spectrum have lost the well-resolved features and are slightly red-shifted with respect to those of the parallel spectrum. These findings are consistent with the results reported by Hagler et al. [5] and imputed to the residuals of non-oriented materials in the film. The film shows a very high dichroic ratio of 58 which is the highest for PFOs up to now.

Photophysical Properties of the PFO/U-PE Blending Film

The influence of the drawing ratios on the PL spectra of the PFO/U-PE films is presented in Figure 2. By comparing the emission spectra of PFO in the unoriented and oriented films, one can find that the shapes and locations of the peaks are different from each other. In the case of unoriented PFO/U-PE film, a spectrum with three well-resolved peaks at 442, 465, and 496 nm is observed with the strongest peak locating at 465 nm. The location of the peaks is similar to those of pure PFO film by drop casting [26] which implies that the PFO molecules in the blending film evidently aggregate due to the phase separation between U-PE and PFO.

After drawing, the emission spectra were changed and all peaks were blue-shifted by increasing the

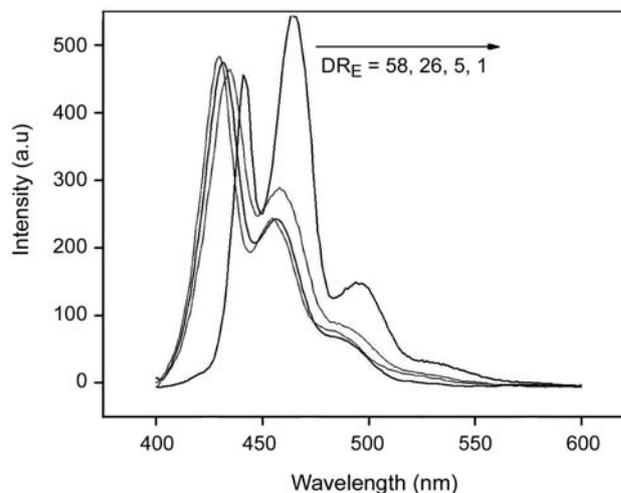


Figure 2. The PL spectra of 1 wt% PFO/U-PE film with different dichroic ratios.

drawing ratio. The peak shifts from 442 to 430 nm for 0-0 transition and from 465 to 456 nm for 0-1 transition when the drawing ratio is increased from 1 to 70, respectively. This suggests that the PFO chains are forced to be more dispersed in the U-PE matrix and the interactions between conjugated polymer chains become weaker.

The absorption spectra of the PFO/U-PE films also vary with the drawing ratio as shown in Figure 3. For the blending films, the maximal absorption peaks are all at 396 nm. In the unoriented blending films, a well-resolved additional peak at 432 nm was observed. By increases in the drawing ratio, the additional peak

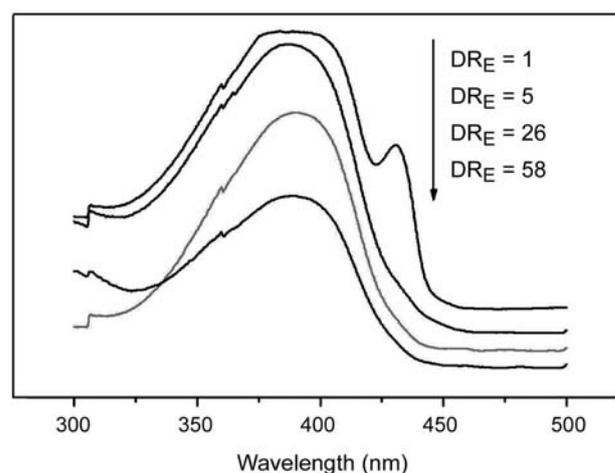


Figure 3. Absorption spectra of 1 wt% PFO/U-PE film with different dichroic ratios.

turned to a shoulder and finally disappeared when the dichroic ratio was beyond 26. This additional peak (or shoulder) in the absorption spectra was always observed in the crystalline samples of PFO, and the shoulder was regarded as a precursor of the fully developed peak [26-29]. Therefore, the variation of absorbance also reflects the physical states of PFO chains in the U-PE matrix.

Combining the variations of the emission and absorption spectra, the dispersion process of PFO in the U-PE matrix can be assumed as follows:

Primarily, the PFO chains easily aggregate to form crystals during the gelation of the PFO/U-PE/xylene solution due to no thermodynamic compatibility of PFO with U-PE.

Secondly, since the crystals of PFO are fragmented during drawing these fragments of the crystals orient along the drawing direction under the drawing stress.

Finally, the PFO chains in the fragments are gradually detached and dispersed in U-PE matrix in molecular level with a macroscopic orientation along the drawing direction, resulting in the remarked blueshift of the emission spectra and a very high dichroic ratio.

Orientation and Photophysical Properties of PFF in U-PE Films

Figure 4 shows the polarized PL spectra of oriented PFF/PFO/U-PE film excited at 380 nm. The spectra of the blending film comprise both blue band and strong green band. The blue band identical to that of the PFO comes from the PFO component. The strong green band is evidently related to the PFF because no green band is observed in PFO/U-PE films. It is found that the dichroic ratio of blue band is 27 at the drawing ratio of 70. The dichroic ratio is much smaller than that of PFO/U-PE film at the same drawing ratio. The depolarization of blue band from the oriented PFF/PFO/U-PE film (with respect to that from the oriented PFO/U-PE film) is possibly due to the energy transfer from the excited fluorene segments to the fluorenone moieties [14,18,30]. The dichroic ratio of green band is 36, which is higher than that of the blue band. But it is also smaller than that of blue band from the PFO/U-PE film at the same drawing ratio. This may be due to the fact that dipoles of fluorenone

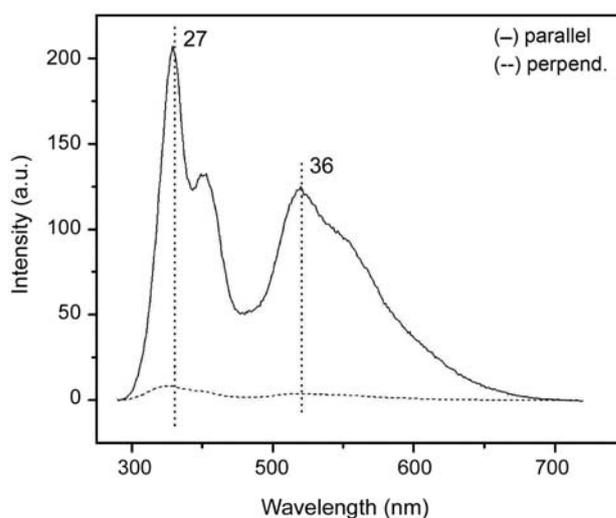


Figure 4. The polarized PL spectra of the blending films excited at 380 nm with the drawing ratio of 70. The composition of the blending film is 2.5 mg PFO, 0.5 mg PFF and 0.5 g U-PE.

moieties are not fully oriented along those of the polymer main chains [14,18]. The same results are also observed in PFF/U-PE film (not shown here).

The PL spectra of the PFF/PFO/U-PE and PFF/U-PE films with different drawing ratios are shown in Figure 5. The PL spectra of the PFF/PFO/U-PE film are shown in Figure 5a. The blending film is composed of 2.5 mg PFO, 0.5 mg PFF, and 0.5 g U-PE. The spectra comprise a blue band and a strong green band. The blue band is well-marked and blue shifted by the increase of the drawing ratio which is the same as that of PFO/U-PE films (mentioned above). This suggests that the conjugated polymer in ternary blending film is also dispersed after drawing. The relative intensity of g-band in the whole spectrum decreases with the increase of the drawing ratio as shown in Figure 5c. The decrease in relative intensity of the g-band can be mainly due to the increase of the luminescent efficiency of PFO resulting from the increase of the drawing ratio. It is demonstrated by evidence that the blue band is blue-shifted and the intensity has increased when the drawing ratios have changed as shown in Figure 5a.

The PFF/U-PE film is only composed of 0.5 mg PFF and 0.5 g U-PE. The spectra also comprise blue band and strong green band in Figure 5b. But the blue peak is very weak and structure-less. It is suggested

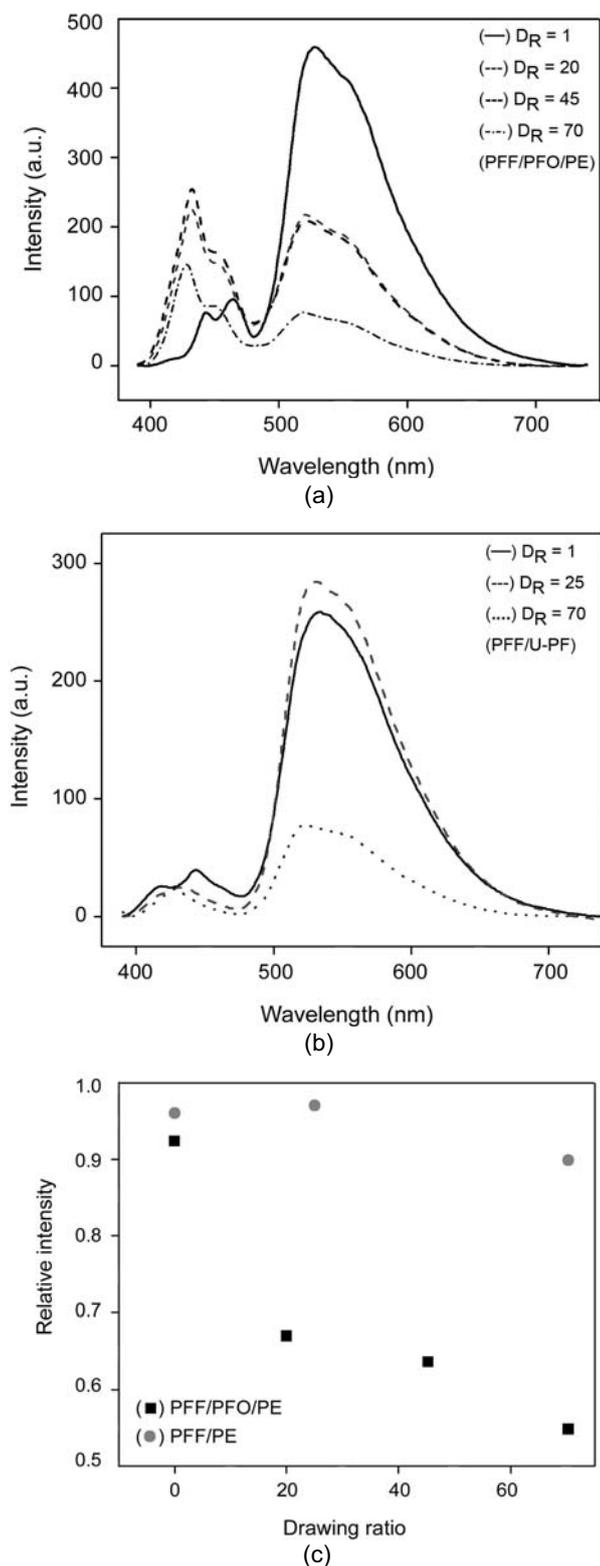


Figure 5. Changes of the g-band intensity in the films of: (a) PFF/PFO/U-PE, (b) PFF/U-PE at different drawing ratios (D_R), and (c) relative integral intensity of g-band in the whole spectra of the blending films vs. drawing ratio.

that the blue band is suppressed which is possibly due to more effective through-bond energy transfer from the excited polyfluorene chains to the fluorenone moieties. However, the relative intensity of the green peak in the whole spectrum is almost unchanged at different drawing ratios as shown in Figure 6c, which is consistent with the invariance of the fluorenone content in the blending films.

From the above results, it is believed that the g-band does not originate from the fluorenone-based excimer but from the fluorenone defect. To create an excimer, an electrically excited unit must react with another one in its ground state within sufficient proximity (about 0.3 nm [31,32]). If the g-band really originated from the fluorenone-based excimers (that should be the main static excimers [32]) the emission of g-band would be suppressed and even disappeared with the increasing of the drawing ratio because the fluorenone-based excimer can be damaged after drawing due to the increase of the distance between two fluorenone units beyond the mentioned distance of an excimer. The relative intensity of g-band is not kept constant, but remarkably decreases even in oriented PFF/U-PE film. Evidently, the experiment results obtained are against the formation of the fluorenone-based excimer and support the keto-defect origin of the g-band.

CONCLUSION

Highly oriented light-emitting blending films of PFO and/or PFF with U-PE are prepared by tensile deformation. The high dichroic ratios of blue band (58 in PL) from the PFO/U-PE film and of green-band (36 in PL) from the PFF/PFO/U-PE film are obtained. The PL spectra are blue shifted and the additional peak at 432 nm in absorption spectra gradually disappears with increasing the drawing ratio of the PFO/U-PE film. It is suggested that the PFO chains in the film change from the initial aggregates to where finally the molecular level disperses in the U-PE matrix with increases in the drawing ratio. In the oriented PFF/PFO/U-PE film, the dichroic ratio of blue band is smaller than that of green one and both are smaller than that of PFO/U-PE film at the same drawing ratio. It is also found that the relative intensity of g-band is

almost unchanged in the PFF/U-PE films and decreases in the PFF/PFO/U-PE film with increasing the drawing ratio which powerfully demonstrates that the g-band originates from fluorenone moieties instead of fluorenone-based excimer.

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SYMBOLS AND ABBREVIATIONS

PL	Photoluminescence
U-PE	Ultrahigh molecular weight polyethylene
PFO	Poly(9,9-dioctylfluorene)
PFF	Poly(9,9-dioctylfluorene) containing one fluorenone unit
g-band	Green band
LCD	Liquid crystal display
EL	Electroluminescence
MEH-PPV	Poly(2-methoxy-5-(2-ethylhexyloxy)- <i>p</i> -phenylenevinylene)
PPE	Poly(<i>p</i> -phenylene-ethynylene)
GPC	Gel permeation chromatography
M_n	Number-average molecular weight
M_h	Viscosity-average viscosity
DR_E	Dichroic ratio for emission
DR_A	Dichroic ratio for absorption
D_R	Drawing ratio

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