Fabrication of Oriented Thin Films Composed of Polyfluorene and Oligothiophene, and Application for Polarized White Light Emitting Devices

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Abstract. We have been studying the production of oriented films of various conjugated polymers by means of the friction transfer technique. The method has been applied to produce oriented poly(9,9-dioctylfluorene) (PFO) films which were then used to produce devices that emit polarized blue light. We fabricate oriented films composed of PFO and sexithiophene (6T), which is an orange emitting dye, for production of white polarized light emitting devices. We make a comparative study of the characteristics of devices produced with different doping techniques and discuss the advantages of each method.

1. Introduction
Light emitting organic materials based on oriented layered structures have been studied for their applications in electroluminescent devices that emit polarized light. There are various possible applications of these polarized light emitting devices in the field of optoelectronics like, for example, as a backlight source of liquid crystal displays or as flat-area light sources that can be produced with low cost. Various techniques, such as blending of polymers of copolymerization[1-3], have been employed for the whitening of the emission of devices based on oriented polymeric layers but most of the successful techniques employ rather complex compounds.

We have been producing oriented polymer films [4,5], by means of the friction transfer technique [6], for the fabrication of polarized electroluminescence (EL) devices. Oriented poly(9,9-dioctylfluorene) (PFO) films were produced with this technique to fabricate polarized blue light emitting EL devices. PFO is a simple structured conjugated polymer that, besides showing efficient blue electroluminescence [4, 5, and 7] and good charge transport, is also a material with easy processability. We have been studying the application of these oriented PFO films combined with some processes that allow the change of the colour of the device in a controlled manner, with the ultimate purpose of producing devices that emit white light [8, 9].

One of the techniques for the whitening of the emitted light is doping α-sexithiophene (6T) molecules into the oriented PFO layers by means of the vapour transportation method [9, 10]. This method is suitable for oriented layers because it allows doping after film production without loss of molecular orientation. With this method the whitening of the emission of a device based on 6T-doped oriented PFO films [9] was possible, but intrinsically it does not allow a good control of the amount of dye doped into the matrix film.
Another method employed to produce white emitting devices is the deposition of 6T molecules, directly on top of the oriented PFO films, before device production. With this method we tried to better understand the light emission mechanisms of the devices by analysing the effect of the amount and morphology of the dye at the interface region. Devices’ colour change and light polarization were analyzed and related to 6T film thickness and morphology.

The photoelectrical characteristics of devices produced with each doping method, i.e., vapour transportation and vacuum deposition, are also analyzed and discussed.

2. Experimental

Oriented PFO films were produced on clean substrates by means of the friction transfer method. This method consists of sliding the PFO polymer block directly onto the substrate by controlling the temperature (95°C) of the substrate, and the sliding speed (0.5 m/min) and the load (2.45 MPa) of the block onto the substrate. With this process the PFO molecules naturally orient themselves in the direction of the sliding movement, but further thermal treatment is performed (at 180°C, in vacuum, during 1 h) to perfect orientation and surface smoothness [6]. The resulting PFO film is about 50 nm thick.

To change the colour of the blue emitting PFO, two methods were employed for comparison. With one method 6T was doped into the oriented PFO films and with the other one 6T was deposited onto the oriented PFO films, as described in the following. For doping 6T into the PFO film the vapour transportation method was employed. With this method the dye and the oriented PFO film are loaded together, without contact, into a glass tube. The whole system is evacuated and then the glass tube is closed/sealed forming an ampoule. Finally this sealed system is heated in an oven at 180°C for about 13 hours, causing the 6T dye to sublimed and diffuse into the PFO film. The other method, for deposition of 6T onto the PFO films, is the conventional vacuum deposition technique, where deposition is performed at room temperature in a vacuum better than 2x10⁻⁴ Pa and 6T deposition rate is about 0.02 nm/s. Films of 6T with various thicknesses, between 0.5 and 5.0 nm, were prepared. For morphological comparison, 6T was also deposited on silicon substrates, which native oxide layer is left on top, degreased with acetone prior to deposition.

EL devices were produced in the following way. Indium thin oxide (ITO) coated glasses were used as substrates, which were initially cleaned in ultrasonic baths of ethanol and acetone, prior to a 30 minutes oxygen plasma treatment. To improve the efficiency of the device a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) hole injection layer was spin coated on top of the clean ITO substrate. The PFO layer was then produced, by the friction transfer method, directly on this PEDOT:PSS/ITO substrate. For the case of 6T doped PFO layers, they were inserted into a vacuum chamber and a 50-nm-thick 2,2',2''-(1,3,5-benzinetryl)-tris(1-phenyl-1H-benzimidazole) (TPBi), which is an electron transport and hole-blocking layer, was evaporated on top at a vacuum better than 2x10⁻⁴ Pa. Finally, a 90-nm-thick magnesium-silver (Mg:Ag, 10:1) cathode was deposited. For the oriented PFO layers were 6T was to be deposited, the PFO layers were inserted into the chamber and 6T deposition was performed prior to the deposition, but without removing from the chamber, of TPBi and the Mg:Ag layers. The active area of the devices was 4 mm².

The PFO used in this work had molecular weight ranging from 20000 to 120000 and was purchased from American Dye Source, catalogue number ADS 129BE. A sublimated grade of 6T was purchased from Tokyo Chemical Industry, and used without further purification. The PEDOT:PSS (CLEVIOS P VP.AI4083) was purchased from H. C. Starck and TPBi from Luminescence Technology.

For the polarized electroluminescence (EL) measurements the light is collected with a glass fiber, dispersed in a spectrograph and detected with a charge coupled device camera (BWTEK BTC112). The Commission Internationale d’Éclairage (CIE) chromaticity coordinates and the luminance are measured by a luminance-colorimeter (Konica-Minolta CS-100A). Atomic Force Microscopy (AFM) measurements are performed by means of a commercial Seiko Instrument SPI-3700. All measurements were performed at room temperature, without sample encapsulation.
3. Doping of 6T into PFO by vapour transportation

The vapour transportation method was employed to dope 6T into oriented PFO films. These oriented PFO/6T doped films were then used for the production of EL devices. Figure 1 (a) shows the polarized EL spectra of the devices where it can be seen that, for both PFO (peaks around 430 and 450 nm) and 6T (broad peak between 510 and 550 nm), the electroluminescence with parallel polarization to the friction direction is much stronger than that with orthogonal polarization. The polarization of PFO originates from the uniaxially oriented PFO main chain along the friction direction. Considering that the peak from 6T also exhibits high polarization we suggest that the 6T molecules are also aligned along the polymer chain direction in the oriented film.

![Figure 1.](image)

**Figure 1.** (a) Polarized EL spectra of the 6T-doped PFO oriented film. The EL device was based on PFO film deposited directly on ITO substrates, without the intermediate PEDOT:PSS film. (b) CIE chromaticity diagram of EL devices based on PFO films with and without 6T-doping.

The degree of orientation was evaluated semi quantitatively using the polarized EL spectra. The orientation of the entire PFO plus 6T structure was evaluated by calculating the dichroic ratio, i.e., the parallel component to the orthogonal component (EL/EL), of the integrated intensities for polarized EL spectra. The average dichroic ratio results were about 25 for both doped and non doped samples. The EL results for non doped samples show that there is a large dichroism due to an excellent uniaxial alignment of the polymer backbone. On the other hand, the results for doped samples show the same or better dichroism, compared to the non doped samples, which indicates that there is also an excellent alignment of the dye molecules parallel to the polymer orientation direction. CIE chromaticity diagram coordinates show the whitening of the device, as can be seen in figure 1 (b), where the blue PFO (0.19, 0.19) coordinates at 11 V bias voltage changed to (0.23, 0.31) for bias voltage 11 V after doping with 6T. These CIE coordinates are very stable with applied voltage up to the break down voltage. These results indicate that by doping the 6T (orange emitting material) into PFO (blue emitting material) the whitening of the EL device is possible with excellent polarization of the emitted light.

To improve the efficiency of the device a PEDOT:PSS layer is inserted between the ITO substrate and the PFO film. The properties of the EL device were then analyzed. For the 6T doped device luminance reached 3800 cd/m² at 10 V and the device without 6T doping reached ~2900 cd/m² at 9 V. Turn on voltage (the bias required to give a luminance of 1 cd/m²) of the device is about 4 V for both doped and non doped devices. Efficiency results show that the doping of 6T leads to about 65% increase in efficiency of the device (from 1.48 to 2.28 cd/A). CIE chromaticity diagram coordinates are (0.19, 0.18) for PFO at 11 V bias voltage and change to (0.22, 0.24) for bias voltage 11 V after doping with 6T. These CIE coordinates are very stable with applied voltage up to the break down voltage.
down voltage. Dichroic ratio was about 16 and 13 for non-doped and doped EL devices, respectively. We observe the reduction of dichroic ratio and of the whitening, probably due to the difference in film thickness when PEDOT:PSS is included, but considering that there is a good improvement of efficiency and luminance, we are continuing the research for optimization of these of PEDOT:PSS based devices.

4. Deposition of 6T on PFO

For a better understanding of the light emission mechanisms of the 6T-oriented PFO based devices, we analyze the influence of the amount of 6T at the interface region, by producing vacuum deposited 6T layers on top of oriented PFO films before device production. Figure 2 (a) shows the normalized EL spectra of these devices with 6T thickness being varied from 2.0 to 4.0 nm (for 5.0 nm see the inset of figure 2(a)). The peaks derived from PFO can be seen at 430 and 450 nm while the broad region seen between 500 and 650 nm derives from 6T. The relative intensity of this region derived from 6T is seen to increases with 6T film thickness. CIE chromaticity diagram coordinates from these devices with 6T thickness between 0.5 and 5.0 nm plus the one for the device without 6T are shown in figure 2(b). A linear variation of the devices’ coordinates with the thickness of the deposited 6T film can be seen. Emitted colour changes from blue for the device without 6T, (0.19, 0.19) coordinates at 11 V bias voltage, to white for the device with 6T around 4.0 nm thick, (0.30, 0.32) coordinates at 10 V bias voltage. These coordinates are stable around the maximum luminance voltage.

These results show that, by varying the thickness of deposited 6T film onto a PFO layer, an excellent control of the emitted colour is possible. A white emitting device can be produced by depositing about 4.0 nm thick 6T (orange emitting) onto the oriented PFO (blue emitting) layer.

The EL spectra, with polarization parallel and orthogonal to the friction direction, of the device produced with 4.0 nm thick 6T on the oriented PFO layer are shown, as a typical example, in figure 3 (a). One can see that the emission from PFO, at 430 and 450 nm, with parallel polarization to the friction direction is much stronger than that with orthogonal polarization. This polarization originates from the uniaxially oriented PFO main chain along the friction direction. In a similar way, the emission region derived from 6T (between 500 and 650 nm) also exhibits high polarization, indicating that the 6T molecules might be aligned along the polymer chain direction in the oriented film. The degree of this orientation was evaluated by calculating the dichroic ratio (EL||/EL⊥), in the same way as described in the previous section. Average dichroic ratio results were around 25 for pure PFO samples (without 6T deposition), and varied from about 8 to 12 (see figure 3(b)) for 6T deposited
samples. These results are interpreted as follows. For devices based on oriented pure PFO layers (without 6T), there is a large dichroism due to an excellent uniaxial alignment of the PFO polymer backbones. On the other hand, 6T deposited samples show a comparatively smaller but still large dichroism, which suggests some level of alignment of the dye molecules parallel to the polymer orientation direction. Furthermore, despite the fact that the emitted colour changes with 6T thickness, the dichroic ratio does not change significantly, which indicates that the orientation of 6T is not significantly affected by film growth, for the analyzed thickness range of this study.

![Figure 3](image-url)  

**Figure 3.** (a) Polarized spectra of a white EL device based on a 4.0 nm thick 6T layer deposited on top of and oriented PFO film. (b) Dichroic ratio determined from the polarized EL spectra of PFO and 6T deposited /oriented PFO based devices.

5. **Morphology studies**

Morphology studies of 6T/PFO films prepared with both vapour transportation and vacuum deposition methods were performed with AFM.

For PFO films doped with 6T by vapour transportation, no significant surface structure could be observed, and morphology was very similar to the oriented PFO film without 6T (data not shown). This is probably due to the fact that 6T molecules are evenly distributed inside the film and that the molecules that rest on the surface do not form aggregates large enough to be clearly observed.

For the case of vacuum deposition a comparative analysis has been performed by depositing 6T films on the oriented PFO and on a Si substrate, whose native oxide layer was kept on top. Figure 4 shows that 30 nm thick 6T films deposited on these substrates form very different structures, namely, drop-like islands are formed on oriented PFO layers while flat-plateaux like islands grow on top of Si. Figure 4(a) shows that on Si the flat islands are about 200 nm wide and 5.0 nm high. This height corresponds to approximately the 6T unit cell parameter $a$ ($a = 4.4708$ nm) [11] indicating that the 6T molecules are aligned with their molecular axis perpendicular or almost perpendicular to the Si substrate. This result is in accordance with previously reported studies for 6T grown on top of flat surfaces [12, 13]. On the other hand, on top of the oriented PFO layer, figure 4 (b), 6T grows forming drop-shaped islands, about 100 nm wide and between 20 and 30 nm high, while flat regions are not noticeable. We suggest that these islands are composed of 6T molecules piled up in a way that their long axis is parallel or almost parallel to the friction direction, i.e., to the orientation direction of the underneath PFO molecules which are parallel to the substrate’s surface. These islands were observed to grow in width and height with the increase of 6T films thickness (not shown here). Similar results have been reported for oriented polytetrafluoroethylene (PTFE) [14] and TiO$_2$ [15] substrates, where 6T molecules were also observed to orient parallel to the orientation of these substrates. These results suggest that for 6T deposited thin films, substrate orientation acts as a driving force to preferentially orient the deposited 6T molecules with their long axis parallel to the underneath molecular orientation. This assumption of molecular orientation between 6T and PFO is also consistent with the present
results that show that the EL devices produced with 6T on oriented PFO films produce polarized light, from both PFO and 6T emissions, with high dichroic ratio (figure 3(a)).

![AFM images of 6T films (30 nm thick) deposited on (a) Si substrate (with native oxide kept on top) and on (b) oriented PFO substrate.](image)

**Figure 4.** AFM images of 6T films (30 nm thick) deposited on (a) Si substrate (with native oxide kept on top) and on (b) oriented PFO substrate.

6. Discussion
For devices produced with 6T deposited/PFO the excellent control of the emission colour by changing the 6T film thickness without losing molecular orientation makes it a promising candidate for application. An interesting feature is the fact that by increasing 6T film thickness, the current density does not change significantly while luminance decreases. Another peculiar result is that the efficiency increases slightly after deposition of 0.5 nm thick 6T (figure 5), compared to the pure PFO based device, and then decreases with further increase of 6T thickness. The mechanism of the increase of efficiency at 0.5 nm 6T deposition is not yet well understood.

![Variation of the maximum current efficiency with deposited 6T film thickness. The highest efficiency is observed for devices produced with a 0.5 nm thick 6T layer deposited on top of oriented PFO.](image)

**Figure 5.** Variation of the maximum current efficiency with deposited 6T film thickness. The highest efficiency is observed for devices produced with a 0.5 nm thick 6T layer deposited on top of oriented PFO.

We compared the photoelectric results of these devices with those for the devices we produced by doping 6T into the oriented PFO. Results show that for the best colour change result for each production method, i.e., the whitest CIE chromaticity diagram coordinates for devices produced with 6T deposition (CIE (0.30, 0.32)), the maximum luminance was about 380 Cd/m² and efficiency 0.1 Cd/A. This is much lower than the results for the 6T doped devices (CIE (0.22, 0.24)) where
maximum luminance was 3850 Cd/m\(^2\) and efficiency 0.75 Cd/A, despite a lack of significant colour change in the doped devices because of the inclusion of a PEDOT:PSS layer. This difference in luminance and efficiency can be explained as follows. Considering that for the deposited samples, the 6T layer is oriented on top of the PFO surface and might act as a quenching interface layer for the emitted light, as suggested by the decrease of luminance despite of constant current density with increase of 6T thickness results. On the other hand, vapour transportation doping leads to a homogenously distributed 6T into the PFO film, and because no quenching layer is formed on top of PFO the device shows a better performance. These results show that while the deposition process allows an excellent control of the colour as well as a better understanding of the emission mechanism of 6T/oriented PFO devices, the doped 6T/oriented PFO devices, despite of a lack of control of doping amount and consequently of the colour of the device, show better photoelectrical characteristics due to the oriented and homogenously distributed 6T in the oriented PFO matrix. Studies are under way to combine both methods, i.e., deposition of 6T on top of a 6T doped PFO layer, to improve the whitening of the highly efficient doped devices.

7. Conclusions
Whitening of the emission color of EL devices was performed by depositing about 4.0 nm thick orange emitting 6T onto blue emitting oriented PFO films. The orientation of deposited 6T molecules parallel to the oriented PFO molecules leads to very good polarization of the light emitted by these EL devices. Excellent control of the color of the emitted light is achieved by controlling the thickness of the 6T film. On the other hand, high luminance and efficiency of devices prepared by doping 6T into oriented PFO layers by means of the vapor transportation process was observed, despite of a lack of control of the color of the device.

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