

Polarized organic electroluminescence: Ordering from the top

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We demonstrate a method for achieving polarized organic electroluminescence for liquid crystalline conjugated polymers that allows the polymer to be deposited directly onto the anode. The technique utilizes a top-down alignment approach whereby the predeposited polymer was aligned from above using a rubbed polyimide master and a smectic liquid crystal transfer layer. The liquid crystal/polyimide master bilayer was sandwiched with the liquid crystalline polymer that had been deposited onto the electrode. The sandwiched layers were then heated to achieve alignment before the removal of the polyimide master and liquid crystal transfer layer. Using this method, poly[2,7-(9,9-di(2-ethylhexyl))fluorene] (PF2-6) was aligned to give an anisotropic polymer film. Light emitted from single layer light-emitting diodes containing the aligned PF2-6 had integrated dichroic ratios of up to 9.7. At 100 cd/m², the single layer devices had external quantum and power efficiencies of 0.08% and 0.05 lm/W, respectively. Bilayer devices containing an electron transport layer between the PF2-6 and the cathode gave emitted light with good dichroic ratios and with the external quantum and power efficiencies at 100 cd/m² being increased to 2.2% and 1.1 lm/W. © 2003 American Institute of Physics. [DOI: 10.1063/1.1632025]

Since the report of Burroughes *et al.*,¹ rapid progress has been made in improving the efficiencies and lifetimes of light-emitting diodes (LEDs) based on conjugated polymers.² Most of the work carried out on organic electroluminescence (EL) has involved unpolarized light emission. However, there have been a number of reports demonstrating polarized EL with the aim of incorporating such polymer LEDs as backlights into liquid crystal displays (LCDs). Although the technical requirements are stringent, the use of polarized EL could lead to more efficient LCDs as losses due to the absorbing polarizers could be avoided. Two main strategies have been adopted for achieving the alignment necessary for polarized EL. The most common method is a bottom-up approach, where an alignment layer is positioned between the electrode and the emissive layer.³⁻⁶ The alignment layers used in this bottom-up approach have consisted of rubbed polymer^{3,5,6} or photopolarized layers.⁴ The problem with both of these methods is that the alignment layer is normally an electrical insulator. Modest improvement in device performance has been achieved by increasing the conductivity of the alignment layer by the inclusion of a charge transport material.^{4,5} However, such a strategy has its drawbacks in that the addition of the charge transport material can, in some cases, reduce the effective alignment of the luminescent material.⁴ The second strategy for achieving polarized EL from light-emitting polymers has been to mechanically align the emissive polymer film once it has been deposited onto the electrode. For example, the sulfonium precursor to

poly(1,4-phenylenevinylene) has been partially converted, mechanically rubbed to align the chains, and then converted to the fully conjugated material.⁷⁻⁹ The advantage of such a route is that there is no insulating alignment layer between the polymer and bottom electrode and, hence, charge transport in the device should be improved. However, the problem with mechanically rubbing the polymer is that it is likely to introduce defects and impurities that could lead to poorer device performance. In this letter, we describe a simple method for obtaining polarized EL that removes the need for an alignment layer between the electrode and the emissive layer and also avoids a potentially damaging rubbing process leading to polarized blue-light emission with good dichroic ratios (DRs) and efficiencies at usable brightnesses.

Most of the effort on polarized EL from conjugated polymers has involved aligned liquid crystalline poly(fluorene)s deposited on rubbed polyimide coated indium tin oxide (ITO) on glass. This bottom-up approach is effective in achieving alignment but has the serious disadvantage that there is an insulating polyimide layer in the LED structure. We show that a poly(fluorene) can be aligned from above and thus avoid having an insulating polyimide layer in the LED. The alignment procedure is shown in Fig. 1, and begins by spin coating the liquid crystalline polymer onto poly(3,4-ethylenedioxythiophene) (PEDOT) coated ITO on glass. A rubbed polyimide master coated with a liquid crystal transfer layer is then placed in contact with the liquid crystalline polymer layer and heated to facilitate alignment. After cooling, the rubbed polyimide master and liquid crystal transfer layers are removed.

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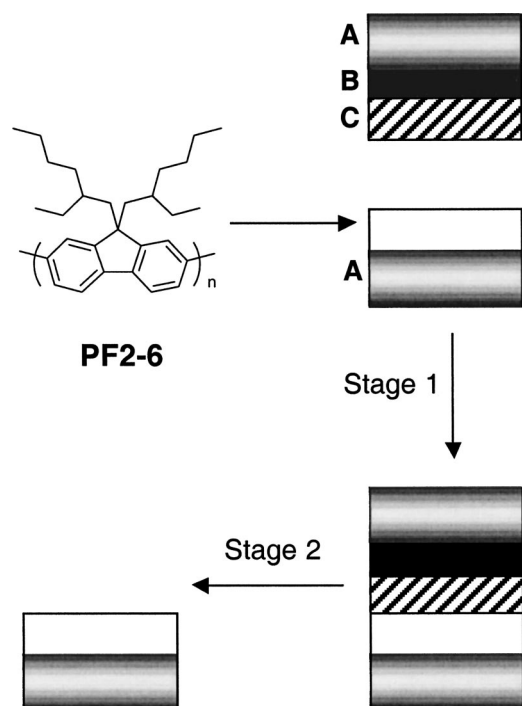


FIG. 1. General method used for the alignment procedure and structure of PF2-6. A=substrate; B=rubbed polyimide master layer; C=liquid crystal transfer layer. Stage 1: The LC coated polyimide layer is "sandwiched" with the spin-coated film of PF2-6 on PEDOT-coated ITO on glass and then heated to achieve alignment. Stage 2: The polyimide master and LC transfer layer are removed.

To demonstrate the practicability of our alignment method, we used poly[2,7-{9,9-di(2-ethylhexyl)}fluorene] (PF2-6) (Fig. 1) formed from a bis(1,5-cyclooctadiene)nickel(0) catalyzed polymerization of 2,7-dibromo-9,9-di(2-ethylhexyl)fluorene.⁵ The PF2-6 had a $\bar{M}_w \approx 40\,000$ and a polydispersity ≈ 2.6 (determined by gel-permeation chromatography against polystyrene standards). A PF2-6 film that had been drop cast from toluene and dried with heating overnight had a glass transition temperature of 78 °C, a melting point of 135 °C, and a nematic liquid crystalline phase from 135 °C to over 250 °C. A chiral liquid crystal mixture SCE8 (Merck, Ltd., UK) was used as the liquid crystal transfer layer. SCE8 undergoes a number of phase transitions upon heating: At 58 °C, it changes from a smectic C* to a smectic A phase; at 78 °C, it becomes nematic; and at 102 °C, it becomes isotropic. For the photophysical and device analyses, PF2-6 films ≈ 40 nm thick were spin coated from toluene solutions of PF2-6 (10 mg/ml) at 2000 rpm for 2 min onto PEDOT-coated ITO on glass. The ITO was cleaned by ultrasonification in acetone followed by 2-propanol and then plasma etched for 5 min under a vacuum of 10^{-2} mbar. The PEDOT was deposited by spin coating Baytron-P (Bayer AG, Germany) at 2200 rpm for 2 min to give ≈ 40 nm thick films. The PEDOT films were baked at 80 °C for 10 min before deposition of the PF2-6. To achieve alignment of the samples, SCE8 was deposited on the rubbed polyimide master layer (PI2555; Dupont, UK) (which was on ITO-covered glass) and then the two slides were sandwiched together. The "sandwich" was then heated at 90 °C for 1 h after which the sample was allowed to cool at a rate of approximately 1 °C/min to room temperature. The

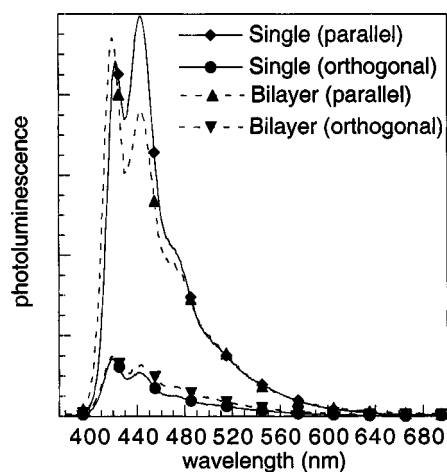


FIG. 2. PL spectra of PF2-6 in the single and bilayer devices taken both parallel and orthogonal to the direction of the rubbed master.

two glass slides were separated and the liquid crystal transfer layer was removed from the surface of the PF2-6 by washing with acetone. UV-visible spectroscopy was used to monitor the complete removal of the SCE8. Single layer LEDs were completed by the evaporation of lithium fluoride (≈ 0.4 nm), calcium (15 nm), and aluminum (100 nm). Bilayer LEDs had a 45 nm evaporated layer of electron transporting 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) deposited before deposition of the cathode layers.

SCE8 had two key properties that were important for the success of the alignment process; first, SCE8 was essentially immiscible with PF2-6; and second, it could be dissolved in acetone without dissolution of the PF2-6 layer. The first part of the study was to determine the effectiveness of the top-down alignment process in device configurations. The level of alignment, or DR, of the PF2-6 film in single and bilayer device configurations was determined from the photoluminescence (PL) and EL spectra measured parallel and perpendicular to the direction of the rubbed polyimide master layer. The spectra have been corrected for the spectral and polarization response of the spectrometers used. The DRs have been calculated from the ratio of the integrated emission spectra parallel and perpendicular to the alignment direction. Figure 2 shows the PL spectra obtained from the single layer (ITO/PEDOT/PF2-6/LiF/Ca/Al) and bilayer (ITO/PEDOT/PF2-6/TPBI/LiF/Ca/Al) device structures. The integrated PL DR for the single and double layer devices were determined to be 7.0 and 5.1, respectively. These good DRs clearly demonstrate that the top-down approach has good potential as an alignment technique. In addition, the similar PL DRs of the two device configurations show that the polymer alignment is stable to cathode and TPBI depositions.

The EL spectra for a single layer LED (ITO/PEDOT/PF2-6/LiF/Ca/Al) are shown in Fig. 3, and the DR is 9.7. In a previous report on EL from aligned PF2-6, where the polymer was aligned by direct contact with an underlying polyimide film, the DR calculated from the ratio of the peak emission parallel and perpendicular to the alignment layer was 15.⁵ For the single layer device used here the ratio of the EL peaks was 19 at 447 nm showing that the top-down approach is at least as good as the bottom up approach for aligning poly(fluorene)s. The dramatic difference though be-

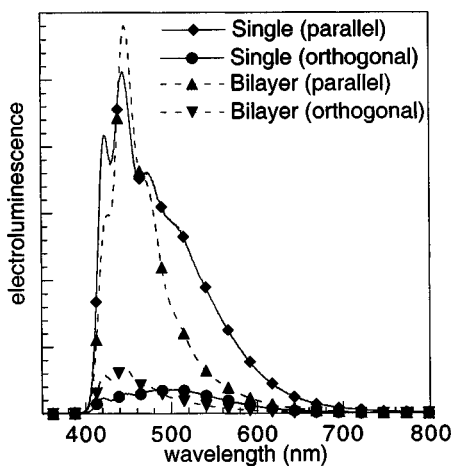


FIG. 3. EL spectra of PF2-6 in the single and bilayer devices taken both parallel and orthogonal to the direction of the rubbed master.

tween the two methods of alignment is in the device performance. The removal of the insulating layer between the anode and the polymer film was expected to give better device performance. For all polarized EL previously reported, the devices tend to have high turn on voltages, low brightnesses at high bias and, hence, low power efficiencies.¹⁰ For example, polarized EL from a device structure ITO/polyimide:hole transport material/PF2-6/Ca/Al had a turn on voltage of around 13 V and brightness of 45 cd/m² at 19 V.⁵ In contrast, the turn on voltage for the single layer device in this work was 4.0 V (1 cd/m²), and 500 cd/m² was achieved at around 7.8 V. The external quantum efficiency of the device at 100 cd/m² (at 5.6 V) was 0.08% and the power efficiency was 0.05 lm/W. Although these efficiencies are much lower than what has been currently achieved for unpolarized EL, they are a significant step forward when compared with the other methods of achieving polarized EL.

Insight into the reason for the modest efficiency of the single layer devices was gained by introducing electron transporting TPBI¹¹ between the aligned PF2-6 and the cathode. The EL spectra and device characteristics of the bilayer device (ITO/PEDOT/PF2-6/TPBI/LiF/Ca/Al) are shown in Figs. 3 and 4. The integrated DR of the EL spectra was again good at 6.8, and at 447 nm, the ratio of the peaks parallel and orthogonal to the alignment direction was 8.4. The incorporation of an electron transport layer substantially improves the device performance. The turn on voltage of the bilayer device was 4.6 V (1 cd/m²) and, at 6.7 V, the brightness was 500 cd/m². At 100 cd/m² (5.8 V), the external quantum efficiency was 2.2% and the power efficiency was 1.1 lm/W. These are excellent results for polarized EL, and the improvement in performance of the bilayer device suggests that electron transport and/or injection is a factor which significantly limits the efficiency of the single layer LEDs. This is consistent with polyfluorenes showing good hole mobility, but much lower electron mobility.¹² The results are also consistent with the observation of slightly higher DRs in EL than PL. In single layer devices, the recombination zone for injected charges will be close to the cathode, while in the bilayer devices, it is close to the polymer/TPBI heterojunction.

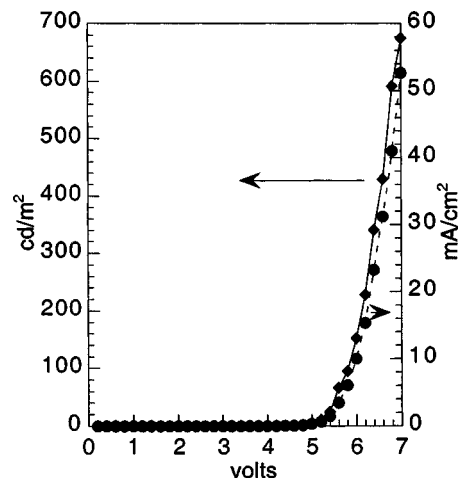


FIG. 4. Luminance (diamonds) and current density (circles) vs voltage for the bilayer device.

Therefore, in both cases the recombination zone is close to the top of the aligned PF2-6 layer, and this is the part of the film that is likely to be most strongly aligned. For the thickness of the PF2-6 films used here, the PL will come from the entire film, and it is possible that the bottom of layers are less effectively aligned, giving a lower dichroic ratio.

In conclusion, we have developed a nondestructive and simple method for obtaining polarized EL which avoids the mechanical damage associated with mechanical rubbing and the placement of a poorly conducting layer between the emissive polymer and an electrode. The device performance and EL DR indicate that the top-down approach to alignment has significant potential as an alignment technique for electronic and optoelectronic devices.

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