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Solution Processed Optical Devices Utilizing Poly(alkylfluorene) Derivatives

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Polymeric materials are one of promising materials for organic electronics devices fabricated by printing technology. Among polymeric materials, poly(9,9-dialkylfluorene) is one of soluble conducting polymers for polymeric light-emitting diodes (PLEDs) and organic field-effect transistors (OFETs), which exhibit high fluorescence quantum yield, high electron and hole mobilities and good thermal stability. Layered PLEDs were fabricated by solution process in order to enhance the emission characteristics, especially, emission intensity and emission efficiency. The PLEDs have been discussed as an electro-optical conversion device for optical signal transmission. The ambipolar and the light emission characteristics of top gated-type ambipolar OFETs utilizing polyfluorene derivatives have been discussed.

Keywords: poly(9,9-dialkylfluorene), organic light-emitting diodes, organic field-effect transistors

1. Introduction

Poly(9,9-dialkylfluorene)[1] (PFO) derivatives are one of soluble conducting polymers for polymeric light-emitting diodes (PLEDs) and organic field-effect transistors (OFETs) because PFO derivatives exhibit high fluorescence quantum yield, high hole and electron mobility, and good thermal stability. PFO derivatives are one of the promising materials for large-area optoelectronic devices such as organic light-emitting diodes (OLEDs) for display and lighting applications. The PLEDs based on PFO derivatives with short fluorescence lifetime can be applied to the electro-optical conversion devices for high-speed switching applications in the field of optical sensors, and optical signal transmission.

High performance of OFETs fabricated using highly crystalline organic materials have been realized; however, solution processing has still attention in simple fabrication process for large area devices. In particular, ambipolar materials are useful for fabricating OFETs because they can be used either as a p-channel or an n-channel by changing the polarity of the gate voltage.

In this report, we demonstrated highly-efficient and high-speed PLEDs by incorporating a thin interlayer. We also discussed the fabrication and the ambipolar and light-emitting characteristics for solution processed OFETs utilizing PFO derivatives.

2. Experimental

The schematic of the device structures and molecular structures of the polymeric materials used in the study are shown in Fig. 1. Commercially available glass substrates on which pre-coated polished indium tin oxide (ITO), which serve as source/drain electrodes were used. The substrate was degreased with solvents and cleaned in a UV ozone chamber. The PLEDs were fabricated by solution process utilizing poly(9,9-dioctylfluorene) (F8) or poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) as an emissive material. First, poly(ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS) hole injection layer with 45 nm was spin-coated on an indium tin oxide (ITO)-coated glass substrate and baked in air at 120 °C for 20 min. Next, the thin-film of poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB) as an interlayer (10 nm in thickness) was spin-coated on the hole injection layer and baked in N_2 gas at 200 °C for 20 min in order to stabilize the thin film to be insolvent. The 50 nm-thick F8BT film was spin coated onto the TFB interlayer using xylene as a solvent. The typical cathode consisting of LiF (0.5 nm) / Al (10 nm) / Ag (100 nm) was vacuum deposited in at a chamber base pressure of about 10^{-4} Pa. Finally, the device was covered with a glass plate and encapsulated by epoxy rein in an argon gas atmosphere to prevent the oxidation of the cathode and the organic layers. The active areas of the device were 4 or 0.3 mm^2, for usual use and for high speed operation, respectively. All of the measurements were carried out at room temperature.

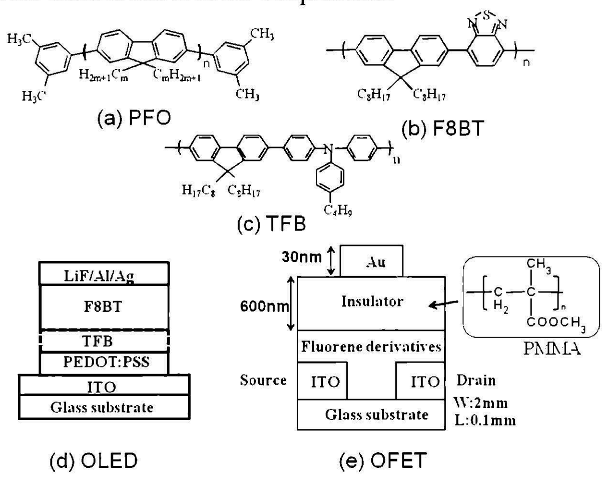

Fig. 1. Schematic of device structures and polymeric materials used in the experiment. (a) PFO, (b) F8BT, (c) TFB, (d) OLED, and (e) OFET

As active semiconducting layers of OFETs, two kinds of PFO derivatives, F8 and F8BT, were tested. Solution processed PFO derivatives were spin coated on patterned ITO (indium-tin-oxide) source/drain electrodes so as to form a channel length and width of 0.1 and 2 mm, respectively. The semiconducting layers were baked at 290 °C in nitrogen gas. Typical layer thickness of the active layer was in the range between 50-100nm.

Then, poly(methyl methacrylate) (PMMA) layer was spin-coated as a gate insulating layer, which was baked above 150 °C. Finally, An Au gate electrode with a 30 nm thickness was vacuum evaporated at a background pressure of about 10^{-4} Pa onto the polymer gate insulating layer formed on the polyfluorene semiconducting layer. The deposition rate and thickness of the deposited electrode were monitored using a quartz crystal oscillator. The measurements of electrical characteristics of OFETs were carried out at room temperature in a vacuum chamber at a background pressure of about 10^{-4} Pa.

The current-voltage characteristics were measured using a 2400 and 6517A source meters (Keithley). The electroluminescence (EL) output characteristics were measured using a photodiode (Hamamatsu Photonics). The EL spectra were measured using a photonic multichannel spectral analyzer (Hamamatsu Photonics PMA-11).

3. Results and Discussions

3.1. Layered polymeric pight-emitting diodes

3.1.1 Emission characteristics of PLEDs

A yellow-green emission was observed from a multi-layer PLED based on F8BT, whose device structure was ITO/ PEDOT:PSS (45nm)/ TFB (10 nm)/ F8BT (50 nm) / LiF/ Al/Ag (Fig. 1(d)). Figure 2 shows the current density-applied voltage-luminance characteristics of the PLED with or without TFB.

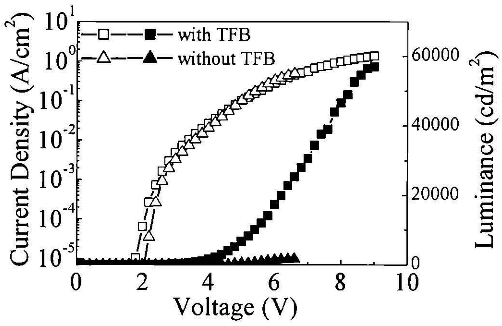

Fig. 2. Current density - applied voltage – luminance characteristics of PLEDs with and without TFB interlayer.

The luminance of the PLED with TFB increased in the forward bias direction above a threshold voltage of about 1.9 V. The emission intensity reached as high as 57,000 cd/m^2 at an applied voltage of 9 V. The PLED showed a peak efficiency of 6.7 cd/A, an improvement of more than 16 times in their performance, compared with the device without TFB interlayer. The increased efficiency is much larger in the low current region than that in high current [2].

3.1.2 Optical signal transmission utilizing PLEDs

The transient response of the luminescence from the PLEDs has been evaluated. The emission life time has been measured by PL decay time excited by short laser pulse. As a result, the decay time of F8 and F8BT was estimated to 1 and 3 ns, respectively. The short emission life time will enable us to expect high response time of EL emission.

In order to obtain a high frequency operation of the PLED, the device size as small as 0.3 mm^2 was used. As increasing the applied voltage, the emission rise and decay times decreased. However, the decrease of the decay time is not as large as the rise time. The decay time is limited by the emission lifetime of the material, and also by the geometrical parameters of the device. Since we choose the small size of the OLEDs, the CR (capacitance - resistance) time constant will be in the order of 10 ns. In Fig. 3, pulsed emission is shown by direct application of pulsed current. While the cut-off frequency of the device, when the output power comes to the half maximum power, is estimated to 50 MHz, 100 MHz operation is realized at the applied voltage of 16 V [2].

Optical signal transmission utilizing the PLED is as follows. Electrical moving picture signals are converted to NTSC (National Television System Committee) signals and then to the PFM (pulse frequency modulation) signals by the electrical circuits. PFM signals with around 10 MHz are applied to the PLEDs, and the signals are converted to optical signals by the PLEDs. The optical signals are transmitted by the polymeric optical fiber, and then they are received by the photo-detector. The optical signals are converted to the electrical signals, and the transmitted pictures signals are displayed in the display device.

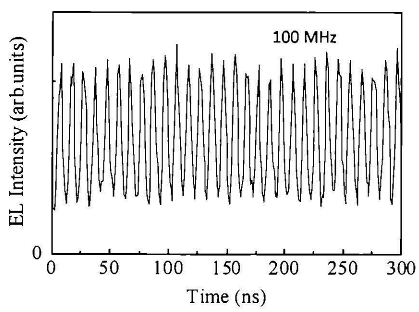

Fig. 3. Direct modulation of PLEDs by applying 100 MHz pulse voltage.

The layered PFO based PLEDs with TFB as an interlayer shows enhanced emission with higher emission efficiency, and high speed operation. The PLEDs are expected to be applicable to the electro-optical conversion devices for high-speed switching applications in the field of optical link [3] and optical sensor systems. They can be fabricated by solution process, and by simple printing fabrication process.

3.2. Light-Emitting Field-Effect Transistors

3.2.1 Device characteristics of poly (9,9-dioctylfluorene) (F8)

F8 which contains only fluorene backbone exhibits a blue emission and is well-known emissive material in OLEDs. Figure 4 shows output characteristics of top-gated type OFETs [4] with F8. It is well-known that the charge carriers run in a few nm at the interface of gate insulator and conducting layer. Since OH groups act as trapping site and affect n-channel conduction, we employed PMMA which has no OH group as an insulating layer. From the characteristics shown in Fig. 4(a), the field-effect hole mobility and the threshold voltage of the top-gate type F8 device were estimated as μ = 0.7 x 10^{-3} cm^2/Vs and V_{th} = -24 V at the drain-source voltage V_{DS} = -100 V, respectively.

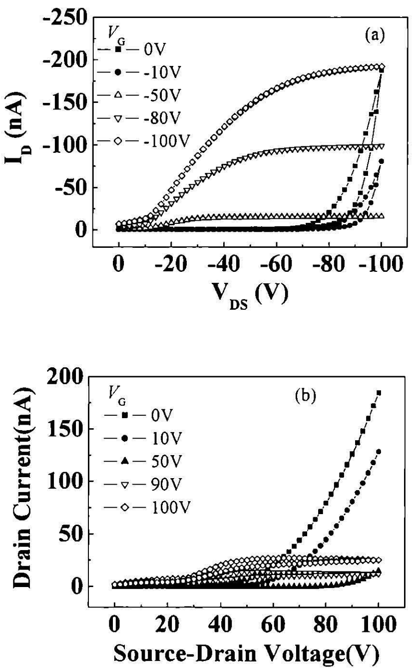

Fig. 4 Output characteristics of F8 OFETs in the (a) hole and (b) electron enhancement modes, respectively.

Output characteristics of the F8 device operated in the electron enhancement mode are shown in Fig. 4(b). The leakage drain-source current increased superlinearly with drain-source voltage at lower gate voltages. Although a hysteresis curve was observed due to the charge trapping, application of positive gate voltage suppressed the component and the typical saturation characteristics of n-channel OFET were observed above the gate voltage of 80V.

For F8 device, the threshold voltage in p-channel conduction regime is lower than that in n-channel conduction regime because the hole injection barrier is lower than the electron injection barrier. For n-channel accumulation regime, the field-effect electron mobility and threshold voltage were estimated as μ = 1.2 x 10^{-3} cm^2/Vs and V_{th} = 61 V at a drain-source voltage V_{DS} = 100 V, respectively. That is, ambipolar characteristics were obtained from the top-gate type F8 device with ITO drain/source electrodes.

The ambipolar OFET with F8 emitted a blue light under the gate voltage application as shown in Figs. 5(a) and (b). A peak of EL intensity was observed when hole current dominated at gate voltages between 0 and 60 V, and between -30 and -100 V, respectively. The EL intensity was at a minimum when the drain current reached a minimum. On the other hand, EL intensity increased with gate voltage when electron current dominated above approximately 60 or -20 V, respectively.

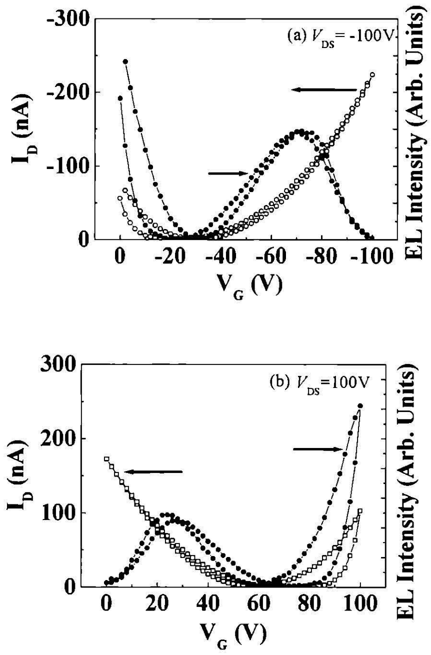

Fig. 5 Transfer and emission characteristics of OFETs with F8 for different drain voltages of (a) -100 V and (b) +100 V.

3.2.2 Device characteristics of poly(9,9-dioctylfluorene--co-(benzothiadia zole) F8BT

Output characteristics of top-gate type OFETs based on F8BT are shown in Figs. 6(a) and 6(b). For p-type characteristics, the field effect mobility and the threshold voltage of F8BT device are estimated as μ = 0.8 x 10^{-3} cm^2 /Vs and V_{DS} = -18 V, respectively. The field-effect electron mobility and the threshold voltage were estimated as μ = 0.4 x 10^{-3} cm^2 /Vs and V_{DS} = 40 V, respectively. The yellow-green light emission was also observed. For n-type characteristics, the threshold voltage of OFET based on F8BT with an electron-withdrawing group was lower than that of the F8 device because the injection barrier of electrons from ITO into the LUMO level of F8BT is relatively lower than that of F8. Although these devices with ITO source/drain electrodes have relatively large contact resistance, these carrier mobilities are relatively in agreement with those of bottom-gate type OFETs with Au and Ca drain/source electrodes for p-channel and n-channel OFETs measurements, respectively.

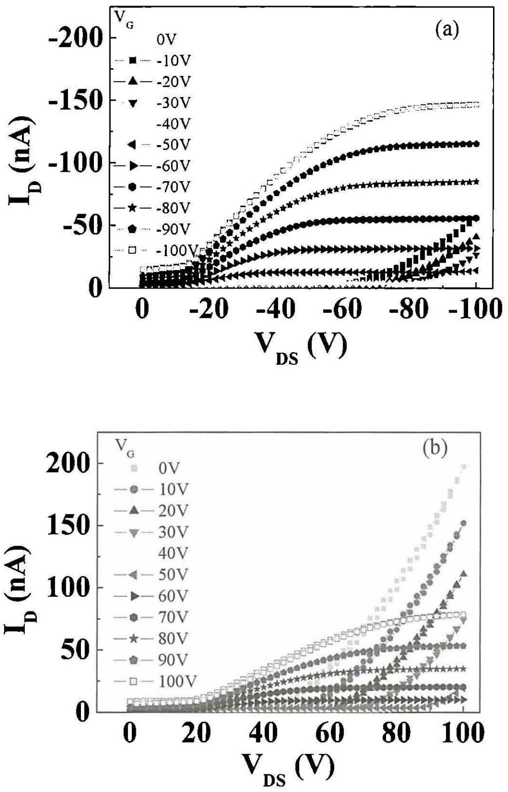

Fig. 6 Output characteristics of F8BT OFETs in the (a) hole and (b) electron enhancement modes, respectively.

For the F8 device, a peak of EL intensity was observed when hole current dominated. On the other hand, for a F8BT device, two peaks of EL intensity were observed when either hole or electron currents dominated. These results suggested that the carrier transport of holes is predominant in F8 film. For the F8 device, a peak of EL intensity was observed when hole current dominated. On the other hand, for a F8BT device, two peaks of EL intensity were observed when either hole or electron currents dominated. These results suggested that the carrier transport of holes is predominant in F8 film.

3.2.3 Device characteristics of F8BT doped in F8

The dye doping method is of practical importance because it allows for easy improvement in performance, such as color tunability. Transfer and emission characteristics of top-gate type OFETs based on 5 wt% F8BT doped in F8 operating at V_D = 100V is shown in Fig. 7. White emission was observed from the F8:F8BT OFET, and the emission spectrum are shown in Fig. 8(a).

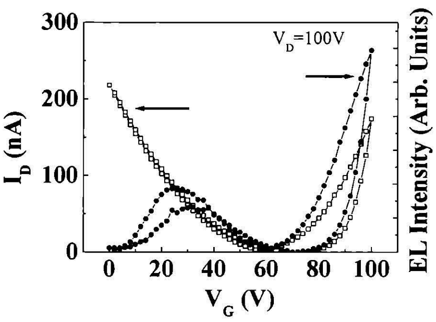

Fig. 7 Transfer and emission characteristics of an OFET with F8BT doped in F8 for a drain voltages of +100 V.

The CIE (Commission Internationale de l'Éclairage) coordinate was (0.34, 0.40) as shown in Fig. 8(b) with the emission picture. Blue and yellow green points show the emission from F8 and F8BT device, respectively. The transfer characteristics of the F8:F8BT device are the same as those of the F8 device as shown in Fig. 5(b). That is, for the F8:F8BT device, carrier transfer is still dominant in the F8 film. This result indicated that excitons are formed on the F8, and the excitonic energy transfers to the F8BT by the Förster energy transfer process, because the band gap of F8BT is lower than that of F8.

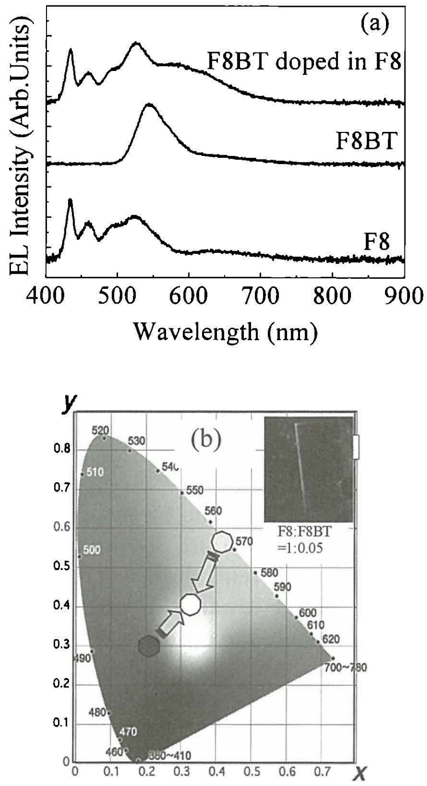

Fig. 8 (a) EL spectra of the OFETs with F8, F8BT and F8BT doped in F8, (b) CIE coordinate of the emission from the device with F8BT doped in F8.

4. Conclusions

In this report, the layered PFO based PLEDs with TFB as an interlayer shows enhanced emission with higher mission efficiency, and high speed operation. The PLEDs are expected to be applicable to the electrooptical conversion devices for high-speed switching applications in the field of optical link [3] and optical sensor systems. They can be fabricated by solution process, and by simple printing fabrication process.

Ambipolar characteristics of solution processed top-gate type OFETs with ITO source/drain electrode utilizing polyfluorene derivatives are demonstrated. All OFETs with fluorene derivatives exhibited ambipolar characteristics. Ambipolar OFETs with F8, F8BT and F8BT:F8 exhibited the blue, yellow and white EL emissions by varying the gate voltage, respectively. Top gate-type fluorene OFETs with ITO drain/source electrodes have been demonstrated as the light-emitting transistors.

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