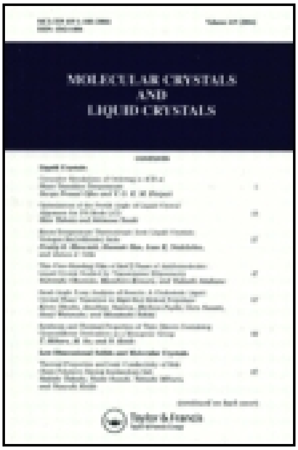

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Application of Maskless Dye-Diffusion Technique to Conducting Polymer for Emission-Color Tuning

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Tuning the emission color of polymer light-emitting devices (PLEDs) based on a conducting polymer poly(9,9-dioctylfluorene) (PDOF) through the maskless dye-diffusion technique has been attempted. Introduction of green-emitting dye Coumarin 6 into PDOF through this technique results in green emission from the PLEDs without notable alteration of the external quantum efficiency, although the onset voltage for emission has much increased. This result suggests that Coumarin 6 plays a role of carrier trap in the polymer.

Keywords: color tuning; conjugated polymers; patterning; polyfluorene derivative; polymer light-emitting devices

1. INTRODUCTION

The conducting polymers have been attracting much attention as an emission layer for polymer light-emitting devices (PLEDs). One of the most important features of conducting polymers is solubility which enables the production of PLEDs through wet-processes such as spin-coating. The spin-coating technology requires only cheap facilities and is used for the monochrome displays with PLEDs in present consumer products. However, this technique is apparently incompatible with the production of multi-colored displays.

We have proposed “maskless dye-diffusion technique” to tackle this problem for a few years [1,2]. Multi-colored displays based on PLEDs are fabricated on substrates with pre-patterned transparent electrodes such as indium tin-oxide (ITO). The maskless dye-diffusion

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technique utilizes the pre-patterned electrodes as heaters to promote local dye-diffusion for emission-color tuning. There are some techniques using thermal dye-diffusion to tune the emission color of PLEDs with spin-coated polymer layer proposed by different groups [3,4]. Among those techniques, our method seems to be unique because of its simplicity.

There are two classes of materials for PLEDs. One includes polymers with saturated main chain with emissive moiety as pendant such as poly(N-vinylcarbazole) (PVK), and the other corresponds to conjugated polymers including poly(*p*-phenylene vinylene) derivatives and poly(fluorene) derivatives. It is usually hard to change the emission with longer wavelength to shorter one, and the suppression of the conversion opposite to this direction is also difficult. Therefore, the polymer materials with wide band-gap energy or blue-emitting polymers have to be selected as host materials. For PLEDs based on PVK, the introduction of large amount of electron transport dyes up to 40 wt% is typically applied to improve the emission efficiency [5,6]. However, this type of composite is apparently incompatible with the maskless dye-diffusion technique, because "back-diffusion" of the electron transport dye from the polymer may take place.

In this paper, we show some preliminary results on the maskless dye-diffusion technique applied to a blue-emitting conducting polymer, poly(9,9-dioctylfluorene) (PDOF).

2. EXPERIMENTAL

Figure 1 shows the molecular structure of PDOF and Coumarin 6. PDOF and Coumarin 6 used were purchased by American Dye Sources and Aldrich, respectively. Aqueous suspension of poly(ethylenedioxythiophene):poly(styrenesulfonate) salt (PEDOT:PSS) used was obtained from Bayer.

The procedure of the maskless dye-diffusion technique is schematically depicted in Figure 2. An ITO film coated on a glass plate was patterned into strips as shown in Figure 3. Then, PEDOT:PSS layer was formed by spin-coating the aqueous suspension. The PEDOT: PSS film was heated to 120°C for 40 min to dry. A PDOF layer, which is indicated as "receiver film" in Figure 2, was also spin-coated from its toluene solution on the PEDOT:PSS layer. Typical thicknesses of PEDOT:PSS and PDOF layers were in the rages of 50–60 nm and 80–90 nm, respectively. The "dye reservoir film" was made on another glass plate by spin-coating from a toluene solution containing equivalent weights of PVK as a matrix and a green-emitting dye Coumarin 6.

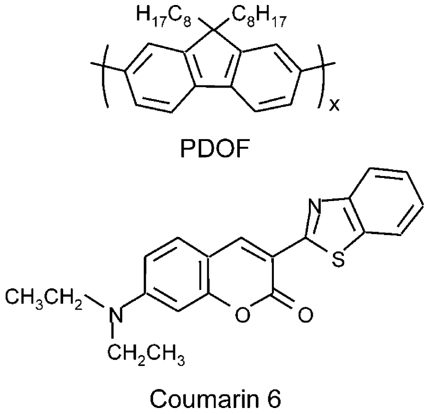

FIGURE 1 Molecular structures of PDOF and Coumarin 6.

The maskless dye-diffusion technique is carried out by bringing the two polymer films into contact followed by Joule heating of selected ITO electrodes. The dye molecules in the reservoir film nearby the ITO heated are thermally activated and start to diffuse into the receiver PDOF film. Since the heating area can be limited by the shape of the electrode, the area where the dye molecules diffuse mimics

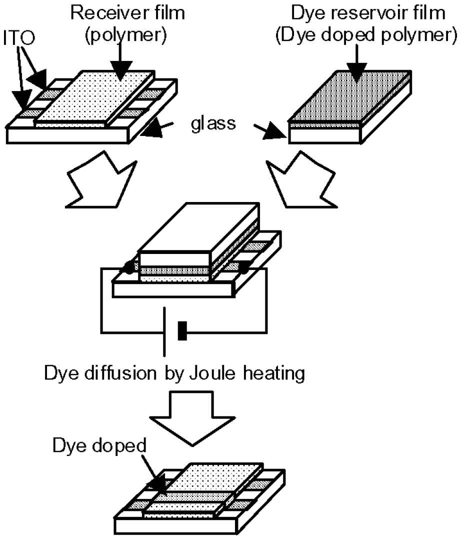

FIGURE 2 A scheme of maskless dye-diffusion technique.

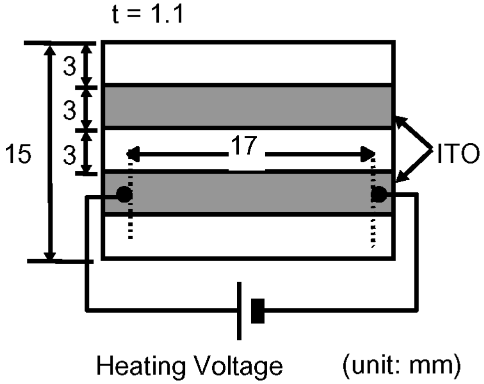

FIGURE 3 Size and pattern of ITO-coated glass substrates.

the ITO electrode. In this study, heating voltage of 15 V was applied between 17 mm.

After the dye-diffusion, the PDOF film was heated to 80°C for 30 min to remove residual solvent. In this study, all processes mentioned above were carried out in air. Then, MgAg cathode was vacuum deposited onto the PDOF film to complete the device. The emission area is 3 mm × 3 mm. The characterization of the devices was carried out in a glove-box filled with nitrogen.

The emission intensity of a PLED was measured by a Hamamatsu S1337-1010BQ photodiode attached on the PLED. The emission intensity shown in the following section corresponds to the short-circuit photocurrent from the photodiode in nA unit. The emission spectra were collected by an Ocean Optics S2000 CCD-spectrophotometer and are shown without any normalization.

3. RESULTS AND DISCUSSION

Figure 4 shows the emission spectra of PLEDs from PDOF films with various dye-diffusion periods. The device with pristine PDOF shows clear blue emission and no notable change was found in emission spectrum up to 20 s of dye-diffusion. However, a sudden change in emission spectrum was found after diffusion for 40 s. The spectrum almost coincides with a PLED from PVK doped with Coumarin 6.

The emission intensity-voltage characteristics of the PLEDs from PDOF with various dye-diffusion periods are shown in Figure 5. It is clearly indicated that green-emitting devices (40 s and 60 s) show much higher onset voltage of about 13 V than blue-emitting devices

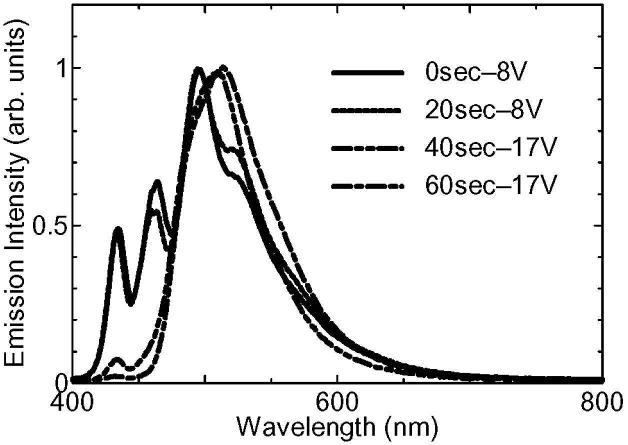

FIGURE 4 Emission spectra of PLEDs from PDOF films with various dye-diffusion periods.

(0 s and 20 s) which show onset voltage of 6 V. This may suggest that Coumarin 6 plays a role of carrier trap in PDOF. Two scenarios seem to be possible for the green emission in PLEDs after dye-diffusion. One is the recombination of carriers to form exciton on PDOF, followed by the energy transfer from PDOF to Coumarin 6. Another one is the

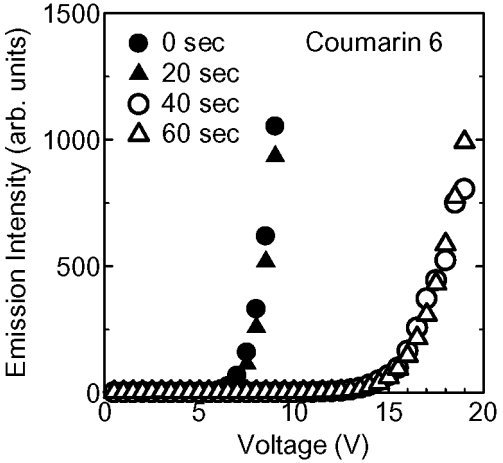

FIGURE 5 Emission intensity-voltage characteristics of PLEDs from PDOF films with various dye-diffusion periods.

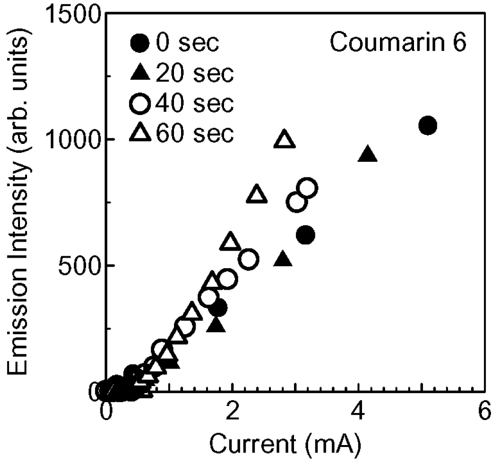

FIGURE 6 Emission intensity-current characteristics of PLEDs from PDOF films with various dye-diffusion periods.

direct recombination on Coumarin 6. The validity of the two scenarios has not been clarified yet.

Figure 6 shows the emission intensity-current characteristics of the PLEDs from PDOF with various dye-diffusion periods. The slope of the characteristics corresponds to the external quantum efficiency of the device. Since the emission intensity was measured by the Si photodiode with almost flat external quantum efficiency over the visible range attached on the PLEDs, the number of photons and thus the external quantum efficiency can be measured regardless of the spectral change. It was found that the quantum efficiency of the PLEDs showed slight enhancement upon Coumarin 6 diffusion. The heat treatment effect during the dye-diffusion seems to contribute to this improvement.

4. CONCLUSIONS

In this paper, we have shown our preliminary results on the application of the maskless dye-diffusion technique to PLEDs based on a conducting polymer PDOF for emission-color tuning. Introduction of green-emitting dye Coumarin 6 into PDOF through this technique results in green emission from the PLEDs without notable alteration of the external quantum efficiency, although the onset voltage for emission has much increased. This result suggests that Coumarin 6 plays a role of carrier trap in the polymer.

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