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Emission-Color Modulation of Polymer Light-Emitting Device Based on Poly(9,9-dioctylfluorene) by Maskless Dye-Diffusion Technique

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Organic light-emitting devices have been used in consumer products for many years. The technology provides brilliant images with thin and light-weight display panels suitable for mobile or car devices. The organic light-emitting devices available in the market are based on low molecular materials, since they show the property of sublimation, which make it quite easy to purify the materials and to deposit patterned thin films through dry-processes under low-pressure. Another class of materials for organic light-emitting devices, the polymeric materials, is also studied for many years. Since they can form uniform films without pin-holes through wet-processes under the atmospheric pressure, they will be attractive candidates if one thinks about wide flat panel displays. However, the short lifetime of the polymer devices compared to the low-molecular devices hinders their commercial launch.

The spin-coating technology yields thin films uniform enough to be used in light-emitting displays. This feature has been recognized as one of the most important advantages of this technology. However, if we target the display with patterned multi-color display, this advantage turns into a kind of drawback, unless some patterning methods compatible with the spin-coating technology. To tackle this problem, the authors developed and studied maskless dye-diffusion technique, which is based on thermally activated diffusion of dye molecules from a reservoir film to a receiver film, for several years. [1] The energy transfer from the polymer to the dye incorporated in the polymer enables the modification of emission color. The preceding studies using poly(N-vinylcarbazole) (PVK) as host material have shown the potential of the technique as a patterning method compatible with the spin-coating, however, their efficiency was poor because of the nature of the material. [1, 2] Polyfluorene derivatives have been found as the first blue-emitting conjugated polymer by Yoshino et al.[3], and are recognized as a key material for polymer light-emitting devices because of their excellent luminescent property.

In this paper, we report on the color modification of polymer light-emitting devices based on poly(9,9-dioctylfluorene) (PDOF) by means of maskless dye-diffusion technique.

Figure 1 shows the schematic procedure of the maskless dye-diffusion technique. A poly(ethylenedioxythiophene):poly(styrene sulfonate acid) salt (PEDOT:PSS) film was spin-coated on a glass substrate with patterned indium tin-oxide (ITO) and was dried at 120 C. The PDOF film, which is indicated as receiver film in the figure, was spin-coated on the film from chloroform

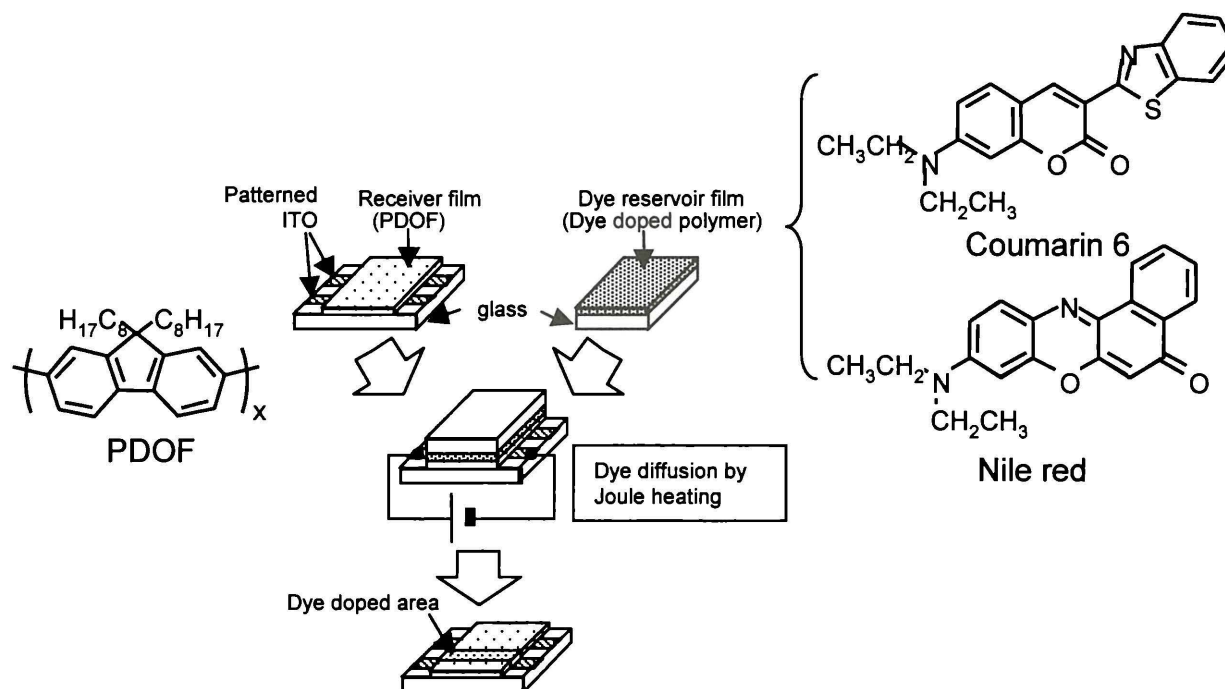


Figure 1 Scheme of Maskless dye-diffusion technique.

solution. The thickness of the PEDOT: PSS and PDOF films are approximately 50 nm and 80 nm, respectively. The dye reservoir film was spin-coated on another glass substrate from chloroform solution containing equivalent weights of PVK and one of the dyes, Coumarin 6 or Nile red. Then, the two polymer films are brought into contact and selected ITO films on the receiver film are heated by means of the Joule heating to initiate the diffusion of dye molecules in the reservoir film into the receiver film. In this study, the heating voltage of 15 V was applied to an ITO strip with 3 mm width and 17 mm long. The sheet resistance of the ITO was 10 Ω/sq . Heating voltage exceeding 15 V sometimes results in crack of glass substrate. The vacuum deposition of MgAg electrode as cathode was carried out to complete the polymer light-emitting device.

Apparently, the maskless dye diffusion process is a dry process under the atmospheric pressure. In this study, all the fabrication steps but the vacuum deposition have been carried out in air. The devices were characterized in a dry-box filled with nitrogen. The current-voltage characteristics were measured with PC-controlled apparatus, and the emission intensity was measured by a Si photodiode attached on the device. Since the spectral response of the photodiode is almost unity over visible wavelengths, this method is quite useful to know how the quantum efficiency of the device changes after the modulation of emission color. The emission spectra were collected by a CCD-spectrophotometer.

Figure 2 shows the emission spectra from devices using pristine PDOF and PDOF upon Coumarin 6-diffusion for 60 s. The emission color of PDOF which is initially blue modified to green peaked at around 500 nm after the diffusion of Coumarin 6. In the case of PVK, the dye diffusion does not give any particular effect on the onset voltage of emission. However, the

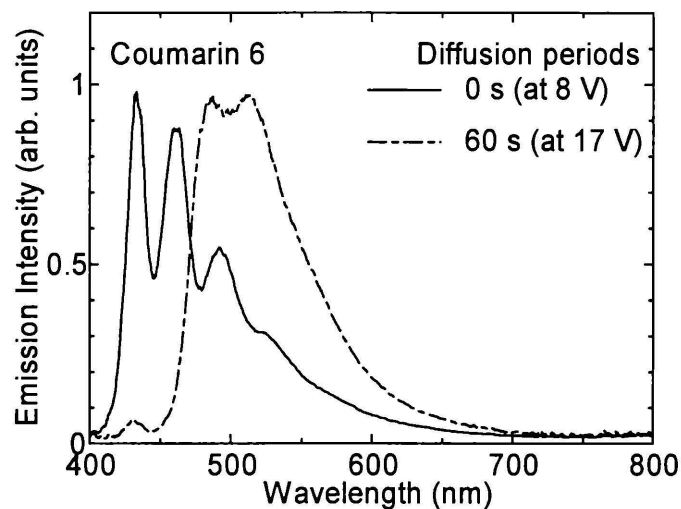


Figure 2 Emission spectra of devices using pure PDOF and PDOF upon Coumarin 6-diffusion for 60 s.

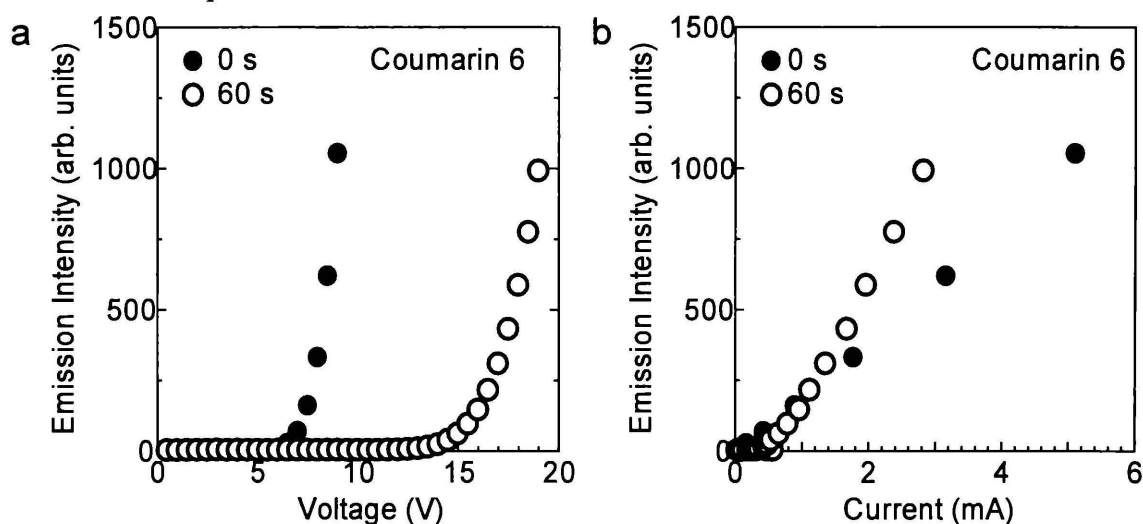


Figure 3 Emission intensity-voltage (a) and emission intensity-current (b) characteristics of devices using pure PDOF and PDOF upon Coumarin 6-diffusion for 60 s.

emission intensity-voltage characteristics shown in Fig. 3(a) clearly indicate the increase of the onset voltage. However, the emission intensity-current characteristics of the device shown in Fig. 3(b) show a slight increase in the quantum efficiency. These results suggest that the Coumarin 6 plays a role of carrier trap in PDOF and the direct recombination on Coumarin 6. The diffusion shorter than 20 s does not give any apparent modification.

Previous study has shown that the Nile red changes the emission color of PVK to red. [1] Contrarily, Nile red does not find as effective red dopant in PDOF. As shown in Fig. 4, the emission spectrum of the device from PDOF after the diffusion of Nile red for 60 s consists of the original emission from PDOF and additional broad emission peaked at around 560 nm. The peak

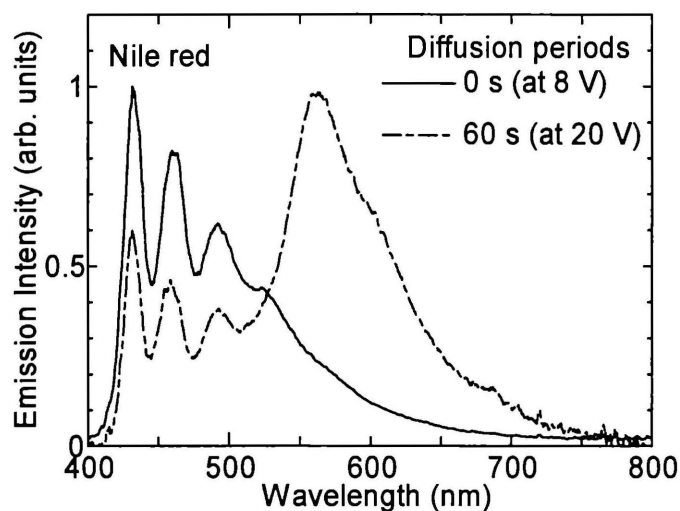


Figure 4 Emission spectra of devices using pristine PDOF and PDOF upon Nile red-diffusion for 60 s.

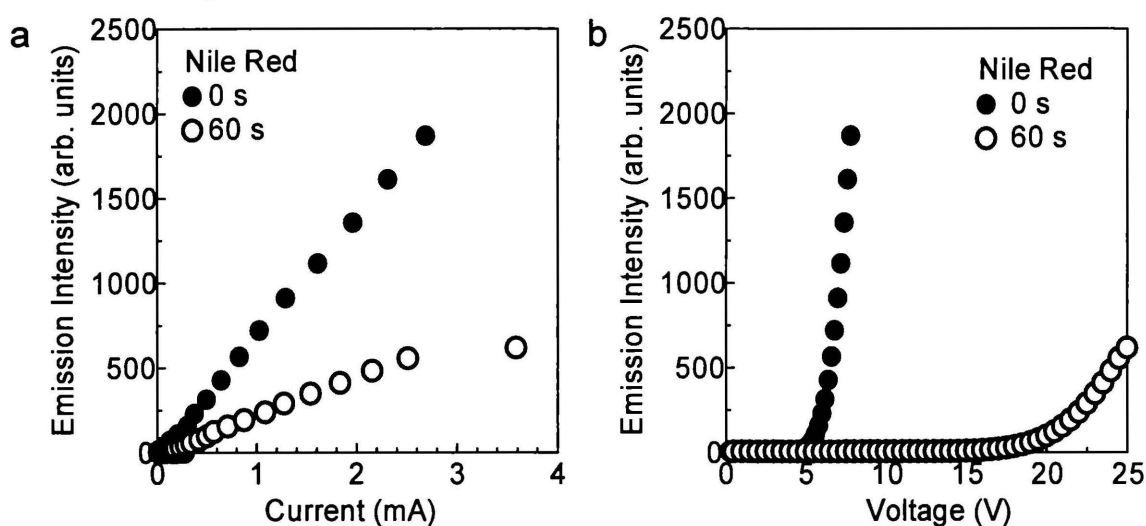


Figure 5 Emission intensity-voltage (a) and emission intensity-current (b) characteristics of devices using pristine PDOF and PDOF upon Nile red-diffusion for 60 s.

wavelength of the additional emission is much shorter than the case of PVK-based device. The emission onset voltage also increased from 6 V to approximately 20 V, and, the quantum efficiency of the device reduced to be 30% of the original PDOF device as shown in Fig. 5. These results suggests that the formation of exciplex of PDOF and Nile red.

References

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