

## THREE-COLOR DOPING OF POLYMER OLEDs BY MASKED DYE DIFFUSION

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### ABSTRACT

A method to locally pattern the distribution of dye by diffusion into the polymer film of organic light-emitting diodes is introduced. Using a large-area diffusion source, the diffusion of dye into the polymer film can be controlled with a shadow mask. The materials used are the polymer poly(9-vinylcarbazole) (PVK) combined with electron transport molecules (PBD), and the dyes bimeane, coumarin 6 and Nile red. The temperature dependence of the diffusion is investigated along with the effect of annealing of the polymer film. A model of the dye distribution is introduced and estimations of the dye profile based on this model and PL measurement are discussed. A 3-color integrated device was demonstrated.

### INTRODUCTION

Organic light-emitting diodes (OLEDs) have demonstrated a remarkable potential for flat-panel display applications because of their relatively simple structure and the use of non-crystalline materials<sup>1,2</sup>. However, the fabrication of color displays, which requires red, green and blue emitters, is a current research challenge. The emission color of OLEDs, both those based on polymers or those based on small molecules, can be tuned by adding small amounts (about wt. 1%) of dyes into the host material<sup>3,4</sup>. Thus the color can be locally adjusted by just patterning the dye material in some way without disturbing the host material.

### EXPERIMENT

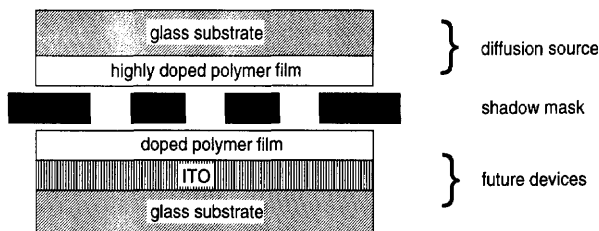


Figure 1: Experimental set-up: a shadow mask is sandwiched between the diffusion source which provides the dye and the device substrate with the polymer film<sup>5</sup>

The experimental set-up is shown in figure 1. The device substrate with the organic film to be patterned were deposited on a glass substrate coated with sputtered ITO ( $30 \Omega/\square$ ). A polymer blend layer with poly(9-vinylcarbazole) (PVK;  $M_w$  ca. 1,100,000 g/mole; 71.5 % by weight in the final film) as a hole transport polymer and 2-(4-Biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD; 28.5 % by weight) as electron transport molecule was created by spin coating<sup>6</sup>. Some blends also contained 9,10-Dioxo-*syn*-dimethylbimeane<sup>7,8</sup> (bimeane; wt 0.2

%) as an emissive dye (emission peak at  $\lambda = 435$  nm). The resulting thickness of the organic film after spin coating was approximately 100 nm. The dye used during the diffusion process was either coumarin 6 (C6, green) or Nile red. The diffusion source consists of a flat plate with a highly doped polymer layer as the dye source. The layer was deposited by spin coating using a solution of equal amounts by weight of PVK and C6 or Nile Red dissolved in chloroform. The shadow mask is a patterned stainless steel foil (200  $\mu\text{m}$  thick). The diffusion source layer, the shadow mask and the polymer film of the device substrate were then placed in close contact as shown in figure 1 to perform the diffusion.

Figure 2 shows the photoluminescence (PL) spectra after different diffusion times in which C6 was diffused into a layer of pure PVK (i.e. the film does not contain PBD or bimane) in an oven at 100 °C in air. In this case, the dye source was a film of pure C6 evaporated on a glass substrate. The PL excitation source was a ultraviolet lamp ( $\lambda = 254$  nm). Before the diffusion, one only observes the emission of PVK with a peak at 407 nm. After 15 min, the C6 emission peak at  $\sim 500$  nm can be detected. After about 50 min the C6 peak dominated the spectrum.

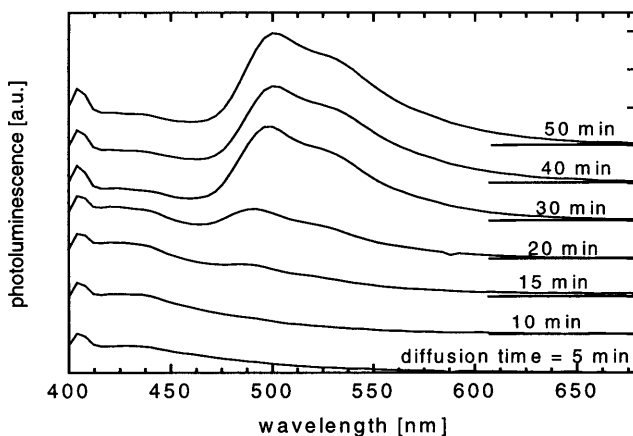


Figure 2: PL spectra of a pure PVK film in which C6 was diffused for different times <sup>5</sup>

This simple experiment demonstrates the feasibility of this method. However, since the quantum efficiency strongly depends on the dye concentration it is imperative to investigate the dye transfer under different conditions in order to be able to control the diffusion process.

The patterning process consists basically of three steps: The dye must diffuse out of the dye source film, travel to the surface of the device substrate and diffuse into the polymer film. The last step appears to be the rate limiting one. After a very long diffusion time, the color of the PL emission of C6 from the top of the target film was shifted from green to orange. Since C6 in its pure form emits in the orange, this fact indicates that C6 was piling up at the surface of the device substrate. An annealing process after the diffusion step was found to be very effective to remove the pile-up of dye. During the anneal, the dye will diffuse deeper into the polymer film and the dye distribution profile will become more homogeneous. Quantitative results of the annealing process are presented later.

Because the concentration of dye has such a strong impact on efficiency, we investigated the diffusion process into the polymer film in more detail. To get some information about the dye content in the film, it is useful to use an internal reference in order to eliminate any variations of the UV-radiation, viewing angle etc. To this goal, we added a fixed amount of the dye bimane to

the PVK-solution and thus obtain a blue emitting film after spin coating. When diffusing the green dye C6, the ratio of the PL emission of bimane and the PL emission of C6 serves as our dye concentration signal rather than the absolute intensity of the PL emission. To verify the validity of this method, we spun-coated glass substrates with a PVK-solution containing 0.3 mg bimane and different amount of C6 (0.05 mg, 0.1 mg, 0.2 mg, 0.3 mg and 0.4 mg). Figure 3 shows the relationship between the ratio of the PL emission of C6 and bimane versus the ratio of the concentration of C6 and bimane. For a homogeneously doped film, the monotonous characteristic allows us to uniquely map a emission ratio to a concentration ratio. A similar characteristic was obtained for Nile red and bimane.

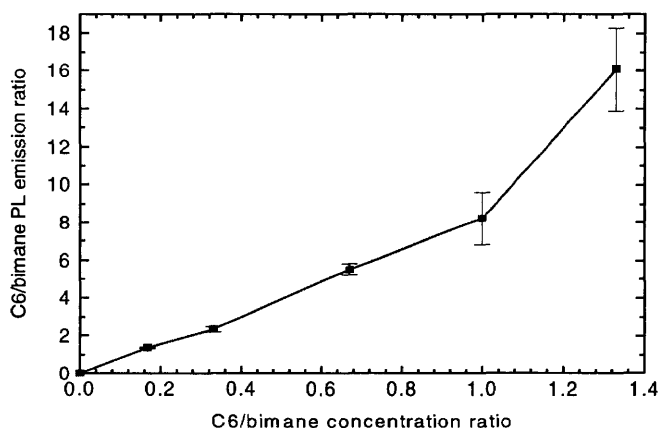


Figure 3: The ratio of the PL emission of C6 and bimane is plotted against the ratio of the concentration of C6 and bimane. The monotonous characteristic allows us to convert the PL ratio of C6 and bimane into the concentration ratio of a homogeneously doped film.

Using this technique, we measured the emission of PVK films containing PBD and bimane in which C6 and Nile red were diffused for 30 min at different temperatures. The PL ratio rises for both dyes exponentially with temperature as shown in figure 4. Because of the nature of the diffusion process, we expected that the dye will accumulate in the PVK layer close to the surface of even on top of the PVK layer. The sample was then annealed at 80 °C for 12 hours. The C6/bimane ration increased by a factor of 6 due to annealing, the Nile red/bimane ration increased by a factor of about 2. This proves that the dye is indeed moving into the polymer film. However, since the dye might have only diffused only into the layer close to the surface of the PVK-film, we can not easily convert the emission into a dye concentration ratio. For this, it is necessary to get some information on the dye distribution within the PVK-film. To this end, we deposited the PVK-film with bimane and PBD on sapphire substrates which are transparent for UV of  $\lambda=254$  nm. The absorption length of the PVK for UV light of this wavelength is about 50 nm<sup>9</sup>, whereas the thickness of the PVK-film is about 100 nm. This fact allows us to probe the front surface and the back side of the PVK-film separately. From the difference in the PL signal, we are able to estimate the dye distribution profile.

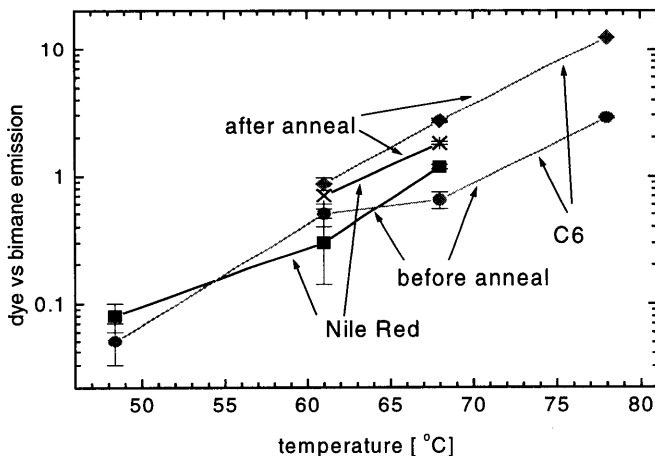


Figure 4: The PL ratio of C6/bimane (circles) and Nile red/bimane (squares) for different diffusion temperatures. The dye was diffused for 30 min into a PVK-film containing bimane. The wavelength of the UV light source is 254 nm. The sample was annealed at 80 °C for 12 hours. Both, PL ratio of C6/bimane (diamonds) and the PL ratio of Nile red/bimane (crosses) increased.

Figure 5 shows the spectra of a PVK-film with bimane and PBD in which C6 was diffused for 60 min at 90 °C. The C6 emission at 500 nm is barely detectable in the PL spectrum taken from the front of the PVK-film. No C6 emission could be seen from the back of the film suggesting that the dye has accumulated very close to the surface of the film. After annealing the substrate at 90 °C for 6 hours, the C6 emission dominated the spectrum taken from the front of the film. The PL spectrum obtained from the back now clearly shows a peak from the C6 emission. The difference of the ratio of the C6/bimane emission between the front PL and the back PL is smaller after the anneal indicating that the dye concentration profile indeed gets flatter.

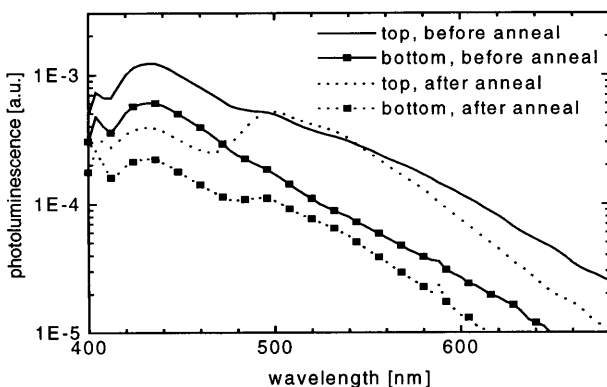


Figure 5: PL spectra (before and after anneal) of a PVK-film containing bimane in which C6 was diffused. The film was spun-on on a sapphire substrate to allow for probing the front and back surface of the polymer film separately.<sup>5</sup>

In order to obtain an OLED, a cathode has to be evaporated on top of the dyed PVK-film. In our case, the cathode material is Mg:Ag<sup>5</sup>. The PL spectrum of the C6 dyed PVK-film and the EL spectrum of a device on the same substrate is shown in figure 6. All of the EL emission comes from the C6 dye. This is surprising because both dyes, bimeane and C6, are present in the film and the PL spectrum exhibits the two corresponding peaks. The reason for the different spectra is still unknown. The non-uniformity of the film as a cause was ruled out because the same characteristic could be observed when we spun-on a PVK-film from a solution containing both dyes and thus forming a film with a homogeneous distribution of bimeane and C6.

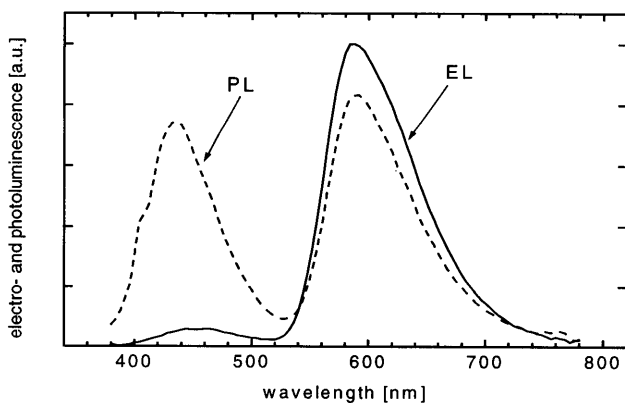


Figure 6: PL and EL spectra of a PVK-film containing bimeane with C6 diffused into it. Nearly all the EL emission is coming from the C6. The PL spectrum shows both of the peaks, the bimeane and the C6 peak.

This fortuitous fact enables us to fabricate a 3-color device with only two diffusion processes. After spin-coating a solution containing PVK, PBD and bimeane onto an ITO coated substrate, we diffused first C6 and then Nile red into the film before we evaporated the cathode material. The EL spectra of the RGB device is shown in figure 7. The external quantum efficiency for the blue device was 0.1%, for the green 0.45% and the red 0.13%. These efficiencies are not much lower than those of the devices which were fabricated with all the dyes already contained in the solution. This makes the dye diffusion technique a promising method for patterning polymer films for OLEDs.

## CONCLUSION

We demonstrated a new patterning technique to tune the color of organic light-emitting devices. Using this method, we fabricated an integrated three color OLED. Initial work was done to characterize and optimize this method. The effect of annealing was studied. The result shows that an annealing process enhances dye diffusion and flattens the dye concentration profile within the film. Furthermore, the EL spectrum of PVK-films containing two dyes only occurs from the dye with the lower emission energy.

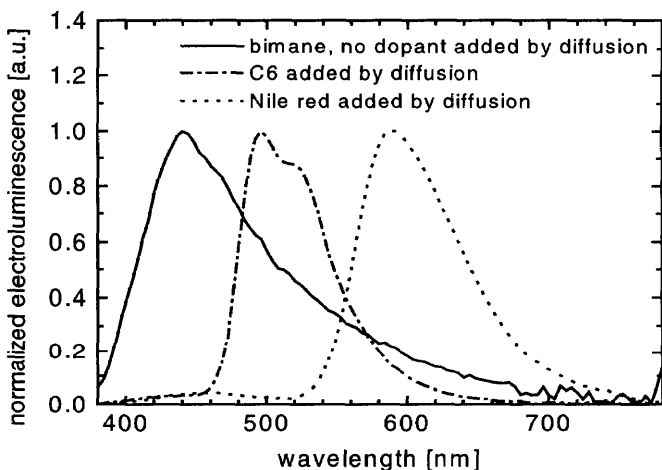


Figure 7: EL spectra of integrated blue, green and red device <sup>5</sup>.

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