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A Thermal Transfer Approach for the Doping of Organic LEDs

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ABSTRACT

An effective process of performing controllable doping of polymer films in organic light-emitting devices is reported. In this approach, a film to be doped is brought into direct contact with a dye-dispersed polymer donor film to permit direct dye-diffusion thermal transfer. Theoretical and experimental studies indicate that this doping process can be modeled by Fick's diffusion theory and that a desired dopant distribution from shallow to flat profiles may be obtained in a single transfer step by adjusting the diffusion conditions. Doped-polymer light-emitting devices made by this process and the conventional blending process exhibited same device characteristics. Along with patterned color donor plates, we demonstrated multicolor OLEDs of arbitrary patterns over large areas with a single thermal transfer step.

Keywords: Organic Light Emitting Diodes; OLEDs; OLED Displays; Dye-Diffusion Thermal Transfer; Color Integration

1. INTRODUCTION

Organic light emitting devices (OLEDs) based on molecular organic materials or on polymer materials have been extensively studied because of their various merits suitable for flat panel display applications.[1,2] The capability of solution processing of polymers leads to manufacturing advantage for large-area coating. However, it is found difficult to integrate multicolor polymer materials or devices for full-color displays by conventional coating and sequential photolithography steps.[3,4] To resolve this issue, printing approaches have been aggressively pursued recently. For instance, ink-jet printing has been used to deposit directly patterned polymers or to introduce color-tuning dye patterns into/onto continuous buffer polymer layers.[5-8] However, ink-jet printing is in general a sequential process and might have a limit for substrate throughput.[9] Alternatively, a large-area thermal transfer process was recently proposed for color patterning of polymer layers in OLEDs.[9] Owing to a transfer mask inserted between the donor and the receiver films, this process involves several mechanisms: the sublimation of dye molecules from the heavily dispersed polymer film, travel of dye molecules to the

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surface of the receiver film, and the diffusion of dye molecules into the receiver film. Interaction of all these mechanisms has led to difficulty in controlling profiles of dye concentration and to complication of processing steps. For instance, long periods of annealing may be required to redistribute dye dopants in the receiver film after the transfer process.

In this paper, we report an effective transfer process for performing controllable doping of polymer films in OLEDs. In this process, the polymer receiver film is placed in direct contact with the dye-dispersed polymer donor film to permit direct dye-diffusion thermal transfer (Fig. 1). We performed theoretical and experimental studies of this doping process and show that it can be modeled by Fick's diffusion theory under impermeable film-substrate boundary conditions. We have therefore named this process as finite-source dye-diffusion thermal transfer (FS-D2T2). Using this process, we demonstrated doped-polymer OLEDs with device characteristics same as those made from the conventional blending process, and demonstrated multicolor OLEDs of arbitrary patterns using only a single thermal transfer step.

2. EXPERIMENTAL RESULTS

2.1. Finite-Source Dye-Diffusion Thermal Transfer (FS-D2T2)

We first explain the concept of finite-source dye-diffusion thermal transfer (FS-D2T2). The arrangement for performing FS-D2T2 is shown in Fig. 1. A pressure (typically ~30 g/cm^2) is applied on top of the receiver plate to ensure intimate contact with the source film. Fig. 2 show the resulting layer geometry, in which the initial distribution of dye concentration is represented by a step from C_0 in the source to zero in the receiver. If the dye diffusion at an elevated temperature obeys Fick's diffusion theory, under the impermeable boundary conditions at two film-substrate interfaces, the spatial distribution of dye concentration $C(x,t)$ at time t is given by an infinite sum of error functions:[10]

$$C(x,t) = \frac{1}{2}C_0 \sum_{n=0}^{\infty} \left\{ erf\left(\frac{-x - 2n(d_S + d_R)}{2\sqrt{Dt}} \right) + erf\left(\frac{x + 2d_S + 2n(d_S + d_R)}{2\sqrt{Dt}} \right) \right\}$$
$$+ \frac{1}{2}C_0 \sum_{n=1}^{\infty} \left\{ erf\left(\frac{-x + 2n(d_S + d_R)}{2\sqrt{Dt}} \right) + erf\left(\frac{x + 2d_S - 2n(d_S + d_R)}{2\sqrt{Dt}} \right) \right\}$$

, where x represents the space variable. d_S and d_R are the thickness' of the source and the receiver layers, and D denotes the diffusion coefficient of dyes in the matrix. Here for mathematical and analytical simplicity, we have assumed that the source and the receiver matrices are of the same composition and that the temperature and D are constant throughout both layers. (x,t) vs. normalized diffusion length ($\sqrt{Dt/d_R^2}$) is shown in Fig. 2, which reveals that dyes originally in the source layer basically undergo a redistribution process. By choosing appropriate conditions (i.e. varying diffusion length), dye profiles into the receiver layer may be controlled from a shallow profile to a flat profile, a feature maybe useful in different designs

of devices. Since dye redistribution is a self-limiting process, there would be no concern of over-doping or consequent concentration quenching even for elongated diffusion time as long as C_0 is chosen to match the desired final concentration in the receiver.
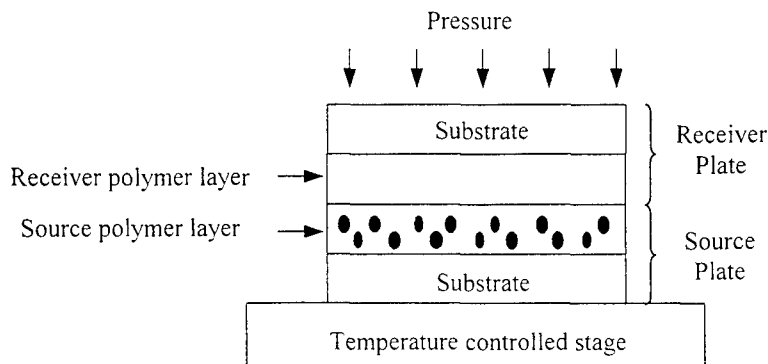

Fig. 1: Experimental arrangement for finite-source dye-diffusion thermal transfer.
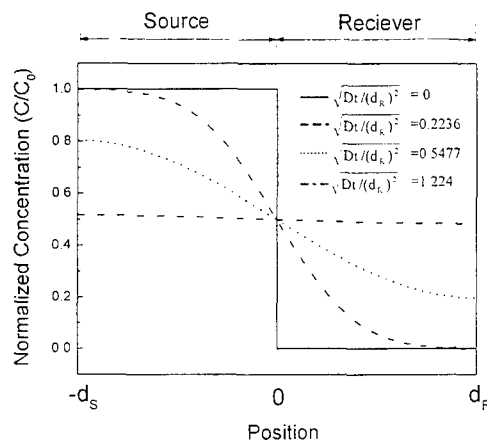

Fig. 2: Calculated normalized profiles of dye concentration $C(x, t)/C_0$ vs. normalized diffusion length $\sqrt{Dt / d_R^2}$.

2.2. Experiment Results of Finite-Source Dye-Diffusion Thermal Transfer

To verify these concepts, we performed a series of dye-diffusion thermal transfer experiments based on the deep-blue-emitting polymer poly(N-vinylcarbazole) (PVK),shown in Fig. 3. Due to same reasons stated previously, results presented in this paper are for source and receiver layers of this same matrix composition and the same thickness (~1000 Å), except that the source is initially charged with an additional small amount of dyes. Dyes such as perylene (blue), coumarin 6 (C_6, green) and nile red (orange-red) were used in this study, shown in Fig. 3. Films were coated onto quartz substrates for photoluminescence (PL) and absorption measurements on the SLM-AMINCO AB2 luminescence spectrometer and the

Shimadzu UV-1601PC spectrophotometer, respectively. All the thermal transfer experiments and characterization were performed in air.

Fig. 4 show the growth with time of absorption spectra associated with the dye (C_6) diffused into the receiver layer for diffusion at 200 °C. Since the dye absorbance is proportional to the total amount of dyes inside the film (i.e. Beer's Law), the ratio of the amount of dyes diffusing into the receiver (M) to the initial amount of dyes in the source layer (M_0) can be obtained by dividing the associated absorbance peak intensities. Results of M/M_0 for different diffusion conditions are plotted in Fig. 5, in which the least-square fitting of experimental data from Fick's theory is also presented. Using diffusion coefficient D as the only parameter, the fitting reasonably follows the trend of experimental data. Fig.6 shows the extracted diffusion coefficients of the dye at different diffusion temperatures. The extracted diffusion coefficient D is strongly dependent on the temperature and ranges from 10^{-12} to 10^{-17} cm^2/sec within the temperature range (130 °C - 240°C) used, indicating that it is a highly thermally activated process. As can be seen in Fig.6, the temperature dependence of D shows different behaviors below and above the glass transition temperature (T_g) of PVK (~210°C). A rapid rise of D with temperature is observed around T_g, consistent with the rapid transfer of dyes around T_g. These diffusion characteristics are consistent with those found in previous study of dye diffusion in glassy polymer matrices around T_g.[11, 12] Fig. 7 shows the PL spectra of the receiver layer vs. diffusion time at 220 °C for C_6. It can be seen that, within a few minutes (or tens of seconds at even higher diffusion temperature), the diffused dye profile is deep enough to completely quench the luminescence from the host, consistent with the results of absorption experiments. The final PL intensity of the diffused film is basically the same as that of the dye-blended films with a similar dye concentration, showing no indication of degradation. All these results show that the FS-D2T2 is a relatively effective technique for doping the organic films.
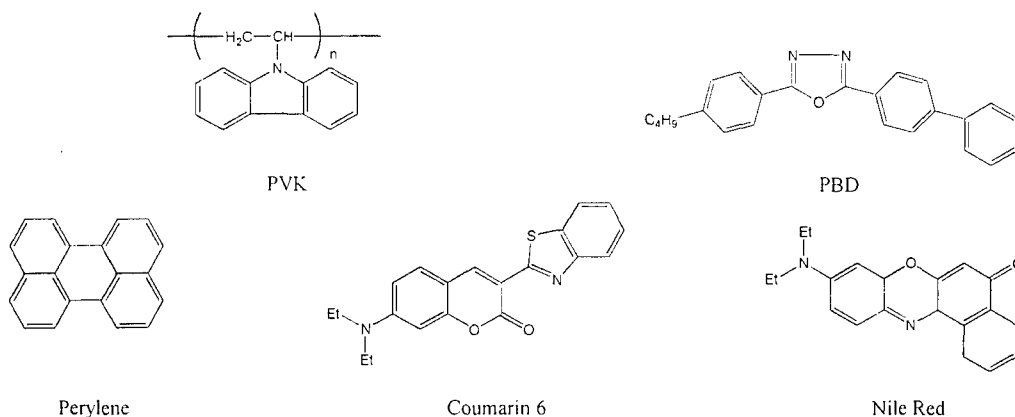

Fig. 3: Molecular structure of the organic compounds used in the present study. PVK is hole transport polymer. PBD is electron transport molecule. The perylene, coumarin 6, nile red are blue, green, orange-red dopants respectively.
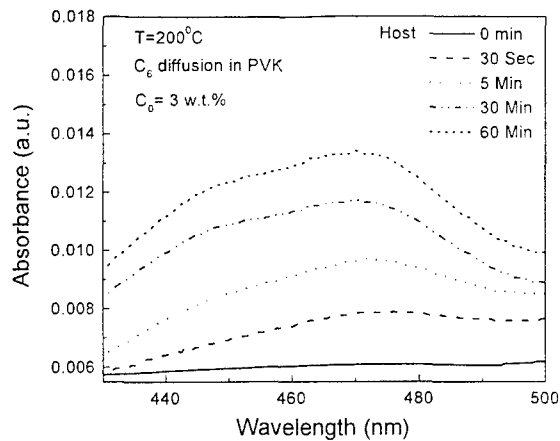
Fig. 4: Absorption spectra of C_6-diffused PVK films vs. diffusion time at T=200°C
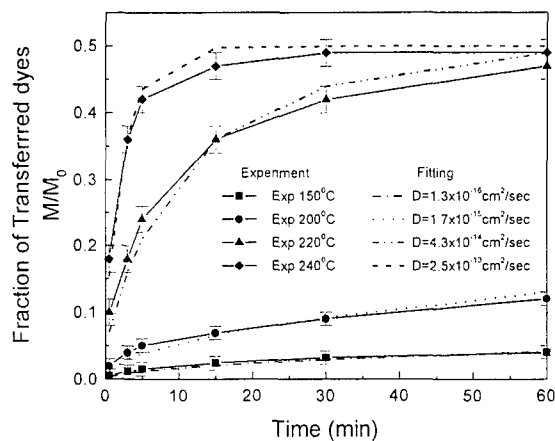

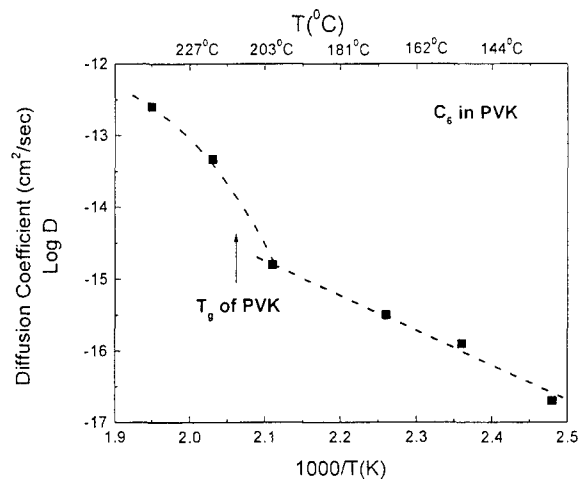Fig. 5: Ratio of dyes transferred for different diffusion condition.

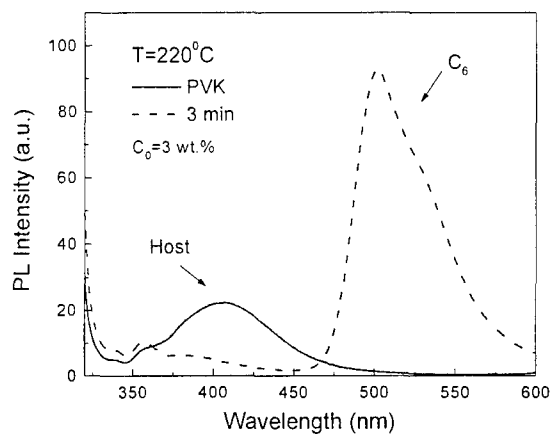Fig. 6: Diffusion coefficients of C_6 in polymer PVK at different diffusion temperatures.

Fig. 7:Photoluminescence spectra of the receiver film vs. diffusion time.

2.3. Color tuning of OLED by Finite-Source Dye Diffusion Thermal Transfer

Since PVK is only hole-transport, in preparing films for OLED fabrication, ~25 wt.% of electron-transport molecules 2-(4-biphenyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD), shown in Fig 3, is added to the PVK matrix by blending before spin coating. To investigate the effect of this doping process on OLED characteristics, we compared devices using

the dye-diffused films and "control" devices using conventional dye-blended films as the active emission layers. Both have the device structure of glass/ITO (indium tin oxide) anode/hole-injection layer (~300 Å)/active emission layer (~1000 Å)/Mg:Ag (10:1) cathode/Ag protection layer. The conducting polymer polyethylene dioxythiophene /polystyrene sulphonate (PEDT/PSS, Bayer Corp.) was used as the hole-injection layer. All the device processing were carried out in air. Fig. 8 compares the device characteristics of OLEDs using C_6-diffused and C_6-blended PVK:PBD films with similar dye concentrations. Within our experimental variation, both types of devices gave nearly the same characteristics with an external quantum efficiency of ~0.8%. By using different dyes in the source polymer layer, the colors of OLEDs made from the FS-D2T2 process can be tuned from blue to orange-red. Fig. 9 show the EL spectra of OLEDs doped with perylene, C_6 & nile red as the blue, green and orange-red emission dopants, all with similar device characteristics. Brightness over several thousand cd/m^2 can be obtained in these devices.
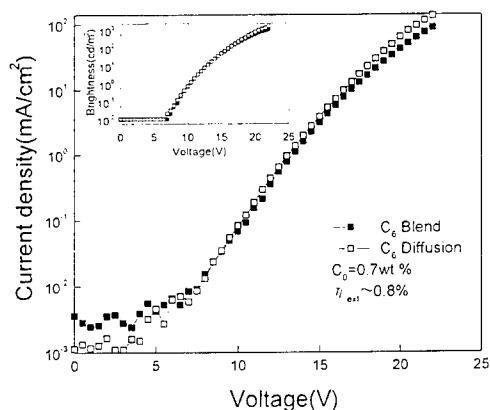

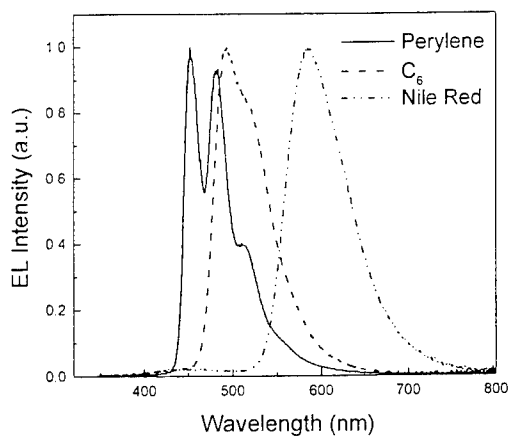Fig. 8: Comparison of device characteristics of OLEDs using C_6-diffused films and C_6-blended films.

Fig. 9: EL spectra of OLEDs doped with perylene (blue), C_6 (green) and nile red(orange-red).

2.4. Color Integration

By using a source plate containing color patterns. FS-D2T2 could be used to accomplish color integration for OLED devices or displays on a substrate in a single thermal transfer step, as shown in Fig. 10. The source plate containing multicolor dye-dispersed polymer patterns may be fabricated with any patterning technique, ranging from photolithography to printing, as long as the fabrication processing does not degrade the emission characteristics of dyes to be transferred. Screen-printing, an additive and high-throughput patterning technique suitable for large areas, has been used as a demonstration to make the color source plates. The details will be discussed in another paper of this proceeding.[13]
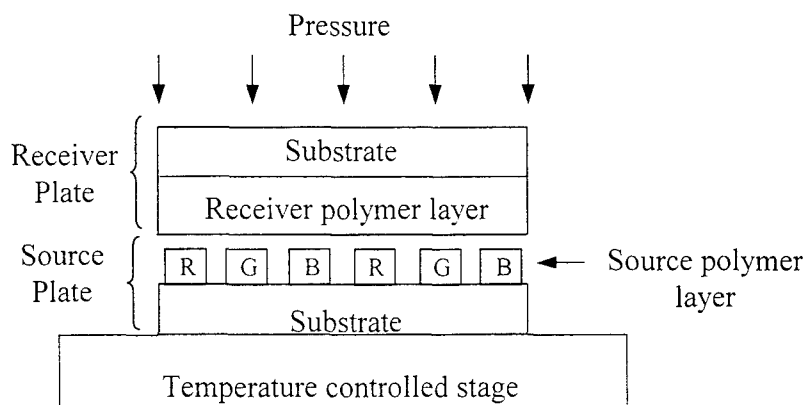

Fig. 10: Color integration of OLED by FS-D2T2 and color source plate.

3. CONCLUSION

We have introduced finite-source dye-diffusion thermal transfer as an effective method of performing controllable doping of polymer films in OLEDs. We show that this doping process can be modeled by Fick's diffusion theory under finite boundary conditions. We successfully applied this doping technique to color tuning of OLEDs without degrading device performance. Along with patterned color source plates, we can fabricate multicolor OLEDs of arbitrary patterns over large areas with a single thermal transfer step.

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