

Dual-color polymer light-emitting pixels processed by hybrid inkjet printing

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A hybrid inkjet printing (HIJP) technology, which combines a pin-hole free polymer buffer layer and an inkjet printed polymer layer, allows the patterning of high quality polymer light-emitting devices. In this letter, we present a successful demonstration of controllable patterning of dual-color polymer light-emitting pixels using this HIJP technique. In this demonstration, the polymer buffer layer is a wide band gap, blue emitting semiconducting polymer prepared by the spin-casting technique. The inkjet printed layer is a red-orange semiconducting polymer which was printed onto the buffer layer. When a proper solvent was selected, the printed polymer diffused into the buffer layer and efficient energy transfer took place generating a red-orange photoluminescence and electroluminescence from the inkjet printed sites. Based on this principle, blue and orange-red dual-color polymer light-emitting pixels were fabricated on the same substrate. The use of this concept represents an entirely new technology for fabricating polymer multicolor displays with high-resolution, lateral patterning capability. © 1998 American Institute of Physics. [S0003-6951(98)03144-1]

Conjugated polymers are a novel class of semiconducting materials which combine the electronic and optical properties of semiconductors and the processability of conventional polymers.¹ Recently, inkjet printing (IJP) technology has attracted considerable attention due to its low cost, large area processing, and multicolor addressable capabilities.²⁻⁴ The intrinsic pin-hole and uneven surface roughness problems of the IJP technology,² which significantly limits its application, have been resolved by a hybrid inkjet printing technology (HIJP).^{3,4} This HIJP technology combines a pin-hole free polymer buffer layer and a regular inkjet printed polymer layer. Below is a brief description of the unique characteristics of the HIJP technology:

- (1) The buffer layer is a pin-hole free layer which can seal the pin-holes produced by the inkjet printed layer.
- (2) The buffer layer is the ink absorbing layer and can effectively "fix" the printed materials when a proper solvent for the ink has been chosen. In addition, this buffer layer effectively planarizes the surface roughness produced by the inkjet printed dots.
- (3) Due to the small diameter of the jet nozzle, and the high molecular weight of the conjugated polymer, IJP is ideal for printing small amounts of materials. Therefore, this technology is ideal for the deposition of dopants. Multicolor emission can be realized from an efficient energy transfer, when the buffer layer is a wide band gap semiconducting polymer layer, and the inkjet printed materials are the dopants with smaller band gaps than the buffer layer.

In this manuscript, we present the successful demonstration of dual-color polymer light-emitting pixels patterned by the HIJP technology. In this demonstration, the buffer layer polymer is a wide band gap, water soluble blue emitting polymer, poly[2,5-bis[2-(N,N,N-triethylammonium)ethoxy]-1,4-phenylene-alt-1,4-phenylene] dibromide (PPP-NEt₃⁺)⁵ and the inkjet printed material is a red-orange emitting, water soluble polymer poly(5-methoxy-(2-propanoxysulfonide)-1,4-phenylene vinylene) (MPS-PPV).⁶ Blue and orange-red dual color electroluminescence emissions are obtained from light-emitting diodes (LEDs) made of PPP-NEt₃⁺ and MPS-PPV doped PPP-NEt₃⁺ (abbreviated as PPP-NEt₃⁺: MPS-PPV) as the active materials, respectively. The advantages of the HIJP technology can be seen immediately in this example. The blue emitting PPP-NEt₃⁺ layer serves as the pin-hole free buffer layer, and it also serves as the ink absorbing layer into which the MPS-PPV diffuses. Subsequently, the dual-color emission is achieved from the PPP-NEt₃⁺ (blue emission) and from the PPP-NEt₃⁺: MPS-PPV (orange-red emission), respectively.

The details of the device preparation are described below. Due to the nature of the commercially available inkjet printer, MEH-PPV was modified to MPS-PPV a water-soluble compound to meet the ink specifications of the printer. The chemical structure of the water-soluble PPP-NEt₃⁺ and MPS-PPV are shown in Fig. 1. The synthesis and characterization of PPP-NEt₃⁺ has been reported earlier⁵ along with its utilization in layer-by-layer deposited, blue emitting LEDs;⁷ and the synthesis of the water-soluble MPS-PPV will be reported elsewhere.⁶ The device structure of the inkjet printed dual-color polymer LEDs is shown in Fig. 2. Four LEDs were fabricated on one substrate. Two were blue

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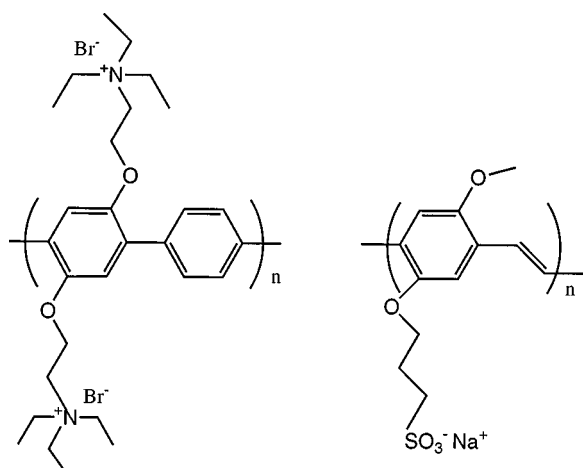


FIG. 1. The chemical structures of water soluble PPP-NEt_3^+ and MPS-PPV.

emission LEDs (devices A and B), and the other two were orange-red emission devices (devices C and D). All four devices were fabricated on a single glass substrate, half coated with indium-tin-oxide (ITO), which served as the anode. A thin layer of conducting polymer, polyaniline, was spin cast onto the ITO as an efficient hole-injection layer.⁸ The PPP-NEt_3^+ solution was prepared in an acidic DI water (pH=4) at 1 wt % concentration, and the MPS-PPV solution was prepared in neutral DI water at 2 wt % concentration. The pin-hole free PPP-NEt_3^+ buffer layer was fabricated by spin casting at a spin speed of 1500 rpm, which yielded a film thickness of approximately 2000 Å as determined by profilometry. This spin-cast thin film was subsequently dried in a vacuum oven at 70 °C for two hours. For the orange-red emission devices (devices C and D), MPS-PPV was printed onto the PPP-NEt_3^+ layer using a commercially available printer (Epson Stylus II) with the capability of handling solid substrates. The spin casting of PPP-NEt_3^+ and the inkjet printing of MPS-PPV was carried out in air. In order to remove the water from the MPS-PPV, the films were further dried inside a vacuum oven at 70 °C for two hours before they were loaded into an evaporator for the deposition of calcium (500 Å) and aluminum (1000 Å) bilayer electrodes. The devices were tested in a nitrogen environment. The current–voltage characteristics were measured using an HP 4145A Semiconductor Parameter Analyzer. The photolumi-

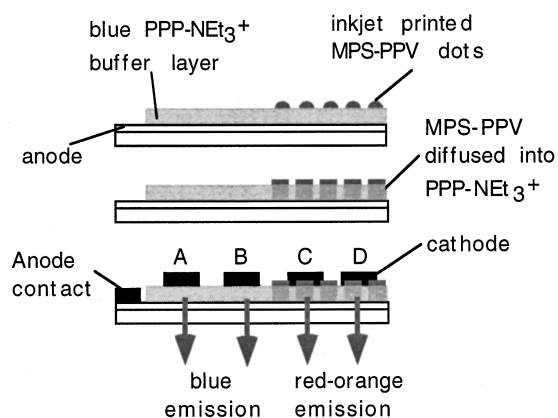


FIG. 2. The device structure of dual-color polymer light-emitting diodes. Devices A and B are blue emitting LEDs with PPP-NEt_3^+ as the active material. Devices C and D are red-orange devices with PPP-NEt_3^+ : MPS-PPV as the active material.

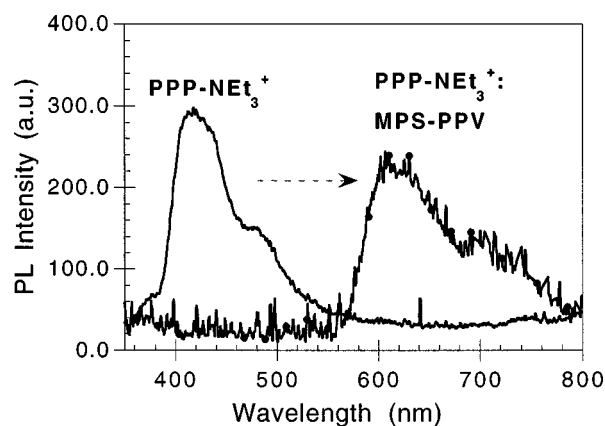


FIG. 3. The PL emission of the PPP-NEt_3^+ and PPP-NEt_3^+ : MPS-PPV. EL spectra are similar. There is no blue emission in the PPP-NEt_3^+ : MPS-PPV blend and this spectrum indicates that the energy has been transferred from PPP-NEt_3^+ to MPS-PPV.

nescence (PL) and electroluminescence (EL) spectra were measured using an Ocean Optics Spectrometer.

The PPP-NEt_3^+ buffer layer plays a critical role in this dual-color device. The PPP-NEt_3^+ is first synthesized as a neutral polymer that is soluble in organic solvents (CHCl_3 , THF) and in acidic water through quaternization of the amine functionality. In a second step, the neutral polymer is subject to treatment with bromoethane to yield the bromide salt of polymer. This form of the polymer has varying neutral water (pH=7) solubility characteristics depending on the number of amine sites quaternized. This particular PPP-NEt_3^+ sample was quaternized such that an aqueous solution of pH=4 was necessary to achieve the desired solubility. This unique property makes PPP-NEt_3^+ an ideal ink absorbing material for the MPS-PPV when neutral DI water is used as the solvent for the MPS-PPV. On the other hand, if PPP-NEt_3^+ were completely soluble in the neutral DI water, then the solvent of MPS-PPV would have smeared the buffer layer. Hence, the concepts of ink absorbing (or dopant diffusion) and energy transfer effect is successfully demonstrated in this PPP-NEt_3^+ : MPS-PPV system. The solvent of the inkjet printed MPS-PPV slightly dissolves the PPP-NEt_3^+ layer and allows the MPS-PPV to diffuse into the PPP-NEt_3^+ layer. The (PL) spectrum of the PPP-NEt_3^+ : MPS-PPV blend is identical to the MPS-PPV PL spectrum, and this is a direct evidence of the dopant diffusion and energy transfer effects discussed earlier. The PL spectra of PPP-NEt_3^+ and PPP-NEt_3^+ : MPS-PPV are shown in Fig. 3. The current–voltage curves of the PPP-NEt_3^+ and PPP-NEt_3^+ : MPS-PPV devices are shown in Fig. 4. The slightly high operating voltage for both types of LEDs was due to the thick PPP-NEt_3^+ layer. The PPP-NEt_3^+ : MPS-PPV system has a much lower turn-on and operating voltage than that of the PPP-NEt_3^+ system. This may be due to the fact that MPS-PPV has a smaller band gap, and subsequently easier carrier injection and carrier transport than that of the PPP-NEt_3^+ system. The brightness of both devices is however not very high. For the blue emission, the peak brightness at 33 V was about 10 cd/m^2 . For the red emission, the peak brightness at 22 V was about 7 cd/m^2 . The reason for such low brightness is probably due to the fact the devices were fabricated in air and photochemical oxidation reaction could have damaged the polymer. In addition, the low efficiency and brightness of the device is

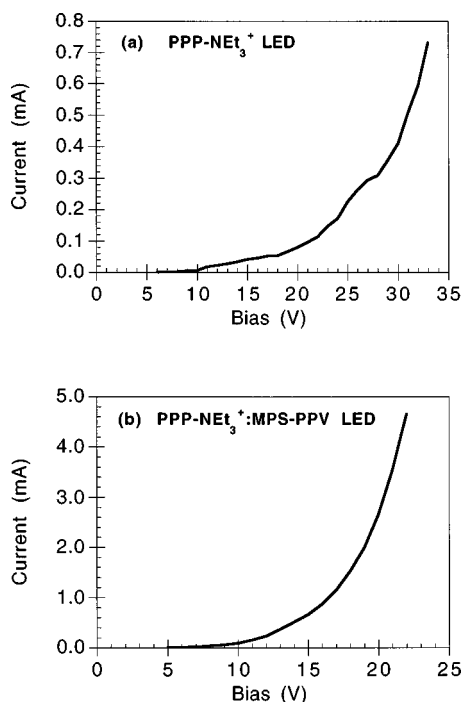


FIG. 4. The current-voltage curves of the two type devices: ITO/PANI/PPP-NEt₃⁺/Ca and ITO/PANI/PPP-NEt₃⁺:MPS-PPV/Ca. The device area is about 0.1 cm².

probably also due to the usage of DI water and acidic DI water as the solvents for the MPS-PPV and PPP-NEt₃⁺, respectively. For the future practical applications such as multicolor displays, special inkjet printers, which are inert to organic solvents, are required to process regular luminescent polymers.

To further illustrate the importance of the dopant diffusion process, we also prepared a bilayer device consisting of a spin-coated PVK layer and an inkjet printed MPS-PPV layer. The device fabrication is similar to the process described above. The PVK layer is not water soluble and there is no diffusion of MPS-PPV into the PVK layer. The inkjet printed MPS-PPV forms isolated dots on top of the PVK layer and the "film surface" is rather irregular. The actual thickness of the inkjet printed MPS-PPV layer was very difficult to determine by a thickness profilometer. The PL and EL spectra of this bilayer structure device consisted mainly of the spectrum from the PVK layer with a small signal from the MPS-PPV dots. Based on the morphology of the MPS-PPV on PVK and the purple color EL emission, we are confident to conclude that there is no significant energy transfer from the PVK to the MPS-PPV due to limited diffusion of the MPS-PPV at the interface of this bilayer system. Finally, a Scotch tape lift-off experiment was also conducted to confirm the diffusion theory. Two pieces of Scotch tape were applied to the MPS-PPV/PPP-NEt₃⁺ and MPS-PPV/PVK systems, respectively. The inkjet printed MPS-PPV dots could not be lifted off from the PPP-NEt₃⁺ surface by the Scotch tape, whereas there was about 30%–40% lift off of the inkjet printed MPS-PPV dots from the PVK system. This simple test demonstrates that the diffusion process significantly enhances the adhesion properties of MPS-PPV to the PPP-NEt₃⁺ layer.

These examples indicate that the choice of the solvent used for the IJP material (the dopant) is critically important

in achieving the dopant diffusion and energy transfer effect. These two examples also illustrate the advantage of the HIJP technology in controlling the local morphology between the dopant and the buffer layer (the host). The details of the diffusion process, the local morphology between the buffer layer and the solvent, and the potential of forming high surface area contact between the dopant polymer and the host polymer are still under investigation. Furthermore, we do not completely rule out devices comprising a bilayer structure, such as the PVK/MPS-PPV system. A different emission will probably be observed if the MPS-PPV layer that is printed above the buffer layer reaches a critical thickness with the EL emission, perhaps occurring at the interface of this bilayer structure. However, it is difficult to demonstrate this approach using the existing commercial inkjet printer, since only small amounts of the polymer can be printed.

In summary, we have successfully demonstrated the patterning of dual-color polymer LEDs by the hybrid inkjet printing technology (HIJP). A blue emitting PPP-NEt₃⁺, which is soluble in acidic water, is used as the buffer layer material deposited via spin casting. A water-soluble MPS-PPV was used as the inkjet printed material, and was printed on top of the PPP-NEt₃⁺ layer. The solvent (DI water) used for the MPS-PPV ink partially dissolved the PPP-NEt₃⁺ layer below permitting the MPS-PPV polymer to diffuse into the PPP-NEt₃⁺ layer. Energy transfer from the PPP-NEt₃⁺ to the MPS-PPV has been confirmed in the PPP-NEt₃⁺:MPS-PPV system through the PL and EL emissions. In addition to the fabrication of multicolor LEDs, this HIJP technology provides the local control of polymer morphology, allows the formation of polymer blends in any desired areas, and allows the control of desired physical properties such as conductivity, photoluminescence, and other interesting physical properties. The diffusion process of the dopant into the host polymer, the morphology, the possible formation of high surface area contact between the dopant and the host, and the control of the doping profile are still under investigation.

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¹ *Handbook of Conducting Polymers*, 2nd ed. edited by T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds (Marcel Dekker, New York, 1998).

² T. R. Hebner, C. C. Wu, D. Marcy, M. L. Lu, and J. Sturm, *Appl. Phys. Lett.* **72**, 519 (1998).

³ (a) Y. Yang, US Patents Pending, Serial No. 60/062,294 and 60/072 709; (b) B. Service, *Science* **279**, 1135 (1998); (c) Y. Yang and J. Bharathan, *Proc. SPIE* **3279**, 78 (1998).

⁴ J. Bharathan and Y. Yang, *Appl. Phys. Lett.* **21**, 2660 (1998).

⁵ P. B. Balanda, Ph.D. Dissertation, University of Florida, 1997.

⁶ R. Helgeson and F. Wudl (unpublished).

⁷ J. W. Baur, S. Kim, P. B. Balanda, J. R. Reynolds, and M. F. Rubner, *Adv. Magn. Reson.* (to be published).

⁸ Y. Yang and A. J. Heeger, *Appl. Phys. Lett.* **64**, 1245 (1994).