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## Multicolor Organic Light-Emitting Diodes Processed by Hybrid Inkjet Printing\*\*

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Organic light-emitting diodes (OLEDs) represent a novel approach for fabricating high quality, multicolor, electroluminescent displays.<sup>[1]</sup> Traditionally the fabrication of OLEDs has been achieved by the thermal sublimation of organic materials in an ultra-high vacuum environment onto transparent substrates, usually glass, coated with indium tin oxide (ITO). This is a rather time consuming process and the patterning of fine multicolor pixels is also quite complicated. The application of inkjet printing (IJP) technology to polymer electroluminescent devices has attracted considerable attention due to its low cost, large area processing, and multicolor addressing capabilities.<sup>[2-6]</sup> However, the IJP technology is afflicted with some serious problems such as uneven surface roughness and the intrinsic pinhole nature of the deposited material, which impede such applications.<sup>[2]</sup> Recently, these drawbacks have been overcome by hybrid inkjet printing technology (HIJP).<sup>[3-6]</sup> HIJP technology combines a pinhole-free polymer buffer layer and a regular inkjet-printed polymer or organic layer

which allows the patterning of high quality polymer light-emitting devices. On proper selection of solvents the buffer layer can serve as an ink-absorbing layer and effectively fix the printed materials. The small diameter of the inkjet nozzles permits printing of minute amounts of materials such as dopants to give rise to displays with high resolution. Multicolor emission can be realized from an efficient energy transfer from an appropriate buffer layer (a semiconducting polymer layer) with a wide bandgap to the inkjet-printed materials (dopants) with smaller bandgaps than the buffer layer. Alternatively, the buffer layer can be a continuous polymer layer insoluble in the solvents used by the IJP droplets. In this case it seals the pinholes and can also function as the hole transport layer (HTL). The later case is ideal for the fabrication of organic LEDs since the most efficient OLEDs comprise a bilayer structure of a HTL and an emissive layer.<sup>[7]</sup>

In this communication we present a successful demonstration of controllable patterning of red-green-blue (R-G-B) multicolor, organic, light-emitting pixels using this HIJP technique. In this demonstration the polymer buffer layer used is the blue-emission, semiconducting polymer, poly-9-vinylcarbazole (PVK), prepared by the spin-casting technique. The inkjet-printed dopants are tris(4-methyl-8-quinolinolato)Al(III) (Almq<sub>3</sub>)<sup>[7]</sup> and DCM (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran) which were inkjet-printed on the PVK buffer layer. Based on this principle, multicolor organic LEDs comprising bilayer structures of PVK/DCM (orange-red-emission) and PVK/Almq<sub>3</sub> (green-blue-emission) were fabricated with the blue-emission PVK buffer layer serving as the hole-transport layer.

The details of the device preparation are given in the experimental section. Due to the inability of commercially available inkjet printers to resist the corrosive action of regular solvents, methanol was chosen as the solvent for DCM and Almq<sub>3</sub>, with each dopant deposited separately. The device structure of the inkjet-printed multicolor organic LEDs is shown in Figure 1. Each substrate consisted of four LEDs, two of these four LEDs were blue-emission LEDs (devices A and B in Fig. 1) with PVK as the active material. The remaining two were either orange-red or green emitting LEDs (devices C and D in the same figure) with the emission obtained from the PVK/DCM or PVK/Almq<sub>3</sub> bilayer structures respectively. Hence, in order to demonstrate R-G-B multicolor LEDs, two sets of devices were fabricated. One set of LEDs demonstrated red and blue emission, whereas the other set demonstrated green and blue emission. Glass substrates measuring 15 mm × 15 mm and half-coated with ITO were used. ITO served as the anode and the pixel size of our OLEDs was about 2 mm × 6 mm. A thin layer of conducting polymer, 3,4-polyethylenedioxythiophene-polystyrenesulfonate (PEDOT), was spin-cast onto the ITO for efficient hole injection.<sup>[8]</sup> PVK was chosen as the buffer layer because of its insolubility in methanol. Hence a well-defined bilayer

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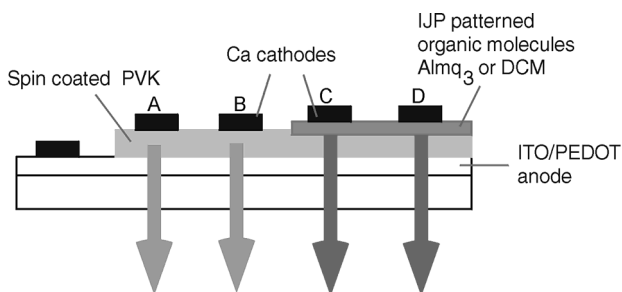


Fig. 1. The device structure of multicolor organic light-emitting diodes processed by HIJP technology. Devices A and B are blue-emission LEDs with PVK as the active material. Devices C and D are red-emission devices with DCM as the active material or green-emission devices when  $\text{Almq}_3$  is used as the emission material.

structure can be obtained by using this layer. This process is ideal for the fabrication of organic LEDs since efficient OLEDs require a bilayer structure. Generally, a hole-transport layer and an electron-transport layer, which also functions as the emissive layer (e.g. an  $\text{Almq}_3$  layer), are used for this purpose.

Figures 2a and b show the pictures of the  $\text{Almq}_3$ -based LEDs fabricated by the thermal deposition process and by the HIJP process respectively. These two pictures were taken under identical conditions of exposure and the results qualitatively reflect the difference in the emission intensities between these two devices. The device fabricated by thermal sublimation shows more uniform emission than the inkjet-printed device. The thin dark lines seen crossing devices fabricated by HIJP are caused by some clogged nozzles in the printer head, which resulted in no material being printed along these lines. This is a common problem afflicting inkjet printers and hence demonstrates the importance of the buffer layer. Without the buffer layer it would be virtually impossible to make good devices due to the unavoidable presence of pinholes that are associated with the IJP technique. The current-voltage ( $I$ - $V$ ) and light-voltage curves ( $L$ - $V$ ) for the PVK/ $\text{Almq}_3$  bilayer LEDs fabricated by HIJP are shown in Figure 3a, and the photoluminescence (PL) and electroluminescence (EL) emission spectra are shown in Figure 3b. The device turned on at around 8 V and the external quantum efficiency was about 0.05%. On the other hand, the devices obtained by the thermal sublimation process were superior to their inkjet-printed counterparts. The device efficiency was about 10 times higher (0.5%) with a much better device stability. One of the reasons for the low efficiency and short lifetime of the LEDs fabricated using the HIJP technology could be due to the fact that since the devices were fabricated in air, significant device degradation could have occurred due to the presence of residual moisture and oxygen. Another possibility for the faster decay of the inkjet-printed devices is the difference in the morphology of  $\text{Almq}_3$ ; the thermal sublimation film is much more uniform than the inkjet-printed film. The PL and EL emission spectra from the devices with the inkjet-printed  $\text{Almq}_3$  are identical with the spectrum obtained from an  $\text{Almq}_3$  thin film deposited by

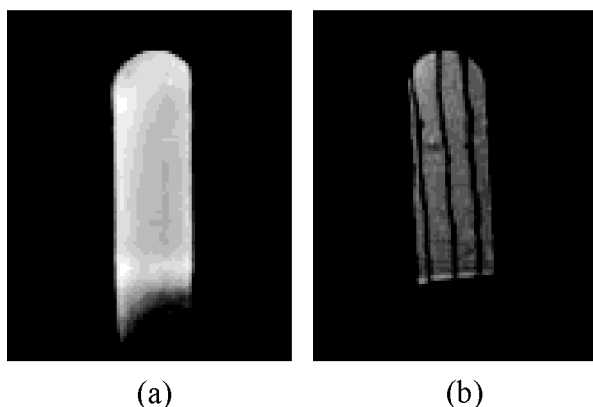


Fig. 2. Color pictures of an OLED with  $\text{Almq}_3$  as the emission material. a)  $\text{Almq}_3$  processed by the thermal sublimation process. b)  $\text{Almq}_3$  processed by inkjet printing.

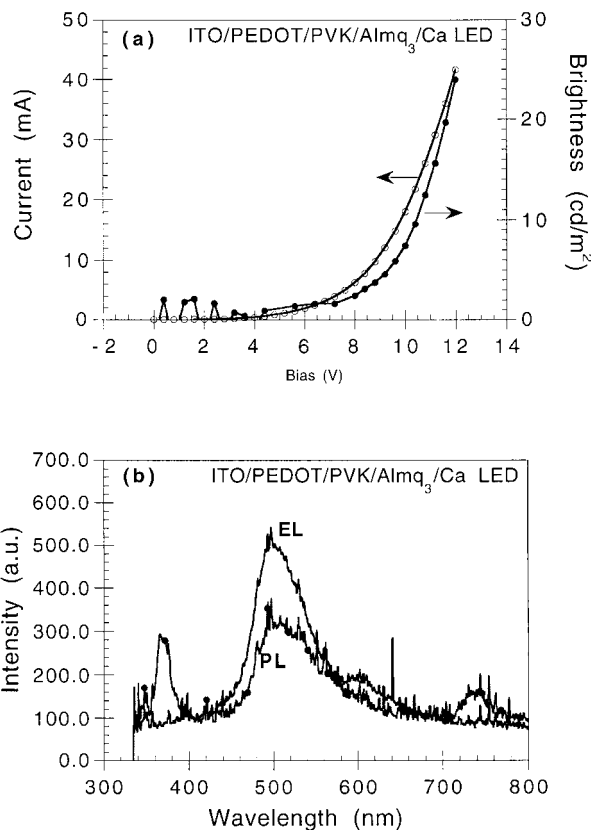


Fig. 3. a) The current-voltage and light-voltage ( $I$ - $V$  and  $L$ - $V$ ) curves for the ITO/PEDOT/PVK/ $\text{Almq}_3$ /Ca LED. b) EL and PL emission spectra for the same device.

thermal sublimation.<sup>[7]</sup> This is an indication that the recombination zone is entirely within the  $\text{Almq}_3$  layer and that the PVK layer functions only as the hole-transport layer. The peaks at 370 nm and 740 nm in the PL spectrum are from the mercury lamp source which was used for the PL measurements.

Figure 4 shows a color picture of red-green-blue LEDs. The red-emission device, with DCM as the emissive materi-

al, has an emission spectrum consistent with regular DCM. Analogous to the PVK/Almq<sub>3</sub> bilayer structure, this is an indication that the recombination zone is entirely within the DCM layer and that PVK functions as the hole-transport layer. The blue devices, with the structure of ITO/PEDOT/PVK/Ca, exhibit a blue-purple color. In this device structure the PVK layer behaves as the active layer for generation of electroluminescence. However, there is a red-emission peak in the spectrum of PVK. This phenomenon has been previously observed and has been attributed to the defects in the PVK film or perhaps to the moisture absorbed during the spin-casting process and the inkjet printing processes, which were carried out in the air.<sup>[9]</sup>

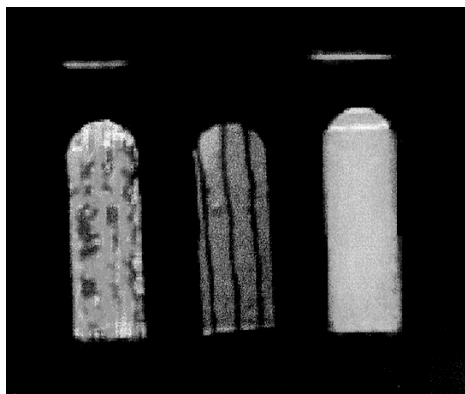


Fig. 4. Color picture of red, green and blue OLEDs. The red and blue LEDs are on the same substrate whereas the green LED was fabricated on a separate substrate.

In addition to the multicolor patterning capability, another important technical issue for the EL display is the patterning of the anode and the cathode. For the organic EL displays, the easiest and lowest cost way of driving the display is the so-called X-Y passive addressable driving scheme, achieved through the patterning of the anode and the cathode materials into mutually perpendicular row and column electrodes. The patterning of ITO is achieved by a regular photolithographic process and the resolution can be very high. On the other hand, the patterning of the cathode is somewhat difficult. The traditional photolithographic process cannot be applied to pattern the cathode since the solvents that process the photoresist would destroy the underlying organic materials. Therefore, the cathode patterning is usually achieved by using stainless steel shadow masks. This technique, however, lacks the required fine resolution. An alternative method could be the use of pre-patterned mushroom shaped photoresist dividers on top of the active organic layers to serve as shadow masks. In this communication, apart from demonstrating the multicolor patterning capability, we have also demonstrated the patterning of a built-in shadow mask through the inkjet printing of inert polymers. Figure 5 shows the picture of patterned metal (cathode) strips using this technique. The printed material is an aqueous solution of poly(vinyl alcohol) (PVA). As can be seen from the figure, the spacing in

between the inkjet-printed lines determines the width of the cathode. The width of the metal strip or the opening of the shadow mask that we have demonstrated is about 1 mm. Eventually the metal line width can be reduced to the resolution of the inkjet printer which has recently been improved to 10  $\mu\text{m}$ .<sup>[10]</sup> The thickness of the final PVA layer is estimated to be more than 1  $\mu\text{m}$ , and it was later removed by a lift-off technology using a weak adhesive tape. In the future, fabrication of shadow masks can be done after the printing of the multicolor organic compounds. This process will significantly simplify the procedure for fabricating organic multicolor, X-Y addressable passive matrix displays.

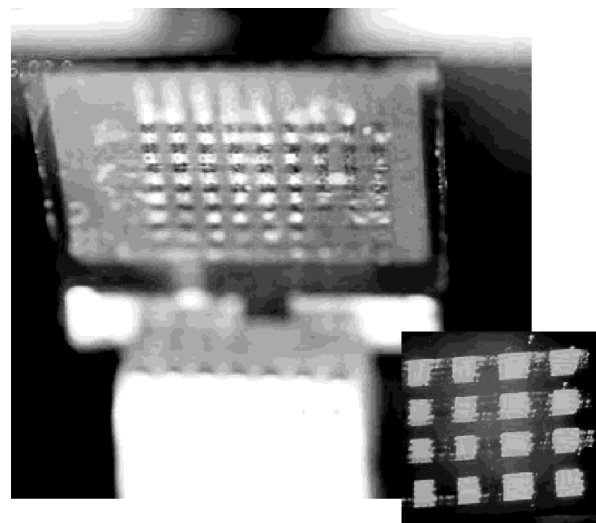


Fig. 5. Column cathode (vertical shining metal strips) patterned by the inkjet-printed built-in shadow mask. Also shown is the row PEDOT anode (horizontal dark strips) printed directly by the IJP technology. The active polymer light-emitting pixels are shown as the inset.

In summary, we have demonstrated red-green-blue (R-G-B) organic LEDs patterned by the hybrid inkjet printing technology. PVK, which has a blue emission, served a multifunction role in this demonstration: (1) it sealed the pinholes in the inkjet-printed layer, (2) it was used as the hole-transport layer for the red- and green-emission LEDs, and (3) it was also the active material for the blue-emission LED. The green emission is achieved by the deposition of the Almq<sub>3</sub> molecules above the PVK buffer layer. Similarly, the red emission is achieved by deposition of the DCM laser dye molecules above the PVK layer. The device performance of the inkjet-printed OLED, however, is still not as good as the OLED prepared by the thermal sublimation process. The device efficiency for the HIJP OLED is about 10 times lower than the regular OLEDs. One factor that could be responsible for this effect is that the R-G-B devices were fabricated in air, thereby causing some environmentally assisted degradation of the device performance. These devices demonstrate the ease of multicolor patterning capability of the hybrid inkjet printing technology. A novel way of patterning the cathode metal strips for the X-Y addressable passive matrix display is also demonstrated by

using the inkjet printing technology. Built-in shadow masks for the cathode deposition can be easily fabricated using this technology. Finally, the fabrication of multicolor organic displays with fine pixels can be achieved if an inkjet printer capable of a better lateral control of the ink materials is available.<sup>[11]</sup>

## Experimental

The pinhole-free PVK buffer layer was fabricated by spin-casting a 2% w/v solution of PVK at 1500 rpm, which yielded a film thickness of approximately 1500 Å as determined by an Alphastep profilometry. The thin films were subsequently dried in a vacuum oven at 70 °C for two hours. For the orange-red-emission devices, DCM was printed onto the PVK layer using a commercially available printer (Epson Stylus II) with the capability of handling solid substrates. For the green-emission device, Almq<sub>3</sub> was inkjet-printed onto the PVK buffer layer using the same printer. The spin-casting of PVK and the inkjet printing process of DCM and Almq<sub>3</sub> was carried out in air. The volatile nature of methanol permits the localized deposition of the Almq<sub>3</sub> and DCM droplets and hence no smearing of these droplets occurred on printing. In order to remove the solvent and moisture from the DCM and Almq<sub>3</sub>, the films were further dried inside a vacuum oven at 70 °C for two hours before being 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 a HP 4145A Semiconductor Parameter Analyzer. The photoluminescence and electroluminescence spectra were measured using an Ocean Optics Spectrometer. For the purpose of comparison, a regular organic LED with the structure ITO/PEDOT/PVK/Almq<sub>3</sub>/Ca was also prepared, with Almq<sub>3</sub> deposited by vacuum sublimation.

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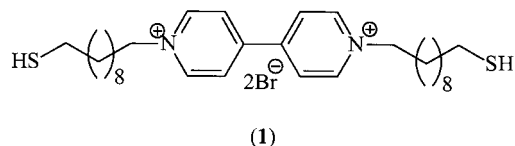
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## Redox-Connected Multilayers of Discrete Gold Particles: A Novel Electroactive Nanomaterial\*\*

By David I. Gittins, Donald Bethell, Richard J. Nichols, and David J. Schiffrin\*

The synthesis of new materials consisting of three dimensional (3D) arrays of nanometer-sized particles is a relatively new but expanding area of research that could find use in the miniaturization of electronic devices, such as the single-electron transistor.<sup>[1,2]</sup> The self-assembly of two dimensional (2D) structures on gold by organosulfur compounds, first reported by Nuzzo and Allara,<sup>[3]</sup> and the synthesis of chemically functionalized nanoparticles by Brust et al.<sup>[4]</sup> have led to significant progress in the drive to develop materials that display single-electron phenomena.<sup>[5–9]</sup> For example, single-electron transfer (coulomb staircase) and bandgap properties in small particles (quantum size effects) have been recently demonstrated by Whetten, Murray, and co-workers.<sup>[9]</sup> A considerable research effort is now directed toward the assembly of discrete metal nanoparticles into (3D) structures.<sup>[10–13]</sup> We now report the synthesis of a viologen dithiol (**1**, see Scheme 1), its use as a redox-active linker between gold nanoparticles in three dimensional structures, and a study of electron transfer processes in such systems.



Scheme 1.

The viologens (1,1'-dialkyl-4,4'-bipyridinium salts, V<sup>2+</sup>) have been widely studied for their redox activity and electrochromic properties.<sup>[14]</sup> Recently Willner et al.<sup>[15]</sup> have constructed gold colloid multilayers using *N,N'*-bis(2-aminoethyl)-4,4'-bipyridinium dibromide, but this viologen does not form tightly packed monolayers on gold surfaces ( $\Gamma = 7.3 \times 10^{-11} \text{ mol cm}^{-2}$  compared with a maximum coverage of  $\Gamma_{\text{max}} = 4.3 \times 10^{-10} \text{ mol cm}^{-2}$ ).<sup>[16]</sup> The viologen derivative prepared in the present work results in thermodynamically stable covalent thiol bonding to gold surfaces, in contrast to the kinetic stability provided by the amine derivative.<sup>[17]</sup> In addition, the inclusion of long alkyl chains gives controlled separation between the gold nanoparticles, which increases stability.<sup>[2]</sup> We report here the assembly of an electroactive material that preserves the integrity and dimensions of the gold nanoparticles used in its construc-

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