High Efficiency AMOLED using Hybrid of Small Molecule and Polymer Materials Patterned by Laser Transfer

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Abstract

Laser-Induced Thermal Imaging (LITI) is a laser addressed patterning process and has unique advantages such as high-resolution patterning with over all position accuracy of the imaged stripes of within 2.5 micrometer and scalability to large-size mother glass. This accuracy is accomplished by real-time error correction and a high-resolution stage control system that includes laser interferometers. Here the new concept of hybrid system that complement the merits of small molecule and polymer to be used as an OLED; our system can realize easy processing of light emitting polymers and high luminance efficiency of small molecules. LITI process enables the stripes to be patlerned with excellent thickness uniformity and multi-stacking of various functional layers without having to use any type of fine metal shadow mask. In this study, we report a full-color hybrid OLED using the multi-layered structure consisting of small molecules and polymers.

Keywords : laser-induced thermal imaging, AMOLED, patterning, hybrid, high efficiency

1. Introduction

The laser induced thermal imaging (LITI) of 3M (St. Paul, MN)[1] has been suggested as a counterpart patterning method against inkjet-printing in order to prepare well-defined full color polymer light emitting diodes (PLED). As a patterning technique for PLED, we have reported 2.2" QCIF and 3.6" QVGA active matrix (AM) PLED last year.[2] The advantageous simple structure of polymer electroluminescent device, however, have some limitations in achieving high efficiency and long lifetime compared to the state-of-the-art small-molecular OLED. In principle, LITI is a solid-to-solid transferring process; the film of light emitting material on the transfer layer is conveyed from the "donor" to a receptor surface. The necessity of suitable layer-to-layer adhesion and film cohesion strength of transferred emitting layer should be involved, which cannot be achieved by merely using the most light emitting polymer (LEP). To overcome this problem, we developed a molecularly doped polymer system[3] to decrease the cohesive forces of the materials for LITI, which gives excellent pattern accuracy. Using the small molecule-polymer hybrid mixtures as emitting layer, small molecular matrix materials are utilized as host systems for energy transfer from fluorescent dye in a light-emitting polymer or dispersed phosphorescent dyes. Hybrid structures with multi-stacked small molecule and polymer hole transport material could provide improved stability irrespective of the solvent compatibility between employed layer structures. Initial studies on the transferring phosphorescent small-molecular emitters to the receptor substrate allows the possibility the laser

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thermal imaging to be applied for the patterning process of highly efficiency small molecular OLED.

2. Experimental

2.1 Laser thermal transfer

An optical imaging system consisting of a CW Nd:YAG laser, acousto-optic modulator, collimating and beam expanding optics, an attenuator, a galvanometer and an f-theta scan lens were utilized. The Nd:YAG laser produced a total power of 8.0 Watts on the image plane. Scanning was accomplished with a high precision GSI galvanometer. The laser was focused to a Gaussian spot with a measured diameter of 300X40 microns at the $1/e^2$ intensity level.

The donor film consists of a transparent base film with several coated layers. The base film is typically a polyester film, for example, a poly (ethylene terephthalate) or poly (ethylene naphthalate). The layer adjacent to the base film is a light-to-heat conversion (LTHC) layer, which converts laser energy in to heat. The transport of material from donor in to receptor is made without significant movement because the donor and receptor are held in intimate contact. The result is the ability to pattern and maintain a uniform, intact thin organic film with a 20-80 nm thickness and 35-100 μm width.

2.2 Materials

Hybrids of small molecule and polymer materials were used for the fabrication of hole-transporting hybrid layers and laser-patternable light-emitting layer. The former is intended to improve the lifetime of conventional small molecule devices and the latter is for a mask less patterning of emission layer. Fabrication of test coupon with 80 μm width striped ITO substrate was as follows; 80 nm-thick PEDOT:PSS (Baytron P TP CH8000, Bayer AG) or polymeric hole injection layer (HIL, 30nm, copolymers of poly (9,9-dioctylfluorene) [PFO] with N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(4,4'-diamine) [TPD])[4] were spun-coated onto the UV-O_3 treated ITO substrates as HIL . Those two HILs can be used as a stacked layer due to their solvent compatibility. For limited cases, α-napthylphenyl-biphenyl (NPB) was evaporated onto the polymer HIL. As a solution-casting hybrid emitting layer, commercial grade of light emitting polymers and wide-band gap hole transporting molecules (supplied by Covion Organic

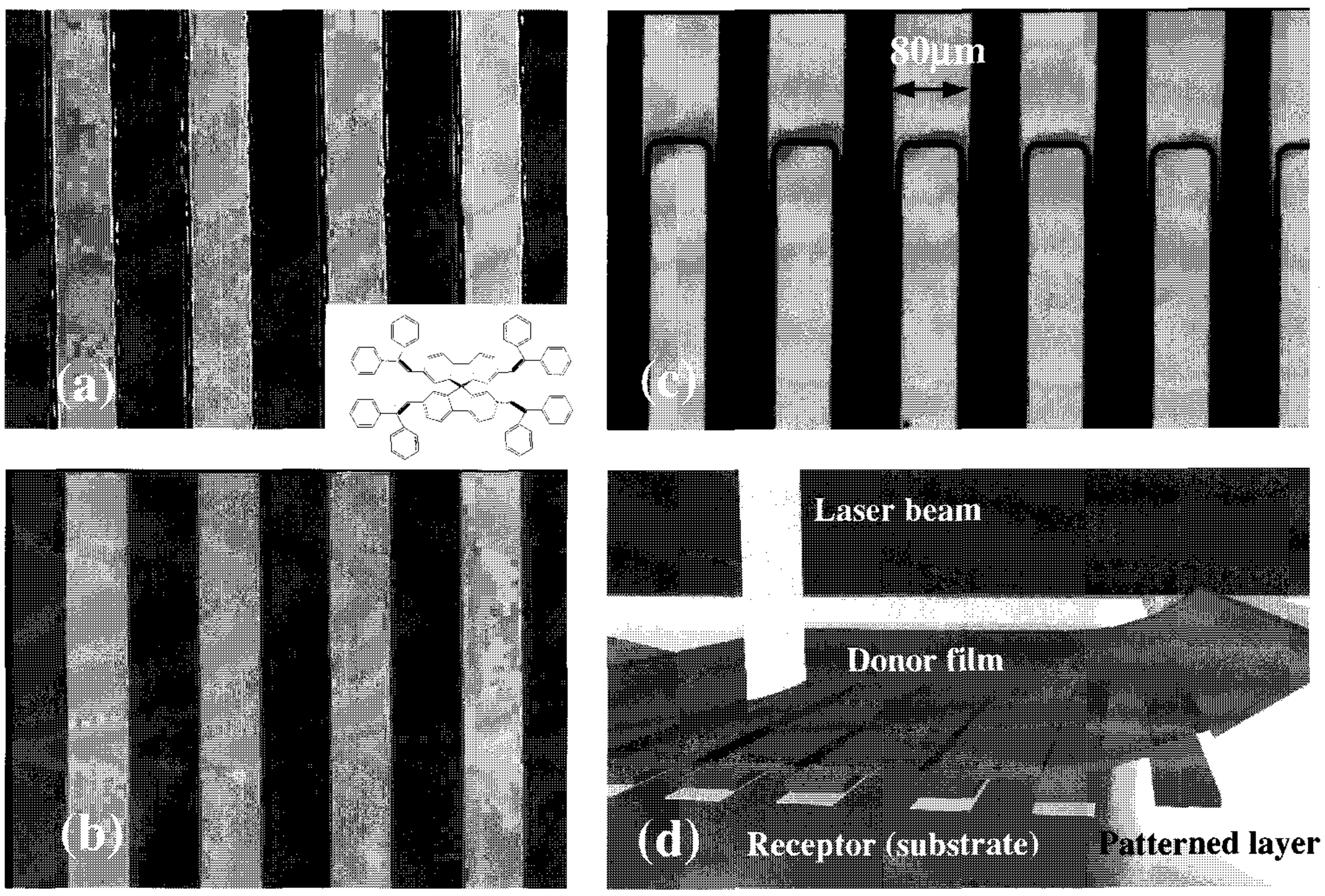

Fig. 1. Microscopic image of hybrid emitting layer which is patterned onto receptor. The ratio of incorporated small molecule (SM: spiro-DPVBi) decides the quality of pattern edge (a) 67 % SM (b) 80 % SM (c) imaging on the patterned ITO (d) schematics of laser-transfer process.

Semiconductor GmbH) were blended and spun-coated onto the donor film to obtain 40~80 nm homogeneous film. Electron transport layer [tris-(8-hydroxy-quinoline) aluminum, Alq3] and cathode (LiF/Al) were evaporated at a pressures of less than 10^{-7} mbar Pa.

3. Results and Discussion

3.1 Image patterns by daser transfer

The principal parameters that determine a laser-transfer characteristic include adhesion between the donor film and the organic film (emitting layer), cohesion between elements of the organic films, and adhesion between the organic film and the receptor material. Since the strong adhesion and film strength of most commercial grade of LEPs (Mw > 20,000) makes it difficult to image by laser transfer, LITI-AMOLED reported at SID2002[1] used the blend of light emitting polymer and optically inert polymers (e.g. polystyrene, PMMA, etc.). The blend of small molecules (light emitter or charge transporting material) and LEPs further improve the pattern quality as well as the efficiency and lifetime of fabricated devices compared to existing PLED technology. Figs.1 (a) and (b) illustrate the imaged stripe using the conventional small molecular light blue emitter (spiro-DPVBi, from Covion) blended with light emitting polymer onto the receptor layer of hole transporting material. The incorporation of spiro-DPVBi (Mw =1,029) lowers the cohesion between elements of the polymer film without greatly weakening the adhesion between the receptor substrate and the polymer film. Further, the increase of the content of small molecules resulted in a clear pattern quality (b). Fig.1. (c) shows the imaged line of optimized hybrid emitters onto our representative patterned ITO (80 μm width) test coupon and this pattern width could be reduced to 35 μm, as observed in our preliminary study. Fig. 1(d) is a schematic view illustrating a laser transfer process for patterning a light-emitting layer, where an hybrid emitting layer formed on a donor film was irradiated by laser beam through the donor film, which in turn resulted in the separation and transfer of a receptor-coated patterned ITO substrate.

3.2 Energy transfer of hybrid emitter

Fig. 2 represents the photoluminescence (PL) and electroluminescence (EL) spectra of small molecular host, light-emitting polymer (polyspiro-LEP green, Covion), and their blends. Photoluminescence of the small molecule host showed the peaks in the region of 430-460 nm (Spiro-4-PP-9) and 350-400 nm (Spiro-4-PP-6). One can find that sufficient energy transfer occurred at the EL spectrum of LEP/small molecule host hybrid device (peak at 520 nm), giving an appropriate CIE1931 coordinate (0.30, 0.60) compared with the color index of neat green LEP (0.26, 0.59, EL peak at 508 nm). Likewise, red emitter showed complete energy transfer using the same type of small molecule host materials. In the case of blue emitter, incorporated host with peak wavelength of lower than 430 nm resulted in a significant increase of in driving voltage, such that blending of small molecular blue emitter (spiro-DPVBi) with blue LEP was selected.

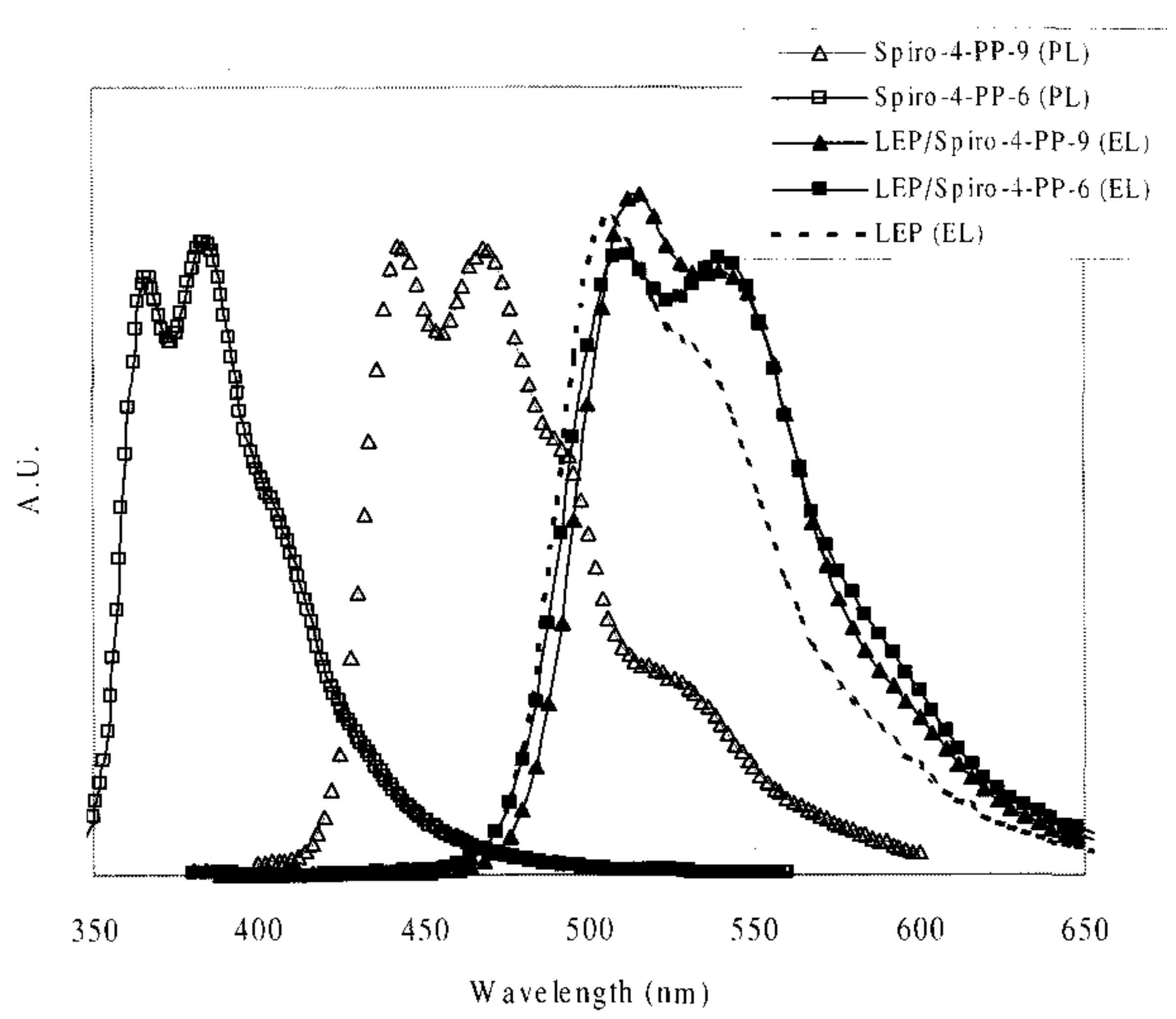

Fig. 2. Photoluminescence and electroluminescence spectra of neat green polymer, small molecule hosts (Spiro-4-PP-9, Spiro-4-PP-6), and their blends.

3.3 Device performances

Fig. 3 represents the CIE1931 chromaticity diagram of small molecule-polymer hybrid OLED devices (white points, patterned by laser transfer) with the conventional small molecular OLED (black, patterned by fine-metal frame mask). Operating voltage, required to obtain 100 Cd/m^2 white brightness with 32 % aperture ratio lies in the range of 5.5~6.0 V for hybrid RGB emitter. The level of efficiency using fluorescent host-polymer hybrid is almost as high as the conventional polymer or fluorescent small molecule devices. In order to further improve device stability, multi-stacked device by LITI method[5] using polymer and small molecule hole transporting material hybrid was found to show longer lifetime than conventional double-layer PLED device using PEDOT:PSS hole injecting layer (Fig. 4).

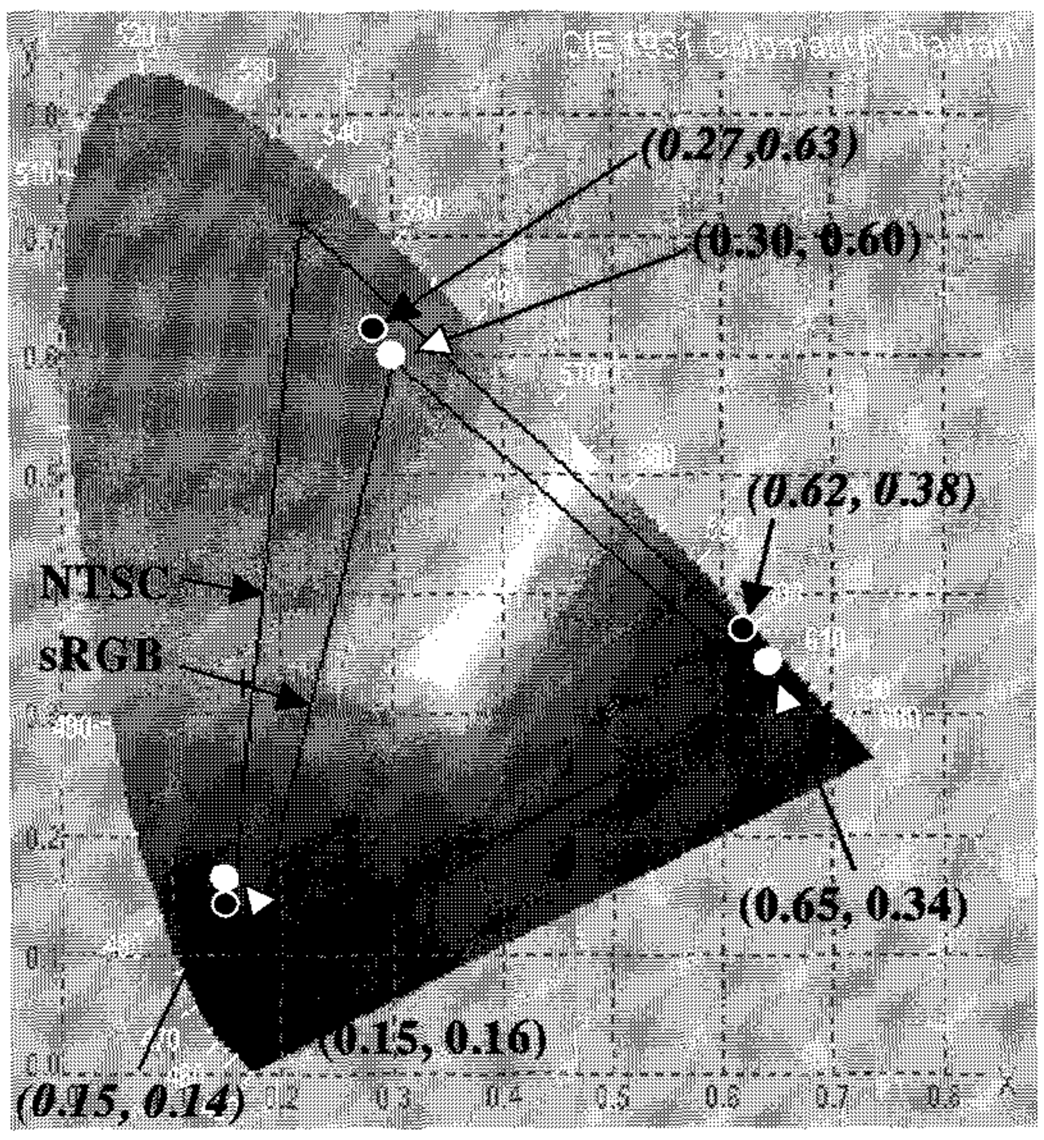

Fig. 3. CIE1931 chromaticity diagram of fluorescent small molecular OLED (black points), hybrid OLED by laser transfer (white points), and NTSC/super RGB.

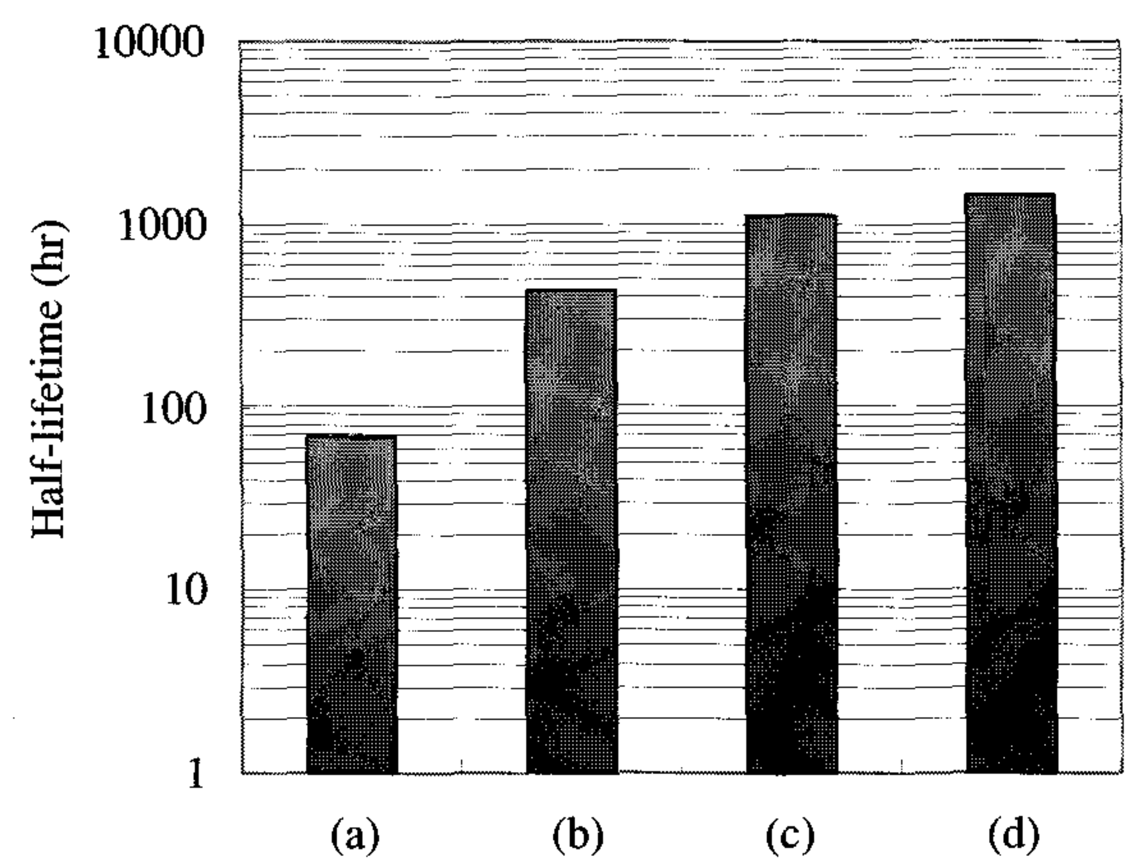

Fig. 4. Half-lifetime of LITI device using hybrid emitting red material; (a) 80 nm PEDOT:PSS as HIL; (b) 30 nm PFO-TPD stacked over PEDOT:PSS; (c) 90 nm stacked small molecules as HIL/HTL; and (d) 30 nm PFO-TPD and 30 nm NPB The initial brightness is 1000Cd/m^2.

We have fabricated a 22″ QCIF (176xRGBx220, 64 gray scale, gate/source driver integrated CMOS) full-color AMOLED without using fine metal frame mask. The white CIE1931 coordinates were (0.33, 0.35). Fig. 5 shows the still images of AMOLED devices. It is important to further improve of pixel uniformity, power consumption, and the lifetime of hybrid AMOLED devices.

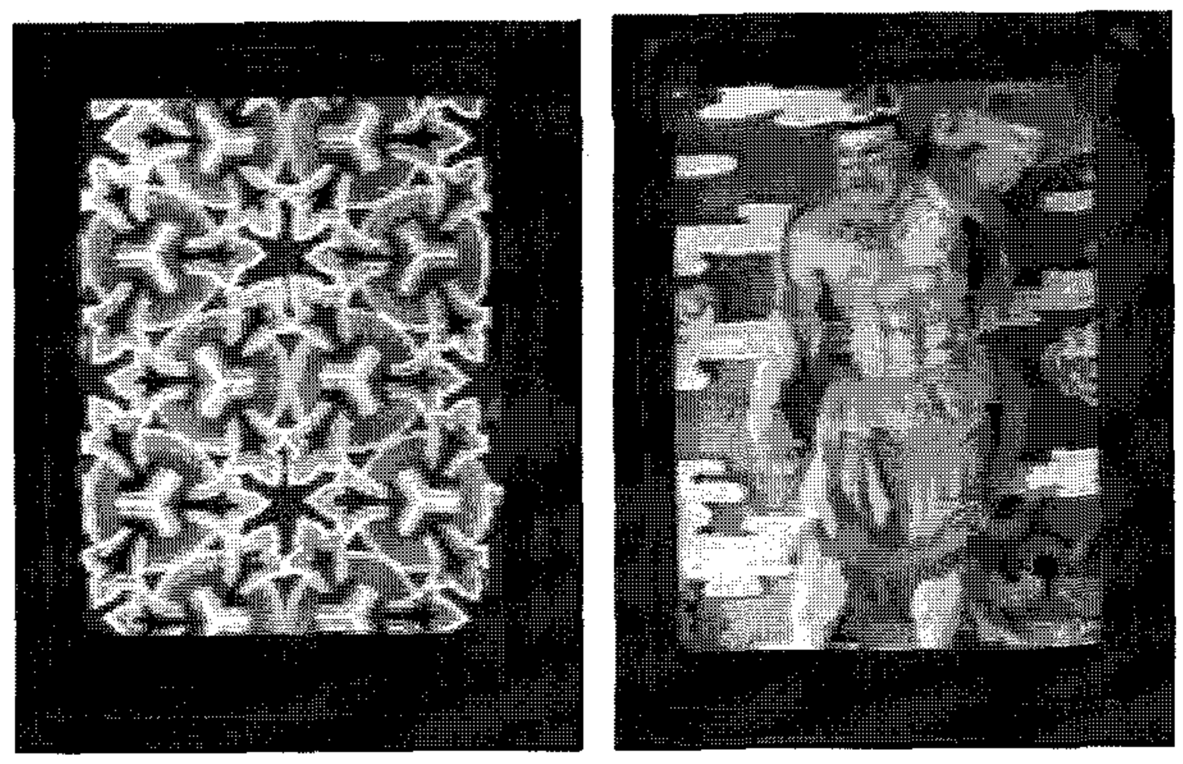

Fig. 5. Images of 2.2″ QCIF active matrix full color hybrid-OLED device patterned by laser transfer.

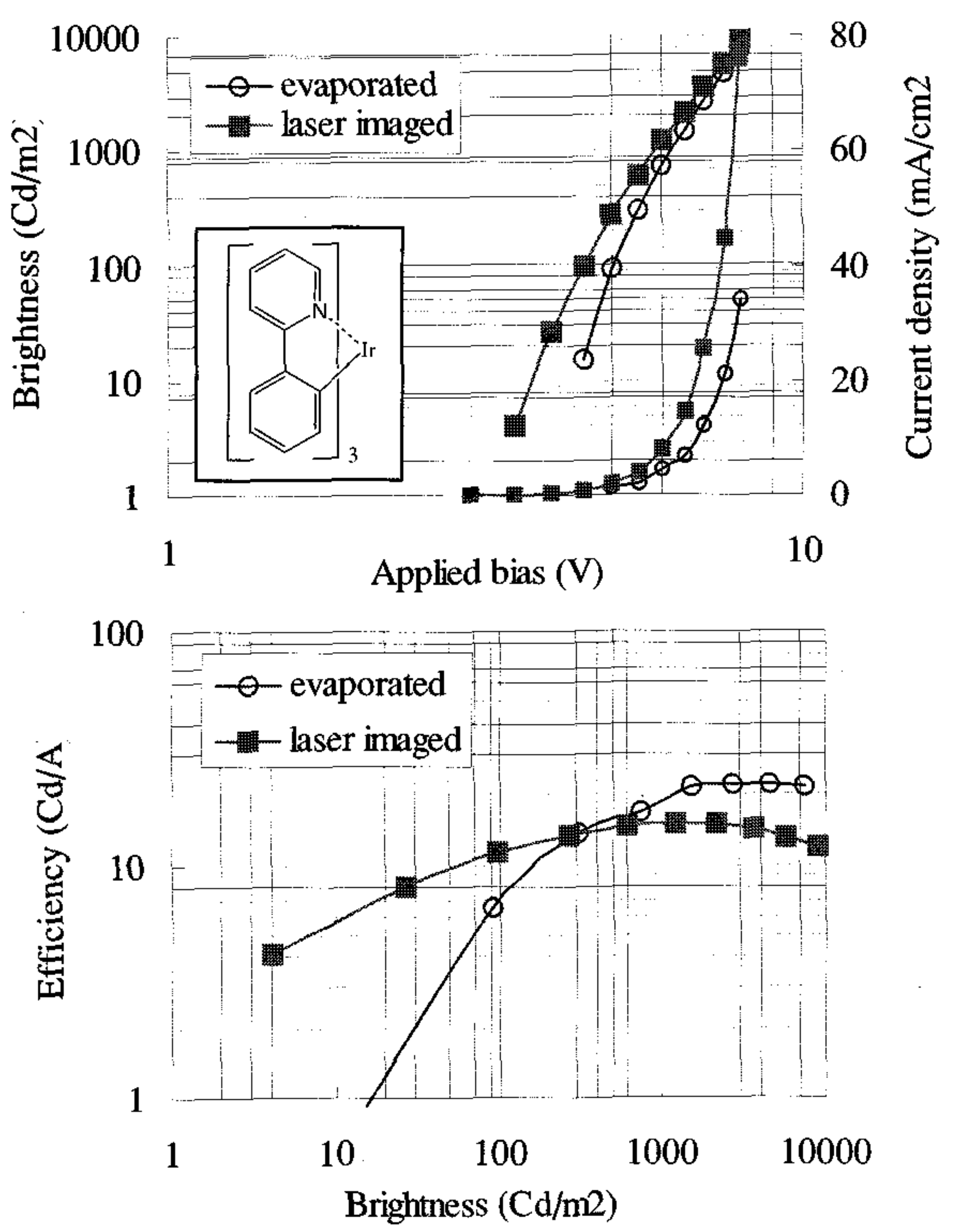

Fig. 6. Luminance-current-voltage(LIV) characteristics of laser-transferred hybrid device using $Ir(ppy)_3$ as phosphorescent dye.

3.4 Application for the highly efficient electro-phosphorescent device.

Although PLED has great potential for full-color flat panel display devices due to its unique easiness of solution processing and low-cost patterning methods, its inferior efficiency and lifetime causes delay of commercialized application for mobile display area. Fig. 6 compares laser-patterned test device using phosphorescent emitter [$Ir(ppy)_3$] with evaporated one, and shows the successful adaptation of phosphorescent small molecular OLED technology for laser-transferred full color device. Details on this subject are currently under intense investigation.

4. Conclusion

A mask-free direct patterning method for LEP and small molecular emitter is essential to the further development of high-precision full-color devices. Laser-transferred small molecule-polymer hybrid shows a promising possibility to incorporate the advantage of solution processing and evaporation method. 176x220 2.2" QCIF AMOLED device with excellent uniformity was fabricated. Solution-processed small molecules-polymer hybrids as well as phosphorescent small molecules were verified to be a promising system to be applied as laser-transferred full color AMOLED.

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