

## 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 within 2.5 micrometer and scalability to large-size mother glass. This accuracy is accomplished using real-time error correction and a high-resolution stage control system that includes laser interferometers. Here the new concept of mixed hybrid system which complement the advantages of small molecular and polymeric materials for use as an OLED; our system can realize the easy processing of polymers and high luminance efficiency of recently developed small molecules. LITI process enables to pattern the stripes with excellent thickness uniformity and multi-stacking of various functional layers without using any type of fine metal shadow mask. In this study, we report a full-color hybrid OLED using the multi-layered structure of small molecular/polymeric species.*

### 1. Introduction

The laser induced thermal imaging (LITI) by 3M (St. Paul, MN)<sup>1</sup> has been suggested as a counterpart patterning method against inkjet-printing in order to prepare well-defined full color polymeric light emitting diodes (PLED). As part of patterning technique for PLED, we have reported 2.2" QCIF and 3.6" QVGA active matrix (AM) PLED last year.<sup>2</sup> The advantageous simple structure of polymeric electro-luminescent device, however, have some limitations to achieve 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 at the use of most light emitting polymer (LEP) s. To overcome this problem, we have developed molecularly doped polymeric system<sup>3</sup> 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 molecular and polymeric hole transporters 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 provides the possibility applying the laser thermal imaging for the patterning process of highly efficiency small molecular OLED.

### 2. Experimental

#### 2.1 Laser Thermal Transfer

An optical imaging system comprised of a CW Nd:YAG laser, acousto-optic modulator, collimating and beam expanding optics, an attenuator, a galvanometer and an f-theta scan lens was utilized. The Nd:YAG laser produced a total power of 8.0 Watts on the image plane. Scanning was accomplished with the 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, 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 to heat. The transport of material from donor 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 20~80nm thickness and 35-100 micrometer width.

## 2.2. Materials

Hybrids of small molecular and polymeric materials were used for a 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 $\mu$ m-width-striped ITO substrate was as follows; 80nm-thick PEDOT:PSS (Baytron P TP CH8000, Bayer AG) or polymeric HIL (30nm, copolymers of poly (9,9-dioctylfluorene) [PFO] with N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(4,4'-diamine) [TPD])<sup>4</sup> were spun-coated onto the UV-O<sub>3</sub> treated indium tin oxide (ITO) substrates as hole-injecting layers (HIL). Those two HIL polymers can be used as a stacked layer due to their solvent compatibility. For limited cases, alpha-naphthylphenylbiphenyl (NPB) was evaporated onto the polymeric 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 Semiconductor GmbH) were blended and spun-coated onto the donor film to obtain 40~80nm homogeneous film. Electron transport layer [tris-(8-hydroxyquinoline) aluminum, Alq3] and cathode (LiF/Al) were evaporated at pressures less than 10<sup>-7</sup> mbar Pa.

## 3. Results and discussion

### 3.1 Image patterns by the laser 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 (m.w. > 20k) makes it difficult to image by laser transfer, LITI-AMOLED reported at SID2002<sup>1</sup> used the blend of light emitting and optically inert polymers (e.g. polystyrene, PMMA, etc.). The hybrid of small molecules (light emitter or charge transporter) and LEPs further improve the pattern quality as well as the efficiency and lifetime of fabricated devices compared to existing PLED technology. Fig.1 (a), (b) illustrates 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 transporter. The incorporation of spiro-DPVBi (m.w. =1029) lowers the cohesion between elements of the polymer film without greatly lowering the adhesion between the receptor substrate and the polymer film. Further 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 micrometer-width) test coupon and this pattern width could be reduced to 35 micrometer according to 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, causing the separation and transfer to a receptor-coated patterned ITO substrate.

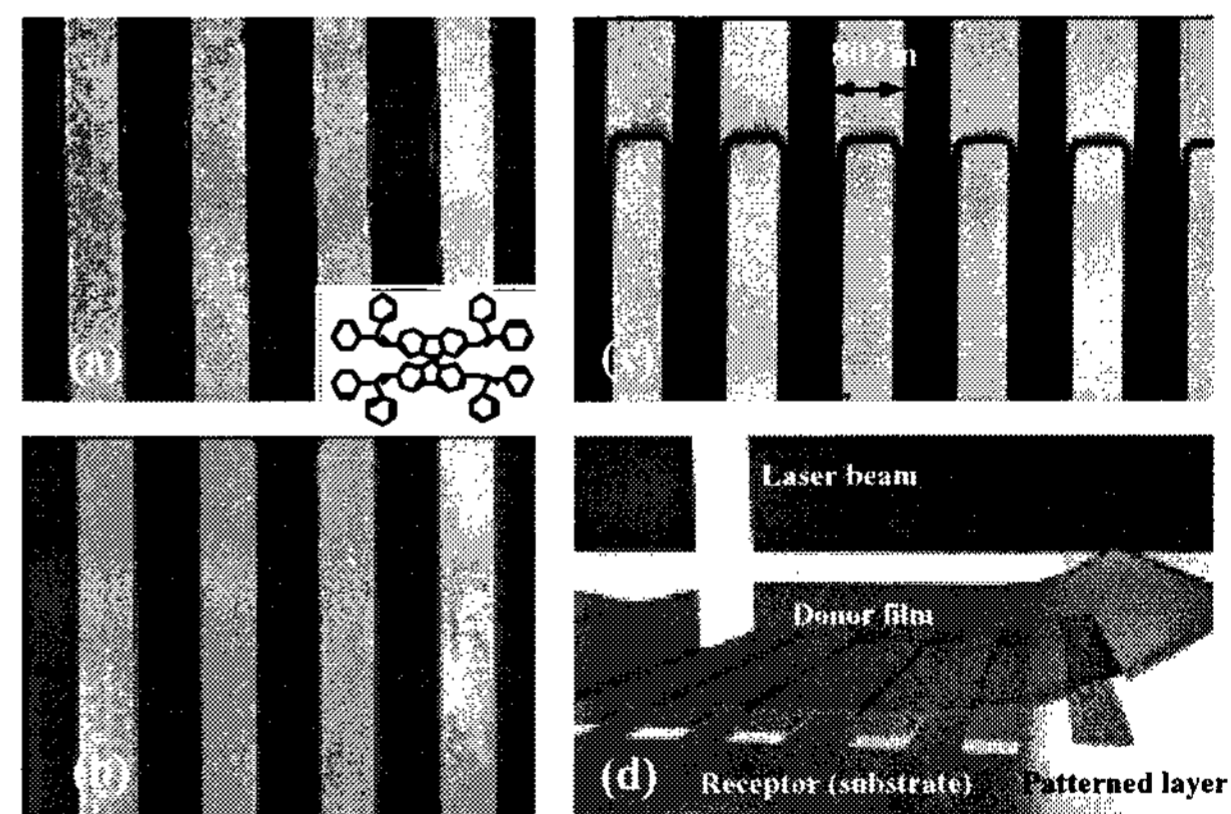


Fig.1 Microscopic image of hybrid emitting layer which is patterned onto receptor. The ratio of incorporated small molecule (SM: spiro-DPVBi) decides the quality of pattern edge (a) 67% SM (b) 80% SM (c) imaging on the patterned ITO (d) schematics of laser-transfer process.

### 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 molecular host showed the peaks in the region of 430-460nm (host 1) and 350-400nm (host 2). One can find that sufficient energy transfer occurred both at the EL spectrum of LEP/host1 hybrid device (peak 520nm), 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 508nm). Slight red shift of the EL spectrum at both cases, however, seems to be responsible for the exciplex formation and change of charge mobility. Likewise, red emitter showed complete energy transfer using same type of small molecular host materials. In the case of blue emitter, incorporated host with peak wavelength lower than 430nm resulted in the significant increase of driving voltage, so that blending of small molecular blue emitter (spiro-DPVBi) with blue LEP was selected.

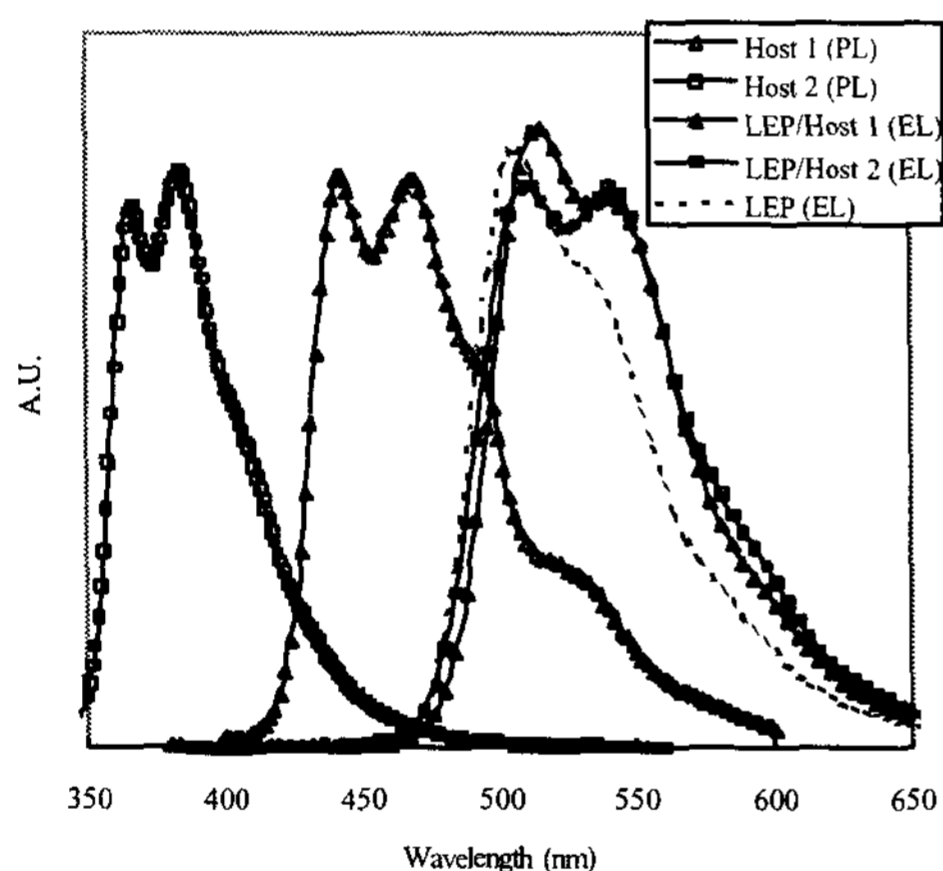


Fig. 2 Photoluminescence and electroluminescence spectra of neat green polymer, small molecular hosts (Host1, Host 2), and their hybrids.

### 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  $100\text{Cd/m}^2$  white brightness with 32% aperture ratio lies in the range of 5.5~6V for hybrid RGB emitter. The level of efficiency using fluorescent

host-polymer hybrid is almost as high as the conventional polymeric or fluorescent small molecular devices. For a further improvement of device stability, multi-stacked device by LITI method<sup>5</sup> using polymer and small molecular hole transporter hybrid was found to show longer lifetime than conventional double-layer PLED device using PEDOT:PSS hole injecting layer (Fig 4).

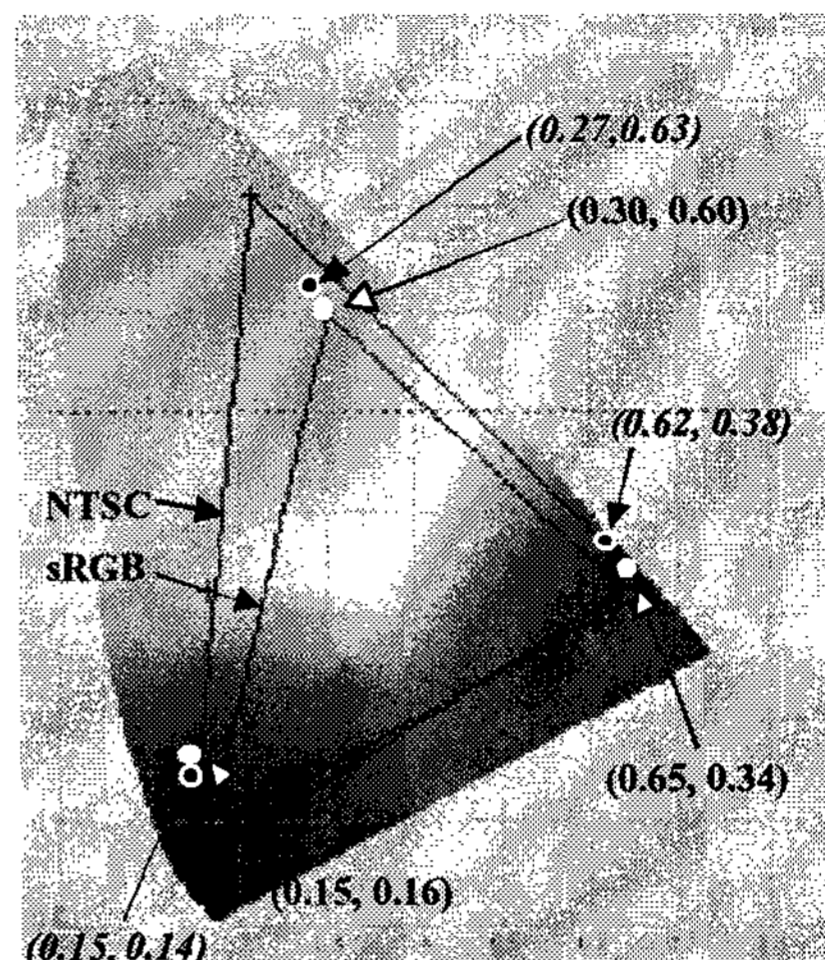


Fig. 3 CIE1931 chromaticity diagram of fluorescent small molecular OLED, hybrid OLED by laser transfer, and NTSC/super RGB.

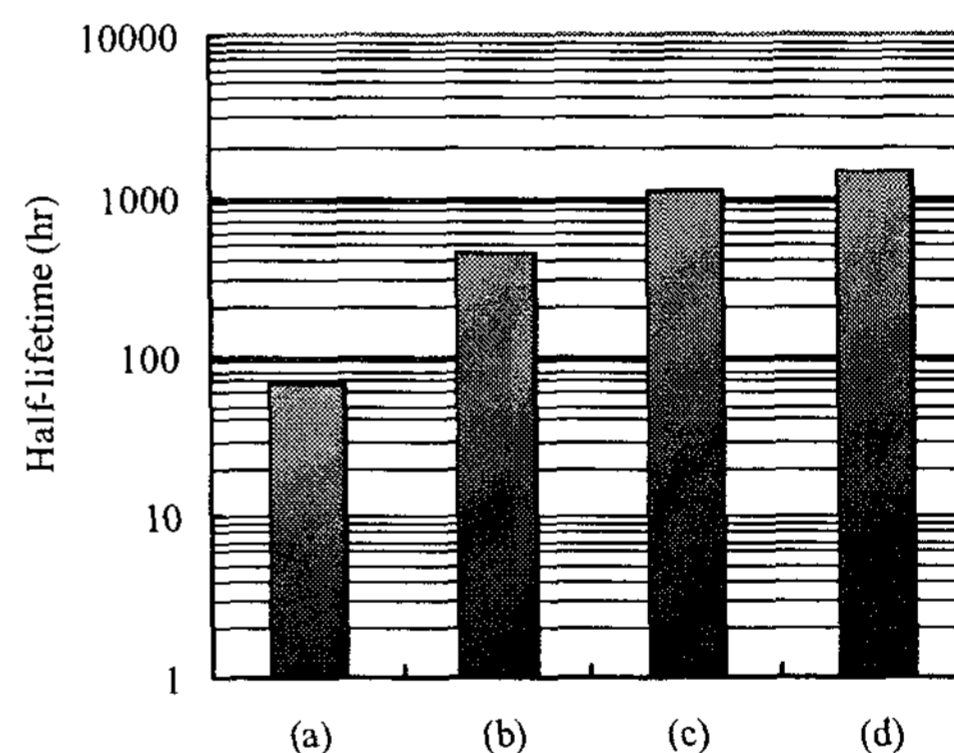


Fig. 4 Half-lifetime of LITI device using hybrid emitting red material (a) 80nm PEDOT:PSS as HIL (b) 30nm PFO-TPD stacked over PEDOT:PSS (c) 90nm stacked small molecules as HIL/HTL (d) 30nm PFO-TPD and 30nm NPB. The initial brightness is  $1000\text{Cd/m}^2$ .

We have fabricated a 2.2" QCIF (176xRGBx220, 64 gray scale, gate/source driver integrated CMOS) full-color AMOLED without using fine metal frame mask. The white CIE1931 coordinates are (0.33,



0.35). Fig. 5 shows the still image of AMOLED devices. Currently, further improvement of pixel uniformity, power consumption, and the lifetime of hybrid AMOLED devices are required.

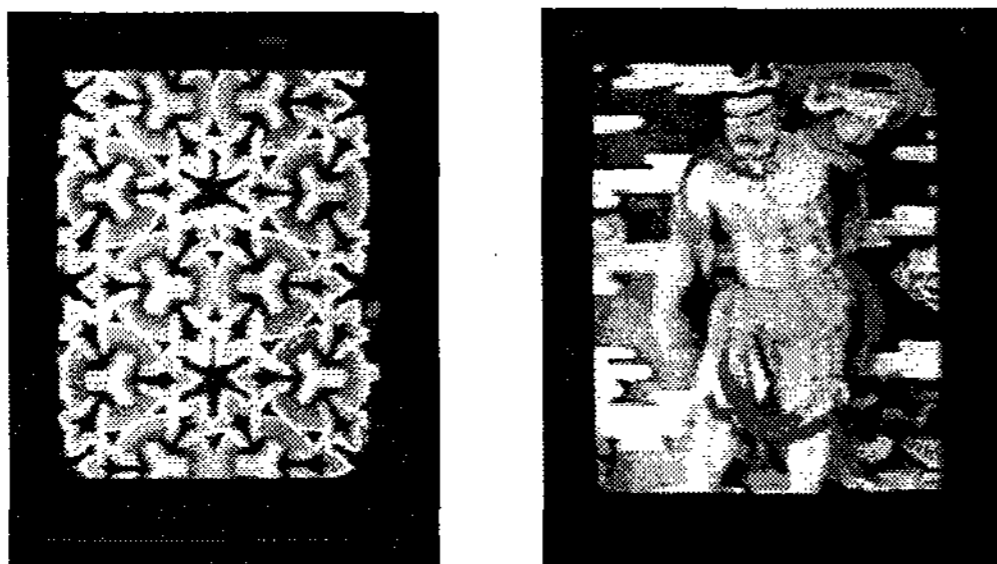


Fig. 5 Images of 2.2" QCIF active matrix full color hybrid-OLED device patterned by laser transfer.

### 3.4 Application for the highly efficient electrophosphorescent 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 the delay of commercialized application for mobile display area. Fig. 6 represents the comparison of laser-patterned test device using phosphorescent emitter ( $\text{Ir(ppy)}_3$ ) with evaporated one, which proves 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 fabricated. Solution-processed small molecules-polymer hybrids as well as phosphorescent small molecules are verified as a promising system for laser-transferred full color AMOLED.

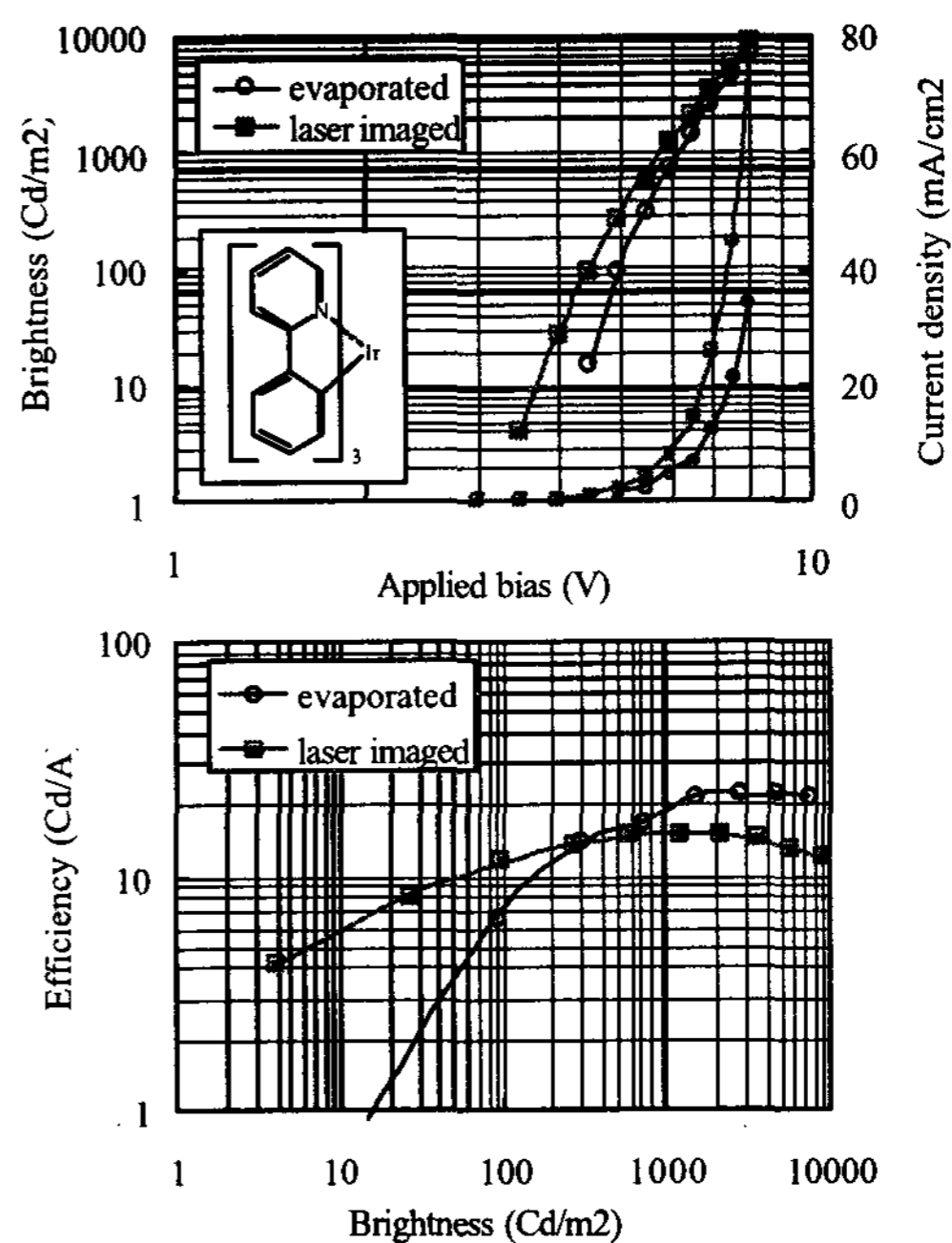


Fig. 6 Luminance-current-voltage(LIV) characteristics of laser-transferred hybrid device using  $\text{Ir(ppy)}_3$  as phosphorescent dye.

### Acknowledgment

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### 5. References

- [1] US Patent 5,521,035; 6,114,088; 6,194, 119
- [2] S.T. Lee, J.Y. Lee, M.H. Kim, M.C. Suh, T.M. Kang, Y.J. Choi, J.Y. Park, J.H. Kwon, and H.K. Chung, J. Baetzold, E. Bellmann, V. Savvateev, M. Wolk, and S. Webster, SID 2002 digest, 784 (2002).
- [3] M.H. Kim, M. C. Suh, S. T. Lee, J.H. Kwon, and H. K. Chung, IMID 2002 Digest, 94 (2002)
- [4] M.Redecker, D.D.C. Bradley, M.Inbasekaran, W. W. Wu, and E. P. Woo, Adv. Mater., 11, 241 (1999)
- [5] US patent 6,242,140; 6,291,116