

P-91: Asia Display/IMID '04: Highly Efficient Blue Organic Light-emitting Devices Based on Copper Phthalocyanine/Aromatic Diamine Composite Hole Transport Layer

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Abstract

Highly efficient blue organic light-emitting devices (OLEDs) utilizing the idea of copper phthalocyanine (CuPc)/*N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl,1,1'-biphenyl-4,4'-diamine (NPB) composite hole transport layer (CPHTL) have been fabricated. The effect of inserting CPHTL upon the performance of blue OLEDs with 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) as the blue emitter has been investigated. Compared with the luminous efficiency of the standard blue device without CPHTL (1.33 cd/A), that of the device with 40:60 CuPc/NPB CPHTL has been increased by more than twice up to 2.96 cd/A with a Commission Internationale d'Eclairage (CIE) coordinates of ($x = 0.15$, $y = 0.10$) and a power efficiency of 1.46 lm/W (20 mA/cm²) at 6.39 V. The increased device efficiency is attributed to an improved balance between hole and electron currents arriving at the recombination zone.

1. Introduction

Since Tang and Van Slyke developed the multi-layer organic light-emitting devices (OLEDs),¹ many efforts have been made to improve the device performance. It was recognized that the external quantum efficiency (EQE) of OLEDs depends on the efficiency of carrier injection and of the carrier recombination as well as the balance of the holes and electrons.^{2,3} Therefore, several approaches, including modification of the anode or cathode contact, have been done in achieving better carrier recombination.

The most often used method is to interpose a CuPc layer between an ITO anode and a hole transport layer (HTL),⁴ which can improve the device stability and efficiency. However, these advantages are compensated by a substantial increase in the device operation voltage. Since introducing the CuPc layer causes a shift in the J-V characteristic to higher voltages, it was expected that the CuPc could impede hole injection into the HTL. Later on, it was demonstrated that the hole-transport from the ITO anode to the NPB is injection limited and that the hole-injection efficiency is reduced progressively as the CuPc thickness is increased in the range of 0-30 nm.⁵ As the result, the increase in device efficiency induced by inserting a CuPc layer is correlated with a decrease in

hole-injection efficiency, which leads to a better recombination of holes and electrons.⁶ Similar to the case of OLEDs with a CuPc layer, doping the HTL with rubrene also leads to a higher EL efficiency and a slightly shift in the J-V characteristics to higher voltages. This shift points to the role of the rubrene as hole traps, thus reducing hole mobility in the HTL.⁷ The more pronounced shift in the J-V characteristics after introducing the CuPc layer than for doping the HTL can be attributed to the different nature of the hole-impeding process in both cases.⁸ The CuPc layer impedes the injection of holes into the HTL, but the dopant molecules reduce their mobility inside the HTL, the effect of which may not be as strongly reflected on the J-V characteristics because of the superior hole mobility characteristics of NPB.⁹

Having this thought in mind, we wish to combine the "hole-impedance" of CuPc with the doping technique and come up with a new OLED structure having CuPc/NPB composite hole transport layer (CPHTL). In this paper, the effect of inserting various ratio of CPHTL upon the performance of blue OLEDs with MADN as the blue emitter has been investigated and we will demonstrate that this new OLED structure can significantly enhance the device efficiency without much sacrifice in device operation voltage.

2. Experimental

In our experiment, four blue devices have been fabricated. Device I is a standard blue device without CuPc/NPB CPHTL, whereas device II, III, and IV are blue devices incorporating various ratio of CuPc/NPB CPHTL. The ratio of CuPc:NPB is 20:80, 30:70, and 40:60 for device II, III, and IV, respectively. The molecular structure and detail device architecture is shown in figure 1, where CF_x is the hole-injection layer¹⁰, CPHTL and *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl,1,1'-biphenyl-4,4'-diamine (NPB) as a whole is the hole transport layer, MADN is the blue emitter, tris(8-quinolinolato)aluminium (Alq₃) is the electron transport layer, and LiF/Al is the cathode. After a routine cleaning procedure, the indium-tin-oxide (ITO)-coated glass was loaded on the grounded electrode of a parallel-plate plasma reactor, pretreated by oxygen plasma, and then coated with a polymerized fluorocarbon film.⁸ Devices were fabricated under the base vacuum of about 10⁻⁶ Torr in a thin-film evaporation coater

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following a published protocol.¹¹ A multi-layer structure of CPHTL/NPB/EML/Alq₃/LiF/Al was deposited on the substrate by resistive heating with a thickness of 40, 30, 40, 10, 1, and 200 nm for CPHTL, NPB, EML, Alq₃, LiF, and Al respectively. In the evaporation of CPHTL, CuPc and NPB was co-deposited at various ratios. All devices were hermetically sealed prior to testing. The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 9 mm². The current-voltage-luminance characteristics of the devices were measured with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled programmable dc source.

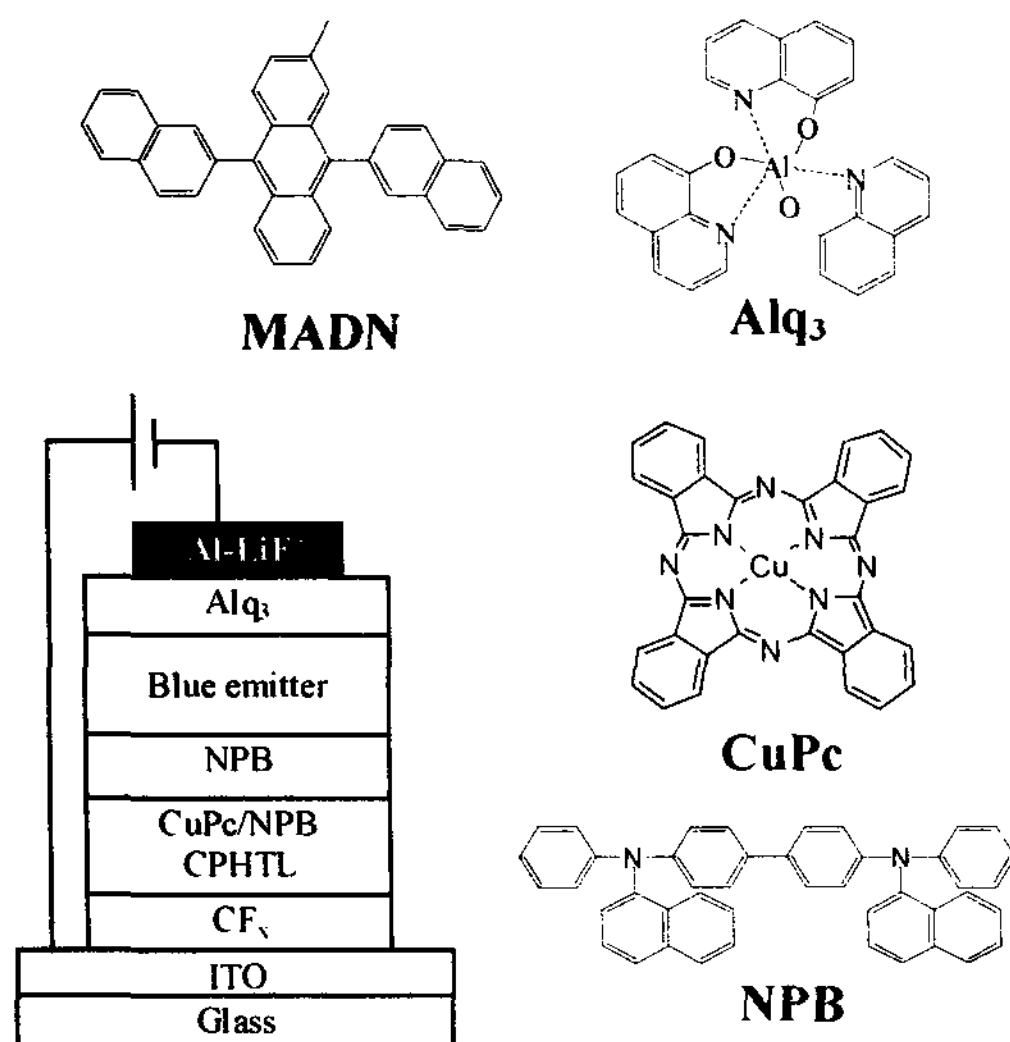


Figure 1. Material and device structures

3. Results and discussion

The B-I-V characteristics of the four blue devices are shown in Figure 2. Higher operation voltage and brightness was observed in the device with CPHTL comparing to that of the standard device. However, by adjusting the ratio of CuPc/NPB CPHTL, operation voltage can be dropped significantly. It is noteworthy that the operation voltage was lowered as the amount of CuPc in the CPHTL was increased. A schematic diagram in Figure 3 may explain this phenomenon. The increase in operation voltage when incorporating CPHTL is expected to arise from two contributions. One is the "hole-impedance" of CuPc, which slows down the hole-transport, hence, increases the operation voltage. The other contribution is the dissipation of energy from the "trapping and detrapping" of holes because the ionization potential of CuPc is lower than that of NPB. By increasing the concentration of CuPc in the CPHTL, the probability for "trapping and detrapping" will be reduced since the intermolecular distance between CuPc molecules will become shorter and holes will tend to travel via CuPc. That is why lower operation voltage was the result when the CuPc concentration was increased.

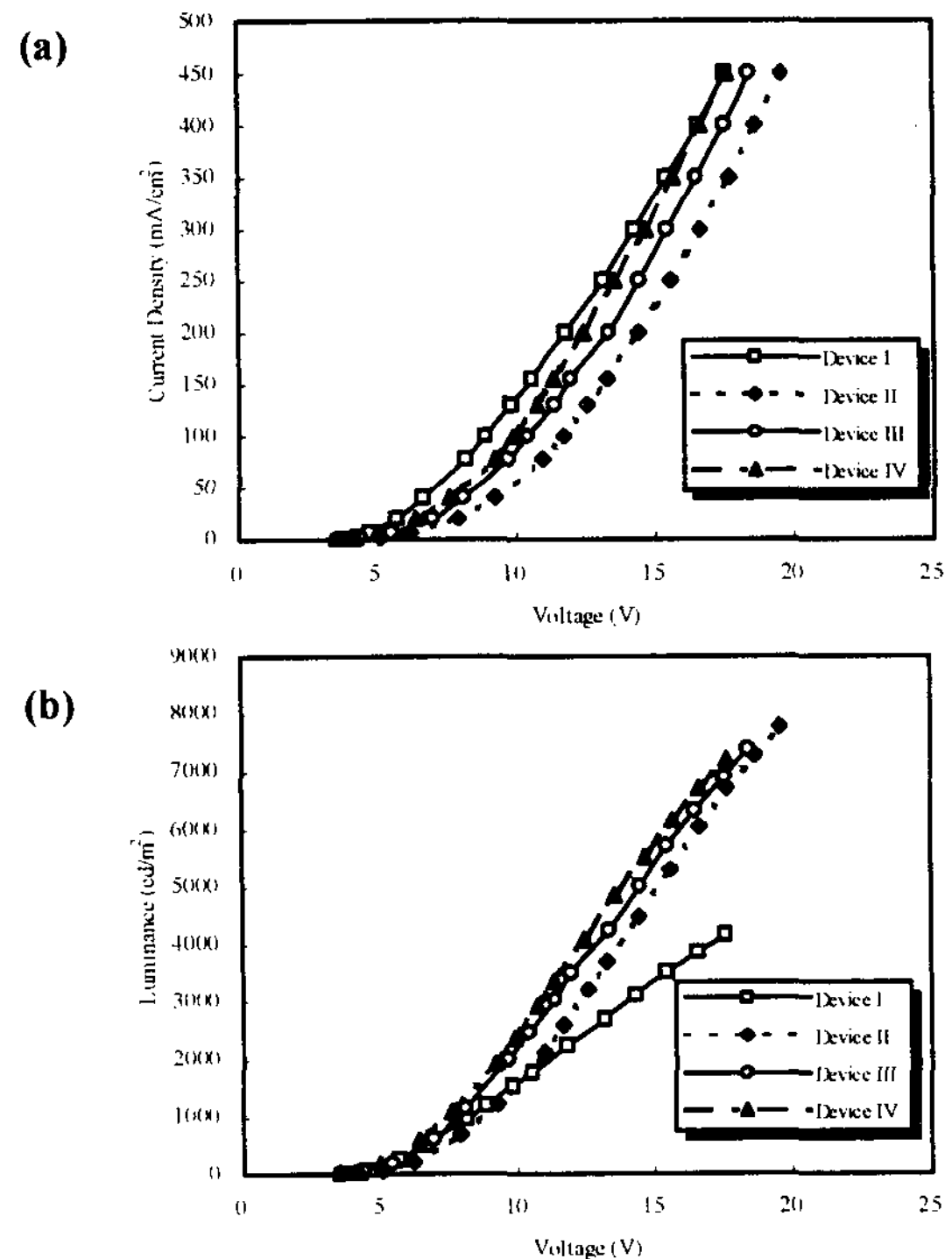


Figure 2. The current density-voltage characteristics (a) and luminescence-current density (b) of the blue devices

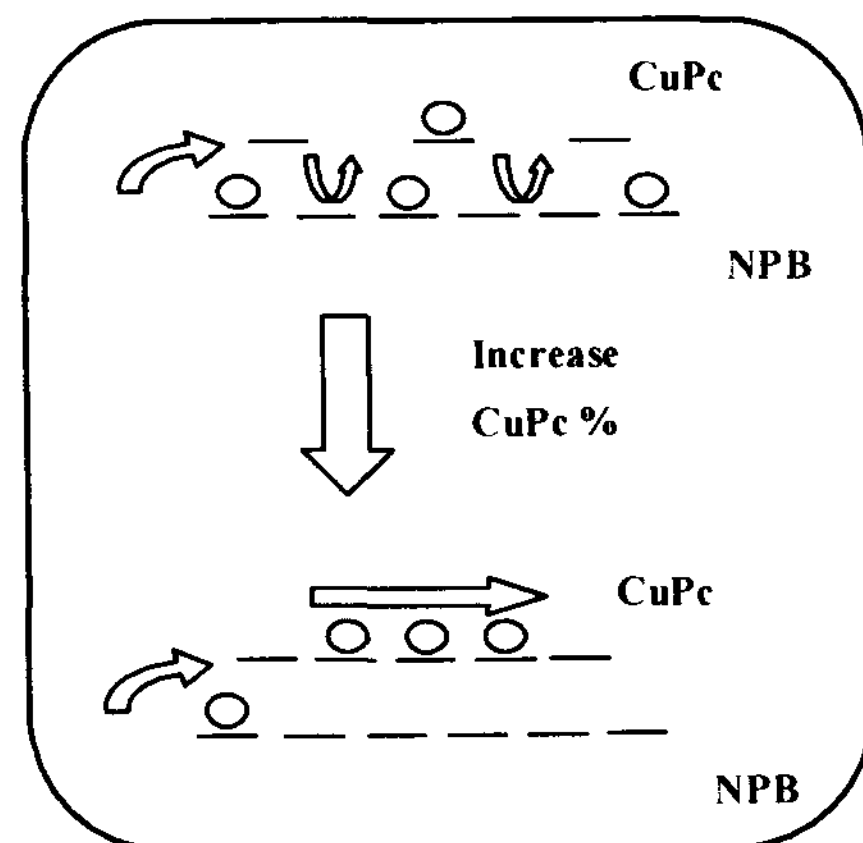


Figure 3. Schematic diagram illustrating the transport of holes on the highest occupied molecular orbital (HOMO) of CuPc and NPB

Figure 4 shows the plot of luminous efficiency vs. current density for these blue devices. The drastic enhancement in luminous efficiency by implementing CuPc/NPB CPHTL is the result of better carrier recombination at the emitting zone. Although the *current induced quenching (CIQ)* is more severe for devices with CuPc/NPB CPHTL, which might be due to the shift of recombination zone, the absolute luminous efficiency still is more superior to that of a standard device at high current drive conditions. It was found that different ratio of CuPc/NPB CPHTL can effectively influence the device performance and, under our experimental conditions, a 40:60 CuPc/NPB CPHTL is optimum for obtaining high performance blue OLEDs.

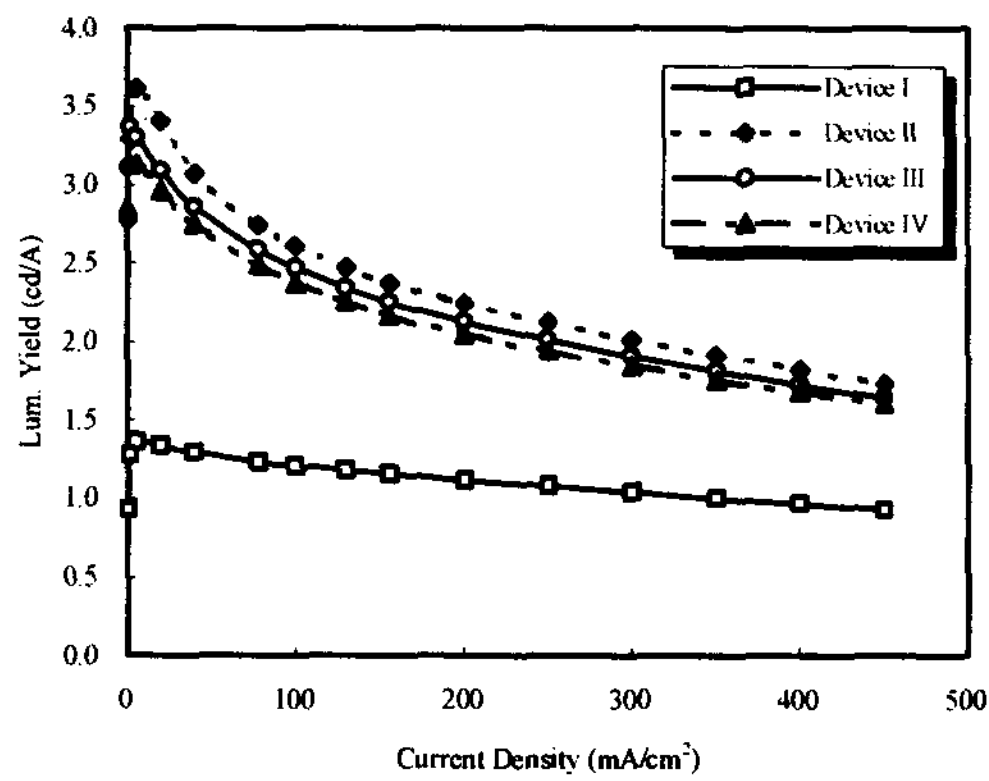


Figure 4. The dependency of the EL efficiency on the drive current density of the blue devices

The overall EL performances of these blue devices are summarized in table 1. Compared with the luminous efficiency of the standard blue device without CPHTL (1.33 cd/A), that of the device with 40:60 CuPc/NPB CPHTL has been increased by more than twice up to 2.96 cd/A with Commission Internationale d'Eclairage (CIE) coordinates of ($x = 0.15, y = 0.10$) and a reasonable device operation voltage of 6.39 V at 20 mA/cm². One additional advantage about incorporating CuPc/NPB CPHTL in blue device is the enhancement of device performance without impacting on the emissive color. Furthermore, the devices with CuPc/NPB CPHTL have shown considerable improvement in both power efficiency and EQE.

Table 1. EL performances of the blue devices driven at 20 mA/cm²

Device	Voltage (V)	Lum. yield (cd/A)	1931 CIE		Power efficiency (lm/W)	EQE (%)
			x	y		
I	5.69	1.33	0.15	0.11	0.74	1.4
II	7.91	3.41	0.15	0.11	1.35	3.5
III	6.97	3.09	0.15	0.10	1.39	3.6
IV	6.39	2.96	0.15	0.10	1.46	3.5

4. Conclusion

Carrier recombination as well as the balance of holes and electrons is considered to be one of the important factors that

determines the EQE of OLEDs. Here, we have developed a simple method, introduction of the CuPc/NPB CPHTL, which can efficiently control the hole-mobility in order to achieve a hole-electron balance. Improvement in the hole/electron recombination efficiency of the device with CuPc/NPB CPHTL was demonstrated by the amazingly high EQE (3.5%) compared to that of the standard device (1.4%). Under our experimental conditions, the device with 40:60 CuPc/NPB CPHTL was found to be optimum which has improved the luminous efficiency to 2.96 cd/A with a CIE coordinates of ($x = 0.15, y = 0.10$) and a power efficiency of 1.46 lm/W (20 mA/cm²) at 6.39 V.

5. Acknowledgement

This work was supported by the MOE Program for Promoting Academic Excellence of Universities under the grant 91-E-FA04-2-4-B and the National Science Council of Taiwan, Republic of China under the grant NSC 92-2215-E-009-045 & NSC 92-2623-7-009-006. We are also grateful to a research grant of Industry/Academia Cooperation Project provided by e-Ray Optoelectronics Technology Co., Ltd.

6. References

- [1] C. W. Tang and S. A. Slyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- [2] J. Pommerehne, H. Vestweber, Y. H. Tak, and H. Bassler, *Synth. Met.* **76**, 654 (1996).
- [3] C. F. Qie, L. D. Wang, H. Y. Chen, M. Wong, and H. S. Kwok, *Appl. Phys. Lett.* **79**, 2276 (2001).
- [4] S. A. Slyke, C. H. Chen, C. W. Tang, *Appl. Phys. Lett.* **69**, 2160 (1996).
- [5] E. W. Forsythe, M. A. Abkowitz, Y. Gao, *J. Phys. Chem. B* **104**, 3948 (2000).
- [6] H. Vestweber and W. Rieb, *Synth. Met.* **91**, 181 (1997).
- [7] J. Yang, and J. Shen, *J. Appl. Phys.* **84**, 2105 (1998).
- [8] H. Aziz, Z. D. Popovic, Nan-Xing Hu, Ah-Mee Hor, Gu Xu, *Science* **283**, 1900 (1999).
- [9] G. G. Malliaras and J. C. Scott, *ibid.* **83**, 5399 (1998).
- [10] L. S. Hung, L. R. Zheng, and M. G. Mason, *Appl. Phys. Lett.* **78**, 673 (2001).
- [11] S. A. Van Slyke C. H. Chen, and C.W. Tang, *Appl. Phys. Lett.* **69**, 2160 (1996).