Small Molecule-based Organic Electrophosphorescent Devices fabricated by Spin Coating

Kenichiro Watanabe^a, Daisuke Kumaki^b, Toshimitsu Tsuzuki^c, Eiji Tokunaga^a,
and Shizuo Tokito^{a,b,c}

^aDepartment of Physics, Faculty of Science, Tokyo University of Science
1-3 Kagurazaka, Shinjuku-ku,
Tokyo, 162-8601, Japan

^bTokyo Institute of Technology
4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8205, Japan

^cNHK Science and Technical Research Laboratories
1-10-11 Kinuta, Setagaya-ku, Tokyo 157-8510, Japan

Organic electrophosphorescent devices using several small molecules as a host and Ir(ppy)₃ as a green emitting guest have been fabricated by spin coating. We used new host materials in which a cyclohexanyl or adamantyl group was inserted between two phenyl rings of CBP (named Cy-Cz, Ad-Cz). The device with Cy-Cz host material and a guest concentration of 24wt% showed an external quantum efficiency of 11% and a power efficiency of 27lm/W at 100cd/m². These results suggest that small molecule-based organic electrophosphorescent devices fabricated by spin coating can be highly efficient.

Keyword: small molecules, solution process, carbazole derivative, OLED

1. Introduction

Because of their many advantages, such as flexibility, low driving voltage, and high luminance, organic light emitting diodes (OLEDs) have attracted a great deal of interest [1]. OLEDs using phosphorescent materials have demonstrated very high quantum efficiencies [2-8]. Recently, an external quantum efficiency of nearly 20% was achieved using small molecular materials emitting green phosphorescence. A solution process such as spin coating or inkjet printing is better for large-area and fine-pixel display than a vacuum deposition process. Polymers have been widely used as solution-processable materials [9]. However, it is well known that polymer-based OLEDs are not as efficient and do not last as long as small molecule-based OLEDs because of their low purity. Some small molecule-based OLEDs fabricated with a solution process have been

Fig.1. Chemical structures of host materials

reported [10-12], but they showed low quantum efficiency. We introduced cyclohexanyl or adamantyl groups between two phenyl rings of CBP (Fig.1) into the chemical structures of the new host materials because we expected that this would improve thermal stability. The resulting devices exhibited a high external quantum efficiency of 11%, and a power efficiency of 27lm/W at 100cd/m². That is, we demonstrated that high efficiency small molecule-based phosphorescent OLEDs using new materials can be fabricated by spin coating.

2. Experimental

The devices were prepared by spin coating a 35-nm-thick layer of PEDOT/PSS on precleaned indium tin oxide (ITO) glass and annealing it at 180°C for 1h in an air atmosphere. Subsequently, a 40~50-nm-thick emitting layer was spin coated onto the PEDOT/PSS and annealed at 100°C for 1h in a nitrogen atmosphere. The substrates coated with PEDOT/PSS and the emitting layer were loaded into a vacuum deposition chamber and held there under a pressure of 10⁻⁵ Pa. Then, a 10-nm-thick hole-blocking layer of BCP and a 35-nm-thick electron-transporting layer of Alq₃ were formed by vacuum deposition. Finally, a bilayer of LiF (0.5nm) and Al (100nm) was deposited as a cathode under the same conditions. After the cathode was deposited, the devices were encapsulated using a UV-epoxy resin and glass plates in a nitrogen atmosphere. The luminance was measured with a luminance meter (Minolta LS-100). The emission spectrum was measured with a luminous spectrometer (Minolta CS-1000). The driving source was a digital source meter (Keithley, 2400). The external quantum efficiency was calculated from the luminance value and emission spectrum. We assumed that the spatial emission patterns from the devices were Lambertian.

The highest occupied molecular orbital (HOMO) levels were obtained with an atmosphere UV photoelectron counter (AC-3, Riken Keiki). The lowest unoccupied molecular orbital (LUMO) levels were estimated by adding the optical energy gap to the HOMO levels.

3. Results and Discussion

3.1. Performances of devices with different host materials.

Table. 1 lists the external quantum efficiency, the power efficiency, and the driving voltage at luminance 100cd/m² of the different devices. All devices showed similar EL spectra with a peak wavelength of ~520nm. The device with the CBP host material exhibited the highest external quantum efficiency of 12%, and the devices with Cy-Cz and Ad-Cz host materials exhibited 6.1%, and 5.1% respectively, at 100cd/m². The driving voltages of the devices using CBP, Cy-Cz, and Ad-Cz as hosts were 4.9V, 6.0V, and 6.8V at 100cd/m², respectively.

Figure 2 is a HOMO and LUMO energy diagram of the host materials. CBP has a deeper LUMO level than Cy-Cz and Ad-Cz. That is, the injection barrier from BCP to CBP is smaller than that from BCP to Cy-Cz or Ad-Cz. CBP also has a bipolar transport ability. Electron injection from BCP into CBP is effective. Hence, it showed high quantum efficiency and low driving voltage due to good carrier balance. The Cy-Cz and Ad-Cz devices exhibited high driving voltage and low quantum efficiency because the charge carriers were not balanced in the emissive layer. In addition, the Ad-Cz device showed a nonuniform emission due to low solubility.

Table. 1. Device Characteristics at 100cd/m².

Host material	η_{ext} (%)	η_{power} (lm/W)	Driving voltage (V)
CBP	12	26	4.9
Ad-Cz	5.1	8.4	6.8
CY-CZ	6.1	13	6.0

Fig. 2. HOMO and LUMO levels of materials and energy diagram of device.

3.2. Optimization of device with the Cy-Cz host

To optimize a charge carrier balance in the device with the Cy-Cz host, we investigated guest concentration dependence on device performance. Guest concentration varied from 6 to 24wt%. Figure 3 (a), (b), and (c) show luminance characteristics versus applied voltage, external quantum efficiency versus current density, and power efficiency versus current density, respectively, of the devices. The external quantum efficiency improved from 7 to 11%, and power efficiency doubled at 100cd/m², when guest concentration was increased from 6 to 24wt%. Maximum external quantum efficiencies were 7, 11, 11, and 12% for guest concentrations of 6, 12, 18, and 24wt%, respectively. In addition, the driving voltage at 100cd/m² decreased from 6.2 to 4.5V by increasing the concentration from 6 to 24wt%. All device performances at 100cd/m² are summarized in Table. 2.

Improvement in external efficiency and decrease in driving voltage suggest that the charge carrier balance was improved in the emissive layer by increasing guest concentration. The charge carrier balance was optimal when guest concentration was

Fig. 3. (a) Luminance characteristics versus applied voltage, (b) external quantum efficiency versus current density, (c) power efficiency versus current density. Concentration ratios of Ir(ppy)₃ are 6, 12, 18, and 24wt%.

Table. 2. Performances of devices with guest concentrations at 100cd/m²

Guest concentration (wt%)	6	12	18	24
Driving voltage (V)	6.2	5.7	4.7	4.5
η_{ext} (%)	7.1	10.3	10.5	11.0
η_{power} (lm/W)	13	20	23.5	27

over 18wt%. The device showed performance comparable to that of CBP. Generally, a high concentration of guest molecules in the emissive layer causes concentration quenching and reduces emission efficiency. In this case, concentration quenching was not observed over 18wt%. Therefore, the guest molecules play roles both as light emission and as carrier transport sites.

The energy diagram shows that there was a large barrier height of 1.0eV for holes injected from PEDOT/PSS into Cy-Cz. Therefore, the holes were directly injected from PEDOT/PSS into the guest because the direct injection from PEDOT/PSS into the guest is energetically more favorable than injection into Cy-Cz. It was also speculated that the electrons were directly injected into the LUMO level of the guest because Cy-Cz had a high electron injection barrier.

4. Conclusion

Organic electrophosphorescent devices using a variety of small molecules as a host and Ir(ppy)₃ as a green emitting guest have been fabricated by spin coating. Devices that used Cy-Cz as a

host and had a guest concentration of 24wt%, exhibited an external quantum efficiency of 11%, and a power efficiency of 27lm/W at luminance of 100cd/m².

References

1. C. W. Tang, S. A. Slyke, *Appl. Phys. Lett.* 51, 913, (1987)
2. M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* 395, 151, (1998)
3. D. F. O'Brien, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* 74, 442, (1999)
4. M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* 75, 4, (1999)
5. S. Lamansky, P. Djurovich, D. Murphy, F. Adbel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* 123, 4304, (2001)
6. M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, *Appl. Phys. Lett.* 79, 156, (2001)
7. C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* 90, 5048, (2001)
8. S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, and F. Sato, *Appl. Phys. Lett.* 83, 569 (2003)
9. M. Suzuki, S. Tokito, F. Sato, T. Igarashi, K. Kondo, T. Koyama, and T. Yamaguchi, *Appl. Phys. Lett.* 86, 103507 (2005)
10. J. LEE, H. Y. CHU, Y. S. YANG, L. Mi DO, S. Mook, C. HWANG, *Jpn. J. Appl. Phys.* 45, 9231, (2006)
11. J. Jou, M. Sun, H. Chou, and C. Li, *Appl. Phys. Lett.* 87, 43508, (2005)
12. M. Ooe, S. Naka, H. Okada, H. Onnagawa, *Jpn. J. Appl. Phys.* 45, 250, (2006)