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Small Molecular Reddish-White Light Emitting Electrophosphorescent Devices with Solution Processed Emission Layer

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We compared the electrical characteristics of polymer, poly(N-vinylcarbazole) (PVK) and small molecule, 4,4′-N,N′-dicarbazole-biphenyl (CBP), N,N′-dicarbazolyl-3,5-benzene (mCP), as host material in white organic light-emitting diodes (OLEDs) fabricated by solution process. In order to obtain the white emission, iridium(III) bis(4,6-difluorophenylpyridinato)-picolinate) (Firpic) and iridium(III) bis(2-phenylquinoline)(acetylaceton) [Ir(pq)$_2$acac] were used as blue and red emitting dopant, respectively. As a result, devices with PVK, CBP, and mCP have the max. luminous efficiencies of 10.5 cd/A, 9.8 cd/A, and 4.2 cd/A, respectively.

Keywords   Host; organic light-emitting diode; polymer; small molecule

Introduction

Organic light-emitting diodes (OLEDs) have been widely recognized as a technology for flat-panel displays due to their low-voltage operation, wide-viewing angle, high contrast, and mechanical flexibility [1]. The development of the first organic material emitting visible light in multilayered structure when a bias voltage was applied on the structure by Tang and coworkers [2,3], had stimulated the research in OLEDs and emitting materials [4,5]. It has been reported that numerous phosphorescent OLEDs have excellent efficiency by thermal evaporation process [6–8]. Thermal evaporation process seems to be a successful technique to obtain high efficiency. However, it is limited by many factors such as relatively high cost and time-consuming as well as low process yield. Their high fabrication cost and limited scalability to large size are still regarded as its critical weak point. On the other hand, the solution processes such as spin coating or ink-jet printing exhibit promising potentials for the low-cost

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and large-area flat panel display technology. In generally, the conjugated polymers have been attracted to solution processed OLEDs due to their high solubility and easy of energy band gap control. However, they show the low efficiency because most conjugated polymers have a low-lying triplet state (T_1) and may acts as a potential quencher at the interface of emitting layer. Although it has been reported that the non-conjugated polymers such as poly(*N*-vinylcarbazole) (PVK) have relatively the high T_1, they indicate the high resistivity and operating voltage in devices. These poor electrical properties cause low efficiency of devices. Therefore, in this study, we studied the soluble small molecular host materials that have the high T_1 and excellent electrical property [9–14].

Experimental

Indium tin oxide (ITO) coated glass with resistance of $30\,\Omega/sq$ was cleaned in an ultrasonic bath by following sequence: in acetone, methanol, diluted water and isopropyl alcohol. Thereafter, pre-cleaned ITO was treated by O_2 plasma with the power conditions of $125\,W$ for $2\,min$ under low vacuum of $2 \times 10^{-2}\,torr$. After the pre-treatment of ITO, We fabricated the devices with a structure of ITO (180 nm)/poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) ($\sim$40 nm)/host:14 wt% iridium(III) bis(4,6-difluorophenylpyridinato)-picolinate) (Firpic):0.8 wt% iridium(III) bis(2-phenylquinoline) (acetylaceton) [Ir(pq)$_2$acac] ($\sim$50 nm)/bathocuproine (BCP) (10 nm)/ET137 (30 nm)/lithium quinolate (Liq) (2 nm)/aluminum (Al) (100 nm), where PVK, 4,4′-*N,N′*-dicarbazole-biphenyl (CBP), and *N,N′*-dicarbazolyl-3,5-benzene (mCP) were used as host. Its chemical structure is shown in Figure 1. PEDOT:PSS, BCP, and Liq/Al were used as hole transporting layer, electron blocking layer, and cathode, respectively. ET137 is new electron transporting layer supplied from SFC Co., Ltd. In order to form the PEDOT:PSS layer on the pre-cleaned ITO, it is spin-coated with 3000 rpm for 60 s and baked at 120°C for 30 min in vacuum oven. The emission layer was also spin-coated from the chloroform (CH_2Cl_2) solution with 0.34 wt% solute. The solute consists of the 6.7619 mg host material, 0.9467 mg Firpic, and 0.0540 mg Ir(pq)$_2$(acac) and they are mixed by using magnetic bar for 15 min. at room temperature. The solution was coated onto the PEDOT:PSS layer at 3000 rpm for 60 s. Then, it was baked
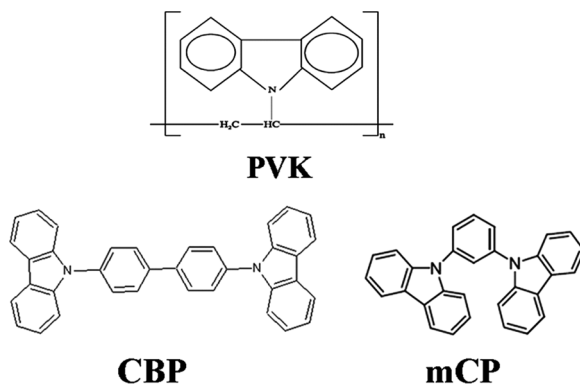

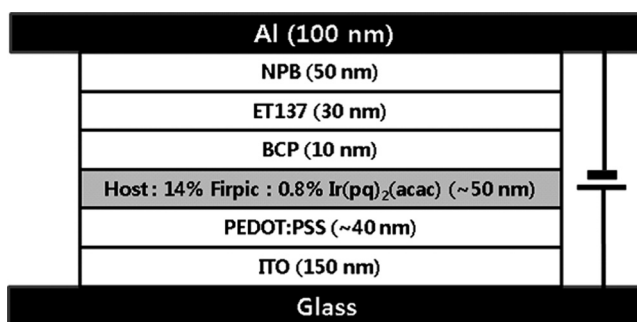**Figure 1.** Chemical structure of host materials used as host in device.

Figure 2. Devices configuration with various host materials.

at $60°C$ for 20 min in vacuum oven. The other layers were deposited by thermal evaporation process for the efficient electron injection and transport except for the PEDOT:PSS and emission layers. The device configuration is shown in the Figure 2. After devices fabrication, the optical and electrical properties of the devices such as the current density, luminance, luminous efficiency, CIE coordinates and electroluminescence (EL) spectra characteristics were measured with CHROMA METER CS-1000 and Keithley 237 instruments, respectively. All measurements were carried out under ambient conditions at room temperature with the DC voltage bias. The emitting area of device is $3\,mm \times 3\,mm$.

Results and Discussion

It is very important that the exciton existed on T_1 of phosphorescent emitting dopant confines within that to obtain high performance OLED. In this case that T_1 of host material is higher than that of emitting dopant, the exciton leakage such as endo-thermic exciton energy transfer from dopant to host can be suppressed and device efficiency can be improved. Although non-conjugated polymers such as PVK have been studied in solution processed device due to the higher T_1 than conjugated polymers, it is not enough to apply for the white phosphorescent OLED because the T_1 ($\sim2.65\,eV$) [15] of Firpic generally used as blue emitting dopant is much higher than T_1 ($\sim2.5\,eV$) [16] of PVK. Therefore, we employed small molecular hosts, CBP (T_1; 2.56 eV) [15] and mCP (T_1; 2.9 eV) [15], with high T_1 to solution processed white OLEDs. Figure 3 and the inset of Figure 3 show the current density and luminance properties of devices with various host materials as increment of the voltage. As a result, the devices with CBP and mCP have lower operating voltage and higher current density at same applied voltage. It proves that the charge injection and transport properties of CBP and mCP are superior than the PVK. It is because that PVK have wide energy band ($\sim3.6\,eV$), high electron injection barrier of 0.8 eV between PVK and BCP, and strong insulator property. Therefore the luminance is also higher in devices with CBP and mCP than that with PVK as shown in the inset of Figure 3. The devices with CBP, mCP, and PVK have $4379\,cd/m^2$, $7026\,cd/m^2$, and $1654\,cd/m^2$, respectively. The efficiency characteristics of devices show similar tendency with luminance and current density flow. Figure 4, the inset of Figure 4, and Figure 5 show the luminous efficiency, power efficiency, and quantum efficiency, respectively, of devices with various host materials. The devices show the max. luminous efficiency
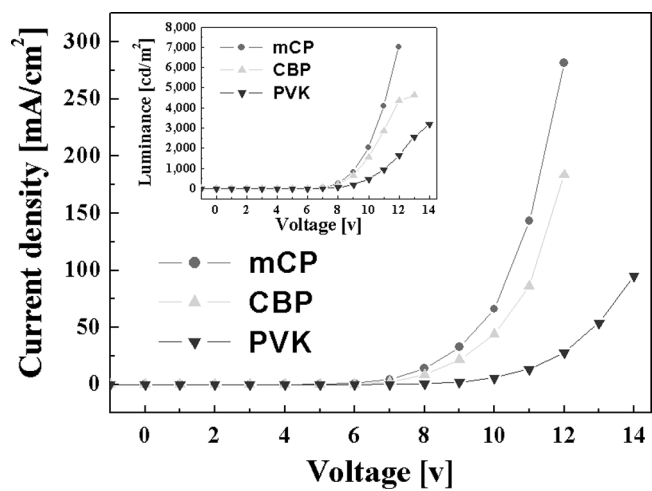
Figure 3. Current density (inset; luminance) vs. voltage curves of devices with various host materials.

of 9.8 cd/A, 10.5 cd/A, and 4.2 cd/A, the max. power efficiency of 3.4 lm/W, 4.7 lm/W, and 2.5 lm/W, and the max. quantum efficiency of 5.2%, 5.7%, and 1.9%, for the devices with CBP, mCP, and PVK, respectively. Therefore, we could confirm that the more the host has higher T_1, the more increased the efficiencies become. On the other hand, Figure 6 and inset of the Figure 6 show the electroluminescence (EL) spectra and CIE coordinates of devices with CBP, mCP, and PVK. The EL spectra were obtained when the voltage of 10 V was applied. The blue emission peaks at near about 470 nm and 500 nm is due to Firpic and the red emission peak at near about 600 nm is obtained from Ir(pq)$_2$(acac). The ratio of blue and red emission intensities was changed due to different HOMO and LUMO of each host material.
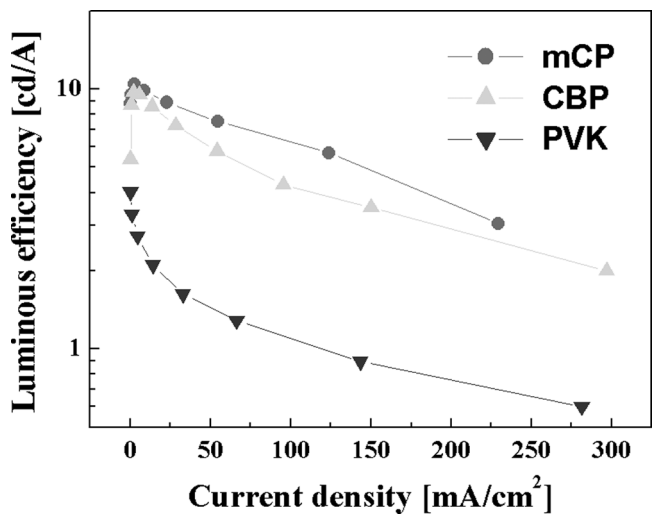

Figure 4. Luminous efficiency vs. current density curves of devices with various host materials.
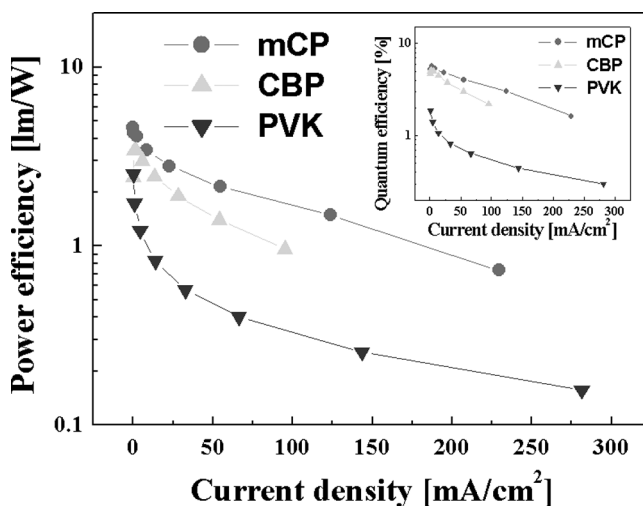
Figure 5. Power efficiency (inset; quantum efficiency) vs. current density curves of devices with various host materials.

And the CIE coordinates of devices with CBP, mCP, and PVK are $(0.48 \pm 0.005, 0.39 \pm 0.005)$, $(0.42 \pm 0.005, 0.39 \pm 0.005)$, and $(0.40 \pm 0.005, 0.39 \pm 0.005)$, respectively, regardless of the applied voltage. These CIE coordinates indicate the reddish-white emission color (warm white). It is because that, in generally, the relatively many excitons existed on the excited state of blue dopant are easily transferred toward the excited state of red dopant when all emitters are mixed in the one emission layer. However, in solution process, it is difficult to fabricate the two-layered device that each emitter is separated. Therefore, we suggest that the pure white emission or bulish white emission (cold white) can be obtained by increasing the doping concentration of Firpic compared with Ir(pq)$_2$(acac) in one emission layer.
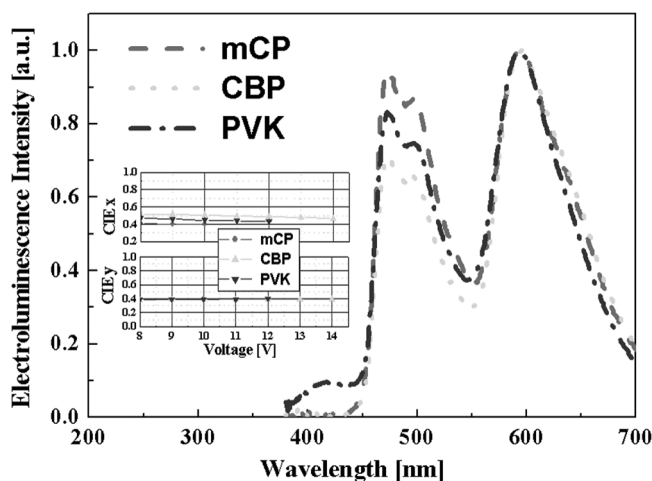

Figure 6. EL spectra (inset; CIE coordinates) of the devices with various host materials.

Conclusions

We demonstrated the devices with small molecular host materials, CBP and mCP, show higher efficiency than that with polymer host material, PVK, in white OLEDs fabricated by solution process because CBP and mCP have relatively excellent electrical properties as well as high T_1 as compared with PVK. As a result, the device with mCP that have the highest T_1 among them have the highest luminous efficiency, power efficiency and quantum efficiency of 10.5 cd/A, 4.7 lm/W, and 5.7%, respectively. We expect that the host materials with high T_1 and excellent charge transporting ability can also lead to the high efficiency in red, green, and blue phosphorescent OLEDs fabricated by solution process.

Acknowledgments

References

[1] Lee, H. K., Seo, J. H., Kim, J. H., Koo, J. R., Lee, K. H., Yoon, S. S., & Kim, Y. K. J. (2006). *Korean Phys. Soc.*, *49*, 1052.

[2] Tang, C. W., & Van Slyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.

[3] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.

[4] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Kwong, R., Tsyba, I., Bortz, M., Mui, B., Bau, R., & Thompson, M. E. (2001). *Inorg. Chem.*, *40*, 1704.

[5] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H. E., Adachi, C., Burrows, P. E., Forrest, S. R., & Thompson, M. E. J. (2001). *Am. Chem. Soc.*, *123*, 4304.

[6] Forrest, S. R., Bradley, D. D. C., & Thompson, M. E. (2003). *Adv. Mater.*, *15*, 1043.

[7] D'Andrade, B. W., Holmes, R. J., & Forrest, S. R. (2004). *Adv. Mater.*, *7*, 624.

[8] Sun, Y., Giebink, N. C., Kanno, H., Ma, B., Thompson, M. E., & Forrest, S. R. (2006). *Nature*, *440*, 289.

[9] Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *75*, 4.

[10] Adamovich, V., Brooks, J., Tamayo, A., Alexander, A. M., Djurovich, P., D'Andrade, B. W., Adachi, C., Forrest, S. R., & Thompson, M. E. (2002). *New J. Chem.*, *26*, 1171.

[11] Kolosov, D., Adamovich, V., Djurovich, P., Thompson, M. E., & Adachi, C. J. (2002). *Am. Chem. Soc.*, *124*, 9945.

[12] Wang, Y. Y., Wang, L. H., Zhu, X. H., Ru, J., Huang, W., Fang, J. F., & Ma, D. G. (2007). *Syn. Met.*, *157*, 165.

[13] Seo, J. H., Park, I. H., Kim, G. Y., Lee, K. H., Kim, M. K., Yoon, S. S., & Kim, Y. K. (2008). *Appl. Phys. Lett.*, *92*, 183303.

[14] Liu, Z. W., Helander, M. G., Wang, Z. B., & Lu, Z. H. (2009). *Appl. Phys. Lett.*, *94*, 113305.

[15] Holmes, R. J., Forrest, S. R., Tung, Y.-J., Kwong, R. C., Brown, J. J., Garon, S., & Thompson, M. E. (2003). *Appl. Phys. Lett.*, *82*, 2422.

[16] Pina, J., Seixas de Melo, J., Burrows, H. D., Monkman, A. P., & Navaratman, S. (2004). *Chem. Phys. Lett.*, *400*, 441.