Electroluminescence enhancement in blue phosphorescent organic light-emitting diodes based on different hosts*

ZHANG Wei (张微)**, **ZHANG Fang-hui** (张方辉), **HUANG Jin** (黄晋), **ZHANG Mai-li** (张麦丽), **and MA Ying** (马颖)

College of Electrical and Information Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

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Blue phosphorescent organic light-emitting diodes (OLEDs) are fabricated by utilizing the hole transport-type host material of 1,3-bis(carbazol-9-yl)benzene (MCP) combined with the electron transport-type host material of 1,3-bis(triphenylsilyl)benzene (UGH3) with the ratios of 1:0, 8:2 and 6:4, and doping with blue phosphorescent dopant of bis(4,6-difluorophenylpyridinato-N,C2)picolinatoiridium (FIrpic). The device with an optimum concentration proportion of MCP:UGH3 of 8:2 exhibits the maximum current efficiency of 19.18 cd/A at luminance of 35.71 cd/m^2 with maintaining Commission Internationale de L'Eclairage (CIE) coordinates of (0.1481, 0.2695), which is enhanced by 35.7% compared with that of 1:0 with (0.1498, 0.2738). The improvements are attributed to the effective carrier injection and transport in emitting layer (EML) because of mixed host materials. In addition, electron and exciton are confined in the EML, and 4,4',4''-Tris(carbazol-9-yl)-triphenylamine (TCTA) and Di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) have the high lowest unoccupied molecular orbital (LUMO) energy level and triplet exiton energy.

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Organic light-emitting diodes (OLEDs) have been actively investigated for their applications in flat panel displays and lighting[1-4] due to the properties of low operating voltage, high luminance efficiency, wide view angle and the suitability on flexible substrates[5,6]. Especially, the internal quantum efficiency of the devices using phosphorescent dyes has achieved almost 100% by using singlet or triplet exciton[7,8]. However, fabricating high-efficiency blue phosphorescent devices is difficult because of intrinsically wide band gap of dyes[9].

Various methods have been suggested to improve the device properties of blue OLED, such as synthesis of new materials and structure optimization[10]. In particular, the mixed host doped with dyes is actively developed. Lee et al[11] have reported the mixed host devices combining 4,4',4''-Tris(carbazol-9-yl)-triphenylamine (TCTA) with 1,3-bis(triphenylsilyl)benzene (UGH3) and doped with the deep blue material of iridium(III)bis(4′,6′-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate (FIr6), which can enhance power efficiency over 40% and maintain the Commission Internationale de L'Eclairage (CIE) coordinates of (0.163, 0.287). However, FIr6 is expensive, which is unfavorable for industry production.

In this paper, we demonstrate a blue phosphorescent OLED with increased luminance efficiency and stability by using 1,3-bis(carbazol-9-yl)benzene (MCP) and UGH3 doped with the conventional material of bis(4,6-difluorophenylpyridinato-N,C2)picolinatoiridium (FIrpic). Besides, we also discuss the carrier injection and transport mechanism, exciton recombination zone, exciton and carrier confinement of TCTA blocking layer.

A series of devices are made using the configuration of ITO/MoO$_3$ (40 nm)/ Di-[4-(N,N-ditolyl-amino)-phenyl] cyclohexane (TAPC) (40 nm)/TCTA (3 nm)/MCP:UGH3: FIrpic8% (30 nm)/ 4,7-diphenyl-1,10-phenanthroline (BPhen) (40 nm)/LiF (1 nm)/Al (100 nm). For the phosphorescent blue OLEDs, three different devices are fabricated to study the performance of devices with different host structures. MCP compositions in the mixed host device are 100%, 80% and 60%, which represent devices A, B and C, respectively. Blue phosphorescent dye of FIrpic is doped in the emitting layer (EML) with the fixed doping concentration of 8%. In addition, we fabricate the device D with the configuration of ITO/MoO$_3$ (40 nm)/TAPC (40 nm)/TCTA (3 nm)/ UGH$_3$:FIrpic8% (30 nm)/BPhen (40 nm)/LiF (1 nm)/ Al (100 nm), which

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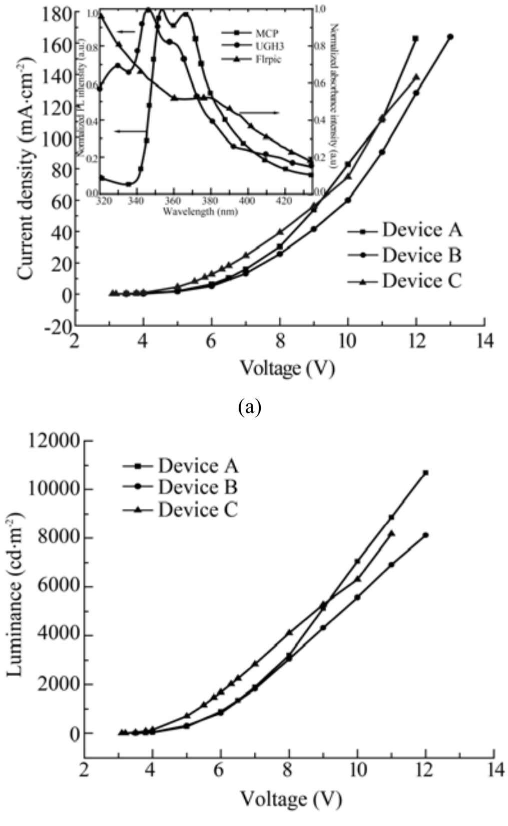
** E-mail: zhangwei198725@126.com

is used to confirm that the triplet of the host (UGH3) can transfer to the triplet of the dopant (FIrpic) and cause the stronger acromion luminescence at 504 nm, compared with the host of MCP.

ITO was purchased from CSG Holding Co., Ltd., and MoO_3 from sigma-Aldrich. CBP, FIrpic, BPhen and UGH_3 were purchased from Bando and Laser Technology Co., Ltd., TAPC, TCTA and MCP were purchased from Agnes Rhea Photoelectric Material Co., Ltd.. ITO was pre-cleaned in the cleaning solution and by ultraviolet (UV)-ozone treatment, and the organic and metallic layers were deposited subsequently in a high chamber below 6×10^{-4} Torr. Electroluminescence (EL) properties were measured using a constant current source (Keithley 2400 SourceMeter) combined with a photometer (Photo Research Spectral Scan PR655). Devices were not encapsulated and tested under atmospheric conditions.

The photoluminescence (PL) spectra of MCP, UGH3 and the absorbance spectrum of FIrpic are shown in the insert of Fig.1. It can be seen that the maximum absorption in the longest wavelength absorption band can be observed at 383 nm, while the PL spectra of MCP and UGH3 reveal the intense peaks at 370 nm and 362 nm. The bigger the overlapping between PL and absorption spectra, the better the energy transfer[12]. Therefore, the phenomenon that PL spectrum overlaps absorption spectrum illustrates the effective energy transfer between the host materials (MCP and UGH3) and the doped material (FIrpic).

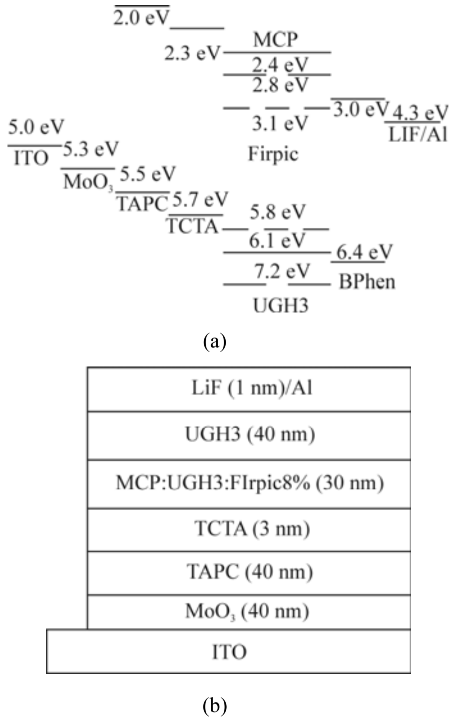
The current density-voltage curves of the devices A, B and C are shown in Fig.1(a). The current density of device is increased at first and then decreased with the decrease of MCP content in the mixed host device. This phenomenon can be explained by the following reasons. The first reason is the facilitated electron injection and transfer from BCP to MCP through UGH3 content. As shown in Fig.2(a), the lowest unoccupied molecular orbital (LUMO) levels of the BCP, MCP and UGH_3 are 3.0 eV, 2.8 eV and 2.4 eV, respectively. The LUMO level of UGH_3 is lower than that of MCP, which leads to a lower energy barrier for electron injection. The second reason is that MCP and UGH3 are the hole-transport-type and electron-transport-type materials, respectively. Moreover, we all know that current is equal to the hole current flow plus electron leakage flow, and the hole current is decreased while electron leakage flow is increased with the decrease of MCP content. The current of device B lower than device A may be mainly ascribed to the former, while device C higher than device B to the latter. As shown in Fig.1(b), the luminance versus voltage is shown, which has the same change trend as the current density versus voltage. Fig.2(b) shows the schematic diagram of the structure of the devices, and the holes can step into the EML by using TAPC/TCTA structure, because the highest occupied molecular orbital (HOMO) energy levels of TAPC and TCTA are 5.5 eV and 5.7 eV, respectively.



(a)

(b)

Fig.1 The relationship of (a) current density-voltage and (b) luminance-voltage (The inset of (a) shows the normalized PL spectra of MCP, UGH3 and UV-absorbance spectrum of FIrpic.)



(a)

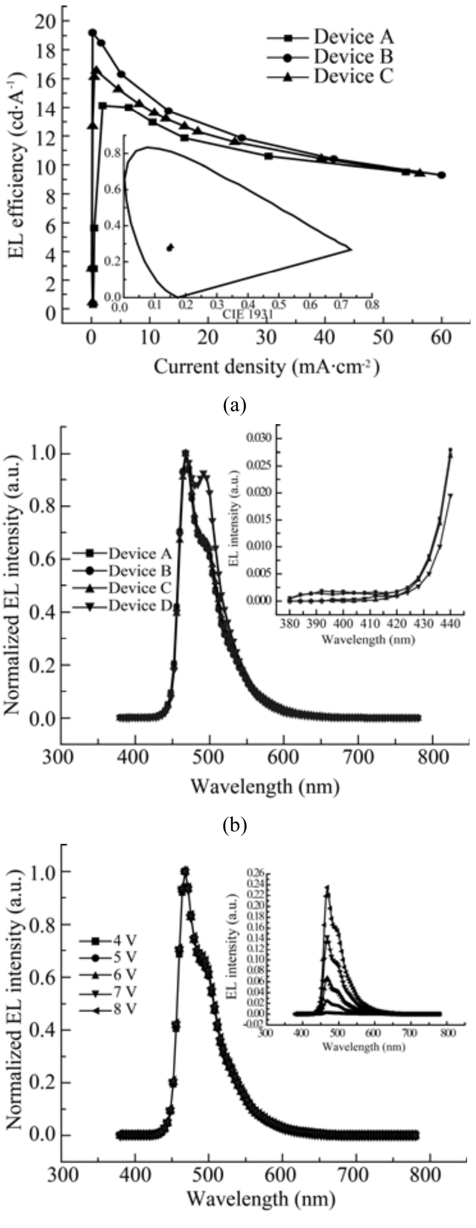
(b)

Fig.2 (a) Energy level diagram of compositions in the devices; (b) Schematic diagram of the structure of the devices

The relationship of EL efficiency and current density is plotted in Fig.3(a). Devices B and C with mixed host structure have remarkably enhanced performance than device A only with MCP host. In case of device B, the peak EL efficiency of 19.18 cd·A^{-1} at luminance of 35.71 cd·m^{-2} (4 V) is obtained, which is about 35.7% higher than that of device A (MCP single host device). The increased EL efficiency in device B with UGH3 and MCP can be explained by holes and electrons balance in the EML. In the case of MCP:UGH3 mixed host devices, the HOMO levels of TCTA, MCP and UGH3 are 5.7 eV, 6.1 eV and 7.2 eV, respectively. Due to the HOMO level differences of 0.4 eV and 1.5 eV between TCTA and MCP, TCTA and UGH3, respectively, the hole injection from TCTA to MCP is easier than to UGH3. However, the LUMO levels of BPhen, MCP and UGH3 are 3.0 eV, 2.4 eV and 2.8 eV, respectively, so the LUMO level of MCP is higher than that of UGH3, which leads to the lower energy barrier for electron injection from BPhen to UGH3. Therefore, efficient hole and electron injections into the EML are achieved though the introduction of electron-transport-type host with adequate LUMO level. Moreover, the recombination zone of mixed host device is positioned at the whole EML due to the electron transport through the molecular UGH3 (high electron mobility) and the hole transport through MCP (high hole mobility), which reduces the exciton quenching process in shallow region. In addition, the triplet energy level of TCTA (2.85 eV) is higher than that of FIrpic (2.65 eV), which confines the triplet exciton into EML, and the triplet energy levels of MCP (2.9 eV) and UGH3 (3.5 eV) both restrict the energy back transfer. The inset of Fig.3(a) shows CIE 1931 coordinates of devices A, B and C at 6 V, and we can find the relatively stable color with different UGH3 contents of host.

As shown in Fig.3(b), devices A, B and C exhibit a similar maximum luminance wavelength near 470 nm and the second vibration peak of approximately 500 nm at 6 V. However, we can find that the intensities of acromion peaks at 500 nm are increased with the increase of UGH3 content, which can be presumed that UGH3 as host could be conductive to this peak emission. To examine this inference, we investigate the EL spectrum of device D (UGH3 single host material) in detail, and then we find that the acromion peak of device D is significantly higher than that of other devices. In case of devices C and D, there is little emission, while in case of the devices A and B, new EL spectra appear near 370 nm. It could be explained by that in BPhen fluorescent emission, triplet energy level of BPhen (2.6 eV) is lower than that of FIrpic (2.65 eV), and the triplet exciton of EML/BPhen interface could transfer to BPhen and cause luminescence.

Normalized EL spectra of device B at different voltages are shown in Fig.3(c). There is a good spectra overlap, which indicates that a stable color coordinate is achieved. Tab.1 shows the color coordinates of devices A, B and C at different applied voltages. We also find that these devices all have slight color coordinate change from 4 V (30 cd·m^{-2}) to 8 V (4000 cd·m^{-2}).



(a)

(b)

(c)

Fig.3 (a) Luminous efficiency-current density curves and CIE 1931 coordinate of devices A, B and C (inset); (b) The relationship of normalized EL intensity and wavelength for devices A, B, C and D at 6 V (The inset is the EL intensity at 380–420 nm); (c) Normalized EL intensities and EL intensities (inset) of device B at different voltages

Tab.1 Color coordinates of devices A, B and C at different applied voltages

	4 V	5 V	6 V	7 V	8 V
Device A	(0.1504, 0.2770)	(0.1498, 0.2738)	(0.1497, 0.2731)	(0.1503, 0.2743)	(0.1508, 0.2755)
Device B	(0.1491, 0.2724)	(0.1481, 0.2695)	(0.1483, 0.2698)	(0.1489, 0.2716)	(0.1500, 0.2754)
Device C	(0.1525, 0.2864)	(0.1524, 0.2854)	(0.1533, 0.2861)	(0.1542, 0.2875)	(0.1546, 0.2881)

We demonstrate the properties of blue phosphorescent OLED utilizing UGH3 mixed into MCP host material, and achieve a significantly improved device. A peak luminance efficiency of 19.18 cd·A^{-1} is achieved at 35.71 cd·m^{-2} (4 V) in the UGH3:MCP (2:8) mixed host device. It is mainly attributed to that the charge injection and transport are more easy and balanced in EML, due to MCP (UGH3) has proper HOMO (LUMO) energy level and is hole(electron)-transport-type material. In addition, the recombination zone distributes on the whole EML because of the electron mobility of UGH3 host material, which reduces the exciton quenching process in shallow region.

References

[1] Yan-Fang Lv, Peng-Chao Zhou, Na Wei, Kui-Juan Peng, Jian-Ning Yu, Bin Wei, Zi-Xing Wang and Chong Li, Organic Electronics **14**, 124 (2013).

[2] G. Krucaite, R. Griniene, D. Mazetyte, G. Puckyte, J. V. Grazulevicius, Y. C. Hsieh, Y. L.Chen, J. H. Jou and S. Grigalevicius, Sythetic Metals **162**, 1079 (2012).

[3] Young Hoon Son, Mi Jin Park, Young Jae Kim, Joong Hwan Yang, Jung Soo Park and Jang Hyuk Kwon, Organic Electronics **14**, 1183 (2013).

[4] ZHAO Juan, YU Jun-sheng, LI Lu and JIANG Ya-dong, Journal of Optoelectronics·Laser **22**, 170 (2011). (in Chinese)

[5] Jonghee Lee, Jeong-Ik Lee and Hye Yong Chu, Sythetic Metals **11**, 991 (2009).

[6] JIAO Zhi-qiang, WU Xiao-ming, HUA Yu-lin, BI Wen-tao, MU Xue, BAI Juan-juan and YIN Shou-gen, Journal of Optoelectronics·Laser **23**, 1252 (2012). (in Chinese)

[7] Yong-hua Chen, Jiang-shan Chen, Yong-biao Zhao and Dong-ge Ma, Appl. Phys. Lett. **100**, 213301 (2012).

[8] Bo Zhao, Zisheng Su, Wenlian Li, Bei Chu, Fangming Jin, Xingwu Yan, Feng Zhang, Di Fan, Tianyou Zhang, Yuan Gao and Junbo Wang, Appl. Phys. Lett. **101**, 053310 (2012).

[9] Qing-Xiao Tonga, Shiu-Lun Lai, Ming-Fai Lo, Mei-Yee Chan, Tsz-Wai Ng, Shuit-Tong Lee, Si-Lu Tao and Chun-Sing Lee, Sythetic Metals **162**, 415 (2012).

[10] Daungratchaneekron Meunmart, Narid Prachumrak, Tinnagon Keawin, Siriporn Jungsuttiwong, Taweesak Sudyoadsuk and Vinich Promark, Tetrahedron Letters **53**, 3615 (2012).

[11] Jonghee Lee, Jeong-Ik Lee, Joo-Won Lee and Hye Yong Chu, Organic Electronics **7**, 1159 (2010).

[12] CHEN Su-jie, YU Jun-sheng, WEN Wen and JIANG Ya-dong, Acta Phys. Sin. **60**, 037202 (2011). (in Chinese)