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Improved current efficiency in organic light-emitting devices with a hole blocking layer*

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A hole-blocking layer (HBL) of 4,7-diphenyl-1,10-phenanthroline (BPhen) is incorporated between the emitting layer (EML) and the electron transport layer (ETL) for a tris-(8-hydroxyqunoline)aluminum based organic light-emitting device (OLED). Such a structure helps to reduce the hole-leakage to the cathode, resulting in an improved current efficiency. The BPhen improves the balance of hole and electron injections. The current efficiency is improved compared with that of the device without the blocking layer. The highest luminous efficiency of the device with 6 nm BPhen acting as a blocking layer is 3.44 cd/A at 8 V, which is improved by nearly 1.5 times as compared with that of the device without it.

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Since the first report on two-layer and three-layer organic light-emitting devices (OLEDs)[1,2], much work was devoted to the electroluminescent devices based on heterojunction of small molecule thin films deposited by vacuum evaporation. An organic heterostructure consists of a stack of layers, i.e., at least two layers of a hole transport layer (HTL) and an electron transport layer which is often the emitting layer (EML) as well. High-performance OLEDs should have low operating voltage, high efficiency and relatively good stability. For applications, the efficiency is one of the key parameters for OLEDs. For improving the OLED's efficiency, one needs to understand all physical processes in the device, properly model them, and optimize the necessary parameters. To achieve highly efficient OLEDs, various approaches have been tried, such as anode[3,4] or cathode[5] modification, hole blocking[6], doping[7], annealing[8] and optical out coupling[9]. Typically, hole-blocking layers (HBLs) are most commonly placed after EML, closer to cathode to confine the carriers and excitons[10]. Another successful approach is the insertion of an HBL between the HTL and EML to improve the efficiency but not the current[11]. Generally, the hole experiences a smaller barrier compared with the electron[12]. Moreover, the hole mobility in HTL is an order of magnitude higher than electron mobility in ETL[13]. External quantum efficiency (EQE) of OLED depends heavily on the efficiency of carrier injection and recombination as well as on the electron-hole balance. Therefore, in order to achieve the maximum efficiency, a balanced carrier recombination in the EML is necessary for the device. However, the commonly used configuration of OLEDs can not provide the required conditions for a balanced carrier injection/transport which leads to efficient recombination. As a result, establishing an electron-hole balance by reducing the number of holes or increasing the number of electrons reaching the EML is considered as one of the most direct and viable solutions to improve the device efficiency. HBLs are generally used for this purpose, but they increase the operating voltages[14-17] in turn. For example, in a typical indium tin oxide (ITO)/NPB/Alq_3/Mg:Ag structure, where NPB is N,N'-Di-(naphth-2-yl)-N,N'-diphenyl-benzidine with hole mobility of 10^{-5} cm^2/Vs and electron mobility of Alq_3 of 10^{-6} cm^2/Vs, the hole is injected from the ITO side, and experiences an overall energy barrier of around 1.7 eV, while the electron has to across a larger barrier of 2 eV before recombination. Such a device suffers a hole leakage to the cathode, which decreases the efficiency.

In this paper, we insert an HBL between EML and ETL for decreasing the hole leakage, and select BPhen as the HBL which is an excellent electron transporting material with high electron mobility and the low highest occupied molecular orbital (HOMO) level. Fig.1(a) shows the energy band diagram of the device. To minimize the increase of the total voltage, a thin HBL is used. The design improves the hole-electron balance at the HTL-ETL interface without significant voltage shift. Tuning of the current

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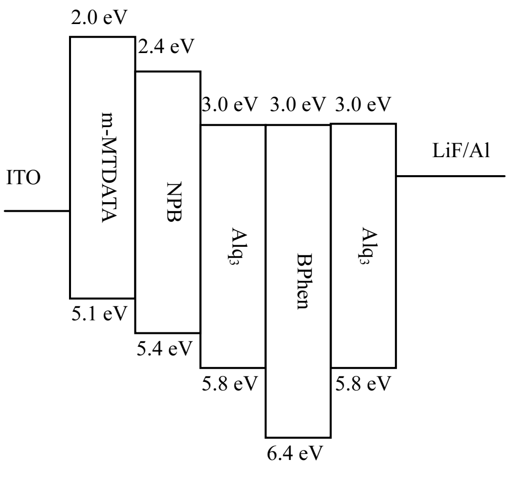
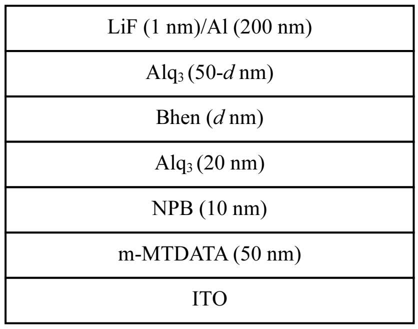
efficiency is possible by varying the thickness of HBL, which controls the hole leakage. To maintain the same optical output coupling, the total thickness of the organic layers is kept constant in our experiment. The insertion of an HBL increases the efficiency of device without much sacrifice on the current injection, and the current efficiency is improved compared with that of the device without the block layer. The highest luminous efficiency of the device with 6 nm BPhen is 3.44 cd/A at 8 V, which is nearly 1.5 times larger than that of the device without it.

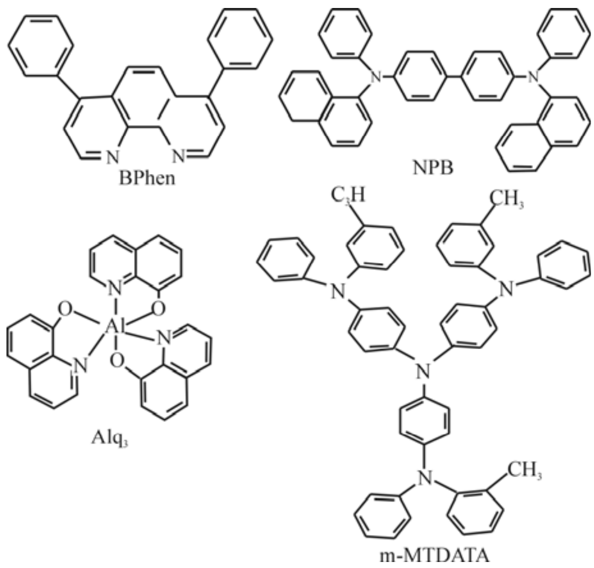
Fig.1(b) shows the structure of device studied in this paper, in which ITO on glass acts as anode, the stacked LiF/Al as cathode, 4,4',4''-tris{N,-(3-methylphenyl)-N-phenylamin}triphenylamine (m-MTDATA) acts as the hole injection layer (HIL) with HOMO level of 5.1 eV, BPhen as HBL with HOMO level of 6.4 eV, NPB as HTL with the HOMO level and lowest unoccupied molecular orbital (LUMO) level of 5.4 eV and 2.4 eV, respectively, and Alq_3 as EML or ETL with the HOMO and LUMO levels of 5.8 eV and 3.0 eV, respectively. Four devices marked as A–D with structure of ITO/m-MTDATA (50 nm)/NPB (10 nm)/Alq_3 (20 nm)/BPhen(d nm)/Alq_3(50-d nm)/LiF(1 nm)/Al (150 nm) were fabricated, where d is chosen as 0 nm, 4 nm, 6 nm and 8 nm, respectively. The routine cleaning procedure, including ultrasonication in acetone and ethanol, and rinsing in deionized water, was firstly carried out to clean ITO glass. The deposition was carried out in a high vacuum condition of about 2×10^{-4} Pa. Except for HBL, all other materials were deposited simultaneously for the four samples with the same evaporation process. Electroluminescence (EL) spectra of the fabricated devices were measured with a PR655 spectra scan spectrometer. The luminance-current density-voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage-current source. All measurements were carried out at room temperature under ambient atmosphere without any encapsulation of the OLEDs.



(a)



(b)



(c)

Fig.1 (a) Schematic diagram of energy band of the devices; (b) The device structure of the OLEDs; (c) Chemical structures of organic materials

Four devices with different thicknesses of the blocking layer were fabricated and tested. As shown in Fig.2, the BPhen layer blocks part of the hole transporting to ETL directly due to the low HOMO level of it. In addition, the NPB also serves as electron blocking layer, and the exciton forms at the Alq_3/BPhen interface. When the thickness of the BPhen is small, the holes can not be blocked effectively. With the increase of d, emission from Alq_3 increases under the same current density. Since the BPhen blocking layer can block the holes and facilitate electron transportation, the exciton recombination region is confined into Alq_3 emissive regions with an improved balance. Fig.2 shows the current density-voltage characteristics of the devices. Under the forward bias conditions, the current increases superlinearly with the increase of applied voltage and retains a small value in the reverse bias case. It is found that the driving voltages (below 13 V) for all the OLEDs with BPhen layers inserted into Alq_3 are lower than that without BPhen layer, due to the effect of hole blocking and exciton confinement within the EML. It is thought that the accumulation of holes occurs at the BPhen/Alq_3 interface. Therefore, the electric field of EML of OLED with the BPhen layer is considered to be enhanced compared with that of the OLED without a BPhen layer, and thus the EL properties are improved. It is also considered that the improvement occurs when there is a good balance between the injected electrons and holes as BPhen owns high electron mobility. In case of the device with 6 nm-thick BPhen layer, the transportation of holes should be partially hindered by the blocking layer due to HOMO. On the other hand, when the thickness of BPhen layer increases to 8 nm, it is expected that the holes flowing towards the cathode are reduced dramatically.

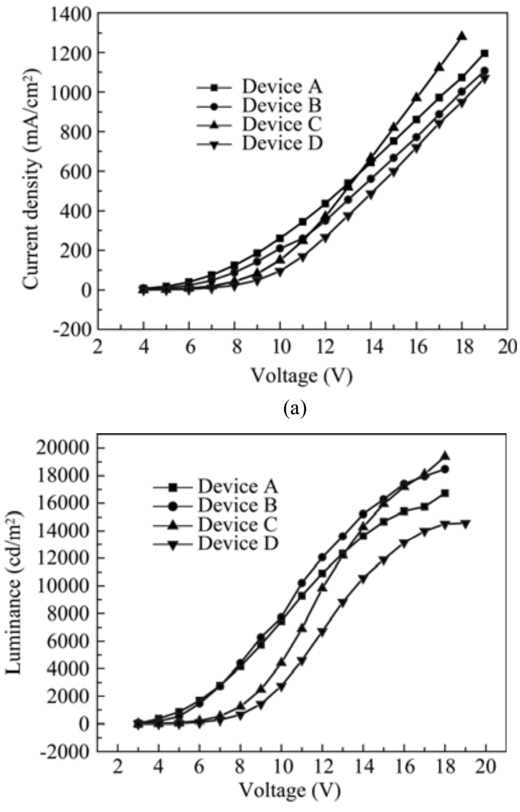


Fig.2 (a) Current density-voltage and (b) luminance-voltage characteristics of devices A–D

The luminance of the devices also shows the same tendency as the current density. The current density of the device is mainly determined by the interfacial energy barrier and charge mobility of the organic materials. The low interfacial energy barrier and the high carrier mobility usually induce low driving voltage. In particular, interfacial energy barrier influences not only the driving voltage but also the turn-on voltage of the devices. In other words, the turn-on voltage is closely related to the interfacial properties of the device, while the driving voltage mainly depends on the charge mobility of the material. It is essential to confine the electrons and holes in the light-emitting layer to get high performance. It's well known that BPhen confines holes effectively in the EML. The improvement seems to be caused by a good balance between the injected electrons and holes when the block layer with proper thickness. The maximum luminances of devices A–D are 16730 cd/m^2, 18480 cd/m^2, 19380 cd/m^2 and 14580 cd/m^2, respectively.

Fig.3 shows the current efficiency-voltage characteristics of the devices. We believe that the improved efficiency of the devices is due to the decrease of hole injection, which results in balancing the number of electrons and holes injected into the emitting layer and thus eliminating the nonproductive hole current. The decrease of injection current in the devices is due to the decrease of hole-injection current, which indicates that the BPhen layer can act as a hole blocking layer when it is inserted into the Alq_3 layers. It is obvious that the device with 6 nm-thcik BPhen as HBL has the highest current efficiency of 3.44 cd/A which is about 1.5 times higher than that of the device without HBL (2.24 cd/A). Tab.1 lists the performance of the devices. We can see that the device with 6 nm-thcik BPhen as HBL (device C) shows the maximum current efficiency of 3.44 cd/A at 9 V and the maximum brightness of 19380 cd/m^2 at 18 V. It indicates that the holes and electrons are more balanced in the OLED with an optimum BPhen thickness of around 6 nm than those in the other three devices. Our results suggest that the optimum thickness of BPhen layer improves the balance of hole and electron, resulting in the improvement of the efficiency.

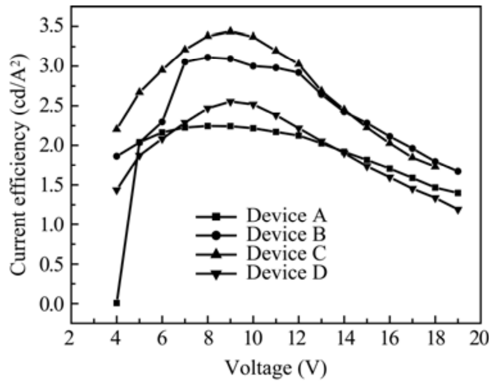


Fig.3 The current efficiency-voltage characteristics of devices A–D

Tab.1 The performance of devices with blocking layer in different thicknesses

Device	Maximum EL efficiency (cd/A)	Maximum luminance (cd/m^2)	Luminance at 4 V
A	2.24 at 8 V	16730 at 19 V	352
B	3.11 at 7 V	18480 at 19 V	174
C	3.44 at 9 V	19380 at 18 V	14.61
D	2.55 at 9 V	14580 at 19 V	6.87

Usually, the mobility of electrons is much lower than that of holes in common organic materials. It gives rise to an accumulation of holes at the BPhen/Alq_3 interface. Either increasing the number of electrons or decreasing the number of holes may improve the balance. Obviously, the presence of BPhen can increase the number of electrons to possess higher mobility in BPhen than Alq_3, while the number of holes can be confined in emitting layer. The phenomena observed experimentally are consistent with such a speculation, which can be discussed by using the simplified energy band model. The BPhen layer blocks part of the holes injected from the anode, and hence balances the injection numbers of holes and electrons in the emission layer. As BPhen thickness increases, the hole blocking effect increases, and thus the turn-on voltage increases as well. As hole-blocking thickness increases, the locally reverse electric field increases. Thus hole injection is impeded in some extent. The further increase of thickness blocks out the hole injection, and thus reduces the efficiency.

In summary, to achieve the high efficiency OLEDs, both carriers and excitons must be well confined within the emissive layer. The approach discussed here is efficiently forcing the carrier recombination and the exciton confinement in the EML by the use of blocking layers. The blocking function can be incorporated as a separate layer which is inserted between the EML and the ETL. Alternatively, the blocking function can be incorporated into the ETL materials, as shown for BPhen, which perform as efficient ETL materials. By carefully controlling the HOMO, LUMO and energy of the HTL and ETL materials, it may be possible to eliminate the need for separate blocking layers at EML/ETL interface. The result shows a simplified structure for high efficiency devices, and we demonstrate a high-efficiency OLED with thin BPhen hole blocking layer. The BPhen blocks part of the injected holes from the ITO anode, and improves the balance of hole and electron injections. The current efficiency is improved compared with that of the device without the blocking layer. The highest luminous efficiency of the device with 6 nm-thick BPhen as blocking layer is 3.44 cd/A at 8 V, which is nearly 1.5 times higher than that of the device without it.

References

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

[2] J. Kido, M. Kimura and K. Nagai, Science **267**, 1332 (1995).

[3] Bing Chen, Yanhu Li, Yueying Chu, Anmin Zheng, Jiwen Feng, Zhitian Liu, Hongbin Wu and Wei Yang, Organic Electronics **14**, 744 (2013).

[4] Dong-Hyun Lee, Jong Hyeok Park, Heeyeop Chae and Sung M. Cho, Organic Electronics **10**, 1345 (2009).

[5] Chih-Hung Hsiao, Shun-Wei Liu, Chin-Ti Chen and Jiun-Haw Lee, Organic Electronics **11**, 1500 (2010).

[6] Takayuki Chiba, Yong-Jin Pu, Ryoichi Miyazaki, Ken-ichi Nakayama, Hisahiro Sasabe and Junji Kido, Organic Electronics **12**, 710 (2011).

[7] Sang-Hyun Eom, Ying Zheng, Edward Wrzesniewski, Jaewon Lee, Neetu Chopra, Franky So and Jiangeng Xue, Organic Electronics **10**, 686 (2009).

[8] Shixiong Liang, Zhaoxin Wu, Xuanke Zhao, Dawei Wang, Xun Hou, Zhijian Chen and Qihuang Gong, Optics Communications **285**, 1625 (2012).

[9] Yu Bai, Jing Feng, Yue-Feng Liu, Jun-Feng Song, Janne Simonen, Yu Jin, Qi-Dai Chen, Jian Zi and Hong-Bo Sun, Organic Electronics **12**, 1927 (2011).

[10] Zhengyi Sun, Xunmin Ding, Baofu Ding, Xindong Gao, Yongmao Hu, Xiaoqing Chen, Yun He and Xiaoyuan Hou, Organic Electronics **14**, 511 (2013).

[11] Yong-Jin Pu, Makoto Yoshizaki, Takahiro Akiniwa, Ken-ichi Nakayama and Junji Kido, Organic Electronics **10**, 877 (2009).

[12] M. B. Khalifa, D. Vaufrey and J. Tardy, Organic Electronics **5**, 187 (2004).

[13] E. Tutis, D. Berner and L. Zuppiroli, J. Appl. Phys. **93**, 4594 (2003).

[14] Young Wook Park, Young Min Kim, Jin Hwan Choi, Tae Hyun Park, Jin Woo Huh, Hong Suk Kim, Min Ju Cho, Dong Hoon Choi and Byeong-Kwon Ju, Appl. Phys. Lett. **95**, 143305 (2009).

[15] Iizumi K., Saiki K. and Koma A., Surface Science **518**, 126 (2002).

[16] Yutaka Noguchi, Naoki Sato, Yukimasa Miyazaki and Hisao Ishii, Appl. Phys. Lett. **96**, 143305 (2010).

[17] Li Y. Q., Fung M. D., Xie Z. Y., Lee S. T., Hung L. S. and Shi J. M., Adv. Mater. **14**, 1317 (2002).