High-brightness blue organic light emitting diodes with different types of guest-host systems^{*}

WANG Xiao (王肖)¹, ZHANG Jing-shuang (张敬爽)², PENG Cui-yun (彭翠云)³, GUO Kun-ping (郭坤平)³, WEI Bin (魏斌)³, and ZHANG Hao (张浩)³**

1. School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

2. Langfang Polytechnic Institute, Langfang 065001, China

3. Key Laboratory of Advanced Display and System Application, Ministry of Education of China, Shanghai University, Shanghai 200072, China

(Received 21 November 2015)

©Tianjin University of Technology and Springer-Verlag Berlin Heidelberg 2016

We demonstrate high-brightness blue organic light emitting diodes (OLEDs) using two types of guest-host systems. A series of blue OLEDs were fabricated using three organic emitters of dibenz anthracene (perylene), di(4-fluorophenyl) amino-di (styryl) biphenyl (DSB) and 4,4'-bis[2-(9-ethyl-3-carbazolyl)vinyl]biphenyl (BCzVBi) doped into two hosting materials of 4,4'-bis(9-carbazolyl) biphenyl (CBP) and 2-(4-biphenylyl)-5(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD) as blue emitting layers, respectively. We achieve three kinds of devices with colors of deep-blue, pure-blue and sky-blue with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.16, 0.10), (0.15, 0.15) and (0.17, 0.24), respectively, by employing PBD as host material. In addition, we present a microcavity device using the PBD guest-host system and achieve high-purity blue devices with narrowed spectrum.

Document code: A Article ID: 1673-1905(2016)02-0089-4

DOI 10.1007/s11801-016-5232-1

Blue organic light emitting diodes (OLEDs) are important for various applications, for example, traffic signals, full color scanners, displays, fluorescence sensor in the field of biochemistry and lighting, including white emission generated by color conversion method^[1]. The luminance efficiency of OLEDs has been greatly improved in recent years^[2-4]. In 2006, Forrest et al^[5] proposed a hybrid fluorescent/phosphorescent route to realize efficient white OLEDs. In this design, white OLEDs with high efficiency can be achieved with the blue fluorescence substituting for the blue phosphors. Therefore, the enthusiasm of electro-phosphorescence might diminish, while that for electro-fluorescent OLEDs might revive^[6-8]. In order to obtain high brightness blue light, microcavity structure device has been studied intensively to narrow spectrum and the luminance has been enhanced so as to get high brightness^[9-11].

In this paper, we report high efficiency blue OLEDs with three different emitters doped in the hosting materials of 4,4'-bis(9-carbazolyl) biphenyl (CBP) and 2-(4-biphenylyl)-5(4-tert-butyl-phenyl)-1,3,4-oxadiazole (PBD), respectively. The blue OLEDs with high brightness and high color-purity are achieved using a microcavity structure.

Fig.1(a) shows the schematic diagram of a series of de-

vices. The structure is glass-indium tin oxide (ITO)/N,N'diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPD)/host: guest/Alq₃/LiF/magnesium (Mg)/silver (Ag). In this paper, we select dibenz anthracene (perylene), di(4-fluorophenyl)amino-di (styryl) biphenyl (DSB) and 4,4'-bis[2-(9-ethyl-3-carbazolyl)vinyl]biphenyl (BCzVBi) doped into CBP and PBD as blue emitting layers, respectively. Fig.1(b) illustrates the chemical structures of guest and host materials.

The devices were fabricated by conventional vacuum deposition of the organic layers and the cathode onto an ITO (15 Ω , 150 nm) coated glass substrate under a base pressure lower than 2.67×10^{-2} Pa. The organic layers consist of the electron transporting layer (ETL), the emitting material layer (EML) and the hole transporting layer (HTL). The substrates were successively cleaned in detergent, de-ionized water, acetone and isopropanol. Immediately, prior to loading into a custom-made high vacuum thermal evaporation chamber, the substrates were exposed to an ultraviolet-ozone environment for 15 min. The typical deposition rates for organic materials, Ag and Mg were 0.06 nm/s, 0.02 nm/s and 0.50 nm/s, respectively. Measurements were carried out and the devices were kept in N2 atmosphere to prevent the negative effects of oxygen and humidity. The active area of

^{*} This work has been supported by the National Natural Science Foundation of China (Nos.51505270 and 61504077), the National Basic Research Program of China (No.2015CB655005), and the Project of Science and Technology Commission of Shanghai Municipality (No.15590500500).

^{**} E-mail: zhkeylab@shu.edu.cn

• 0090 •

the devices defined by the overlap between the electrodes is 4 mm^2 in all cases. The current-voltage-luminance (*J-V-L*) characteristics and electroluminescence (EL) spectra were measured and recorded by a Keithley 2 400 source-meter and a Minolta PR-6 500 spectrometer.



Fig.1 (a) The structural schematic diagram of devices with different guest-host systems and (b) the molecular structures of materials used in host-guest systems

The photo-physical properties of the CBP and PBD were measured using photoluminescence (PL) spectroscopy, as shown in Fig.2. The emission areas of CBP and PBD cover from 350 nm to 550 nm, while the excitation peak wavelengths of DSB and BCzVBi locate at 420 nm and 370 nm, respectively, which proves that CBP and PBD can be the host materials for DSB and BCzVBi. This indicates that the emission of CBP and PBD can be absorbed by the guest materials, so the energy from the host molecule can be transferred to the guest molecule. In addition, as seen from Fig.2, the most appropriate host molecular for perylene is the one that emits at about 300 nm. Although CBP and PBD are not the most suitable host material, the carrier trap instead of energy transfer exists as the primary mechanism between CBP or PBD and perylene. The interaction between dipoles depends on the distance R of the molecules and the orientation of their transition dipoles. This kind of interaction along with energy transfer is called as Förster resonance energy transfer (FRET). The rate constant $K_{\rm ET}$ of FRET can be expressed as^[12]

$$K_{\rm ET} = \frac{1}{\tau_{\rm D}} \left(\frac{R_0}{R}\right)^6,\tag{1}$$

where τ_D is the lifetime of the donor in the absence of acceptor, and R_0 is a constant for the donor-acceptor pair, which is usually called Förster radius with unit of nm and expressed as

$$R_{_{0}} = 0.0211 \cdot \left(n^{-4} Q Y_{_{\rm D}} J \kappa^{^2} \right)^{\frac{1}{6}}, \qquad (2)$$

where *n* is the refractive index of the medium, QY_D is the quantum yield of donor, κ is orientation of the dipoles, and *J* describes normalized overlap integral of donor and acceptor spectra as

$$J = \int_{0}^{\infty} f_{\rm D}(\lambda) \mathcal{E}_{\rm A}(\lambda) \lambda^4 \mathrm{d}\lambda , \qquad (3)$$

where $\varepsilon_A(\lambda)$ is the molar extinction coefficient, and $f_D(\lambda)$ is the normalized spectral distribution of fluorescence.

From Fig.2(a), we find that the overlap integral of CBP and acceptor spectra is close to that of PBD and acceptor. Therefore, the energy transfer efficiencies are comparable for two hosting materials.



Fig.2 The PL spectra of host materials and the absorption spectra of guest materials

Fig.3(a) and (c) reveal that the change of the guest materials affects the luminance, the turn-on voltage and the current efficiency of the devices. The turn-on voltages (measured at the luminance of 1 cd/m^2) of the devices using the DSB, BCzVBi and perylene as the guest materials are ~4.0 V, ~4.7 V and ~5.5 V, respectively. The maximum current efficiencies of 4.84 cd/A, 1.47 cd/A and 0.43 cd/A are obtained at the current densities of 9.8 mA/ cm^2 , 360 mA/cm² and 2.6 mA/cm² for the devices using the DSB, BCzVBi and perylene as the guest materials, respectively. As shown in Fig.3(a), the maximum luminances of the devices using DSB, BCzVBi and perylene as the guest materials are 33 420 cd/m², 20 130 cd/m² and $8\,226\,\text{cd/m}^2$, respectively. The maximum current efficiency and luminance of 4.84 cd/A and 33 420 cd/m² are obtained for the device using the DSB as the guest material, which are higher than those of devices with other guest materials. The maximum quantum efficiencies of DSB, BCzVBi and perylene are ~2.43%, ~0.97% and $\sim 0.21\%$, respectively, which shows that the quantum efficiency is greatly improved using the DSB as guest material. Changing the guest material of the lighting-emitting layer, we find that the device using DSB as the guest material is the best when CBP is used as the host material.

As shown in Fig.3(b), the emission peaks of the device with DSB as guest material are 480 nm and 514 nm, those of the device with perylene as guest material are 458 nm, 486 nm and 524 nm, while those of device with BCzVBi as guest material are 456 nm and 478 nm. As illustrated in Fig.3(b), we can see that the device with DSB as guest material has a narrower spectrum compared with the other two devices. The spectrum of device with perylene is much wider than those of the others, which will be suitable for white OLEDs, while the device with BCzVBi has two blue emission peaks and a narrower EL spectrum compared with the device with perylene, which will be better for blue OLEDs.



Fig.3 (a) Voltage-luminance characteristics, (b) normalized EL spectra and (c) current efficiency and external quantum efficiency characteristics of devices using CBP as host material and DSB, BCzVBi and perylene as guest materials

As shown in Fig.4, we research the properties of the devices using PBD as host material without guest material or using perylene and BCzVBi as the guest materials, respectively. Fig.4(a) reveals that the external quantum efficiency of pure PBD device (0.72%) is very close to that of PBD:perylene device (0.69%), while that of the device with BCzVBi as guest material (0.43%) is much lower. The emission spectra of PBD devices are shown in Fig.4(b). The device without guest material primarily has two deep blue emission peaks (λ_{peak1} =407 nm and λ_{peak2} =430 nm). According to the Commission Internationale de L'Eclairage (CIE) coordinates of (0.16, 0.10) as shown in Tab.1, the device without guest material emits deep blue light. In addition, the devices with perylene and BCzVBi as guest materials emit pure blue light with CIE coordinates of (0.15, 0.15) and sky blue light with CIE coordinates of (0.17, 0.24), respectively.



Fig.4 (a) External quantum efficiency characteristics and (b) normalized EL spectra of devices using PBD as host material

Tab.1 CIE coordinates of the devices with PBD as host material

EML materials	Х	Y	Description
PBD	0.16	0.10	Deep blue
PBD:perylene	0.15	0.15	Pure blue
PBD:BCzVBi	0.17	0.24	Sky blue

Fig.5(a) shows the schematic diagram of microcavity OLED with one metal mirror and three pairs of dielectric mirrors. As shown in Fig.5(b), the normalized EL spectra indicate that the full width at half maximum (*FWHM*) values are 9.5 nm, 12.6 nm and 21.6 nm for the micro-

• 0092 •

cavity devices with PBD, PBD:BCzVBi and PBD:perylene as EML, respectively. Compared with the conventional non-cavity devices with a broader EL spectrum, the microcavity device will be of great benefit in optimizing the color purity of blue OLED.



Fig.5 (a) Schematic diagram and (b) normalized EL spectra of the microcavity devices

We fabricated high-brightness and high-purity blue OLEDs using two types of guest-host systems by doping three emitters into three kinds of hosting materials. We achieve the maximum luminance of 33420 cd/m^2 and the

maximum current efficiency of 4.84 cd/A at the current density of 9.8 mA/cm^2 . In addition, we developed three types of high color-purity deep-blue, pure-blue and sky-blue devices with CIE coordinates of (0.16, 0.10), (0.15, 0.15) and (0.17, 0.24), respectively, by employing PBD as host material.

References

- Jinwen Li, High Color Purity Blue Phosphorescent Organic Lighting Emitting Devices, International Conference on Materials for Renewable Energy and Environment 2, 666 (2013).
- [2] H. Shen, X. Bai, A. Wang, H. Wang, L. Qian, Y. Yang, A. Titov, J. Hyvonen, Y. Zheng and L. Li, Advanced Functional Materials 24, 2367 (2014).
- [3] J.-A. Seo, C.-W. Lee and M.-S. Gong, Dyes & Pigments 96, 211 (2013).
- [4] Y. Qian, F. Cao and W. Guo, Tetrahedron 69, 4169 (2013).
- [5] L. Zhu, Z. Wu, J. Chen and D. Ma, Journal of Materials Chemistry C 3, 3304 (2015).
- [6] W. H. Choi, H. L. Tam, F. Zhu, D. Ma, H. Sasabe and J. Kido, Applied Physics Letters 102, 153308 (2013).
- [7] M. Mesta, M. Carvelli, R. J. de Vries, H. van Eersel, Jeroen J. M. van der Holst, M. Schober, M. Furno, B. Lüssem, K. Leo, P. Loebl, R. Coehoorn and Peter A. Bobbert, Nature Materials 12, 652 (2013).
- [8] T. Higuchi, H. Nakanotani and C. Adachi, High-Efficiency Organic Light-Emitting Diodes with Blue Fluorescent Emitter, Optical Nanostructures and Advanced Materials for Photovoltaics, Optical Society of America, 2014.
- [9] S. H. Rheea, C. S. Kimb, M. Songb, K. B. Chungc and S. Y. Ryua, ECS Solid State Letters 3, R49 (2014).
- [10] J. W. Shin, D. H. Cho, J. Moon, C. W. Joo, S. K. Park, J. Lee, J. H. Han, N. S. Cho, J. Hwang, J. W. Huh, H. Y. Chu and J. I. Lee, Organic Electronics 15, 196 (2014).
- [11] Cy He, Hq Guo, Qm Peng, Sz Dong and F. Li, Journal of Materials Chemistry C 3, 9942 (2015).
- [12] T. Förster, Discussions of the Faraday Society 27, 1959 (1959).