Efficient Solution-Processed Blue and Yellow Phosphorescent Organic Light-emitting Diodes Using Binary Blend Hosts

Yuxin GUAN [1], Wenjing LIN [2], Qiannan WANG [3], Pengchao ZHOU [4], Bin WEI [4], Yingjie LIAO [4] *

[1] *School of Materials Science and Engineering, Shanghai University, 99 Shangda Road BaoShan District, Shanghai, 20444, P.R.China*
[2] *OLED (Shanghai) Material Tech Co., Ltd & Shanghai Shinsee Optoelectronics Technology Co., 666 Ltd, Xianing Road, Shanghai, 201506, P.R.China*
[3] *Sino European School of Technology of Shanghai, Shanghai University, 99 Shangda Road BaoShan District, Shanghai, 20444, P.R.China*
[4] *School of Mechatronic Engineering and Automation, Shanghai University, 99 Shangda Road BaoShan District, Shanghai, 20444, P.R.China*

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The appropriate hosts of emitting layers (EMLs) play an important role in determining the overall performance of solution-processed phosphorescent organic light emitting diodes (PhOLEDs). We have investigated the effect of three species of host molecules, 1,3-bis(carbazol-9-yl)benzene (mCP), 10-(4-(5,5dimethylbenzofuro[3,2-c]acridin-13(5H)-yl)phenyl)-10-phenylanthracen-9(10H)-one (DpAn-5BzAc) and poly(9-vinylcarbazole) (PVK), on the performance of solution-processed blue and yellow PhOLEDs. We have found that compared to the widely used single-host EMLs, the devices using the binary blend of mCP: DpAn5BzAc as hosts, can achieve more efficient optoelectrical characteristics. The maximum current efficiencies of 11.84 and 16.61 have been realized for blue and yellow OLEDs, respectively. The superior electroluminescence performance for binary blend host-based PhOLEDs was attributed to the enhanced charge carrier balance and multi-component miscibility, which has a dramatic influence on the morphology of the emissive layer. These results demonstrate the great potential of the multi-hosts in solution-processed organic optoelectronic devices. The development of complementary colour OLEDs with blue and yellow can provide a simple approach to fabricate solution-processed white PhOLEDs.
Keywords: organic light-emitting diodes, solution-processed, binary blend.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) have many advantages over inorganic ones, such as their high contrast, bendability, self-illumination and low-power consumption [1 – 4], thus resulting in their wide application in the flat-panel display and illumination. At present, the preparation methods of mainstream OLEDs include vacuum evaporation, ink-jet printing and solution-processing. Among them, solution-processing OLEDs have attracted much attention due to the advantages such as low cost, high material- utilization rate, simple fabrication process and large-area preparation [5 – 8].

However, the solution processed OLEDs faced some issues, for example, low efficiency, poor stability, unevenness and low repeatability. Some researchers have made great effort to solve them. Chiba et al. improved the performance of solution-processed OLEDs by interface modification [9]. Doh et al. demonstrated a soluble blue phosphorescent OLEDs (PhOLEDs) with a small molecular mixed host system [10]. We have also reported multicomponent host-guest systems to improve the efficiency and reduce the roll-off of green PhOLEDs [11]. In particular, the solution-processed small molecule host and phosphorescent dopant materials have been paid intense attention in achieving efficient and stable PhOLEDs [12].

In addition, there are two approaches to fabricating white OLED, which are three-primary color mixing and complementary color mixing [13 – 16]. In this paper, we propose a simple preparation method of blue and yellow light by binary system, which is promising to be applied to the preparation of white OLEDs.

2. EXPERIMENTAL SECTION

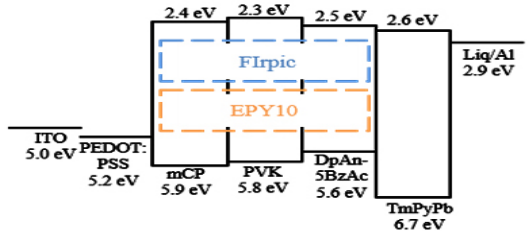
2.1. Materials

Indium tin oxide (ITO, 15Ω/sheet)-coated glass substrates were ordered from CSG Holding Co. Ltd (China). The bipolar and thermally activated delayed fluorescent (TADF) host DpAn-5BzAc was synthesized in our previous work [11, 17]. The hole injection material PEDOT:PSS was purchased from Heraeus, Germany. The other organic functional molecules were obtained from e-Ray Optoelectronics Corp, China. All chemicals and reagents in this work were used as received from commercial sources without purification unless otherwise stated. The hole injecting material PEDOT:PSS was obtained from Heraeus. Other organic functional molecules were purchased from China e-Ray Optoelectronics.

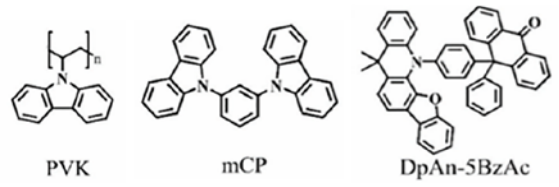
* Corresponding author. Tel.: 56333362; fax: 56333362
E-mail address: *yjliao@shu.edu.cn* (Y. Liao)

2.2. Device manufacturing

The configuration of the devices and chemical structures of host molecules are depicted in Fig. 1 a and b, respectively. Manufacturing equipment using ITO/PEDOT:PSS (40 nm)/EML (20 nm)/TmPyPB (40 nm) /Liq (1 nm)/Al (100 nm) configuration, as shown in Fig. 1, ITO (indium tin oxide) was used as the anode, PEDOT:PSS (conductivity 2×10^{-4} S/cm) was used as the hole injection layer; 1,3,5-tris(m-pyridin-3-ylbenzene) Benzo)benzene (TmPyPB) is used as an electron transport layer; 8-hydroxyquinolinyllithium (Liq) and Al are an electron injection layer and a cathode, respectively. As a common electron injection layer material, Liq has excellent electron transport characteristics and matches the electron transport layer in terms of energy level, as shown in Fig. 1 a. The prepared ITO glass substrate was firstly treated with detergent, deionized water, acetone and isopropanol in uv-ozone environment for about 15 minutes. Then, a 40 nm PEDOT: PSS film is dripped onto the ITO surface. After baking at 130 °C for 20 minutes, transfer the substrate to a nitrogen-filled glove box. The mCP, DpAn-5BzAc, PVK, FIrpic and EPY10 were all dissolved in chloroform with a concentration of 10 mg/ml.The an emissive layer (EML) coating was then spin-coated and annealed at 65 °C for 15 minutes to remove residual solvents. Finally, the upper layers which are the TmPyPB of 40 nm, the Liq of 1 nm and the Al of 100 nm were sequentially evaporated through a shadow mask to complete device fabrication in a vacuum chamber at a base pressure of about 1.0×10^{-6} mbar. The entire organic layer and the Al cathode were deposited without exposure to air, wherein the active area of the OLED was 4 mm^2.



a



b

Fig. 1. a – the device configuration and the energy level diagram; b – the chemical structures of the hosting materials in light-emitting layer

3. RESULTS AND DISCUSSION

3.1. EL properties of the blue solution-processed PhOLEDs

Here, we fabricated three solution-processed blue PhOLEDs with different host-guest system, which are a single host of mCP, and two binary hosts of mCP:PVK and mCP:DpAn-5BzAc, following the structure of ITO/PEDOT: PSS (40 nm)/host: 10 wt.% FIrpic [18, 19] (20 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm). The mCP was selected as host in PhOLEDs for their relatively high triplet energy (ET). The DpAn-5BzAc functioned as another small-molecule host for its high thermal stability, TADF characteristics and bipolar transport. The polymer PVK was used to be matrices for its good film-deposition evenness. The current density–voltage–luminance (J–V–L) characteristics, current efficiency-luminance (CE–L), the EL spectra, the external quantum efficiency (EQE) versus luminance and CIE diagram of the related devices are shown in Fig. 2 a – d, respectively. From Fig. 2 a, we can find that the turn-on voltage (Von) of Device B-1(mCP:FIrpic) is same as that of Device B-3(mCP: DpAn-5BzAc:FIrpic), which are both 5.2 V, while the Von of Device B-2(mCP:PVK:FIrpic) is as high as 6.5 V. In addition, Fig. 2 b reveals that Device B-3 employing the mCP:DpAn-5BzAc binary co-host exhibits superior current efficiency to Devices B-1 and B-2. The maximum CE of Device B-3 reached 16.61 cd/A, while the maximum CEs of Device B-1 and Device B-2 are only 10.54 and 7.87 cd/A, respectively. The enhanced performance of Device B-3 was attributed to the easier hole and electron injection from adjacent hole and electron transport layer compare to other systems [20, 21]. The hole and electron barriers are only 0.4 and 0.1 eV respectively for DpAn-5BzAc-containing binary hosts, while the hole and electron barriers are 0.6 and 0.2 eV respectively for PVK matrices.

It is worth to note that the two blue emission peaks (472 and 500 nm) of Device B-3 can be observed, while the emission peak locate at 476 nm for both Devices B-1 and B-2, as shown in Fig. 2 c. The hole and electron trapping site on the host molecule of DpAn-5BzAc produce a greenish blue emission, leading to the second peak in EL spectra of Device B-3. The optoelectrical properties of devices with single and mixed binary host are summarized in Table 1.

Table 1. Summary of PhOLED blue characteristics based on different host materials

Device [a]	V_{on} [b], V	L_{max} [c], cd/m^2	CE_{max} [d], cd/A	EL [e], nm
B-1	5.2	12200	10.32	472
B-2	6.5	7852	7.87	472
B-3	5.2	17700	16.61	476

[a] – device configuration: ITO/PEDOT:PSS (40 nm)/EML (20 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm); [b] – the operating voltage at a brightness of 1 cd/m^2; [c] – the maximum luminance; [d] – CE at the maximum value; [e] – the EL emission wavelength of the maximum intensity.

3.2. EL properties of the yellow solution-processed PhOLEDs

To verify the above inference, we also fabricated the yellow devices with single and binary blend host using a similar configuration to the blue devices, ITO/PEDOT:PSS (40 nm)/host: 10 wt.% EPY10 (20 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm), where the three types of hosts, mCP (Device Y-1), mCP:PVK (Device Y-2) and mCP:DpAn-5BzAc (Device Y-3).

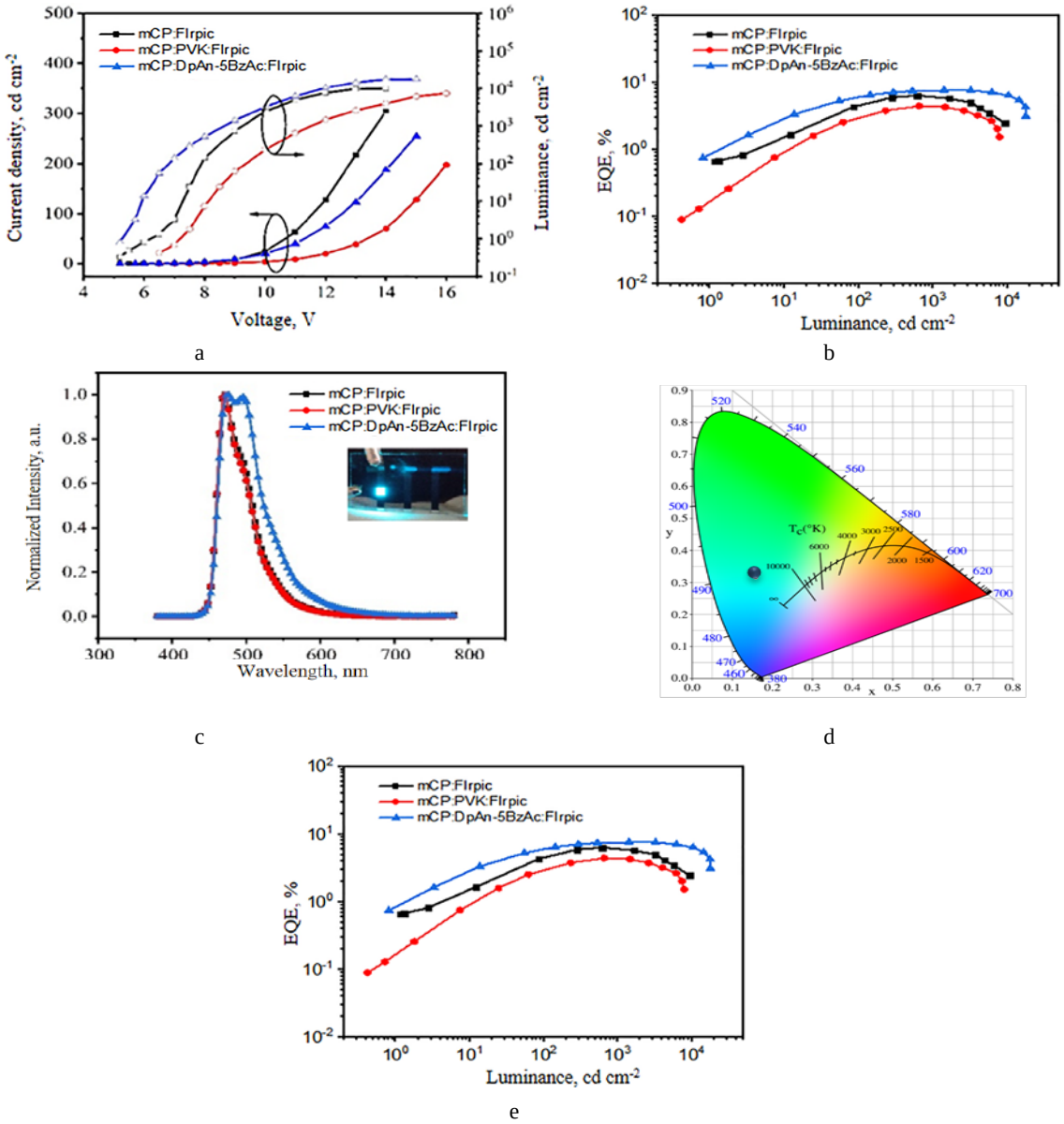


Fig. 2. Comparison of: a – J–V–L; b – CE–L; c – the corresponding EL spectral characteristics of single and binary host-based devices. The inset in Fig. 2 c is the emitting image of Device B-3; d – CIE diagram for blue device; e – the external quantum efficiency (EQE) versus luminance

The J–V–L characteristics, CE–L, the EL spectra, the EQE versus luminance and CIE diagram of the three devices are shown in Fig. 3 a – d, respectively. The typical optoelectrical properties of devices with single and binary mixed hosts are summarized in Table 2.

Table 2. Summary of PhOLED yellow characteristics based on various host materials

Device [a]	V_{on} [b], V	L_{max} [c], cd/m^2	CE_{max} [d], cd/A	EL [e], nm
Y-1	3.1	11360	10.54	584
Y-2	5.2	9311	6.5	584
Y-3	3.2	14270	11.84	584

[a] – device configuration: glass/ITO/PEDOT:PSS (40 nm)/EML (20 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm); [b] – the operating voltage at a brightness of 1 cd/m^2; [c] – the maximum luminance; [d] – CE at the maximum value; [e] – the EL emission wavelength at the maximum intensity.

Device Y-3 with the EML of mCP:DpAn-5BzAc:EPY10 shows the best EL performance with maximum luminance and CE values of 14270 cd/m^2 and 11.84 cd/A, respectively. Most importantly, there is extremely reduced efficiency roll-off for DpAn-5BzAc-based yellow OLED. Moreover, the Von was the highest and the CE was lowest for PVK-based yellow device, which is consistent with our conjecture that the macromolecular material PVK will affect the performance of the solution-processed device. Therefore, we conclude that the binary small-molecule host is an appropriate candidate for solution-processed PhOLEDs.

3.3. The energy transfer mechanisms of the binary system

As shown in Fig. 4, we plot the energy transfer mechanisms of the binary-host-based Devices B-2 and B-3. The Fig. 4 shows that the presence of macromolecular PVK blocks the energy transfer from mCP to FIrpic, resulting in reduced efficiency, higher turn-on voltage.

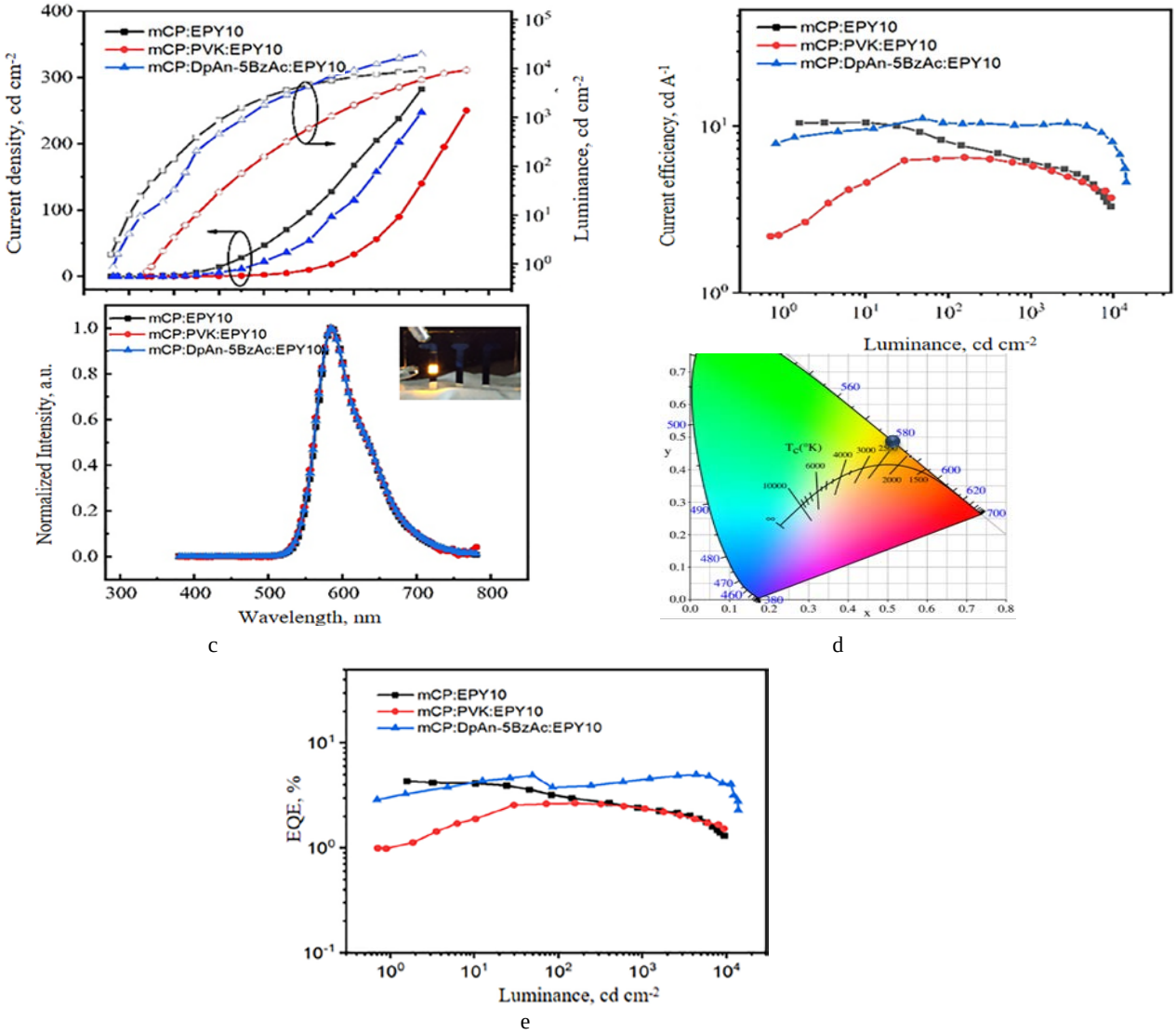


Fig. 3. Comparison of: a – *J–V–L*; b – *CE–L*; c – the corresponding EL spectral characteristics of single and binary host based devices. The inset in Fig. 3 c is the emitting image of Device Y-3; d – CIE diagram for yellow device; e – the External quantum efficiency (EQE) versus luminance

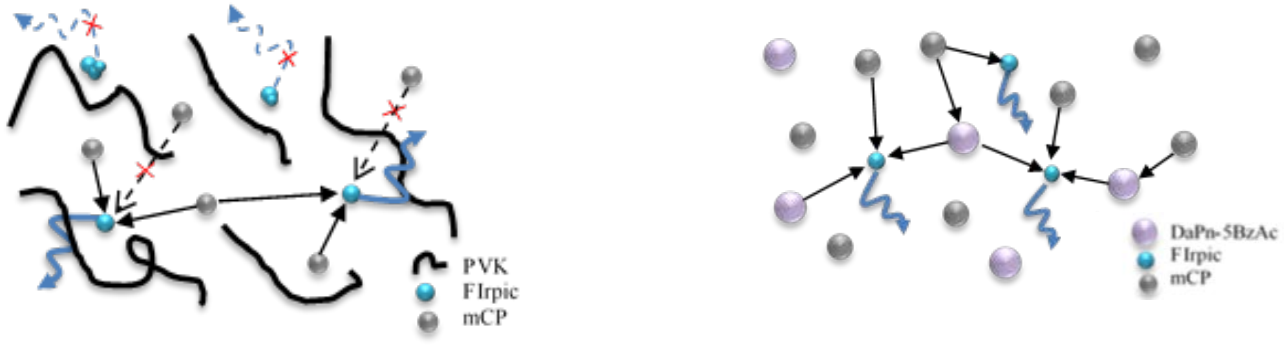


Fig. 4. The energy transfer mechanisms of: a – mCP:PVK:FIrpic; b – mCP:DaPn-5BzAc:FIrpic binary system

In addition, the presence of polymer making emitter more likely to aggregate, resulting in molecule-molecule quenching. Further, the deeper HOMO and shallower LUMO of PVK also severely hamper charge injection and/or transport in the device [22]. There are two possible energy transfer processes in the guest-host complex, Förster transfer and Dexter transfer [23]. For phosphorescent acceptor in the emitting layer, the transfer mechanism of energy has been demonstrated to be a short range. Dexter transfer is the diffusion of excitons from donor to acceptor via the Wigner-Witmer spin conversation rules.

4. CONCLUSIONS

In general, we have investigated the mixed host system using small molecular materials (mCP and DpAn-5BzAc) to enhance the hole injection ability of solution-processed OLEDs. The blue and yellow devices give efficiency with maximum luminance of 17700 and 14270 cd/m^2, peak CE of 16.61 and 11.84 cd/A, respectively, which mCP:DaPn-5BzAc was chose as binary mixed hosts. In addition, the polymer PVK is found to reduce the performance of the device by severely hampering charge injection and transport characteristics. The improved performance of the binary-host-based device is realized by accelerating the balance of charge carrier, optimizing the miscibility of solution-processed EMLs, and improving the film of structural order. This work demonstrates a simple way to fabricate a high performance solution-processed PhOLEDs by using the mixed binary host system. This work could be applied to fabricate the white solution-processed OLED devices achieved by a simple method [23, 24].

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