Highly Efficient and Stable Hybrid White Organic Light Emitting Diodes with Controllable Exciton Behavior by a Mixed Bipolar Interlayer *

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Highly efficient and stable hybrid white organic light-emitting diodes (HWOLEDs) with a mixed bipolar interlayer between fluorescent blue and phosphorescent yellow emitting layers are demonstrated. The bipolar interlayer is a mixture of p-type diphenyl (10-phenyl-10H-spiro [acridine-9,9'-fluoren]-3'-yl) phosphine oxide and n-type 2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole). The electroluminance and Commission Internationale de l'Eclairage (CIE1931) coordinates' characteristics can be modulated easily by adjusting the ratio of the hole-predominated material to the electron-predominated material in the interlayer. The hybrid WOLED with a p-type:n-type ratio of 1:3 shows a maximum current efficiency and power efficiency of 61.1 cd/A and 55.8 lm/W, respectively, with warm white CIE coordinates of (0.34, 0.43). The excellent efficiency and adaptive CIE coordinates are attributed to the mixed interlayer with improved charge carrier balance, optimized exciton distribution, and enhanced harvesting of singlet and triplet excitons.

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Intrigued by extraordinary characteristics, such as high efficiency, fast response and flexibility,[1,2] white organic light-emitting diodes (WOLEDs) are being aggressively explored for large-area flat panel displays and solid-state lighting.[3–5] WOLEDs can be generally classified into three classes; all-phosphorescent WOLEDs, all-fluorescent WOLEDs and hybrid WOLEDs. Though all phosphorescent devices are desirable since both singlet and triplet excitons can be harvested, allowing for a conversion of up to 100%, their performance exhibits poor lifetime and poor color-stability.[6–8] All-fluorescent WOLEDs are also not good enough for practical applications due to low efficiency as fluorescence emission is theoretically limited to an internal quantum efficiency of 25% due to singlet-triplet statistics.[9] However, hybrid WOLEDs, which combine stable fluorescent (F) blue emitters and phosphorescent (P) orange/green-red emitters, have many merits, such as excellent efficiency, long lifetime and stable CIE coordinates.[10,11] Since the energy transfer between the F emitter and P emitter may induce energy loss and quenching, a thin interlayer which separates and harvests the singlet and triplet excitons is usually placed between the fluorescent and the phosphorescent emitting layers in most reported F/P WOLEDs configurations.[12–15] For hybrid WOLEDs, the use of interlayers is important. Interlayers not only prevent the energy transfer between the emitting layers (EMLs) but also tune the colors of the white OLEDs.

Some effective interlayers have been reported. The 4,4-N,N-dicarbazolebiphenyl (CBP) is the most popular and efficient spacer owing to its high triplet energy (2.56 eV) and bipolar conducting properties.[16–18] Sun *et al.* developed the first successful hybrid WOLEDs with a maximum power efficiency (PE) of 22.1 lm/W[12] using CBP as the interlayer. Despite CBP being a common interlayer, it is not an ideal material as its hole mobility (10^{-3} cm^2/Vs) is ten times higher than its electron mobility (10^{-4} cm^2/Vs).[19] Zhou *et al.* used the p-type interlayer NPB to develop hybrid WOLEDs and achieved a maximum PE of 24.3 lm/W.[20] Liu *et al.* used single n-type material 2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) as the interlayer and obtained a current efficiency (CE) of 8.5 cd/A and a PE of 6.5 lm/W at 100 cd/m^2.[21] As a consequence, carriers in a single interlayer are unbalanced and difficult to manipulate. Therefore, the excellent manipulative ability of mixed interlayers with different transport characteristics and energy levels between two emitters have been extensively discussed. For instance, Liu *et al.* utilized CBP:Bebq$_2$ as a mixed interlayer in hybrid WOLEDs, obtaining a maximum PE of 16.2 lm/W.[22] Other mixed interlayers such as 4,4',4"-tri(Ncarbazolyl) triphenylamine (TCTA):hydroxyphenyl-pyridine beryllium complex (Bepp$_2$)[23,24] and TCTA:TPBi[25,26] have also been reported. To achieve higher efficiency in hybrid WHOLED, the interlayer should be able to balance the carriers and adjust the energy levels between the F and P emitters.

In this Letter, we develop a highly efficient mixed interlayer for applications in two-color fluorescent-phosphorescent hybrid WOLEDs. Particularly, we systematically investigate the influence of different doping ratios of interlayer by combining a novel p-type material diphenyl (10-phenyl-10H-spiro[acridine-9,9'-fluoren]-3'-yl) phosphine oxide (3SAFDPPO) with n-type TPBi. Through investigation and optimization of

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the hybrid WOLEDs, the forward-viewing CE and PE of the hybrid WOLED reach 58 cd/A and 53 lm/W, respectively, at 100 cd/m^2. By combining this p-type material with the n-type material (TPBi), the devices show low efficiency roll-off and stable color. Currently, there exist limited hybrid WOLEDs that can simultaneously show high efficiency, low efficiency roll-off and stable color.

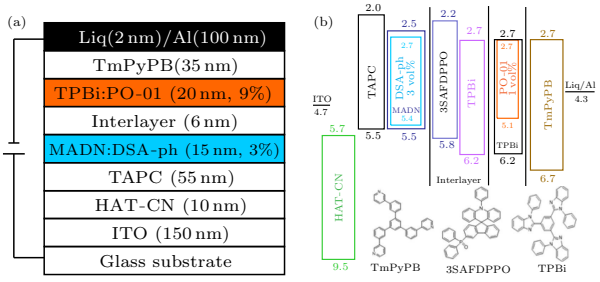

Fig. 1. (a) Structure of devices and (b) energy-level diagram of hybrid WOLEDs and materials used in this work.

As shown in Fig. 1(a), the configuration of the two-color hybrid WOLED is ITO/HAT-CN (10 nm)/TAPC (55 nm)/MADN:DSA-ph (15 nm, 3%)/interlayers (6 nm)/TPBi:PO-01 (20 nm, 9%)/TmPyPB (35 nm)/Liq (2 nm)/Al (150 nm). Here ITO is the anode, HAT-CN (1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile) is the hole injection layer, TAPC(4,4'-Cyclohexylidenebis[N,N-bis(4-methylphenyl) aniline]) acts as the hole transport layer, DSA-ph (pbis(p-N,N-di-phenyl-aminostyryl) benzene) is the blue fluorescent dopant doped into the blue host material MADN (2-methyl-9, 10di(2-naphthyl) anthracene), TPBi (1(3,5-tris(N-phenylbenzimidazol- 2-yl) benzene) acts as both interlayer and host materials for phosphorescent emitting layer, PO-01(iridium(Ⅲ) bis(4-phenylthieno [3,2-c]pyridinato-N,C20)) is the yellow phosphorescent dopant in phosphorescent emitting layer, TmPyPB (3,3'-[5'-[3-(3-Pyridinyl)phenyl][1,1':3',1" terphenyl]-3,3'-diyl]bispyridine) is the electron transport layer, the thickness of Liq is 2 nm and Al is 150 nm, which were evaporated in sequence acting as the cathode. The interlayers are made of different ratios of 3SAFDPPO:TPBi.

The devices were fabricated in a vacuum deposition instrument. Prior to organic layer deposition, indium-tin-oxide (ITO) glass substrates (sheet resistance of about 10 Ω/sq) were cleaned successively with acetone and alcohol in an ultrasonic bath, dried in a drying cabinet and exposed to a UV-ozone environment for 15 min. All organic layers were thermally deposited at the base pressure of $\leq 5 \times 10^{-6}$ Torr without breaking the vacuum. The typical deposition rates were 2–4 Å/s for organic materials and 8.0 Å/s for Al. The devices were encapsulated immediately under nitrogen atmosphere by using UV glue, desiccant and glass lids. The electroluminescent (EL) spectra and the Commission International de I' Eclairage (CIE) coordinates of devices were measured by a PR-655 photometer. Current density–voltage (J–V) measurements were carried out by using a Keithley 2400 Source Meter. The emission area of the white OLED devices was 3×3 mm^2. All the measurements were taken in ambient atmosphere.

As shown in Fig. 1(b), we applied MADN doped with DSA-ph as a blue fluorescent emitting layer for its efficient emission of blue light. PO-01 was used as phosphorescent dopant in TPBi host material for yellow light emission. TmPyPB with high electron mobility of 10^{-3} cm^2/Vs was used as the electron transporting layer (ETL) to improve the electron carrier concentration.[27] In the design of hybrid WOLEDs, the most important thing is to identify the interlayers which can function most effectively between the F emitter and the P emitter. This is to adequately prevent the Főrest energy transfer from the blue F emitters to the orange P emitters. Ideally, not only can they confine singlet and triplet excitons to the layers where they were formed, they can also reduce the energy barriers and facilitate carrier transport to both F and P emitters. For this concern, we used a p-type material 3SAFDPPO with high triplet energy (2.87 eV) as part of the mixed interlayer in the hybrid WOLED. Owing to the high lowest unoccupied molecular orbital (LUMO) of 2.2 eV, 3SAFDPPO can effectively prevent the electron leakage and confine excitons to the P emitter. To further improve the electron mobility of the interlayer and to balance the carriers in the hybrid WOLED, TPBi was used as both interlayer and host material for P emission due to its excellent electron transport ability and deep highest occupied molecular orbital (HOMO) of 6.2 eV, which can decrease the hole leakage. In addition, the electron mobility of TPBi is about 10^{-4} cm^2/(Vs) and its triplet energy (E_T) can be as high as 2.74 eV. On the one hand, this suitable E_T promises excellent energy transfer from host P to dopant PO-01 for yellow emission. On the other hand, the application of the same material as interlayer and emitter eliminates structural heterogeneity between the interlayer and the emitter, boosting carrier transport and efficiency.

To obtain high-performance WOLEDs, a mixed interlayer of p-type 3SAFDPPO and n-type TPBi exhibiting high E_T (2.87 eV) was employed in the device fabrication. Since the Dexter triplet energy transfer requires spatial overlap of the donor/accepter molecular orbitals within a range of 1–2 nm and the Főrest energy transfers which occurs within 5 nm, the thickness of the interlayer was fixed at 6 nm. To extensively study the nature of the interlayer, five devices with 3SAFDPPO:TPBi ratios of 1:0, 1:1, 1:2, 1:3 and 1:4 were fabricated and named as devices 1, 2, 3, 4 and 5, respectively.

Figure 1(b) shows the energy-level diagram of the hybrid WOLEDs, the HOMO of MADN is 5.5 eV while the HOMOs of 3SAFDPPO and TPBi are 5.75 eV and 6.2 eV, respectively. It shows that without the introduction of an interlayer, the hole transport from MADN to TPBi will experience an energy barrier of 0.8 eV. This energy barrier could block hole transport and cause carriers to accumulate at the sur-

faces of MADN and TPBi. With the addition of 3SAFDPPO, there exists only 0.3 eV energy barrier between MADN and 3SAFDPPO. Holes can therefore be easily transported to 3SAFDPPO. Furthermore, the lower HOMO energy barrier of 0.4 eV between 3SAFDPPO and TPBi also facilitates carrier transport. The lowest unoccupied molecular orbitals (LUMO) of TPBi and 3SAFDPPO are 2.7 eV and 2.2 eV, respectively. This 0.5 eV energy barrier can block the electron transport from yellow emitter to blue emitter which can in-turn reduce the intensity of blue emitter. Although the 3SAFDPPO possesses bipolar characteristic, the addition of TPBi will enhance hole blocking ability in the interlayer.

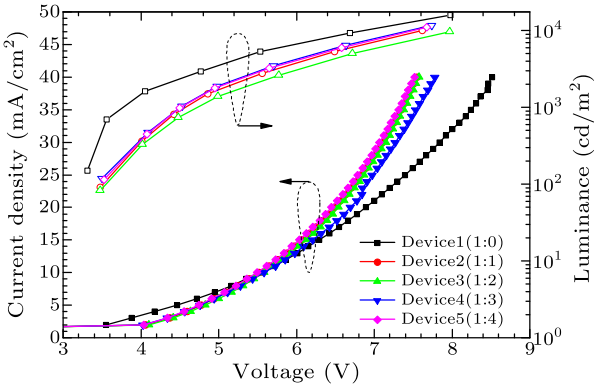

Fig. 2. Current density–voltage-luminance characteristics of devices 1, 2, 3, 4 and 5.

Current density and luminance versus voltage curves of five devices are shown in Fig. 2. It can be seen that the devices with different doping ratios exhibit similar driving voltage at the luminance of 100 cd/m^2. However, device 1 shows the lowest current density at the same voltage, especially at high driving voltage. This is as a result of the poor hole blocking ability of its 3SAFDPPO interlayer. Therefore, exciton recombination could be realized as holes could easily transport to the P emitter. This gives the reason for the highest luminance exhibited by device 1. Although device 1 shows the best electrical characteristic compared with other devices, it only gives yellow emission without blue emission. For this reason, it is required that TPBi is doped into the interlayer. The devices fabricated based on this doping approach exhibit slightly different characteristics from each other. It can be seen that device 4 with the 3SAFDPPO:TPBi interlayer doping ratio 1:3 exhibits the best charge balance characteristics. On the contrary, device 4 shows higher luminances of 6391 cd/m^2 and 11600 cd/m^2 at the current densities of 20 mA/cm^2 and 40 mA/cm^2, respectively.

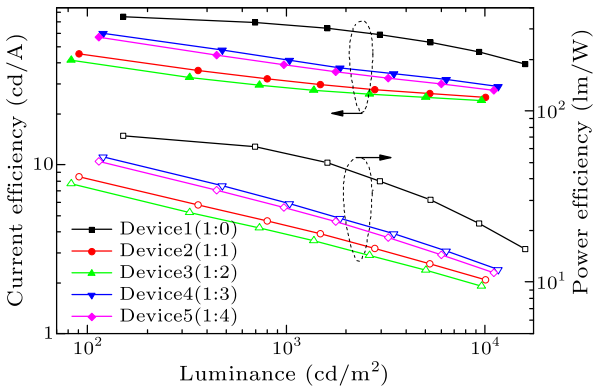

Fig. 3. Current efficiency–luminance-power efficiency characteristics of devices.

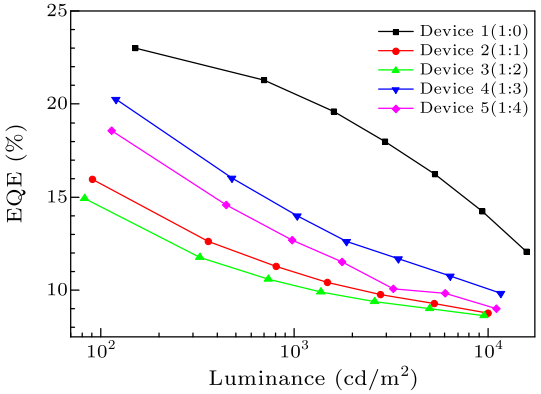

Fig. 4. External quantum efficiency (EQE) versus luminance curves for the five devices.

Table 1. Electroluminescence characteristics of the devices.

Device[a]	V^{b} (V)	η^{c}_{ce} (cd/A)	η^{c}_{pe} (lm/W)	EQE (%)	CIE $(x, y)^{d}$
Device 1 (1:0)	3.3	77, 67.3, 45.7	74.5, 55.9, 21.3	23, 20.5, 13.9	(0.46, 0.50)
Device 2 (1:1)	3.4	45, 31.4, 25.2	40.5, 21.4, 10.4	15.9, 10.9, 8.8	(0.36, 0.44)
Device 3 (1:2)	3.4	40.1, 28.6, 24.1	35.8, 18.9, 9.3	14.9, 10.2, 8.6	(0.34, 0.43)
Device 4 (1:3)	3.4	61.1, 42, 28.2	55.8, 29.1, 11.9	20.2, 14.1, 10.1	(0.39, 0.45)
Device 5 (1:4)	3.4	58.1, 38.9, 29.8	52.7, 27.1, 12.7	18.5, 12.6, 9.1	(0.42, 0.47)

[a]Four devices with interlayers having different doping ratios. [b]Voltages at 100 cd/m^2. [c]Efficiencies in the order of maximum, at 1000 cd/m^2 and at 10000 cd/m^2. [d]CIE coordinates measured at 20 mA/cm^2.

Figure 3 shows the current efficiency and power efficiency versus luminance. Device 1 emitting mainly yellow light also shows the highest efficiency. For the devices with different 3SAFDPPO:TPBi interlayers, device 4 with ratio of 1:3 shows the best efficiencies. Its maximum CE and PE are 61.1 cd/A and 55.8 lm/W, respectively. These values are higher than those reported for hybrid WOLEDs in recent times. In addition, device 4 shows a low efficiency roll-off. By increasing the doping ratio of TPBi in the interlayer, electrons may compensate the unbalanced charge carrier. The highest current efficiency obtained was 57 cd/A. This is one of the highest values obtained for WOLEDs.[28] For instance, the maximum CE of 61 cd/A only shifts to 57 cd/A from 100 cd/m^2 to 180 cd/m^2 and remains as high as 42 cd/A at

1000 cd/m^2.

Figure 4 shows the EQE versus luminance. Device 1 also exhibits the highest EQE and also shows relatively flat EQE roll-off. At 1000 cd/m^2, the EQE is reduced from the maximum value 23% to 20.5%. Even at 10000 cd/m^2, the EQE is still above the maximum EQE with 13.9% for device 1. The device parameters are summarized in Table 1.

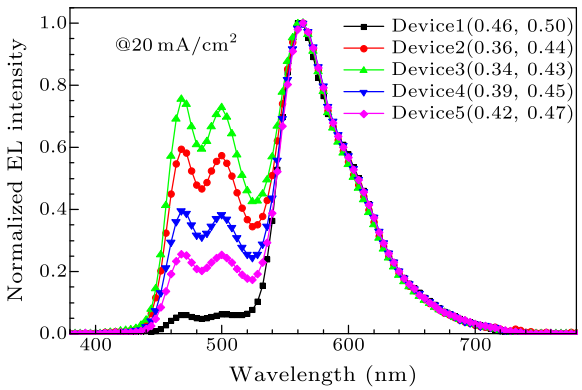

Fig. 5. The EL spectra of five devices in the visible region at 20 mA/cm^2.

Figure 5 shows the normalized EL spectra of five devices at current density of 20 mA/cm^2. The blue emission changes significantly compared with the yellow emission with variation in the interlayer composition. It can be seen that device 1 shows the lowest blue intensity. It also proves that the 3SAFDPPO used as the interlayer could not block the holes in the F emitter, especially at low driving voltage. With the 3SAFDPPO:TPBi interlayer, holes and electrons can be effectively manipulated by using different mixed ratios. The strongest blue emission is observed in device 3, with the CIE coordinates of (0.34, 0.43) which is for warm white light. Interestingly, if the ratio of 3SAFDPPO:TPBi is higher or lower than 1:2, the blue light intensity of devices is lower than that of device 3. This is due to the fact that more electrons reach the blue EML with increasing the ratio of TPBi, which will reduce the effect of 3SAFDPPO. Although the p-type material creates a large LUMO barrier with the blue EML.

Nevertheless, when the ratio of interlayer is higher than 1:2, $E_{\rm T}$ of the blue emitter would transport to the P emitter through the mixed interlayer. This causes energy loss and triplet–triplet quenching in the blue emitter. This is why the blue emission becomes weaker with a decrease in ratio of 3SAFDPPO in devices 4 and 5. Despite these changes, all the devices exhibit warm white light.

From the above results, it can be seen that all these changes are induced by the interlayer. Since the TPBi is an n-type material with high electron mobility, its existence in the interlayer eliminates the barrier between the interlayer and the P emitter as the P emitter is made of the same TPBi material. Furthermore, unlike the higher 0.32 eV energy barrier created by 3SAFDPPO, the slightly lower energy barrier (0.3 eV) between the interlayer and the F emitter promises efficient electron injection into the F emitter, which leads to strong F emission. This explains why device 3 exhibits the strongest blue emission closest to the standard CIE coordinate (0.33, 0.33) than devices 1, 2, 4 and 5. Since 3SAFDPPO has higher $E_{\rm T}$ (2.87 eV) than TPBi (2.6 eV), 3SAFDPPO plays a crucial role in separating the triplet energy transfer between the F emitter and the P emitter.

In summary, with the new 3SAFDPPO:TPBi interlayer, holes and electrons can be effectively manipulated by using different mixed ratios. If the content of TPBi is higher than that of 3SAFDPPO, electrons are more easily transported from the interlayer to the blue EML. However, if the content of 3SAFDPPO is higher than that of TPBi, holes are more easily transported from the interlayer. In addition, 3SAFDPPO plays a key role in preventing the triplet-triplet quenching between the F emitter and the P emitter. Hence we obtain the WOLEDs with the highest current and power efficiency of 61.1 cd/A and 55.8 lm/W, respectively. Due to the excellent manipulative ability of the mixed interlayer, stable CIE coordinates of (0.34, 0.43) was achieved at a current density of 20 mA/cm^2. This is the best emission for both the blue fluorescent emitting layer and the yellow phosphorescent emitting layer. Furthermore, devices with the 3SAFDPPO:TPBi interlayer show much higher performance than devices with the most commonly used CBP and NPB interlayers. These results provide a guide to design high-performance WOLEDs for display and lighting applications.

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