Materials Horizons

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/materials-horizons

Harnessing charges and excitons distribution towards extremely high performance: the critical role of guests in single-emitting-layer white OLEDs

Baiquan Liu[1], Lei Wang[1], Dongyu Gao[2], Miao Xu[1], Xuhui Zhu[1], Jianhua Zou[1*], Linfeng Lan[1], Honglong Ning[1], Junbiao Peng[1**] and Yong Cao[1]

[1]Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

[2]New Vision Opto-Electronic Technology Co., Ltd, Guangzhou 510530, China

Currently, high efficiency, low efficiency roll-off and stable color white organic light-emitting diodes (WOLEDs) are still challenging to realize via simplified structures. Herein, the simplicity/ extremely high efficiency/ low efficiency roll-off/ stable color trade-off has been accomplished in a single-emitting-layer (single-EML) phosphorescent WOLED. The WOLED exhibits total efficiencies of 111.7 cd A^{-1} and 75.5 lm W^{-1} at the practical luminance of 1000 cd m^{-2}, which are the highest among single-EML WOLEDs. Even at 5000 cd m^{-2}, the efficiencies are remained as high as 101.3 cd A^{-1} and 58.8 lm W^{-1}. Besides, the color variation in the whole range of luminances is (0.00, 0.00), which is the first single-EML WOLED with an extremely stable color. The origin of the high performance is unveiled. Particularly, the role of guests, which is often ignored in single-EML WOLEDs, on the origin of color-stability is systematically revealed and the harnessment of charges and excitons distribution by using multifunctional guests is demonstrated to be critical to stabilizing the color. Such marvelous results not only represent a significant step towards the realization of simplified WOLEDs, but also provide a new opportunity to achieve extremely stable colors [ΔCIE (Commission International de I'Eclairage)= (0.00, 0.00)].

Keywords: efficiency; efficiency roll-off; stable color; white organic light-emitting diodes.

Introduction

White organic light-emitting diodes (WOLEDs) have been the object of intense research because of their striking advantages, like high efficiency, long lifetime and flexibility.[1-5] In order to boost the efficiency, phosphorescent emitters are usually imperative to achieving an internal quantum efficiency of 100% by consuming both singlet and triplet excitons (generated at a ratio of 1: 3 owing to their multiplicity).[3] As a consequence, the thoughtful design and understanding of the emitting layer (EML) may be the room for further enhancing the performance of WOLEDs.

Generally, mixing two complementary colors (i.e., blue/orange and blue/red) or three primary colors (blue/green/red) is required to generate white emissions. To date, numerous methods have been reported to realize WOLEDs, including managing singlet and triplet excitons in hybrid structures,[6] harvesting triplet excitons from fluorescent blue emitters with high triplet energies,[7] having carrier- and exciton-confining structures for reduced efficiency roll-off,[8] combining blue/green/red phosphors with light-outcoupling enhancement techniques,[9] adopting color down-conversion media,[10] comprising ultrathin EMLs,[11] exploiting tandem architectures,[12] employing excimer/exciplex systems,[13] and so forth. However, multiple EMLs are widely required to give off white emissions, resulting in complex structures. In addition, the recombination zone usually changes with the increasing voltages, leading to unstable colors.[14] Besides, the charge injection/transfer, exciton diffusion/confinement and energy transfer between or within the different EMLs should be considered, further complicating the structures. Moreover, more heterojunctions would emerge from the various EMLs, which is detrimental to the device lifetime.[15]

To loosen the bottleneck, elaborate structures have to be developed, aside from the synthesis of elegant materials. Since single-EML WOLEDs, which only need one EML comprised of a versatile host doped with different color guests to furnish white emission, can

offer many unique merits (i.e., simpler structures, shorter fabrication processes, easier control, lower voltages and lower cost, and so forth.), compared with their multi-EML counterparts, they have been studied for both polymer and small-molecule WOLEDs.[16] For example, Zhang et al. recently developed a single-EML WOLED based on the solution-processed dendritic host and new orange-emitting Ir-complex, achieving a maximum forward-viewing power efficiency (PE) of 47.6 lmW^{-1} (23.3 lmW^{-1} at 1000 cd m^{-2}), which is the most efficient polymer WOLED.[17] In the case of small-molecule WOLEDs, plenty of endeavors have been made by using the single-EML method as well. Ma et al. used the p-type material mCP as the host to set up a single-EML WOLED with PE of 42.5 lm/W at ~ 7 cd m^{-2} (19 lmW^{-1} at 500 cd m^{-2}).[18] Huang et al. also fabricated a single-EML WOLED by using a unipolar host, obtaining a maximum efficiency of 14.2 lmW^{-1} (6.8 lmW^{-1} at 1000 cd m^{-2}).[19] However, relatively low efficiency, serious efficiency roll-off and poor color-stability are commonplace for the single-EML WOLEDs comprising unipolar hosts. The unsatisfactory performance can be attributed to the intrinsic quality of unipolar host materials, since they usually only transport holes or electrons, resulting in the charge accumulation/ recombination close to the EML/ electron transporting layer (ETL) interface or the hole transporting layer (HTL)/ EML interface. As a consequence, narrow recombination zones and then triplet-triplet annihilation (TTA), triplet-polaron quenching (TPQ) and exciton diffusion are possible to occur, which is detrimental to the device performance.[20]

To solve these issues, the introduction of single-EML WOLEDs employing bipolar hosts is one of the most ideal solutions. As bipolar materials facilitate both holes and electrons transport, more balanced charges as well as broader recombination regions within the EMLs can be guaranteed, resulting in devices with the potential of higher efficiency, lower efficiency roll-off and more stable color.[21] Gong et al. utilized the new silicon-bridged molecule as the bipolar material of a single-EML WOLED, achieving a maximum PE of 42.7 lmW^{-1} at ~30 cd m^{-2} (25.2 lmW^{-1} at 1000 cd m^{-2}) and ΔCIE (Commission International de

I'Eclairage)= (0.01, 0.00) during 8- 12 V.[22] They also developed a single-EML WOLED by utilizing the bipolar tetraarylsilane compound as the host, achieving a maximum PE of 51.9 lmW^{-1} (22.2 lmW^{-1} at 1000 cd m^{-2}) and ΔCIE = (0.01, 0.00) during 8- 12 V.[23] Wu and Wong's group constructed a single-EML WOLED by incorporating a CN group into mCP to design a bipolar host, attaining a maximum PE of 49.7 lmW^{-1} at ~1 cd m^{-2} (25 lmW^{-1} at 1000 cd m^{-2}) but no color-stability information.[24] More recently, Pan et al. prepared a single-EML WOLED with bipolar hosts, yielding a maximum efficiency of 60.4 lmW^{-1} at ~ 10 cd m^{-2} (27.4 lmW^{-1} at 1000 cd m^{-2}, ΔCIE = (0.02, 0.01) during 5- 10 V).[25] Previously, we also developed a series of high-performance polymer/small-molecule WOLEDs with single-EML structures due to the above mentioned merits.[26-28] Thus, the use of single-EML architecture is a very promising, simplified as well as effective way to realize WOLEDs. However, despite performances of single-EML WOLEDs have steadily increased, it still faces at least three challenges: i) the efficiency is not high enough, particularly single-EML WOLEDs with forward-viewing PE exceeding 30 lmW^{-1} at the practical luminance of 1000 cd m^{-2} are rarely reported; ii) the efficiency roll-off is afflicting the development of single-EML WOLEDs, although numerous bipolar hosts are adopted; iii) the color-stability is not good enough, the reported colors are only relatively stable during a very limited luminance/voltage. In fact, no single-EML WOLED with extremely stable color [ΔCIE= (0.00, 0.00)] has been documented.

In this paper, we have accomplished the simplicity/ extremely high efficiency/ low efficiency roll-off/ excellent color-stability trade-off in a single-EML WOLED. The optimized device exhibits total efficiencies of 111.7 cd A^{-1} and 75.5 lm W^{-1} at the practical luminance of 1000 cd m^{-2}, which are the highest among single-EML WOLEDs so far, to the best of our knowledge. Besides, a maximum current efficiency (CE) and PE of 113.6 cd A^{-1} and 92.5 lm W^{-1} are obtained, respectively, which only slightly decrease to 101.3 cd A^{-1} and 58.8 lm W^{-1} even at an ultrahigh luminance of 5000 cd m^{-2}, indicating a rather low efficiency roll-off. Additionally, the color variation in the whole range of luminances is (0.00, 0.00),

which is the first single-EML WOLED with an extremely stable color. The origin of high performance has been comprehensively unveiled. In particular, we have systematically revealed the role of guests, which is often ignored in single-EML WOLEDs, on the origin of the color-stability and demonstrated that the harnessment of charges and excitons distribution by using multifunctional guests is crucial to stabilize the color. Such marvelous results not only represent a significant step towards the realization of simplified WOLEDs, but also provide a new opportunity to achieve extremely stable colors [ΔCIE= (0.00, 0.00)].

Materials and Methods

As shown in figure 1, the WOLED (W1) has the configuration of ITO (indium tin oxide)/ MeO-TPD (N, N, N',N'- tetrakis(4-methoxyphenyl)-benzidine): F4-TCNQ (tetrafluoro-tetracyanoqino dimethane) (100 nm, 4%)/ TAPC (1-bis[4-[N,N-di(4-tolyl)amino]phenyl]-cyclohexane, 20 nm)/ 26DCzPPy: FIrpic: $Ir(dmppy)_2(dpp)$ (11 nm, 1: 22.5%: 1.1%)/ TmPyPB (1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene, 50 nm)/ LiF (1 nm)/ Al (200 nm), in which iridium(III)bis[(4,6-difluo-rophenyl)-pyridinato-N,C2] (FIrpic) and bis(2-phenyl-4,5-dimethylpyridinato)[2-(biphenyl-3-yl)pyridinato] iridium(III) [$(Ir(dmppy)_2(dpp)$] are used as the blue and orange emitter, respectively, to codope into the host 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy). ITO, MeO-TPD: F4-TCNQ, TAPC, 26DCzPPy: FIrpic: $(Ir(dmppy)_2(dpp)$, TmPyPB, LiF and Al are functioned as the anode, hole injection layer (HIL), HTL, EML, ETL, electron injection layer (EIL) and cathode, respectively. These material layers have been evaporated in sequence at a base pressure of 2×10^{-7} Torr without breaking the vacuum, after cleaning the ITO surface by utilizing the ultrasonic water for 3 minutes and then dried at 80 ℃ for 20 minutes. All of these materials were commercially purchased and no further purification has been done. After preparation under a nitrogen atmosphere using epoxy glue and glass lids, the devices were immediately encapsulated. The CIE color coordinates and electroluminescent (EL) spectra were obtained by a Konica

Minolta CS2000 spectra system. The emission area of the devices is 3×3 mm^2 as defined by the overlapping area of the anode and cathode. The luminance- current density (J)-voltage (V) characteristics were recorded simultaneously, using a computer-controlled source meter (Keithley 2400) and multimeter (Keithley 2000) with a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions.

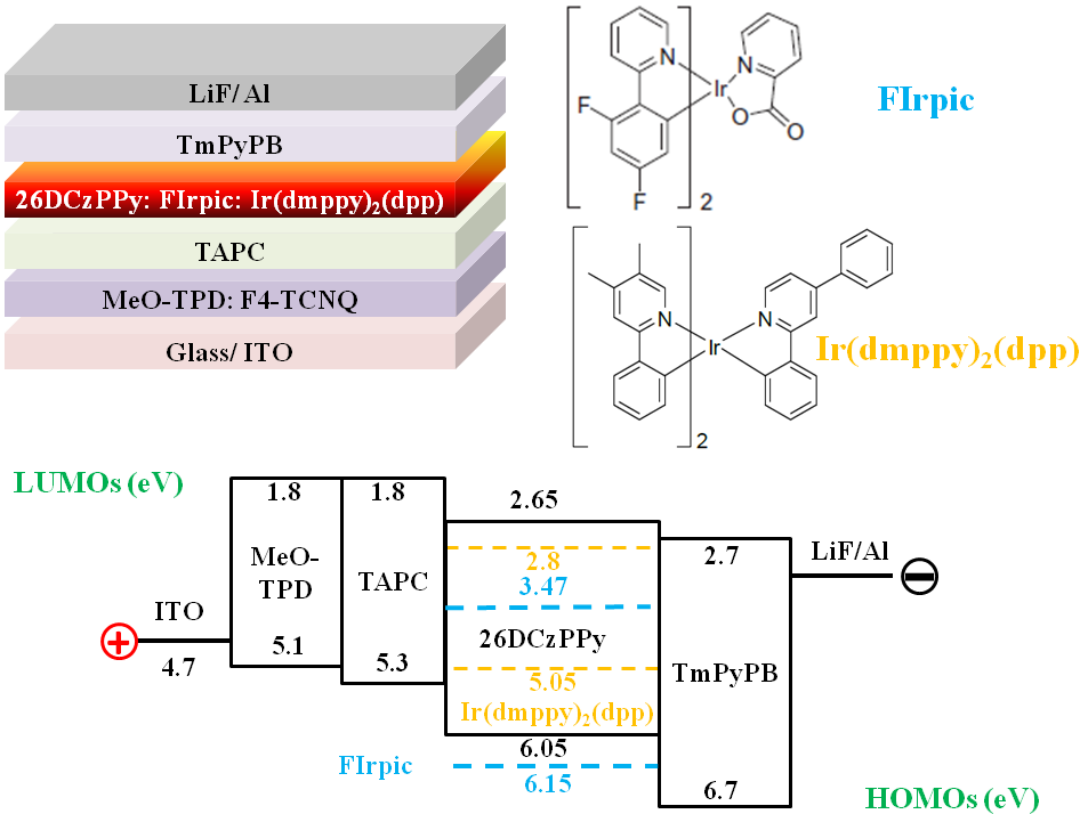


Figure 1. Top: The structure of W1 and the chemical structure of guests. Bottom: The proposed highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the device.

Results and Discussion

The forward-viewing efficiencies of W1 as a function of the luminance have been displayed in figure 2. The peak CE and PE are 66.8 cd A^{-1} (201 cd m^{-2}) and 54.4 lm W^{-1}(33 cd m^{-2}), respectively. And 65.7 cd A^{-1}, 44.4 lm W^{-1} are retained at the illumination-relevant of 1000 cd m^{-2}. Since illumination sources have been generally represented by the total emitted power,[1-7] the peak total CE and PE of W1 are 113.6 cd A^{-1} and 92.5 lm W^{-1}, respectively,

which only slightly decreased to 111.7 cd A^{-1} and 75.5 lm W^{-1} at the practical luminance of 1000 cd m^{-2}. In fact, the efficiency has already overtaken the fluorescent lamps (with typical PE of 40- 70 lm W^{-1}) at 1000 cd m^{-2}, demonstrating a significant step in simplified WOLEDs.[17] Besides, it is noted that the efficiencies have exceeded most of state-of-the-art WOLEDs with multi-EML structures, as shown in table 1. Table 1 also shows that the efficiency/ efficiency roll-off/ color-stability trade-off is rarely accomplished by these multi-EML WOLEDs, which further demonstrates the advantages of our single-EML WOLED.

Remarkably, even at an ultrahigh luminance of 5000 cd m^{-2}, the CE of 101.3 cd A^{-1} and PE of 58.8 lm W^{-1} have still been recorded, demonstrating that W1 has a very low efficiency roll-off.[1-37] Notably, W1 exhibits an excellent color-stability, as illustrated in figure 2 inset. As the luminance ranges from 1, 1000 to 50000 cd m^{-2}, the color experiences almost no shift from (0.2858, 0.4811), (0.2876, 0.4853) to (0.2864, 0.4856). The total variation in the whole range of luminance is ΔCIE $\leq$(0.0022, 0.0045). To appropriately compare it with the color-stability of previous WOLEDs, the total variation is (0.00, 0.00) if we compute to two decimal places. Unlike the previous concept that phosphorescent WOLEDs should exhibit unstable colors since they comprise blue phosphors (i.e., FIrpic) which are usually detrimental to the color-stability,[6] we have demonstrated that the excellent color-stability can be realized in single-EML phosphorescent WOLEDs, indicating a significant breakthrough in WOLEDs.

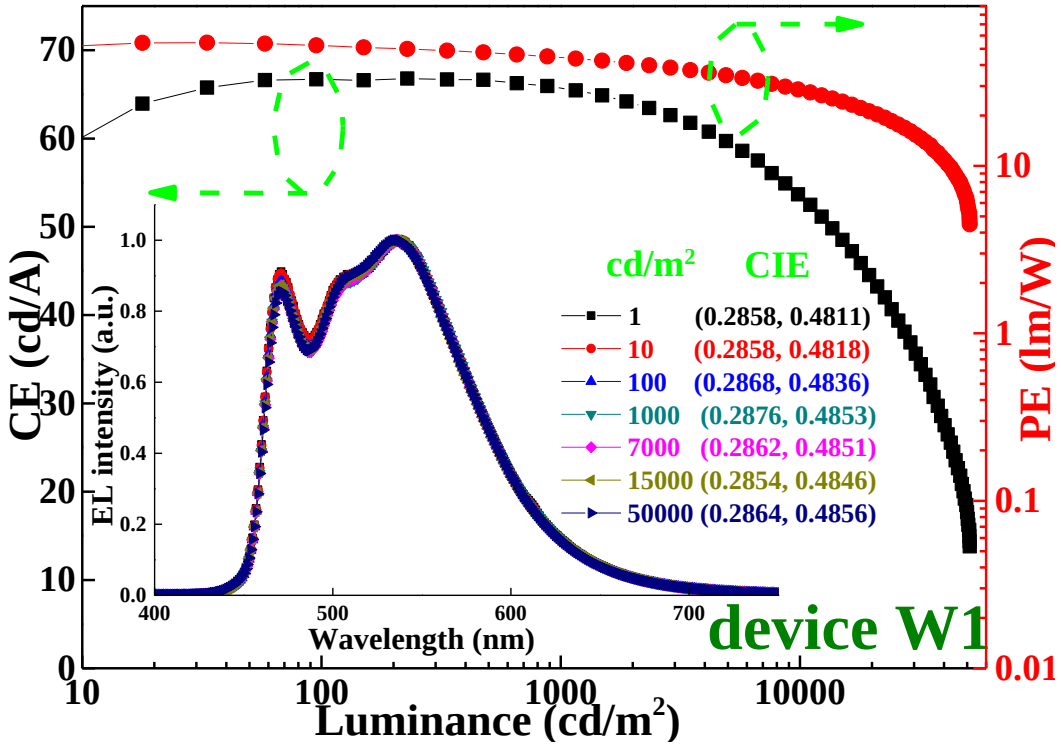


Figure 2. Forward-viewing CE and PE in dependence of luminance for device W1.

Inset: Normalized EL spectra in the whole range of luminances.

Table 1

Summary of most advanced, representative performances of multi-EML WOLEDs in recent four years (without outcoupling technology).

Device	$PE_{max/100/1000}$ [a] (lm/W)	CIE_{1000} [b]	Color shift
Ref. [29] (2 EMLs)	34/-/-	(0.35, 0.44)	(0.006, 0.009) @ 6-10 V
Ref. [30] (2 EMLs)	49.5/-/30.0	(0.44, 0.47)	(0.00, 0.00) @ 3-7 V
Ref. [31] (2 EMLs)	68.8/-/60.0	(0.347, 0.461)	-
Ref. [32] (2 EMLs)	47.2/32.9/15.6	(0.42, 0.42)	(0.01, 0.01) @ 5-8 V
Ref. [33] (2 EMLs)	63/-/52	(0.359, 0.498)	good @ 1-10 mA cm^{-2}
Ref. [34] (3 EMLs)	61/37/12	(0.34, 0.44)	-
Ref. [35] (4 EMLs)	-/42.6/33.8	(0.44, 0.46)	-
Ref. [36] (4 EMLs)	48.2/45.3/26.8	(0.38, 0.45)	(0.08, 0.12)

			@ 10-10000 cd m^{-2}
Ref. [37] (4 EMLs)	~40/-/35.8	(0.507, 0.449)	-
This work (single-EML)	92.5/88.9/75.5	(0.288, 0.485)	(0.00, 0.00)[c)]

[a)]PE in the order of maximum, at 100 cd m^{-2} and at 1000 cd m^{-2}. [b)] The CIE coordinates of devices at 1000 cd m^{-2}. [c)]Color shift in the whole range of luminances.

Galvanized by the superior properties obtained from such simplified device, we then make a comprehensive investigation in order to reveal the origin of high performance. Particularly, we will unveil the role of guests in the color-stability. Before we explore the impact of guests, several other important factors for the high performance will be discussed.

First, two-complementary color (blue/orange) WOLEDs can not only lower the manufacturing cost but also show higher efficiency, compared with three-color WOLEDs.[3] Besides, the correlated color temperature (i.e., cool or warm white) are readily modified by regulating the concentration of blue and orange guests.[34] Therefore, high-performance WOLEDs can be expected by taking advantage of this strategy.

Next, the bipolar host 26DCzPPy plays a vital role, because: i) the triplet energy (T_1) is (2.71 eV),[38] satisfying the blue FIrpic guest (2.65 eV)[38] as well as the orange $Ir(dmppy)_2(dpp)$ emitter (< 2.25 eV),[39] which can not only prevent the reverse energy transfer from FIrpic/ $Ir(dmppy)_2(dpp)$ to 26DCzPPy but also confine triplets in the whole EML, effectively enhancing the efficiency.[3] ii) the similar hole and electron mobility [~10^{-5} $cm^2/(V\ s)$][38] can broaden the excitons recombination zone and achieve balanced charges transport for the recombination procedure. Therefore, TTA and TPQ can be effectively eliminated via 26DCzPPy, leading to the high efficiency, low efficiency roll-off as well as good color-stability.[22] iii) the LUMO and HOMO of 26DCzPPy are 2.65 eV and 6.05 eV, respectively, well matching with those of HTL and ETL to diminish the charge transport barrier, which can lower the driving voltages and further boosting the efficiency. To illustrate the importance of 26DCzPPy, other devices using 4,4-N,N-dicarbazolebiphenyl (CBP) and TAPC hosts have

been fabricated, which exhibit poor performances, as shown in figure S1 and S2, respectively (see the supplementary figure S1 and S2).

Additionally, the utilization of carriers/ excitons confining structure has a substantial influence on ensuring the performance. As shown in figure 3, TAPC is selected as the HTL due to i) the high hole mobility (10^{-2} $cm^2/(V\ s)$),[40] giving an effective hole injection. ii) a higher T_1 (2.87 eV) than the host and guests,[40] effectively confining excitons in the EML. iii) high LUMO (1.8 eV),[40] a great energy offset of LUMO (0.85 eV) between TAPC and 26DCzPPy, decreasing the electron leakage.[3] On the other hand, TmPyPB is chosen as the ETL because of: i) its high electron mobility [10^{-3} $cm^2/(V\ s)$],[41] resulting in an enhanced charge balance due to the effective electron injection. ii) a higher T_1 (2.75 eV) than the host and guests,[41] confining triplets in the whole EML. iii) a deep HOMO of 6.7 eV,[41] the big difference in HOMO levels (0.55 eV) between TmPyPB and the guest FIrpic (or 0.65 eV between TmPyPB and the host 26DCzPPy), reducing the hole leakage. Therefore, both charges (holes and electrons) and excitons (singlets and triplets) can be well confined within the EML via this excellent confining structure, enhancing the efficiency, efficiency roll-off and color-stability, as illustrated in figure 3. To illustrate the importance of TAPC and TmPyPB, other devices using N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB) as the HTL or bis(10-hydroxybenzo[h] quinolinato)beryllium complex ($Bebq_2$) as the ETL have been fabricated, which exhibit poor performances, as shown in figure S3 and S4, respectively (see the supplementary figure S3 and S4).

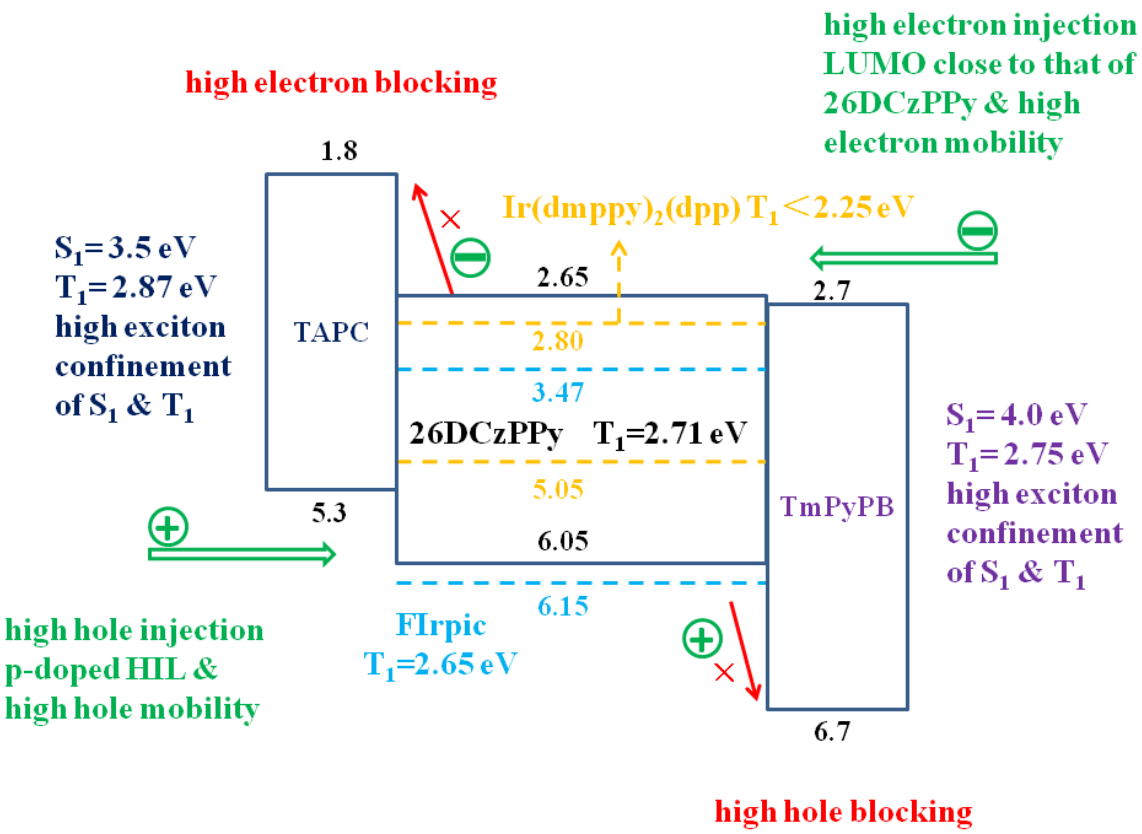


Figure 3. The charge/exciton confining structure for device W1 and the schematic diagram of EL procedures.

Furthermore, the appropriate thickness of EML is one of the main reasons for the high performance. Although no work has been systematically investigated the effect of EML thickness in single-EML phosphorescent WOLED, a further understanding of its impact is still needed. As shown in figure 4 and table 2, when a thin EML thickness is used, a poor color-stability is observed. For example, devices comprising 4 nm, 6 nm and 8 nm EML exhibit the variation of (0.0150, 0.0169), (0.0093, 0.0086) and (0.0024, 0.0045) during 1-10000 cd m^{-2}, respectively. The color shift of these devices in dependence of the thickness of EML is clearly shown in figure 4d. On the other hand, devices comprising 4 nm, 6 nm and 8 nm EML exhibit the forward-viewing efficiencies of 54 cd A^{-1} (42.6 lm W^{-1}), 60.3 cd A^{-1} (44.1 lm W^{-1}) and 62.8 cd A^{-1} (44.3 lm W^{-1}) at 1000 cd m^{-2}, respectively, which are lower than those of W1, as shown in figure 4e. This is because when the thickness of EML is too

thin, the emission zone is very narrow, which easily causes the TTA due to a high triplet exciton density, leading to an evident deterioration of the color-stability.[42] As a result, the device comprising 4 nm or 6 nm EML shows a serious color shift of (0.02, 0.02) and (0.01, 0.01) if we compute to two decimal places, respectively. However, the device comprising 8 nm EML shows a stable color with the color shift of (0.00, 0.00), almost similar to that of W1, suggesting that the 8 nm EML may be enough to widen the main recombination zone. Besides, too thin EML cannot effectively trap or harvest excitons, leading to a low efficiency.[3] However, there is an offset between CE and PE, as shown in figure 4e. A higher CE can be expected when a thick EML thickness is used, however, the PE will be weakened since the thick EML thickness usually results in higher voltages. This is the reason why W1 shows a higher CE but almost the same PE as the device comprising 8 nm EML. This may also be the reason why previous WOLEDs comprising relatively thick EMLs can be used to pursue very high CE but poor PE.[29] However, the thickness of W1 (11 nm) is still much thinner than most of previous WOLEDs, lowering voltages and thus improving the efficiency.

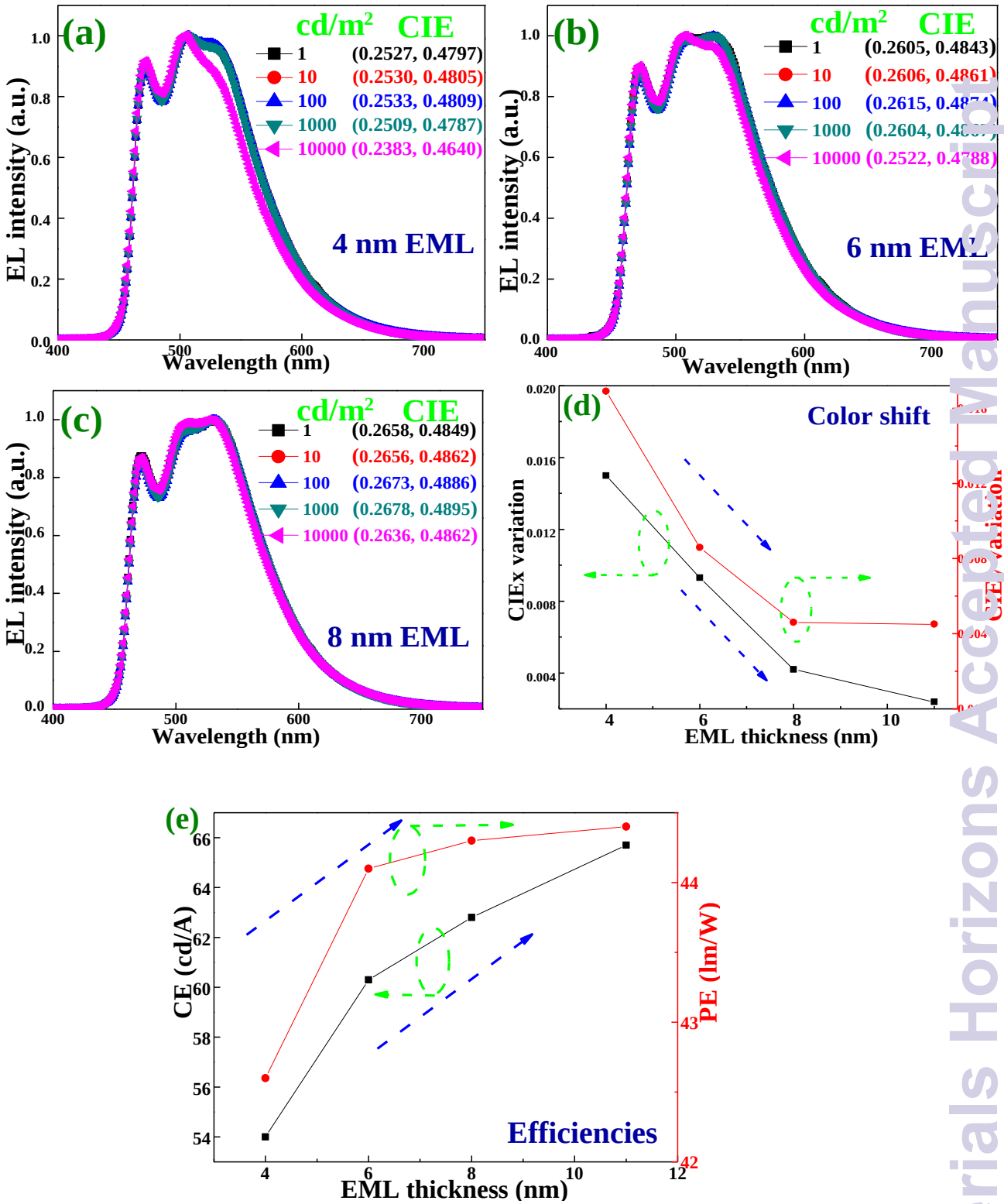


Figure 4. Normalized EL spectra of the devices comprising various EML thicknesses during 1- 10000 cd m^{-2}: a) 4 nm. b) 6 nm. c) 8 nm. d) The color variation as a function of EML thickness. e) Forward-viewing efficiencies at 1000 cd m^{-2} as a function of EML thickness.

Table 2

Summary of WOLEDs with various thick EMLs.

Device	CE_{1000} [a)] (cd/A)	PE_{1000} [b)] (lm/W)	CIE_{1000} [c)]	Color shift
W1 (11 nm EML)	65.7	44.4	(0.288, 0.485)	(0.00, 0.00)
4 nm EML	54	42.6	(0.251, 0.479)	(0.02, 0.02)
6 nm EML	60.3	44.1	(0.260, 0.487)	(0.01, 0.01)
8 nm EML	62.8	44.3	(0.268, 0.490)	(0.00, 0.00)

[a)] Forward-viewing CE at 1000 cd m^{-2}. [b)] Forward-viewing PE at 1000 cd m^{-2}. [c)]The CIE coordinates of devices at 1000 cd m^{-2}.

Apart from the above-mentioned reasons (i.e., adopting the rational design strategy, introducing the bipolar host, using carriers/ excitons confining structures, and exploiting the appropriate EML thickness), other factor may be also attributed to the high performance, particularly for the color-stability. Since the influence of each organic layer has been investigated, the effect of guests should also be considered despite it has been usually overlooked. Therefore, we will systematically reveal the role of guests on the origin of color-stability.

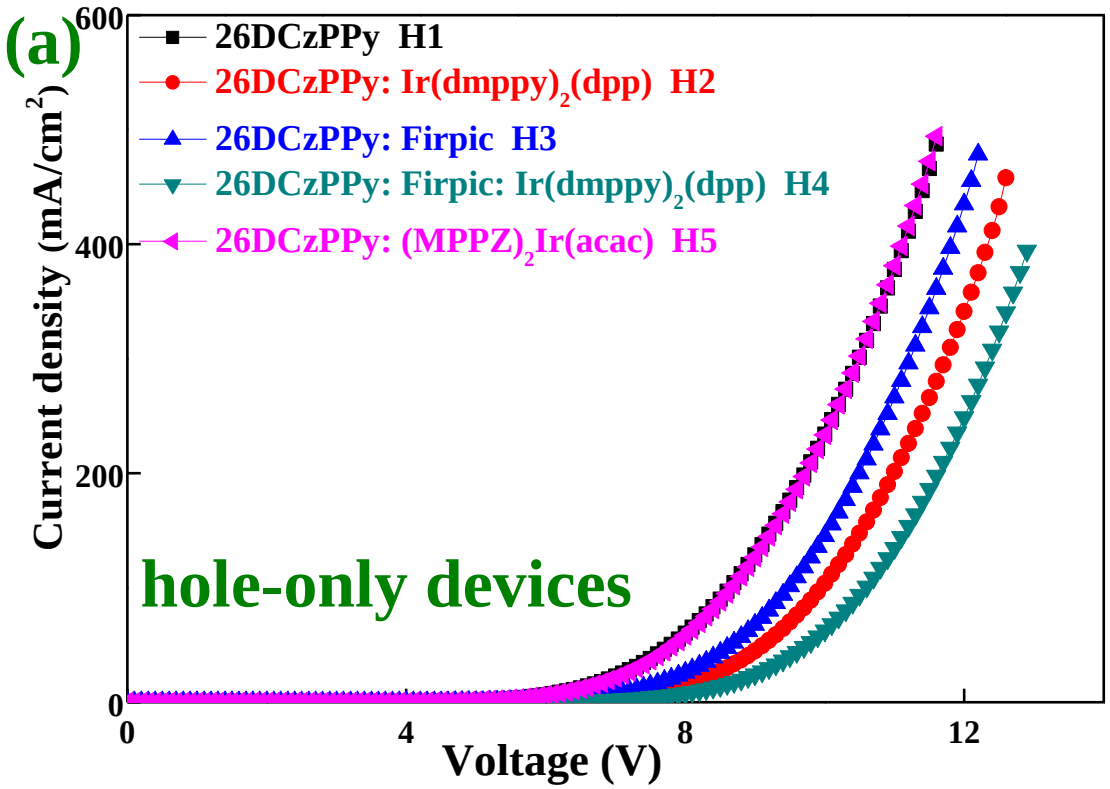
For the excellent color-stability, the recombination ratio should be constant, or else the color variation is easily observed.[3, 42-44] Since the charges transport can be slowed down by the host-guest energy level discrepancy in the EML, the recombination ratio can be constant, thus greatly stabilizing the color. As shown in figure 3, since the HOMO of 26DCzPPy and FIrpic are 6.05 eV and 6.15 eV, respectively,[38] there is a positive barrier (0.1 eV) between the host and guest. As a result, injected holes are possible to occur the collision with this barrier and be scattered, which reduces the drift velocity because of the added transit path.[43] Therefore, the holes transport are slowed down via the blue guest FIrpic. Besides, the HOMO of the orange guest $Ir(dmppy)_2(dpp)$ is 5.05 eV,[39] which is much higher than that of

26DCzPPy (6.05 eV) and lower than that of TAPC (5.3 eV),[40] leading to holes being trapped by $Ir(dmppy)_2(dpp)$.[3] As a result, the holes transport is greatly decreased via the orange guest because of additional traps residing times.[43] Therefore, both the blue and orange guest can lower the hole mobility due to the host-guest energy level discrepancy. On the other hand, since the LUMO of FIrpic and $Ir(dmppy)_2(dpp)$ are 3.47 eV[38] and 2.8 eV[39], respectively, which are lower than those of TmPyPB (2.7 eV) and26DCzPPy (2.65 eV), electrons can be easily trapped guests.[3] As a consequence, the electrons transport is vastly reduced. In a word, both holes and electrons transport have been greatly reduced due to these two multifunctional guests, resulting in the recombination ratio being unchanged with the raising luminance/ current, which is beneficial to obtaining stable colors.

To demonstrate the above analyses, hole-only and electron-only devices have been fabricated comprising configurations of anode/ HIL/ HTL/ EML/ TAPC(50 nm)/ cathode and anode / LiF (1 nm)/TmPyPB (20 nm)/ EML/ ETL / EIL/ cathode, respectively, in which the anode, HIL, HTL, ETL, EIL and cathode are same with those of W1, while the 11 nm EML is constitute of the host 26DCzPPy and guests signifying nothing to device H1 and E1, 1.1% $Ir(dmppy)_2(dpp)$ to device H2 and E2, 22.5% FIrpic to device H3 and E3, 22.5% FIrpic and 1.1% $Ir(dmppy)_2(dpp)$ codoped to device H4 as well as E4. For these single-charge transport devices, electrons cannot be injected from the cathode due to the high LUMO of TAPC (1.8 eV) and holes are impossible to be injected from the anode due to the LiF as well as the deep HOMO of TmPyPB (6.7 eV).[3] As shown in figure 5a, both the J of H2 and H3 are lower than that of H1 due to the effect of guests. In particular, although the concentration of $Ir(dmppy)_2(dpp)$ is low (1.1 %) and the concentration of FIrpic is high (22.5%), H2 shows a lower J than H3, suggesting that $Ir(dmppy)_2(dpp)$ exhibits a strong hole trapping ability. Hence, it is no wonder that H4 shows the smallest J among these four devices. On the other hand, as shown in figure 5b, both the J of E2 and E3 are lower than that of E1 owing to the electron trapping of guests. In particular, although FIrpic is an electron-type material,[7] FIrpic

exhibits a great electron trapping ability, vastly reducing the electron transport in E3in comparison to the J of E1. As expected, it is reasonable that E4 shows the smallest J in these four electron-only devices. Therefore, both the hole and electron mobility are greatly decreased via these two guests, experimentally demonstrating the above analysis.

In addition, based on the above analysis, it can be concluded that excitons can be directly formed on the guests, improving the efficiency since the need to electrically excite the host is eliminated, while allowing for efficient carrier collection, exciton formation, and recombination at the guest molecular sites.[3] Moreover, the charge trapping procedure is also responsible for the low efficiency roll-off, because the proportion of trapped charges are unnecessary to suffer the diffusive transport loss, together with the fact that the decreased charge and exciton accumulation at the EML broaders can reduce TTA and TCQ.[45]



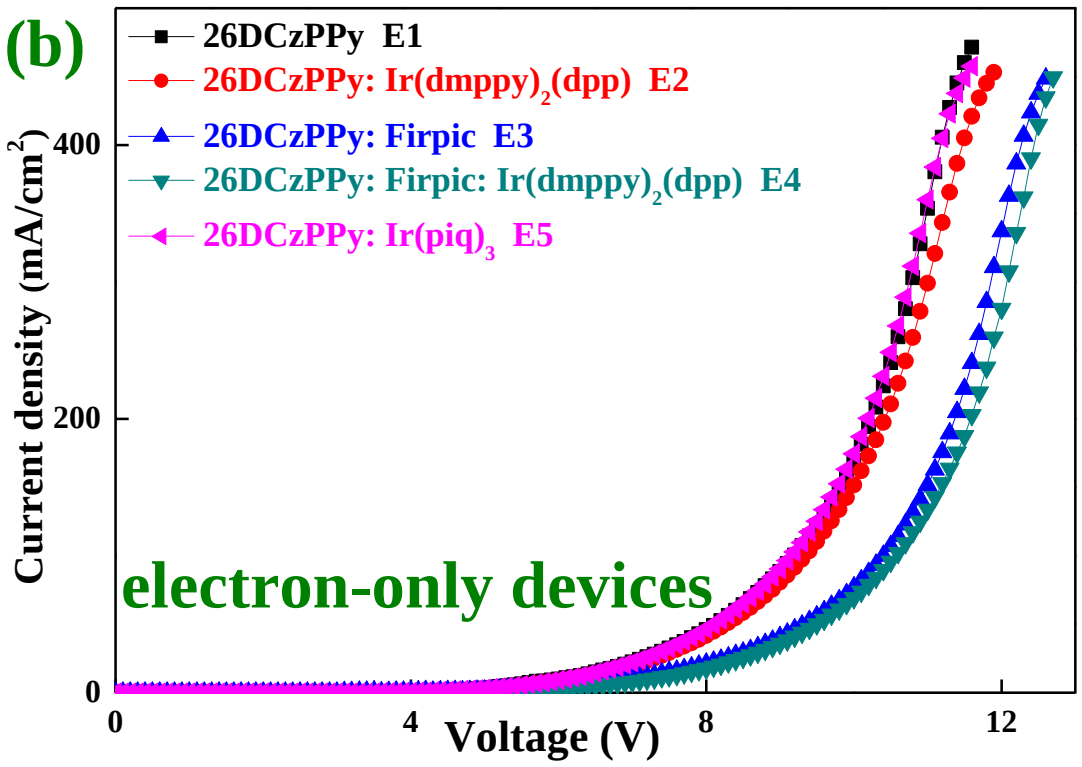


Figure 5. The J-V characteristics of single-charge transport devices with guests FIrpic, $Ir(dmppy)_2(dpp)$, $(MPPZ)_2Ir(acac)$ and $Ir(piq)_3$-doped the host 26DCzPPy. a) hole-only devices. b) electron-only devices.

To further verify the above analysis and illustrate the importance of the orange guest $Ir(dmppy)_2(dpp)$ in making a contribution to maintaining the color constancy resulting from the decreased hole mobility, we have fabricated another device (W21) by replacing $Ir(dmppy)_2(dpp)$ with iridium (III) diazine complexes [$(MPPZ)_2Ir(acac)$], who has a HOMO of 5.31 eV and LUMO of 3.13 eV.[46] The configuration of W21 is similar to that of W1 except the orange guest $(MPPZ)_2Ir(acac)$. As shown in figure 6a, the CIE coordinates variation of W21 is (0.03, 0.00) during 1- 10000 cd m^{-2}, suggesting that W21 exhibits an unstable color compared with W1, which can be understood as follows. According to previous reports, low-concentration guests play a negligible role in the electrical property if the energy barrier between charge transport layers and guests is similar.[39,47] Because of a low concentration of the guest $(MPPZ)_2Ir(acac)$ (1.1%) together with the fact that $(MPPZ)_2Ir(acac)$ has a similar HOMO with TAPC, it is inferred that $(MPPZ)_2Ir(acac)$ cannot lower the hole mobility. To

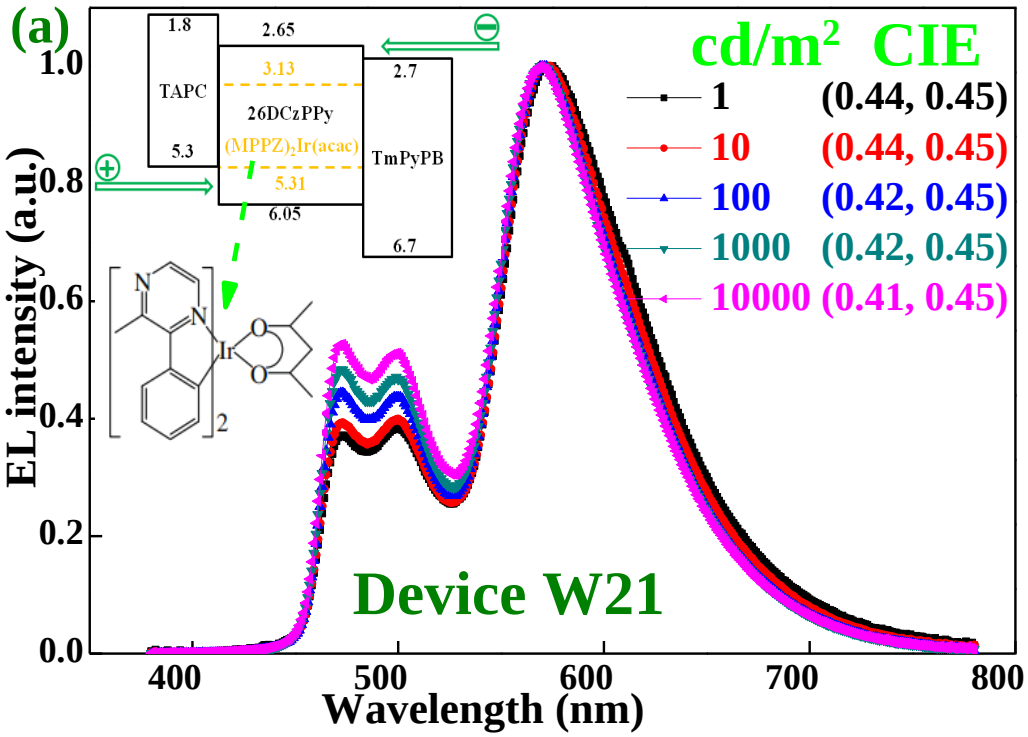
demonstrate this phenomenon, we have fabricated a hole-only device (H5) with the same configuration with H2 except the orange guest $(MPPZ)_2Ir(acac)$. As shown in figure 5a, H5 shows a similar J with H1, indicating that $(MPPZ)_2Ir(acac)$ cannot lower the hole transport characteristic.

On the other hand, to illustrate the importance of $Ir(dmppy)_2(dpp)$ in making a contribution to maintaining the color constancy by decreasing the electron mobility, we have fabricated another device (W22) by replacing $Ir(dmppy)_2(dpp)$ with tris(1-phenylisoquinolinolato-C^2,N) iridium(III) [$Ir(piq)_3$], who has a HOMO of 5.0 eV and LUMO of 2.7 eV.[48] The configuration of W22 is similar to that of W1 except the guest $Ir(piq)_3$. As shown in figure 6b, the total CIE coordinates variation is (0.04, 0.02) during 1- 10000 cd/m^2, indicating that W22 exhibits an unstable color. Owing to the low concentration of $Ir(piq)_3$ (1.1%) and $Ir(piq)_3$ has a similar LUMO with TmPyPB, it is inferred that $Ir(piq)_3$ cannot lower the electron mobility.[39,47] To demonstrate this phenomenon, we have fabricated an electron-only device (E5) with a same configuration with H2 except the guest $Ir(piq)_3$. As shown in figure 5a, E5 shows a similar J with E1, indicating that $Ir(piq)_3$ cannot lower the electron transport characteristic

Therefore, although $(MPPZ)_2Ir(acac)$ exhibits a lower LUMO (3.13 eV) than TmPyPB (2.7 eV) and 26DCzPPy (2.65 eV), electrons can be trapped by $(MPPZ)_2Ir(acac)$, decreasing the electron mobility, the hole mobility of W21 cannot be lowered by $(MPPZ)_2Ir(acac)$. On the other hand, despite $Ir(piq)_3$ exhibits a higher HOMO (5.0 eV) than TAPC (5.3 eV) and 26DCzPPy (6.05 eV), holes can be trapped by $Ir(piq)_3$, decreasing the hole mobility, the electron mobility of W22 cannot be lowered by $Ir(piq)_3$. As a result, compared with W1 in which both the hole and electron mobility are reduced via $Ir(dmppy)_2(dpp)$, the recombination ratio is much more inconstant in W21 and W22, leading to poor color-stabilities.[3,42-44] Besides, since $(MPPZ)_2Ir(acac)$ cannot lower the hole transport and $Ir(piq)_3$ cannot lower the electron transport, more holes are accumulated at the 26DCzPPy/ TmPyPB interface in W21 and more

electrons are accumulated at TAPC/ 26DCzPPy interface in W22, compared with W1, as shown in figure 6c. As a result, a narrower exciton generation zone is formed and an increasing TTA and TPQ can occur in W21 and W22, which is further detrimental to the color-stability.[42] In the case of W1, the charges and excitons distribution are well harnessed, resulting in the recombination ratio being more constant. Therefore, it is reasonable that the color-stability of W21 or W22 is not as stable as W1. These results also show that excellent color-stability cannot be achieved only by using bipolar hosts, since the host of W1, W21 and W22 is similar, indicating that the role of guests should be payed more attention.

Since efficiencies of WOLEDs have been step-by-step enhanced in the last few years, recent research focuses have been shifted towards the difficulties, like prolonging device lifetimes and achieving extremely stable colors [ΔCIE= (0.00, 0.00)], to meet the demand of future display and lighting. In terms of extremely stable colors, only few approaches have been reported. Zhao et al. reported a double-EML hybrid WOLED with ΔCIE= (0.00, 0.00) during 100- 10000 cd m^{-2} by using a bipolar spacer to control the exciton recombination.[49] Sun et al. reported a triple-EML hybrid WOLED with ΔCIE= (0.00, 0.00) during 500- 10000 cd m^{-2} via a bipolar blue host to suppress the mutual quenching between the fluorescent and phosphorescent emitters.[50] However, virtually no phosphorescent WOLED with ΔCIE= (0.00, 0.00) in the whole range of luminance has been documented. Herein, we, for the first time, have demonstrated that the single-EML WOLED can show extremely stable color, by using the multifunctional role of each guest to harness the charges and excitons distribution, providing a new opportunity to achieve extremely stable colors [ΔCIE= (0.00, 0.00)]. Finally, it is deserved to note that W1 exhibits a cool white color with a color-correlated temperature of 6718 K at 1000 cd/m^2, and the color rendering index is not high enough (i.e., 43 at 1000 cd/m^2) due to the two-color system.



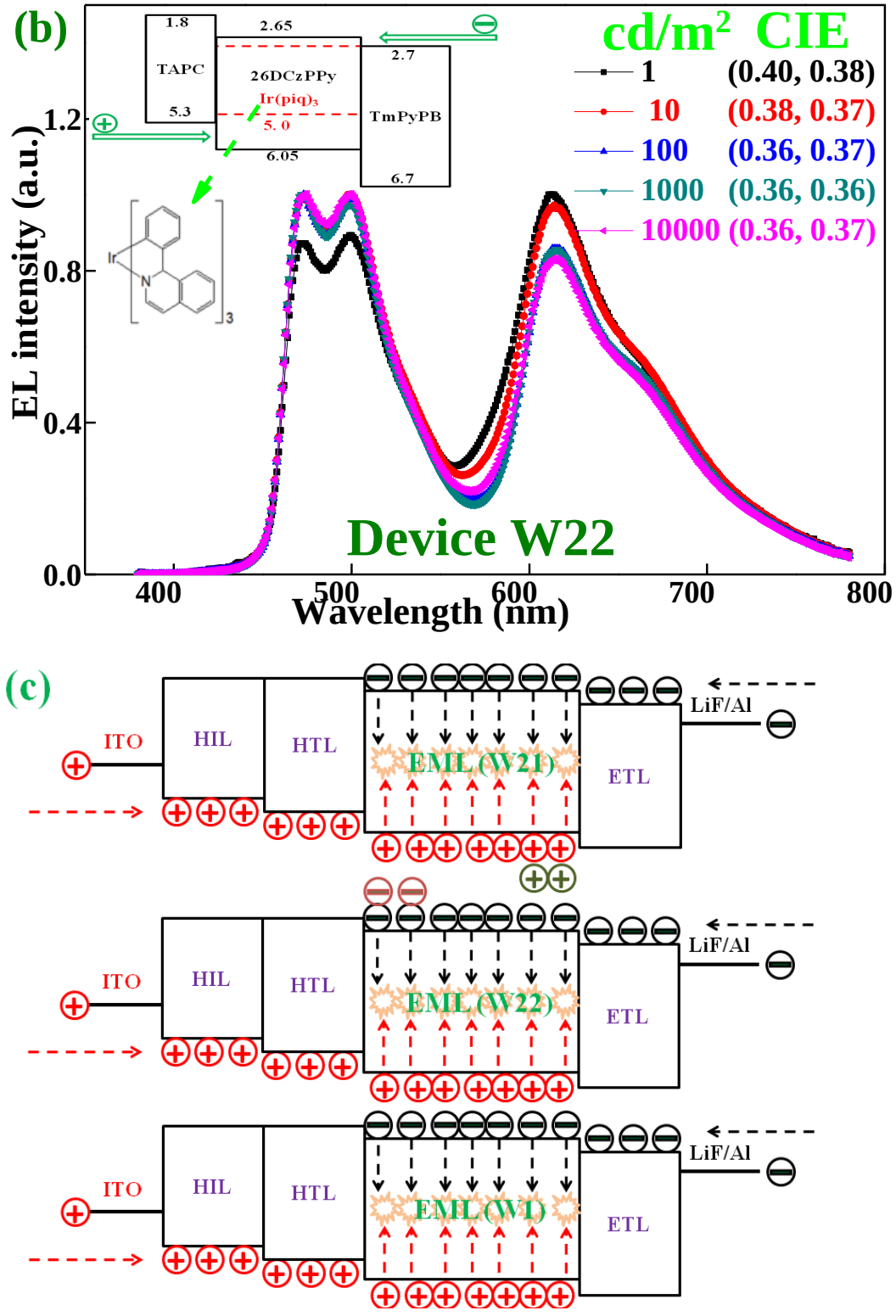


Figure 6. a) Normalized EL spectra of W21. b) Normalized EL spectra of W22. c) Diagrams of EL processes in W21, W22 and W1.

Conclusions

In summary, a single-EML WOLED has been designed, which can simultaneously achieve the simplicity, extreme efficiency, reduced efficiency roll-off and excellent color-stability. The resulting WOLED shows the maximum CE and PE of 113.6 cd A^{-1} and 92.5 lm W^{-1}, respectively, which only slightly decrease to 111.7 cd A^{-1} and 75.5 lm W^{-1} at 1000 cd m^{-2} as well as 101.3 cd A^{-1} and 58.8 lm W^{-1} at 5000 cd m^{-2}. Besides, excellent color-stability with a color variation of (0.00, 0.00) is obtained. The origin of the high performance is comprehensively unveiled. Particularly, we have systematically revealed the role of guests on the origin of the color-stability and demonstrated that the harnessment of charges and excitons distribution by using the multifunctional guests is crucial to stabilize the color. Such marvelous results not only represent a significant step towards the realization of simplified WOLEDs, but also provides a new opportunity to achieve extremely stable colors, which will be beneficial to the design of both material and device structure for extremely high-performance WOLEDs.

AUTHOR INFORMATION

Corresponding Author

E-mail: zou1007@gmail.com (J. Zou); E-mail: psjbpeng@scut.edu.cn (J. Peng).

Acknowledgments

This work was supported by the National “973” Project of China (Grant No. 2015CB655000), National Natural Science Foundation of China (Grant No. 61401156 and U1301243), Guangdong Innovative Research Team Program (Grant No. 201101C0105067115), Educational Commission of Guangdong Province(No. 2014KZDXM010 and 2014GKXM012), National Laboratory for Infrared Physics Open Project (Grant No. M201406) and Guangzhou Science and Technology Plan (Grant No. 2013Y2-00114).

References

1 X. Yang, G. Zhou and W. Y. Wong, *J. Mater. Chem. C* 2014, **2**, 1760.

2 H. Sasabe and J. Kido. *J. Mater. Chem. C* 2013, **1**, 1699.

3 Q. Wang and D. Ma, *Chem. Soc. Rev.* 2010, **39**, 2387.

4 G. Zhou, W. –Y. Wong and S. Suo, *J. Photochem. Photobio. C: Photochem. Rev.* 2010, **11**, 133.

5 L. Ying, C. –L. Ho, H. Wu, Y. Cao and W. –Y. Wong, *Adv. Mater.* 2014, **26**, 2459.

6 Y. Sun, N. Giebink, H. Kanno, B. Ma, M. Thompson and S. R. Forrest. *Nature* 2006, **440**, 908.

7 G. Schwartz, M. Pfeiffer, S. Reineke, K. Walzer and K. Leo. *Adv. Mater.* 2007, **19**, 3672.

8 S. J. Su, E. Gonmori, H. Sasasbe and J. Kido, *Adv. Mater.* 2008, **20**, 4189.

9 S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature* 2009, **459**, 234.

10 J. Lee, N. Chopra, D. Bera, S. Maslow, S. H. Eom, Y. Zhang, P. Holloway, J. Xue and F. So, *Adv. Energy Mater.* 2011, **1**, 174.

11 Y. Zhao, J. Chen and D. Ma, *ACS. Appl. Mater. Interfaces* 2013, **5**, 965.

12 Y. H. Son, Y. J. Kim, M. J. Park, H. Y. Oh, J. S. Park, J. H. Yang, M. C. Suh and J. H. Kwon, *J. Mater. Chem. C* 2013, **1**, 5008.

13 T. Fleetham, H. Liang and J. Li, *Adv. Funct. Mater.* 2014, **24**, 6066.

14 E. Mondal, W. Y. Hung, H. C. Dai and K. T. Wong, *Adv. Funct. Mater.* 2013, **23**, 3096.

15 F. So, D. Kondakov, *Adv. Mater.* 2010, **22**, 3762.

16 H. Wu, G. Zhou, J. Zou, C. –L. Ho, W. –Y. Wong, W. Yang, J. Peng and Y. Cao, *Adv. Mater.* 2009, **21**, 4181.

17 B. Zhang, G. Tan, C. -S. Lam, B. Yao, C. -L. Ho, L. Liu, Z. Xie, W. -Y. Wong, J. Ding and L. Wang, *Adv. Mater.* 2012, **24**, 1873.

18 Q. Wang, J. Ding, D. Ma, Y. Cheng, L. Wang, X. Jing and F. Wang, *Adv. Funct. Mater.* 2009, **19**, 84.

19 W. Y. Huang, Z. W. Chen, H. W. You, F. C. Fan, H. F. Chen and K. T. Wong, *Org. Electron.* 2011, **12**, 575.

20 X. H. Zhao, Z. S. Zhang, Y. Qian, M. D. Yi, L. H. Xie, C. P. Hu, G. H. Xie, H. Xu, C. M. Han, Y. Zhao and W. Huang, *J. Mater. Chem. C* 2013, **1**, 3482.

21 B. S. Kim and J. Y. Lee, *Org. Electron.* 2013, **14**, 3024.

22 S. Gong, Y. Chen, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Mater.* 2010, **22**, 5370.

23 S. Gong, Y. Chen, J. Luo, C. Yang, C. Zhong, J. Qin and D. Ma, *Adv. Funct. Mater.* 2011, **21**, 1168.

24 M. -S. Liu, S. -J. Yang, H. -W. Chang, Y. -H. Huang, Y. -T. Tsai, C. -C. wu, S. -H. Chou, E. Mondal and K. -T. Wong, *J. Mater. Chem.* 2012, **22**, 16114.

25 B. Pan, B. Wang, Y. Wang, P. Xu, L. Wang, J. Chen and D. Ma, *J. Mater. Chem. C* 2014, **2**, 2466.

26 J. Zou, H. Wu, C. S. Lam, C. Wang, J. Zhu, C. Zhong, S. Hu, C. L. Ho, G. J. Zhou, H. Wu, W. C. H. Choy, J. Peng, Y. Cao and W. Y. Wong, *Adv. Mater.* 2011, **23**, 2976.

27 L. Tu, J. Liu, S. Hu, R. He, W. Yang, H. Wu, J. Peng, R. Xia and D. D. C. Bradley, *Adv. Funct. Mater.* 2013, **23**, 4366.

28 B. Liu, L. Wang, M. Xu, H. Tao, X. Xia, J. Zou, Y. Su, D. Gao, L. Lan and J. Peng, *J. Mater. Chem. C* 2014, **2**, 5870.

29 R. Wang, D. Liu, H. Ren, T. Zhang, H. Yin, G. Liu and J. Li, *Adv. Mater.* 2011, **23**, 2823.

30 Q. Wang, I. W. H. Oswald, M. R. Perez, H. Jia, A. A. Shahub, Q. Qiao, B. E. Gnade and M. A. Omary, *Adv. Funct. Mater.* 2014, **24**, 4746.

31 Q. D. Ou, L .Zhou, Y. Q. Li, S. Shen, J. D. Chen, C. Li, Q. K. Wang, S. T. Lee and J. X. Tang, *Adv. Funct. Mater.* 2014, **24**, 7249.

32 S. Gong, N. Sun, J. Luo, C. Zhong, D. Ma, J. Qin and C. Yang, *Adv. Funct. Mater.* 2014, **24**, 5710

33 S. Lee, H. Shin and J. -J. Kim, *Adv. Mater.* 2014, **26**, 5864.

34 S. -L. Lai, W. -Y. Tong, S. C. F. Kui, M. -Y. Chan, C. -C. Kwok and C. -M. Che, *Adv. Funct. Mater.* 2013, **23**, 5168.

35 Y. L.Chang, Y. Song, Z. Wang, M. G. Helander, J. Qiu, L. Chai, Z. Liu, G. D. Scholes and Z. Lu, *Adv. Funct. Mater.* 2013, **23**, 705.

36 C. -J. Zheng, J. Wang, J. Ye, M. -F. Lo, X. -K. Liu, M. -K. Fung, X. -H. Zhang and C. -S. Lee, *Adv. Mater.* 2013, **25**, 2205.

37 W. Gaynor, S. Hofmann, M. G. Christoforo, C. Sachse, S. Mehra, A. Salleo, M. D. McGehee, M. C. Gather, B. Lussem, L. M. Meskamp, P. Peumans and K. Leo, *Adv. Mater.* 2013, **25**, 4006.

38 C. Cai, S. J. Su, T. Chiba, H. Sasabe, Y. J. Pu, K. Nakayama and J. Kido, *Org. Electron.*, 2011, **12**, 843..

39 B. Liu, L. Wang, M. Xu, H. Tao, D. Gao, J. Zou, L. Lan, H. Ning, J. Peng and Y. Cao, *J. Mater. Chem. C* 2014, **2**, 9836.

40 Y. Chen, F. Zhao, Y. Zhao, J. Chen and D. Ma, *Org. Electron.* 2012, **13**, 2807..

41 S. J. Su, T. Chiba, T. Takeda and J. Kido, *Adv. Mater.* 2008, **20**, 2125.

42 S. Chen, Q. Wu, M. Kong, X. Zhao, Z. Yu, P. Jia and W. Hung, *J. Mater. Chem. C* 2013, **1**, 3508.

43 Y. -S. Park, J. -W. Kang, J. -W. Park, Y. -H. Kim, S. -K. Kwon and J. -J. Kim, *Adv. Mater.* 2008, **20**, 1957.

44 Y. Shao and Y. Yang, *Appl. Phys. Lett.* 2005, **86**, 073510.

45 N. Sun, Y. Zhao, F. Zhao, Y. Chen, D. Yang, J. Chen and D. Ma, *Appl. Phys. Lett.* 2014, **105**, 013303.

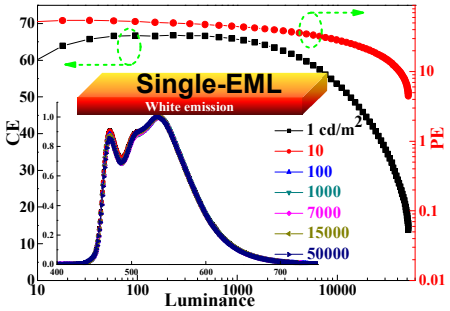
46 G. Ge, J. He, H. Guo, F. Wang and D. Zou, *J. Organomet. Chem.* 2009, **694**, 3050.

47 H. I. Baek and C. H. Lee, *J. Phys. D: Appl. Phys.* 2008, **41**, 105101.

48 D. -H. Lee, Y. -P. Liu, K. H. Lee, H. Chae and S. M. Cho, *Org. Electron.* 2010, 11, 427.

49 F. Zhao, N. Sun, H. Zhang, J. Chen and D. Ma, *J. Appl. Phys.* 2012, **112**, 084504.

50 N. Sun, Q. Wang, Y. Zhao, Y. Chen, D. Yang, F. Zhao, J. Chen and D. Ma, *Adv. Mater.* 2014, **26**, 1617.



The simplicity/ extremely high efficiency/ low efficiency roll-off/ stable color trade-off has been accomplished in a single-EML WOLED.

White organic light-emitting diodes (WOLEDs) are the object of intense research since they are promising to future displays and lightings. This work demonstrates that it is possible to accomplish the simplicity/ extremely high efficiency/ low efficiency roll-off/ stable color trade-off in a single-emitting-layer WOLED, although it is still a big challenge. Unprecedented efficiencies of 111.7 cd A^{-1} and 75.5 lm W^{-1} at 1000 cd m^{-2} have been achieved, which have already overtaken the fluorescent lamps and most of state-of-the-art multi-emitting-layer WOLEDs. Besides, rather low efficiency roll-off is realized, since the efficiencies are remained as high as 101.3 cd A^{-1} and 58.8 lm W^{-1} even at 5000 cd m^{-2}. Moreover, this is the first single-EML WOLED with an extremely stable color, since the color variation in the whole range of luminances is (0.00, 0.00). Then, the origin of high performance is unveiled. Particularly, we have systematically revealed the role of guests, which is often ignored, on the origin of the color-stability and demonstrated that the harnessment of charges and excitons distribution by using multifunctional guests is crucial to stabilize the color. The presented results here will be beneficial to the design of both material and device structure for extremely high-performance WOLEDs.