Highly Efficient White Organic Light-Emitting Diodes Based on Phosphorescent Iridium Complexes with Multi-Light-Emitting Layers

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Abstract: White organic light-emitting diodes (WOLEDs) incorporating a blend of blue, green and red phosphorescent small molecular materials are presented in this article. 4,4′,4′′-Tris(carbazol-9-yl)triphenylamine (TcTa) and 9-(4-tert-Butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole (CzSi) with different transmission characteristics were selected as hosts for different emitting layers aim to promote holes transport, which will reinforce carriers’ balance and broaden carrier composite. On account of adaptive energy levels of the utilized dopants and hosts, secured phosphorescent WOLED displayed high efficiencies, low operating voltage and slow efficiency roll-off. In addition, distribution of carriers’ recombination zone and spectral of change were studied in detail to further understand the light-emitting mechanisms of obtained WOLEDs. Finally, by majorizing the dosage concentration of (fbi)Ir(acac) (bis(2-(9,9-diethyl-9H-fluoren-2-yl)-1-phenyl-1H-benzimidazol-N,N,C3)iridium(acetylacetonate)) and the architectures of WOLEDs, the optimal device exhibited the maximum efficiencies of 44.92 cd A⁻¹, 42.85 lm W⁻¹, 16.8%, respectively, turn on voltage of 2.6 V and Commission International de l’Eclairage coordinates of (0.337, 0.458) at the brightness level of 3000 cd m⁻².

Keywords: white organic light-emitting diodes; efficiency; efficient energy transfer; phosphorescent luminescence

1. Introduction

White organic light-emitting diodes (WOLEDs) have achieved intense attention because of their unique features such as environment-friendly lighting source, easy-flexibility, good color rendering index and physiological friendly in flat panel displays and lighting fields [1–7]. To accomplish high performance WOLEDs, three primary (e.g., red, green, blue) or two adscititious (e.g., blue, orange or yellow) dyes are indispensable. At present, fluorescent and phosphorescent hybrid WOLEDs that integrate stable blue fluorescent and red/green/orange phosphorescent emitters have realized certain success in relatively high efficiency and excellent stability [8–13]. Whereas, to obtain high electroluminescent (EL) efficiency, it is necessary to design reasonable device structure and select matched blue fluorescent materials with high photo-luminescent quantum yields (PLQYs). Generally, the fabrication of phosphorescent WOLEDs, which possess inherent 4-fold higher efficiency than those of fluorescent diodes since all excitons could be effectively utilized, is particularly desired [14–18]. Multiple EMLs structures are often used to physically separate two or more phosphorescent materials with different colors from each other. To realize white light, the thickness of each emitting layer should to be designed skillfully and the doping concentration of guests should be accurately adjusted. However,
the design of multi-emitting-layers WOLEDs will also leads to the complexity of device fabrication and difficulty in adjusting the emitting spectrum.

Therefore, the general challenge in designing multilayer WOLEDs is ensuring the balanced emissions from different emitting layers. Meanwhile, being able to exactly regulate the thickness of each layer and achieving low dopant concentrations of lower energy emitters are crucial to realize balanced white light. Recently, tremendous efforts have been made to develop WOLEDs. For instance, Zhu et al. fabricated the multi-emitting-layers WOLEDs with slow decay of efficiency only 1.8% at practical brightness level of 1000 cd m⁻² by constructing reasonable emissive layer to make full use of carriers [19]. Miao and co-works designed high performances hybrid WOLEDs with three ultrathin phosphorescent emitting layers and one blue fluorescent emitting layer. Finally, the optimal multilayer WOLED exhibited high external quantum efficiency (EQE) close to 20% and high CRI of 90 [20]. To satisfy the requirements of practical application, multi-emitting-layers WOLEDs are expected to be also efficient in improving efficiency and slowing the attenuation of efficiency [21–23].

According to our previous work, warm white device with simple structure was prepared by employing trace doping technology based on typical orange thermally activated delayed fluorescent material 2,3,5,6-tetrakis(3,6-diphenyl-carbazol-9-yl)benzene (4CzTPN-Ph) through skillfully controlling the contribution ratio of carrier trapping in the device. However, relatively low device performances with CE,max, PE,max and EQE,max of 32.33 cd A⁻¹, 32.75 lm W⁻¹ and 10.2% were obtained, respectively [24]. To increase WOLED performances, we designed the white OLEDs based on three phosphorescent iridium complexes Flrpic (iridium(III)bis(4,6-difluorophenyl)pyridinato-N,C20′]picolinat, blue emitter), Ir(mppy)₃ (tris(2-(4-tolyl)-phenyl)pyridine)iridium, green emitter) and (fbi)Ir(acac) ((bis(2-(9,9-diethyl-9H-fluoren-2-yl)-1-phenyl-1H-benzoimidazol-N,C3)iridium (acetylacetone), orange-red emitter). In this case, these three iridium complexes were utilized as the dopants because of their excellent luminescent efficiencies. The experiment results made clear that adaptive energy levels of dopants and hosts exert a beneficial impact on broadening carrier composite and motivating the balance of carriers. Therefore, the optimal device displayed turn-on voltage of 2.6 V, maximum current efficiency of 44.92 cd A⁻¹, power efficiency of 42.85 lm W⁻¹, EQE of 16.8%, and CIE coordinates of (0.337, 0.458) at the brightness level of 3000 cd m⁻². With increasing current density from 10 to 100 mA cm⁻², CIE changed gradually from (0.337, 0.458) to (0.292, 0.438).

2. Materials and Methods

The dopants of Flrpic, Ir(mppy)₃, (fbi)Ir(acac) and functional materials of TAPC, TcTa, CzSi, Tm3PyP26PyB were obtained commercially and used directly. Patterned indium-tin-oxide (ITO) glass (10 Ω sq⁻¹) was taken as the anode which were cleaned and rinsed with abluent and ultra-pure water, respectively, after that put it into an oven dried at 120 °C for 60 min before film deposition. Organic layers were continuously deposited at the rate of 1 Å s⁻¹ in a specialized organic vacuum chamber (≤2.0×10⁻⁵ Pa). All of the EMLs were manufactured by using co-doping technology from two or three separate evaporator sources. Afterward, the devices were transferred to another vacuum chamber (≤8.0×10⁻⁵ Pa) through a transition rod to deposit LiF and Al at rates of 0.1 and 10 Å s⁻¹, respectively. The thicknesses of organic or metal films and the rate of materials used in these devices were monitored with crystal oscillator sensors. An ultrathin metal mask was made into determining cathode position and preparing eight 9 mm² emitting dots for device performances testing. The overall electroluminescent performances, absorption spectra and photoluminescence (PL) spectra were measured with Brightness Light Distribution Characteristics Measurement System C9920-11, Shimadzu UV-3600 and Hitachi F-7000 fluorescence spectrophotometer, respectively.
3. Results and Discussion

To enhance the utilization probability of excitons, realize 100% internal quantum efficiency and thus achieve white emission device with slow efficiency roll-off, it is crucial to deftly construct device structure by selecting suitable materials. As depicted in Figure 1, device configuration and HOMO/LUMO levels diagram, 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN) and LiF serve as anode and cathode interface modified layers to ameliorate the injection of holes and electrons, respectively [25]. We used p-type HAT-CN (0.2 wt%) doped into di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) and 1,3,5-tris(6-(3-(pyridin-3-yl)phenyl)pyridin-2-yl) (Tm3PyP26PyB) as hole transport layer (HTL) and electron transport layer to improve hole mobility from p-doping technology and achieve highly effective transport of electrons [26,27]. FIrpic, Ir(mppy)$_3$ and (fbi)$_2$Ir(acac) with high photoluminescent quantum yields (PLQYs) and matched energy levels were selected as three emitters [17,28,29]. For these three elements WOLEDs, 4,4',4''-tri(9-carbazoyl)triphenylamine (TcTa) and 9-(4-tert-Butylphenyl)-3,6-bis (triphenylsilyl)-9H-carbazole (CzSi) were chosen as the host materials for their complementary transport types [30,31]. The triplet energies (T$_1$) of TcTa and CzSi are 2.83 and 3.02 eV, respectively, while those of (fbi)$_2$Ir(acac), Ir(mppy)$_3$ and FIrpic are 2.20, 2.38 and 2.62 eV, respectively. In this case, the T$_1$ of TcTa and CzSi are more than adequate to restrict triplet excitons on emitter molecules and hinder from the back transmission of triplet exciton energy from emitter to host. Thus, using TcTa as the host of EML1 and EML2 is beneficial for the transmission of triplet exciton energy from emitter to host. The utilization of bipolar host CzSi helps to facilitate carriers' balance and broaden recombination zone. The structures of FIrpic, Ir(mppy)$_3$, (fbi)$_2$Ir(acac), and other organic functional materials used in these WOLED are given in Scheme S1.

![Figure 1. The WOLEDs device structure researched in this paper and the energy level of the used materials.](image-url)
The absorption spectra of (fbi)$_2$Ir(acac), Ir(mppy)$_3$ and Flrpic, and the PL spectra of Ir(mppy)$_3$, Flrpic, TcTa and CzSi in dichloromethane (CH$_2$Cl$_2$) were measured and illustrated in Figure 2. The PL spectra of Ir(mppy)$_3$, Flrpic, TcTa and CzSi peaked at 517, 484, 395 and 376 nm, respectively. Interestingly, metal-to-ligand charge transfer bands from singlet (1MLCT) and triplet (3MLCT) are clearly resolved at 405 and 460 nm for (fbi)$_2$Ir(acac), 410 and 470 nm for Ir(mppy)$_3$, 380 and 420 nm for Flrpic, respectively [32,33]. Simultaneously, large segregation between absorption spectra of guests and emission spectra of hosts was observed, which means efficient energy transmission from hosts to guests is feasible. In addition, obvious segregation between the emission spectrum of Flrpic and the absorption spectra of (fbi)$_2$Ir(acac) and Ir(mppy)$_3$ indicated that energy transmission from blue to red and green emitters is possible. However, PL spectrum of Ir(mppy)$_3$ has no marked segregation with absorption spectrum of (fbi)$_2$Ir(acac), indicating energy transmission from Ir(mppy)$_3$ to (fbi)$_2$Ir(acac) is impossible.

Figure 2. Absorption spectra of (fbi)$_2$Ir(acac), Ir(mppy)$_3$, Flrpic and PL spectra of Ir(mppy)$_3$, Flrpic, TcTa and CzSi measured in CH$_2$Cl$_2$.

To determine the concentration of (fbi)$_2$Ir(acac), a set of co-doped single-EML ((fbi)$_2$Ir(acac) (x wt%):Ir(mppy)$_3$ (10 wt%):TcTa (10 nm)) and double-EMLs ((fbi)$_2$Ir(acac) (x wt%):Ir(mppy)$_3$ (10 wt%):TcTa (10 nm)/(fbi)$_2$Ir(acac) (x wt%):Flrpic (18 wt%):CzSi (8 nm)) devices with the structures of ITO/HAT-CN (6 nm)/HAT-CN (0.2 wt%):TAPC (50 nm)/single-EML or double-EMLs/Tm$_3$PyP$_2$6PyB (60 nm)/LiF (1 nm)/Al (100 nm) were firstly prepared by adjusting x from 1 to 3 with interval of 1. Tables S1 and S2, in Supporting Information, summarized the key EL performance parameters of these devices. As shown in Figs. S1(a), S1(b), S2(a) and S2(b), in Supporting Information, for single-EML devices, when the dosage concentration of (fbi)$_2$Ir(acac) was 1 wt%, the green emission intensity is higher than that of red emission, indicating that most carriers recombined on Ir(mppy)$_3$ molecules. In regard to double-EMLs devices, weak blue emission was observed. So, blue emission ratio should be enhanced to achieve white emission.
Then, based on common ETL, HTL and electrode interface modified layers in the device mentioned above, Device W1 with the EML structure of (fbi):Ir(acac) (1 wt%):Ir(mppy)₃ (10 wt%):TcTa (7 nm)/(fbi):Ir(acac) (1 wt%):Flrpic (18 wt%):TcTa (3 nm)/Flrpic (18 wt%):CzSi (8 nm) was manufactured and examined. With the insertion of blue emitting layer, which is constructed by doping Flrpic into CzSi film, not only device performances were improved but also the blue emission ratio was increased significantly. Device W1 procured the maximum current efficiency (CE_{max}) of 66.97 cd A⁻¹, power efficiency (PE_{max}) of 59.47 lm W⁻¹, external quantum efficiency (EQE_{max}) of 24.4% and CIE coordinates of (0.260, 0.436) at the brightness of 3000 cd m⁻². Meanwhile, as depicted in Figure 3, greenish-white and bluish-white light was obtained by Device W1 at relatively low and high current densities, respectively. Three characteristic emissions centered at 471, 507 and 556 nm originating from Flrpic, Ir(mppy)₃ and (fbi):Ir(acac), respectively, were observed. Simultaneously, blue and red emission in EL spectra exhibited a large variation with increasing current density. Based on Device W1, Device W2 was fabricated with the increased dosage concentration of (fbi):Ir(acac) within EML1 to be 2 wt%. As shown in Figure 4, with aggrandizing dosage concentration of (fbi):Ir(acac) within EML1, more carriers were recombined in red emitter, the relative intensities of red emission increased obviously but still dissatisfied with the requirement of standard white emission.

![Normalized EL spectra of device W1 operating at different current densities.](image-url)
To further enhance the intensity ratios of red and blue emissions, the dosage concentration of \((fbi)\text{-Ir(acac)}\) within EML2 was adjusted to be 1.4 wt% based on Device W2. Surprisingly, the obtained device (Device W3) achieved higher EL efficiency and brightness compared with Device W2 mainly due to the broadening recombination zone. As illustrated in Figure 5, the intensity ratios of blue and green emissions in Device W3 were lower than those of Device W2. At low current density, red emission intensity is the highest one among the three emissions in Device W3. Importantly, with the increasing current density, blue emission increased gradually, while red emission decreased slightly. At the same time, it is presumed that the recombination center is near the interface between 7 nm \((fbi)\text{-Ir(acac)} (2 \text{ wt\%})\text{-Ir(mppy)} (10 \text{ wt\%})\text{-TcTa} and 3 nm \((fbi)\text{-Ir(acac)} (1.4 \text{ wt\%})\text{-Flrpic} (18 \text{ wt\%})\text{-TcTa} layers rather than near the interface between 3 nm \((fbi)\text{-Ir(acac)} (1.4 \text{ wt\%})\text{-Flrpic} (18 \text{ wt\%})\text{-TcTa} and 8 nm Flrpic (18 \text{ wt\%})\text{-CzSi} layers. Carriers were firstly captured by the orange-red \((fbi)\text{-Ir(acac)}\) molecules near the interface between 7 nm \((fbi)\text{-Ir(acac)} (2 \text{ wt\%})\text{-Ir(mppy)} (10 \text{ wt\%})\text{-TcTa} and 3 nm \((fbi)\text{-Ir(acac)} (1.4 \text{ wt\%})\text{-Flrpic} (18 \text{ wt\%})\text{-TcTa} layers, then diffused into Ir(mppy) (10 \text{ wt\%})\text{-TcTa} and Flrpic (18 \text{ wt\%})\text{-CzSi} emitting layers and were captured by Ir(mppy) and Flrpic molecules. Device W3 obtained the CE\text{max} of 44.92 \text{ cd A}^{-1}, \text{PE}\text{max} of 42.85 \text{ lm W}^{-1}, \text{EQE}\text{max} of 16.8\%, which are higher than those of reported works in Table S3, in supporting information [34–36], maximum brightness (B\text{max}) of 38,150 \text{ cd m}^{-2} and CIE coordinates of \((0.337, 0.458)\) at the brightness of 3000 \text{ cd m}^{-2}. 

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**Figure 4.** Normalized EL spectra of device W2 operating at different current densities.
Continuously, the doping concentrations of (fbi)2Ir(acac) within EML1 and EML2 were modulated to be 2.4 wt% and 0.6 wt%, respectively, and the obtained device was defined as Device W4. As shown in Figure 6, the intensity ratios of blue and green emissions in Device W4 were higher than those of Device W3, while the intensity ratio of red emission decreased in some degree compared with Device W3. The CIE coordinates of Device W4 is (0.283, 0.415) at 10 mA cm$^{-2}$. Finally, based on Device W4, the concentration of (fbi)2Ir(acac) within EML1 was modulated to be 3.0 wt%, and the obtained device was defined as Device W5. With the increment of current density, as illustrated in Figure 7, the intensity ratios of blue and green emissions have no marked change, while the intensity ratio of red emission dropped gradually. CIE coordinates of Device W5 is (0.211, 0.388) at 10 mA cm$^{-2}$.
Figure 6. Normalized EL spectra of device W4 operating at different current densities.

Figure 7. Normalized EL spectra of device W5 operating at different current densities.
To prove the emission zone is located near the interface between 7 nm (fbi):Ir(acac) (2 wt%):Ir(mppy) (10 wt%):TcTa and 3 nm (fbi):Ir(acac) (1.4 wt%):FIrpic (18 wt%):TcTa layers rather than the interface between 3 nm (fbi):Ir(acac) (1.4 wt%):FIrpic (18 wt%):TcTa and 8 nm FIrpic (18 wt%):CzSi layers, as well as lower energy gap increased carriers’ smoothly transport. Then, Device W6 with the EML structure of Ir(mppy) (10 wt%):TcTa (7 nm)/(fbi):Ir(acac) (0.2 nm)/FIrpic (18 wt%):TcTa (3 nm)/FIrpic (18 wt%):CzSi (8 nm) was further designed and compared. As shown in Figure 8, the intensity ratios of blue and green emissions increased gradually with adding current density from 0.1 to 200 mA cm$^{-2}$. Interestingly, as the current density of Device W6 leaps to 100 and 200 mA cm$^{-2}$, the relative intensity of red emission tends to drop, plausibly because the recombination zone located near the interface between 7 nm (fbi):Ir(acac) (2 wt%):Ir(mppy) (10 wt%):TcTa and 3 nm (fbi):Ir(acac) (1.4 wt%):FIrpic (18 wt%):TcTa layers. So, carriers are firstly captured by (fbi):Ir(acac) molecules, and then transported to 7 nm Ir(mppy) (10 wt%):TcTa and 8 nm FIrpic (18 wt%):CzSi emitting layers. The CIE coordinates of Device W6 are (0.317, 0.438) at 10 mA cm$^{-2}$. Simultaneously, Figure 9 compared the EL efficiency-current density (η- J) characteristics and current density-brightness-voltage (J-B-V) characteristics of Devices W1-W6. In addition, these WOLEDs exhibited slow efficiency roll-off as depicted in Figure S3, in Supporting Information.

Figure 8. Normalized EL spectra of device W6 operating at different current densities.
Figure 9. EL efficiency-current density ($\eta$-$J$) characteristics of devices W1-W6. Inset: Current density-brightness-voltage ($J$-$B$-$V$) characteristics of devices W1-W6.

Furthermore, the PL spectra of 30 nm (fbi)$_2$Ir(acac) (2 wt%):Ir(mppy)$_3$ (10 wt%):TcTa and (fbi)$_2$Ir(acac) (1 wt%):FIrpic (18 wt%):TcTa films were depicted in Figure 10 to better understand the photo-physical properties of these three-elements WOLEDs. Clearly, these two films exhibit the typical emissions of FIrpic (473 nm), Ir(mppy)$_3$ (507 nm) and (fbi)$_2$Ir(acac) (560 nm). Compared with the EL spectra of Device W3 as depicted in Figure 4, the peaks of blue, green and orange-red emissions were consistent with their EL spectra, which indicates the well energy transfer within Device W3, which caused the high performances.
Figure 10. Normalized PL spectra of 30 nm (fbi)\textsubscript{2}Ir(acac) (2 wt%):Ir(mppy) (10 wt%):TcTa film and 30 nm (fbi)\textsubscript{2}Ir(acac) (1 wt%):Flripic (18 wt%):TcTa film.

4. Conclusions

In summary, highly efficient WOLEDs with slow efficiency roll-off have been designed and fabricated by selecting host materials and three phosphorescent emitters with well-matched triplet energies and energy levels. Importantly, the change of EL spectra at different dosage of red emitter in different emitter and location of EL recombination zone were analysed in detail. By majorizing dosage concentration of orange-red emitter and structure of devices, the optimal WOLED obtained the C\textsub{E}\textsub{max}, P\textsub{E}\textsub{max} and EQE\textsub{max} up to 44.92 cd A\textsuperscript{-1}, 42.85 lm W\textsuperscript{-1} and 16.8%, respectively. At the practical brightness level of 1000 cd m\textsuperscript{-2}, the same device exhibited the CE of 38.05 cd A\textsuperscript{-1} (EQE = 14.28%), PE of 28.46 lm W\textsuperscript{-1}, and CIE of (0.357, 0.468).

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/article/10.3390/photonics9100767/s1, Scheme S1: The molecular structures of organic materials used in this work.; Table S1: The key properties of single-EML devices with different doping concentrations of (fbi)\textsubscript{2}Ir(acac).; Figure S1: (a) EL efficiency-current density (\(\eta-J\)) characteristics of single-EML devices with (fbi)\textsubscript{2}Ir(acac) at different doping concentrations. Inset: Current density-brightness-voltage (J-B-V) characteristics of single-EML devices with (fbi)\textsubscript{2}Ir(acac) at different doping concentrations. (b) Normalized EL spectra of single-EML devices with (fbi)\textsubscript{2}Ir(acac) at different doping concentrations operating at 10 mA cm\textsuperscript{-2}; Table S2: The key properties of double-EMLs devices with different doping concentrations of (fbi)\textsubscript{2}Ir(acac).; Figure S2: (a) EL efficiency-current density (\(\eta-J\)) characteristics of double-EMLs devices with (fbi)\textsubscript{2}Ir(acac) at different doping concentrations. Inset: Current density-brightness-voltage (J-B-V) characteristics of double-EMLs devices with (fbi)\textsubscript{2}Ir(acac) at different doping concentrations. (b) Normalized EL spectra of double-EMLs devices with (fbi)\textsubscript{2}Ir(acac) at different doping concentrations operating at 10 mA/cm\textsuperscript{2}. 
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References


