High-efficiency organic light-emitting diodes based on ultrathin blue phosphorescent modification layer*

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Yellow organic light-emitting devices (YOLEDs) with a novel structure of ITO/MoO_3(5 nm)/NPB(40 nm)/TCTA(15 nm)/CBP:$(tbt)_2$Ir(acac)(x%)(25 nm)/FIrpic(y nm)/TPBi(35 nm)/Mg:Ag are fabricated. The ultrathin blue phosphorescent bis[(4,6-difluorophenyl)-pyridi-nato-N,C2′](picolinate) iridium (III) (FIrpic) layer is regarded as a high-performance modification layer. By adjusting the thickness of FIrpic and the concentration of $(tbt)_2$Ir(acac), a YOLED achieves a high luminance of 41618 cd/m^2, power efficiency of 49.7 lm/W, current efficiency of 67.3 cd/A, external quantum efficiency (EQE) of 18%, and a low efficiency roll-off at high luminance. The results show that phosphorescent material of FIrpic plays a significant role in improving YOLED performance. The ultrathin FIrpic modification layer blocks excitons in EML. In the meantime, the high triplet energy of FIrpic (2.75 eV) alleviates the exciton energy transport from EML to FIrpic.

Keywords: modification layer, ultrathin, YOLEDs, phosphorescence

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1. Introduction

Because of their unique properties, organic light-emitting devices (OLEDs) are continuously and increasingly being studied nowadays, especially white OLED that has promising applications in the fields of display and solid-state lighting.[1] Due to the commercial success of OLEDs, enhancing the performances of OLEDs is becoming more and more important. Not only device performances such as high efficiency, high luminance, and excellent color stability are indispensably improved, but also production costs desperately need to lower.[2] The phosphorescent or fluorescent materials have high-frequency usage in EMLs. Meanwhile, maximum internal quantum efficiency of 100% extremely enhances the performance of phosphorescent OLEDs (PHOLEDs). For the conventional OLEDs, there are two common systems: non-doped and host-guest EML. The two EML systems have been widely employed to construct EMLs. However, the doping concentrations of emitters are usually very low ($\sim$ 0.2%–1.5%) to have high device efficiency, so this requires the use of a precise method to control the variation of doping concentration. The above method of low doping concentration makes the utilization of the material low besides the fact that the reproducibility of the devices cannot be guaranteed,[3] which may result in unsatisfactory performance and degradation of properties.

In general, white OLEDs(WOLEDs) are comprised of three primary colors: red, green, blue, or two complementary colors: blue and yellow. The conventional structures of the light-emitting layer are composed of multiple single-doped EMLs or a single doped emitting layer with multiple emitters. In a previous report white light can be realized by mixing blue, green, yellow, and red with multiple doped emitting layer (EML).[4] In our previous experiments, we found that blue phosphorescent bis[(4,6-difluorophenyl)-pyridi-nato-N,C2′](picolinate) iridium (III) (FIrpic) can be used as not only an EML, but also a modification layer, and the novel usage of phosphorescent material can extremely improve YOLED performance. The ultrathin FIrpic layer allowed the convenient handling process and accurate thickness control, it enabled high device efficiency with simple architecture. We fabricated YOLEDs with different concentrations of $(tbt)_2$Ir(acac) and thickness values of ultrathin FIrpic, and explored the performances of these devices. According to our survey, research about this topic has seldom been carried out, so it is necessary to study in depth the effects on device performance.

In this work, we introduce an unprecedented method for high efficiency YOLEDs. In the study of FIrpic thickness, we note that using a non-doped ultrathin material of phosphorescent FIrpic as a modification layer can improve the device performance: power efficiency, current efficiency, EQE, and lu-

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minance. As we expected, the devices can be optimized by adjusting the concentration of $(tbt)_2Ir(acac)$ and the thickness of ultrathin FIrpic. In the following sections, we investigate the function of FIrpic as a modification layer, and explore different- thickness FIrpics in YOLEDs in detail. In sum, the novel usage of phosphorescent material is a special measure that can achieve high-performance YOLEDs.

2. Experimental details

The indium tin oxide (ITO) in an ultrasonic device was pretreated by using four cleansers: detergent water, acetone, deionized water and isopropyl alcohol, in sequence. Each cleaning step takes 15 min. All materials were deposited on ITO glass substrates with 10 Ω/sq sheet resistance in vacuum deposition equipment, the organic material was deposited in an organic vacuum cavity and metallic material was deposited on a 5 mm×5 mm emission area in a metal vacuum cavity. The two cavities were under pressures of 10^{-4} Pa and 10^{-5} Pa, respectively. A 5-nm molybdenum trioxide (MoO_3) was used as the hole injecting layer, two different materials N′-Di-[1-naphthalenyl-N,N′-diphenyl]-1,1′-biphen-yl-4,4′-diamine (NPB) and 4,4′, 4′-Tri(9-carbazoyl)triphenylamine (TCTA) were used as 40-nm and 15-nm hole transporting layers. Then, a 25-nm-thick yellow EML was constructed by doping yellow phosphorescent bis[2-(4-tertbutylphenyl)benzothiazolato-N,C2′] iridium (acetylacetonate)($(tbt)_2r(acac)$) into a carbazole-based host 4, 4′-Bis(carbazol-9-yl)-biphenyl (CBP). An ultrathin layer of non-doped blue phosphorescent bis[(4,6-difluorophenyl)-pyridi-nato-N,C2′](picolinate) iridium (III) (FIrpic) was sandwiched between the doping yellow EML and a 35-nm 1,3,5-Tris(1-ph-enyl-1H-benzimidazol-2-yl)benzene (TPBi) electron transporting layer, which has hole blocking function. Finally, the cathode used Mg:Ag alloy. Electroluminescent (EL) spectrum was measured with an OPT-2000 spectrometer and luminance–current density–voltage characteristics were recorded with a Keithley 4200 semiconductor source.[5] All the measurements were carried out at room temperature. The devices were given as ITO/MoO_3(5 nm)/NPB(40 nm)/TCTA(15 nm)/CBP:$(tbt)_2Ir(acac)$(*x*%)(25 nm)/FIrpic(*y* nm)/TPBi(35 nm)/Mg:Ag. Figure 1 shows molecular structures of organic semiconductors and an energy diagram. For convenience, the doping concentration of the yellow EML(*x*) varied from 5% (device A1), 6% (device A2), 7% (device A3), 10% (device A4) to 13% (device A5) respectively, while the thickness of FIrpic(*y*) was fixed to be 0.3 nm. In addition, for studying the ultrathin FIrpic function as a modification layer, five devices with different-thickness FIrpics were fabricated, the structures of these devices were similar to those of device A3:ITO/MoO_3(5 nm)/NPB(40 nm)/TCTA(15 nm)/CBP:$(tbt)_2Ir(acac)$(10%)(25 nm)/FIrpic(*y* nm)/TPBi(35 nm)/Mg:Ag, which has been discussed above. Their thickness values are 0 nm (device B1), 0.05 nm (device B2), 0.1 nm (device B3), 0.3 nm (device B4), 0.5 nm (device B5), 0.7 nm (device B6), respectively. It should be noted that the ultrathin thickness of FIrpic could not be measured as the layer was discontinuous, and all the thickness values were calibrated in an evaporator thickness monitor.

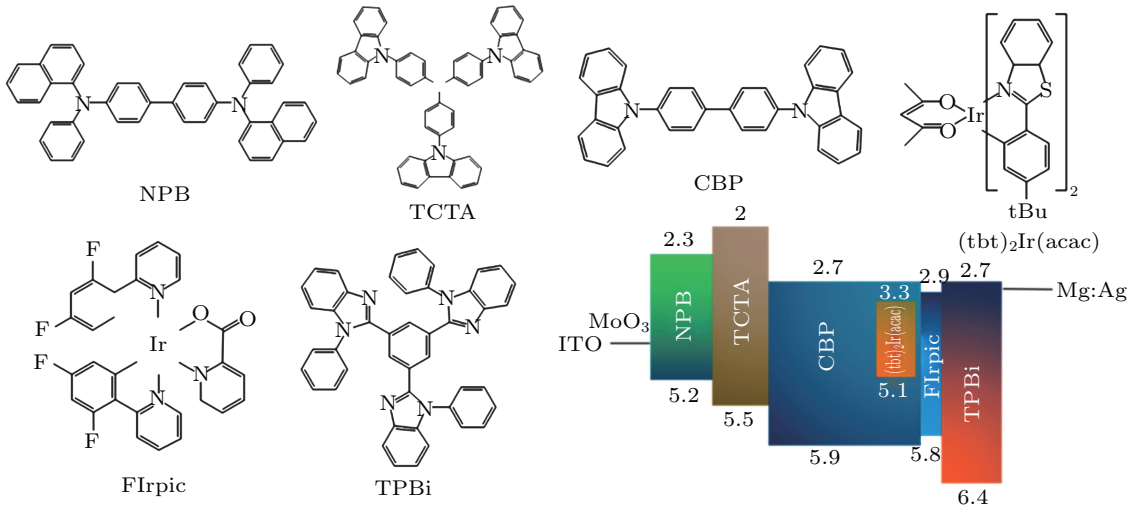


Fig. 1. (color online) Molecular structures of organic semiconductors and energy diagram.

3. Results and discussion

Figure 2(a) shows the luminance–current density–voltage (*L*–*J*–*V*) characteristics of devices A1–A5, and Table 1 presents the detailed characteristics. It can be seen that with $(tbt)_2Ir(acac)$ doping concentration increasing from 5%, 6%, 7% , 10%, and 13% in devices A1, A2, A3, A4, and A5, the current density decreases. In addition, the luminances of A1-A5 are gradually enhanced with the increase of voltage, V, and

the luminances of 6044, 9765, 11024, 41618, 40954 cd/m^2 are obtained at a bias of 13, respectively. As is well known, the hopping mechanism[6,7] in doped devices always plays a significant role in charge transport, with the increase of doping concentration, the hopping mechanism is more remarkable. To investigate the effects of $(tbt)_2Ir(acac)$ molecules on current density, performances of A1–A5 devices are investigated as shown in Table 1.

Table 1. Performances of devices A1–A5.

Device	CBP:x% $(tbt)_2Ir(acac)$	FIrpic (0.3 nm)	V_{on}/V	Max.L /(cd/m^2)	Max.CE /(cd/A)	Max.PE /(lm/W)
A1	5	0.3	3.9	6461	2.8	1.3
A2	6	0.3	3.71	9502	8.7	5.4
A3	7	0.3	3.7	10752	9.2	5.3
A4	10	0.3	3.5	41618	67.3	49.7
A5	13	0.3	3.65	40952	34.1	16.6

Simultaneously, we can see that the maximum power efficiencies and current efficiencies of devices A4 and A5 are higher than those of devices A1, A2, and A3. When the doping concentration of $(tbt)_2Ir(acac)$ reaches to 10%, the current efficiency and the power efficiency attain the highest values: 67.3 cd/A and 49.7 lm/W, respectively. Therefore, a higher doping concentration of $(tbt)_2Ir(acac)$ is available for more radiative recombinations[8] and contributes to higher luminance and high efficiency. Meanwhile, we can clearly see that the turn-on voltage is the lowest (3.5 V) in device A4. Comparing with devices A1, A2, and A3, the efficiencies and luminances of devices A4 and A5 shown in Fig. 2(a) are obviously enhanced. However, the efficiency decreases when the $(tbt)_2Ir(acac)$ doping concentration reaches 13%, the concentration quenching effect is more serious, if the doping concentration continues to increase, it results from intermolecular dipole–dipole interaction caused due to the short distance between the emitter molecules.[9,10] In Fig. 2, the normalized EL spectra of the five representative devices can evidence the above arguments.

In the normalized EL spectra, we can learn from the spectra at 10 V that the blue intensity in device A1 is indeed sufficiently strong compared with those in devices A2, A3, A4, and A5; A1 has no yellow intensity scarcely but blue intensity can be seen clearly, due to the number of $(tbt)_2Ir(acac)$ molecules in a low standard and host material CBP used as the hole transporting layer in the A1 device, so the $(tbt)_2Ir(acac)$ molecules in EML are negligible. In addition, blue intensity cannot be observed in A4 and A5 devices, because with the $(tbt)_2Ir(acac)$ concentration increasing, more charge carriers gather in the $(tbt)_2Ir(acac)$ layer, so the hole-trapping effect on ultrathin FIrpic is negligible.[11] Furthermore, the $(tbt)_2Ir(acac)$ concentration increases, and more charge carriers gather in the $(tbt)_2Ir(acac)$ layer. Therefore, the concentration quenching effect is more serious in device A5. This is proof of the higher efficiency in device A4 instead of device A5.

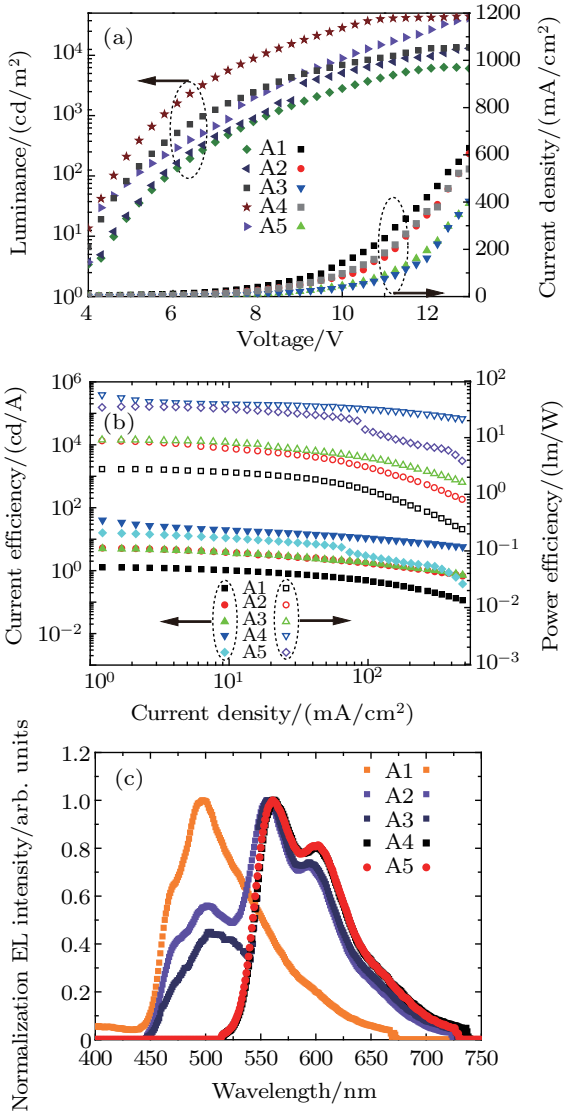


Fig. 2. (color online) (a) Luminance–current density–voltage, (b) current efficiency–power efficiency–current density, and (c) normalization EL spectra of devices A1–A5.

From the above analysis, there are two roles for the $(tbt)_2Ir(acac)$ we can reasonably speculate: (i) trap centers, (ii) emission centers. In the beginning, the device A1 has low concentration of $(tbt)_2Ir(acac)$, the carrier trapping effect is not obvious and an emission center does not exist in the yellow EML either. With the increase of $(tbt)_2Ir(acac)$ concentration, the charge carrier trapping effect is much stronger, more excitons accumulate in EML, the emission center is controlled by $(tbt)_2Ir(acac)$ which contributes to yellow emission. When the concentration of $(tbt)_2Ir(acac)$ increases, more $(tbt)_2Ir(acac)$ molecules are drifted away from EML, rendering more trap centers and emission centers. Two contradictive results emerge, the exciton formation induced by charge carrier recombination would decrease due to more trap centers, but the yellow emission could be intensified due to more emission centers. The results imply that when the concentration

of $(tbt)_2Ir(acac)$ is 10%, the balance between charge carriers and light emission can be enhanced, hence, the high performance of device A4 is obtained. Considering the noticeable trapping effect of $(tbt)_2Ir(acac)$, we believe that the charge carrier balance should also be properly enhanced by using a suitable concentration of $(tbt)_2Ir(acac)$ in device A4. Besides, charge carrier injection and the transport property have a profound influence on device performance. As a result, it can prove the electrical field distribution changes with the change of the concentration of $(tbt)_2Ir(acac)$.

Table 2. Performances of devices B1–B6.

Device	CBP:10% $(tbt)_2Ir(acac)$	FIrpic (y nm)	V_{on}/V	Max.L /(cd/m^2)	Max.CE /(cd/A)	Max.PE /(lm/W)
B1	10	0	4.0	35959	29.1	26.2
B2	10	0.05	3.9	35094	26.2	21.7
B3	10	0.1	3.8	44316	28.6	21.1
B4	10	0.3	3.55	41617	67.3	49.8
B5	10	0.5	3.7	41767	30.9	22.4
B6	10	0.7	3.6	40486	23.3	19.6

Figure 3(a) shows the luminance–current density–voltage (L–J–V) characteristics of devices B1–B6, the detailed characteristics of all the device are summarized in Table 2. It can be seen that from the thickness values of the FIrpic layer between B1–B6, the intensity of yellow is scarcely changed and the intensity of blue is non-existent, the performance of the device is gradually enhanced from B1 to B4. In Table 2 when the thickness of FIrpic reaches 0.3 nm, the device performance becomes best, the power-efficiency is 49.7 lm/W, the current-efficiency is 67.3 cd/A, the lunminance is 41618 cd/m^2. Figure 3(b) shows current-efficiency power efficiency current density characteristics of devices B1–B6. The efficiency increases with increasing the thickness of FIrpic, but the concentration quenching effect is serious if the thickness continues to increase. The results confirm that FIrpic can improve the performances of YOLEDs and an appropriate thickness of FIrpic can optimize the properties of YOLEDs. Reasonable explanations of high performance of B4 will be explored from two aspects as follows.

Figure 3(a) shows that the FIrpic and EML have matched highest occupied molecular orbital (HOMO) level, thereby excitons accumulate at the interface between EML and ETL. Furthermore, FIrpic provides an additional channel to facilitate charge transport for the EML,[12] which can also be inferred from its lowest unoccupied molecular orbital (LUMO) level.[13] On the other hand, the high triplet energy of FIrpic (2.75 eV)[14] prevents exchange energy from being lost from host–guest EML to ETL and suppresses the energy transport from EML to ETL. To summarize, the FIrpic enhances the efficiency and luminance of the device.

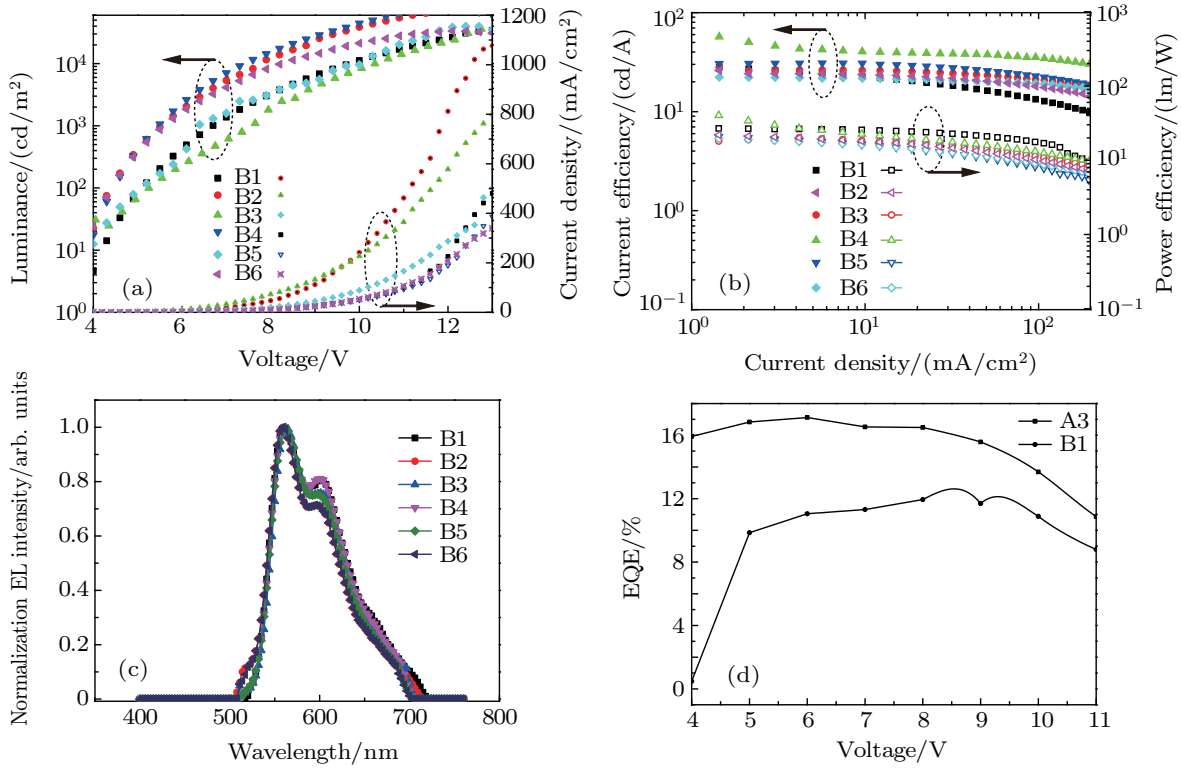


Fig. 3. (color online) (a) Luminance–current density–voltage, (b) current efficiency–power efficiency–current density, and (c) normalization EL spectra of devices B1–B6. (d) External quantum efficiencies–voltage characteristics of devices A3 and B1.

It is generally known that energy transfer and direct charge trapping[15] are the significant mechanisms for exciton formation and emission. In Fig. 3(a), with the increase of FIrpic thickness, the J–V curves show an obvious reduction trend, indicating that direct charge trapping may exist in the emission process. The J–V curves reveal that host-guest energy trans-

fer dominates the EL process, indicating the complete energy transfer from the FIrpic to $(tbt)_2Ir(acac)$. However, we find that J–V curves of devices B4, B5, and B6 are almost overlapped. It means that the trapping effect is much more serious in FIrpic with the increase of FIrpic thickness. On the other hand, the ultrathin FIrpic layer forms discontinuous film, and this layer can be treated as a doped layer with a low concentration, in which the distance between exciton donor and acceptor is too large to facilitate efficient Dexter energy transfer,[16] and this further affects the current density and efficiency. As shown in Fig. 1, we can sum up two mechanisms: one is the host-guest CBP:$(tbt)_2Ir(acac)$ EML system owning 100% photo-luminescence quantum efficiency,[17] and the other is the energy level differences between CBP and $(tbt)_2Ir(acac)$. The two mechanisms directly lead to charge trapping on $(tbt)_2Ir(acac)$ and limit short-distance Dexter energy transfer but promote the Förster energy transfer.[18] Moreover, the concentration quenching[19] is caused by molecular aggregation, but the thickness of neat emitter layer (B4) is larger than quenching radius ($\sim$ 1 nm–1.3 nm), accordingly it prevents the quenching effect. In addition, high triplet energy of FIrpic (2.75 eV)[20,21] can effectively prevent excitons from being generated in the blue modification layer. While the FIrpic layer thickness changes from 0 nm to 0.7 nm, the yellow intensity does not have any change in Fig. 3(c) normalization EL spectra. This is because the ultrathin FIrpic restricts the hole injection even if the thickness of FIrpic is only 0.05 nm.[22] As shown in Fig. 3(d), it can be clearly seen that the EQEs[23,24] of devices A3 and B1 are different, the high EQE close to 18% is realized in device A3. The maximum EQE of A3 is 17.13% that is 1.45 times higher than that of B3 (11.86%), indicating that appropriate thickness of FIrpic as an electron transporting layer close to the EML improves the device of EQE.

4. Conclusions

In this work, phosphorescent YOLEDs with a FIrpic ultrathin modification layer are fabricated, by doping yellow phosphorescent $(tbt)_2Ir(acac)$ into host CBP with a non-doped blue ETL. The concentration of $(tbt)_2Ir(acac)$ and the thickness of FIrpic are adjusted for systematic investigation, and the results indicate that the concentration of $(tbt)_2Ir(acac)$ and the thickness of FIrpic play a significant role in device performance. High concentration of $(tbt)_2Ir(acac)$ makes more excitons accumulate in EML and charge carrier trapping is dominant, while ultrathin FIrpic close to the cathode side makes a major contribution to yellow emission because the FIrpic has high triplet energy (2.75 eV) and provides an additional channel, which allows more carriers to accumulate in EML. Furthermore, an ultrathin FIrpic layer has a high HOMO level with EML, which can limit holes in the EML favorably and adjust for efficient hole collection in the EML. Meanwhile, the recombination zone is well confined in the EMLs, enabling a high-efficiency device. Therefore, it is demonstrated that the FIrpic layer has a great effect on device performance although it is ultrathin, which could provide a direction for high performance YOLEDs with an easy fabrication process.

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