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CHIN. PHYS. LETT. Vol. 33, No. 3 (2016) 038501

Highly Efficient Greenish-Yellow Phosphorescent Organic Light-Emitting Diodes Based on a Novel 2,3-Diphenylimidazo[1,2-a]Pyridine Iridium(Ⅲ) Complex

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(Received 19 August 2015)

A cyclometalated greenish-yellow emitter 2,3-diphenylimidazo[1,2-a]pyridine iridium(Ⅲ) complex is successfully synthesized and used to fabricate phosphorescent organic light-emitting diodes. The optimized device exhibits a greenish-yellow emission with the peak at 523 nm and a strong shoulder at 557 nm, corresponding to Commission Internationale de l'Eclairage coordinates of (0.38, 0.58). The full width at half maximum of the device is 93 nm, which is broader than the fac-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] based reference device of 78 nm. Meanwhile, a maximum current efficiency of 62.6 cd/A (47.5 lm/W) is obtained. This result is higher than a maximum current efficiency of 54.8 cd/A (43 lm/W) of the Ir(ppy)$_3$ based device. The results indicate that this new iridium complex may have potential applications in fabricating high color rendering index white organic light emitting diodes.

PACS: 85.60.Jb, 42.15.Eq, 85.60.Pg, 42.79.Bh   DOI: 10.1088/0256-307X/33/3/038501

Organic light-emitting diodes (OLEDs) have attracted great attention due to their applications in high-resolution, full-color, flat-panel displays and lighting sources.[1−3] The search for highly efficient three primary color (red, green, and blue) emitters is an important subject for OLEDs.[4,5] Compared with fluorescent OLEDs, phosphorescent OLEDs using transition metal complexes as emitters can harvest both singlet and triplet excitons, which can achieve an internal quantum efficiency as high as 100%.[6,7] To become a viable technology for next-generation solid-state light sources, however, phosphorescent organic light-emitting diodes (PHOLEDs) face the challenge of achieving simultaneously a high color rendering index (CRI) and a high efficiency at high luminance.[8,9] To improve the CRI, several groups have incorporated four or more emitters to cover the entire range of the visible spectrum.[10−12] However, the use of such high number of emitters not only increases device complexity, but also makes it less straightforward to achieve high device efficiency. A more convenient approach to improve the CRI of a standard three-color white (i.e. blue, green and red combination) PHOLED without sacrificing the overall device simplicity is to employ a greenish-yellow emitter to replace the green emitter such that the gap in emission wavelength between standard green and red emitters is eliminated.[13] Unfortunately, there are only a few reports on greenish-yellow emitters for PHOLEDs. So *et al.*[14] synthesized a trimethylsilylxylenebased greenish-yellow Ir(Ⅲ) emitter with a peak wavelength at 532 nm, and demonstrated PHOLEDs with maximum external quantum efficiency (EQE) and current efficiency (CE) of 12.7% and 45.7 cd/A, respectively. More recently, Chen *et al.*[15] reported a yellowish-green Ir(Ⅲ) emitter with a peak wavelength at 544 nm, which exhibits a high CE of 63.0 cd/A at a luminance of 100 cd/m^2, corresponding to an EQE of 16.3% and power efficiency of 36.6 lm/W. However, these emitters have no obvious shoulder peak, thus it is difficult to realize a high CRI lighting device based on a three-emitter pattern.

In this Letter, we demonstrate a greenish-yellow PHOLED based on a newly synthesized emitter 2,3-diphenylimidazo[1,2-a]pyridine iridium(Ⅲ) ([Ir(3MPIPy)$_2$tmd]). The synthesis procedure of Ir(3MPIPy)$_2$tmd is shown in Fig. 1. Due to 2,3-diphenylimidazo[1,2-a]pyridine consisting of bidentate ancillary ligands, with increasing the Ir-complex electron transporting ability, the emission of the iridium complex red shifts from green to greenish-yellow compared with the Ir(ppy)$_3$. The optimized device exhibits a greenish-yellow emission with the peak at 523 nm and a strong shoulder at 557 nm, corresponding to Commission Internationale de l'Eclairage (CIE) coordinates of (0.38, 0.58). The full width at half maximum (FWHM) of the device is 93 nm, which is broader than the fac-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] based reference device of 78 nm. Meanwhile, the device shows a maximum current efficiency and a maximum power efficiency of 62.6 cd/A and 47.5 lm/W, respectively, which are higher than the

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$Ir(ppy)_3$-based device.

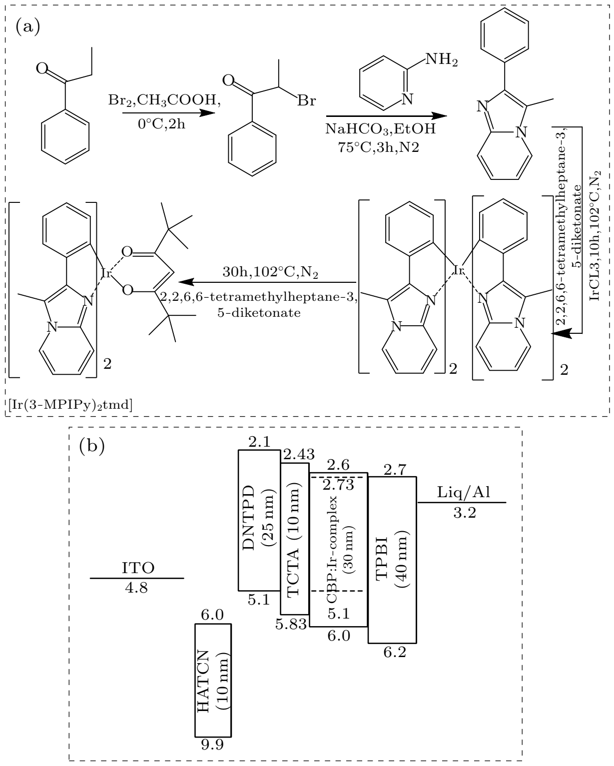

Fig. 1. (a) Synthesis and structure of the green-yellow dopant used in this study. (b) The device structure and energy level diagrams of all materials used in the device.

To evaluate the EL performance of the new Ir(Ⅲ) emitter, the fabricated devices based on [Ir(3MPIPy)$_2$tmd] have structures of indium tin oxide (ITO)/HATCN (10 nm)/DNTPD (40 nm)/TCTA(10 nm)/CBP: [Ir(3MPIPy)$_2$tmd] (∼X%, 30 nm)/TPBI (40 nm)/Liq (2 nm)/Al (100 nm), as well as $x = 8$ (device A), 10 (device B) and 12 (device C). Here DNTPD, CBP and TPBI denote N,N'-diphenyl N,N'-bis[4(phenylmtolylamino)-phenyl]-biphenyl 4,4'-diamine, (4,4'-bis(N-carbazolyl)-2,2'-biphenyl) and (2,2',2"-(1,3,5-benzinetriyl)-tris (1-phenyl-1-H-benzimidazole)), which are exploded as the hole transporting layer, host of the emitter and electron-transporting layer, respectively. TCTA (tris(4-carbazoyl-9-ylphenyl)amine served as the exciton blocking layer due to the high triplet power. Here 1, 4, 5, 8, 9, 11-Hexaazatriphenylene-hexacarbonitrile (HATCN) and 8hydroxyquinolinolatolithium (Liq) served as the hole and electron-injecting layers, respectively. All organic materials were supplied from Xi'an Manareco New Materials Co., Ltd and purified by gradient sublimation with purity higher than 99.95% prior to use. The detailed device structure is shown in Fig. 1, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the materials are taken from Refs. [16–18], the HOMO and LUMO levels of Ir(3MPIPy)$_2$tmd were measured by ourselves. For reference, the device with a widely used green emitter $Ir(ppy)_3$ was also fabricated (device D), and the doping concentration was fixed at the optimized one of 10%. Organic layers and the Al cathode were fabricated by thermal evaporation under 4×10^{-4} Pa onto the pre-cleaned ITO glass substrates with a resistance of 20 Ω/sq. Current density-voltage-luminance characteristics of the devices were measured with Keithley 2400 and a PR670 spectrophotometer, all measurements were carried out in air at room temperature.

The electrochemical properties of [Ir(3MPIPy)$_2$tmd] were investigated by cyclic voltammetric studies and the cyclic voltammogram (CV) curve is shown in Fig. 2. Electrochemical measurements were made by using a CHI model 600C electrochemistry station. A conventional three-electrode configuration, consisting of a platinum working electrode, a Pt-wire counter electrode and a Ag/AgCl reference electrode, was used. The HOMO and LUMO levels of the [Ir(3MPIPy)$_2$tmd] sample were determined to be 5.1 eV and 2.73 eV, respectively, from the electrochemical data and the edge wavelength of the UV-visible absorption spectrum.

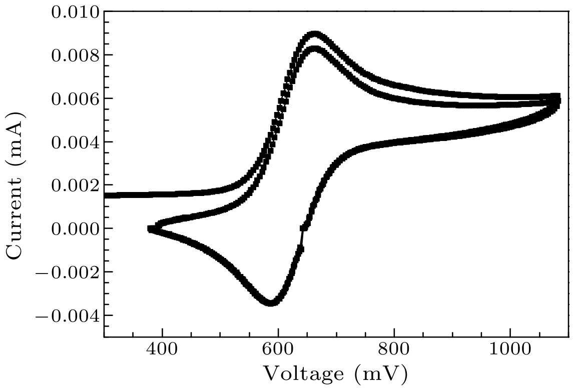

Fig. 2. Cyclic voltammogram of [Ir(3MPIPy)$_2$tmd] complex.

The absorption and photoluminescence spectra of [Ir(3MPIPy)$_2$tmd] in dichloromethane at room temperature are shown in Fig. 3. The absorption and photoluminescence (PL) spectra of iridium(Ⅲ) complexes in degassed toluene solution have been measured on a Shimadzu UV-2550 UV-VIS spectrometer and on a fluorescence spectrometer Shimadzu RF-5301PC with a xenon arc lamp excitation source, respectively. The absorption features of the higher energies (280–320 nm) are assigned mostly to the $^1\pi$–$\pi*$ transitions of the ligand centered states. The moderate intensity of the absorption peaks in the range of 350–450 nm can be attributed to the spin-allowed metal charge transfer (^{1}MLCT) transition from the

Ir atom to the ligands (C^N)[dπ (Ir)→ π*(C^N)]. [Ir(3MPIPy)$_2$tmd] fluoresce intensely when fabricated into solid film, excitation wavelength optimization 290 nm. The film of [Ir(3MPIPy)$_2$tmd] shows an emission maximum at 517 nm and a strong shoulder at 551 nm, which emits greenish-yellow light.[19]

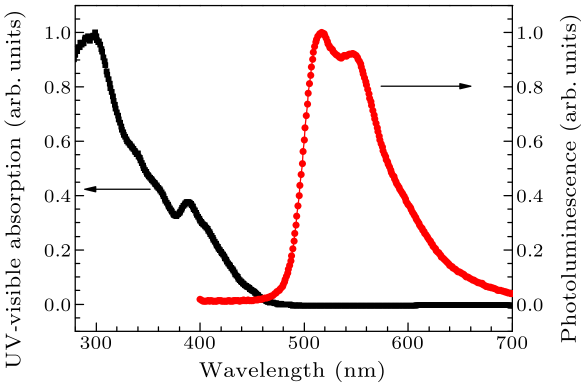

Fig. 3. UV visible absorption (in chloroform) and photoluminescence spectra (in solid film) of the [Ir(3MPIPy)$_2$tmd] complex at room temperature.

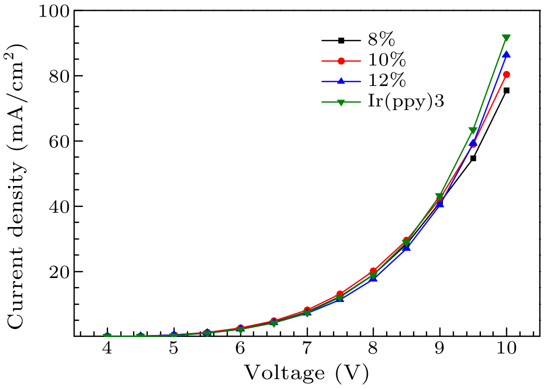

Fig. 4. Voltage–current density characteristics of devices.

Figure 4 shows the voltage–current density characteristics of the fabricated devices based on Ir(3MPIPy)$_2$tmd and Ir(ppy)$_3$ (device D) with different concentrations. The results show that the high-doping-concentration device has slightly higher current density at the same driving voltage. It is known that holes are much easier to transport than electrons in an OLED because the hole mobility is much higher than the electron mobility of an organic semiconducting material. Due to the fact that phenylimidazo shows a weak electron transporting ability, the electron transporting ability of the EML is increased when the doping concentrations of Ir(3MPIPy)$_2$tmd increase from 8% to 12%, which results in more electron injection into the EML and hence raises the current density of the device. We notice that when the voltage exceeds 8 V, device B presents the current density slightly lower than device D under the same doping concentration. This should be attributed to the lower LUMO of Ir(ppy)$_3$ (−2.8 eV) than Ir(3MPIPy)$_2$tmd (−2.73 eV), which facilitates the injection of electrons into the EML.

Figure 5 shows the current efficiencies of devices A–D as a function of luminescence, and the EL data are listed in Table 1. The efficiency of devices based on [Ir(3MPIPy)$_2$tmd] shows a strong dependence on the doping concentration. Device A with 8% Ir(3MPIPy)$_2$tmd shows a maximum current efficiency (CE) and a maximum power efficiency (PE) of 59.6 cd/A and 46.8 lm/W, respectively. With the Ir(3MPIPy)$_2$tmd doping concentration increasing to 10%, both the maximum CE and the maximum PE of device B are increased, up to 62.6 cd/A and 47.5 lm/W, respectively. Further increasing the doping concentration to 12% results in obvious descent of the maximum CE and PE of the device. Device C shows a maximum CE and a maximum PE of only 59.0 cd/A and 46.4 lm/W, respectively. This is possible due to the fact that high doping concentration of the phosphorescent emitter in the device increases the nonradioactive quenching processes, including triplet–triplet annihilation and triplet–polaron annihilation.[20] On the other hand, device D presents a maximum CE of 54.8 cd/A (43.0 lm/W). More interestingly, device B shows higher CE and PE than device D in the whole luminescence region. For example, the current efficiencies at 1000 and 5000 cd/cm^2 of device B are 54.0 and 41.5 cd/A, respectively, while they are 45.6 and 34.4 cd/A for device D. These results indicate that the new Ir(3MPIPy)$_2$tmd greenish-yellow emitter may be useful in highly efficient organic light emitting diodes and lighting sources.

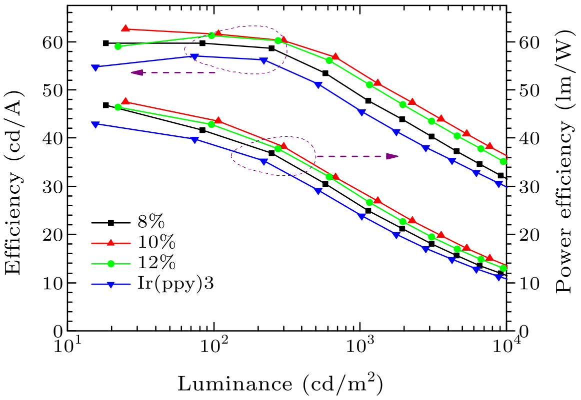

Fig. 5. Luminance–current efficiency characteristics of PHOLEDs.

Figure 6 shows the normalized EL spectra at applied bias of 7 V of devices A–D. The EL spectra of devices A–C show an emission peak at about 523 nm with a strong shoulder at about 557 nm. Meanwhile, we can note that the emission intensity of the shoulder decreases with the increase of the doping concentration of Ir(3MPIPy)$_2$tmd. This proves our conjecture that Ir(3MPIPy)$_2$tmd is a dominant electron transporting material. With the increase of the Ir(3MPIPy)$_2$tmd doping concentration, electrons more easily inject into the EML, which shifts the charge recombination zone close to the HTL/EML interface. As a result, the shoulder emission decreases due to the increasing distance between the charge recombination zone and Al cathode.[21,22] The CIE chromaticity coordinates of devices A, B, and C are (0.39, 0.58), (0.38, 0.58), and (0.38, 0.57), while the FWHMs of corresponding devices are 93, 84, and 84 nm, respectively. In contrast, device D shows an EL emission at about 516 nm, corresponding to the CIE coordinates of (0.34, 0.61) and the FWHM of 78 nm, respectively. For a three-emitter (blue, green, red) system of lighting applications, the emitters must be carefully chosen. The emission spectra of the emitters should compensate for each other so that the generated white spectrum can cover the whole visible region with a uniform emission intensity. Compared with Ir(3MPIPy)$_2$tmd, commercially available green emitters, such as Ir(ppy)$_3$, generally have a shorter emission wavelength and a smaller FWHM, thus it is difficult to realize high CRI white light emission. As Ir(3MPIPy)$_2$tmd has a large FWHM and a strong shoulder peak at about 557 nm, it can effectively complement the yellow region emission when it is used as a primary emitter with suitable blue and red emitters to realize high CRI three-emitter white lighting device. Such works are ongoing in our research group and the results will be reported on in another work.

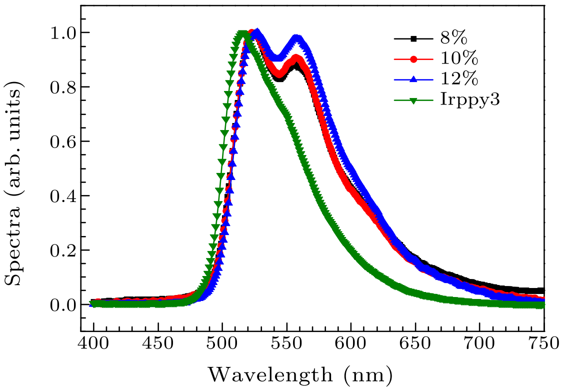

Fig. 6. The electroluminescence spectra of the devices.

Table 1. EL date of PHOLEDs A B C and D.

Device	$\mathrm{CE}_{\max}$ (cd/A)	$\mathrm{PE}_{\max}$ (lm/W)	EQE(%)^{a}	$\lambda_{\max}$ (nm)	FWHM (nm)	CIE$(x,y)^{b}$
Device A	59.6	46.8	22.5	527	93	(0.39, 0.58)
Device B	62.6	47.5	23.9	523	84	(0.38, 0.58)
Device C	59.0	46.4	22.4	524	84	(0.38, 0.57)
Device D	54.8	43.0	21.9	516	78	(0.34, 0.61)

[a] External quantum efficiency of maximum. $\mathrm{PE}_{\max}$: maximum power efficiency, and $\lambda_{\max}$: peak wavelength.
[b] Commission Internationale d'Eclairage chromaticity coordinates. $\mathrm{CE}_{\max}$: maximum current efficiency.

In conclusion, a new iridium(Ⅲ) complex Ir(3MPIPy)$_2$tmd is successfully synthesized. The phosphorescent organic light emitting diodes based on Ir(3MPIPy)$_2$tmd-doped CBP host exhibits a greenish-yellow emission at 523 nm with a strong shoulder peak at 557 nm, corresponding to the FWHM of 93 nm. Compared with Ir(ppy)$_3$, the emission peak is shifted to long wavelength and the emission band is broadened. Furthermore, the optimized device based on Ir(3MPIPy)$_2$tmd shows a maximum current efficiency of 62.6 cd/A, the maximum power efficiency of 47.5 lm/W, which is also higher than the Ir(ppy)$_3$ reference device. These results indicate that Ir(3MPIPy)$_2$tmd may have a potential application in constructing highly efficient PHOLEDs, especially for high-performance white-light-emitting OLEDs.

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