

Color tunable phosphorescent light-emitting diodes based on iridium complexes with substituted 2-phenylbenzothiozoles as the cyclometalated ligands

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Abstract

Several iridium complexes {iridium(III)bis[2-(3-methoxyphenyl)-1,3-benzothiazolato-N,C^{2'}] acetylacetonate (MeO-BT)₂Ir(acac), iridium(III)bis[2-(2,4-difluorophenyl)-1,3-benzothiazolato-N,C^{2'}] acetylacetonate (2F-BT)₂Ir(acac), and iridium(III)bis[2-(2,4-difluorophenyl)-6-fluoro-1,3-benzothiazolato-N,C^{2'}] acetylacetonate (3F-BT)₂Ir(acac)} having different substituents on 2-phenylbenzothiazole have been synthesized. The phosphorescent light emitting diodes (PHOLEDs) using these iridium complexes as dopant emitters were fabricated. The experimental results revealed that the emissive colors of PHOLEDs could be finely tuned by suitable modification of the substituents on the 2-phenylbenzothiazole ligands. Furthermore, these iridium complexes show better emissive properties than the known iridium(III)bis(2-phenylbenzothiazolato-N,C^{2'}) acetylacetonate (BT)₂Ir(acac).

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1. Introduction

Recently, organic light emitting diodes (OLEDs) have attracted worldwide attention for their high emission efficiency and low operating voltage in flat panel displays. An important breakthrough is phosphorescent light emitting diodes (PHOLEDs) with the use of the heavy metal complexes, particularly iridium complexes [1–8]. The PHOLEDs have four-fold theoretical efficiency than the fluorescent light emitting diodes, assuming electron–hole recombination is statistically controlled. The highly efficient emission of PHOLEDs results from strong spin–orbit coupling effect of the electronic states in the heavy metal

complexes, facilitating the population accumulation of triplet state. Since singlet and triplet excitons can be fully utilized, the PHOLEDs thus can theoretically attain 100% internal quantum yield and ca. 20% external quantum yield. As a result, the PHOLEDs with fac-tris(2-phenylpyridine)iridium (Ir(ppy)₃) exhibit green emission with an external quantum efficiency (η_{ext}) of 15% [9,10].

Both the electroluminescent (EL) efficiency and the emissive wavelength of devices based on iridium complexes are affected greatly by the organic ligands. Thompson et al. [11] reported a series of neutral iridium(III) complexes that exhibit different emissive colors. Recently, Grushin's group synthesized a series of iridium(III) complexes with fluorinated 2-arylpyridines and showed that the emissive colors of the materials can be finely tuned by systematic control of the nature and position of the substituents on the ligands [12,13]. These results

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prompted us to systematically study the substitution on 2-phenylbenzothiazole and their effect on emissive colors. In this paper, we report the synthesis and characterization of a series of iridium complexes having different substituted 2-phenylbenzothiazole ligands. The experimental results reveal that the devices based on these iridium complexes exhibit different emissive colors with high brightness, external quantum efficiency and power efficiency.

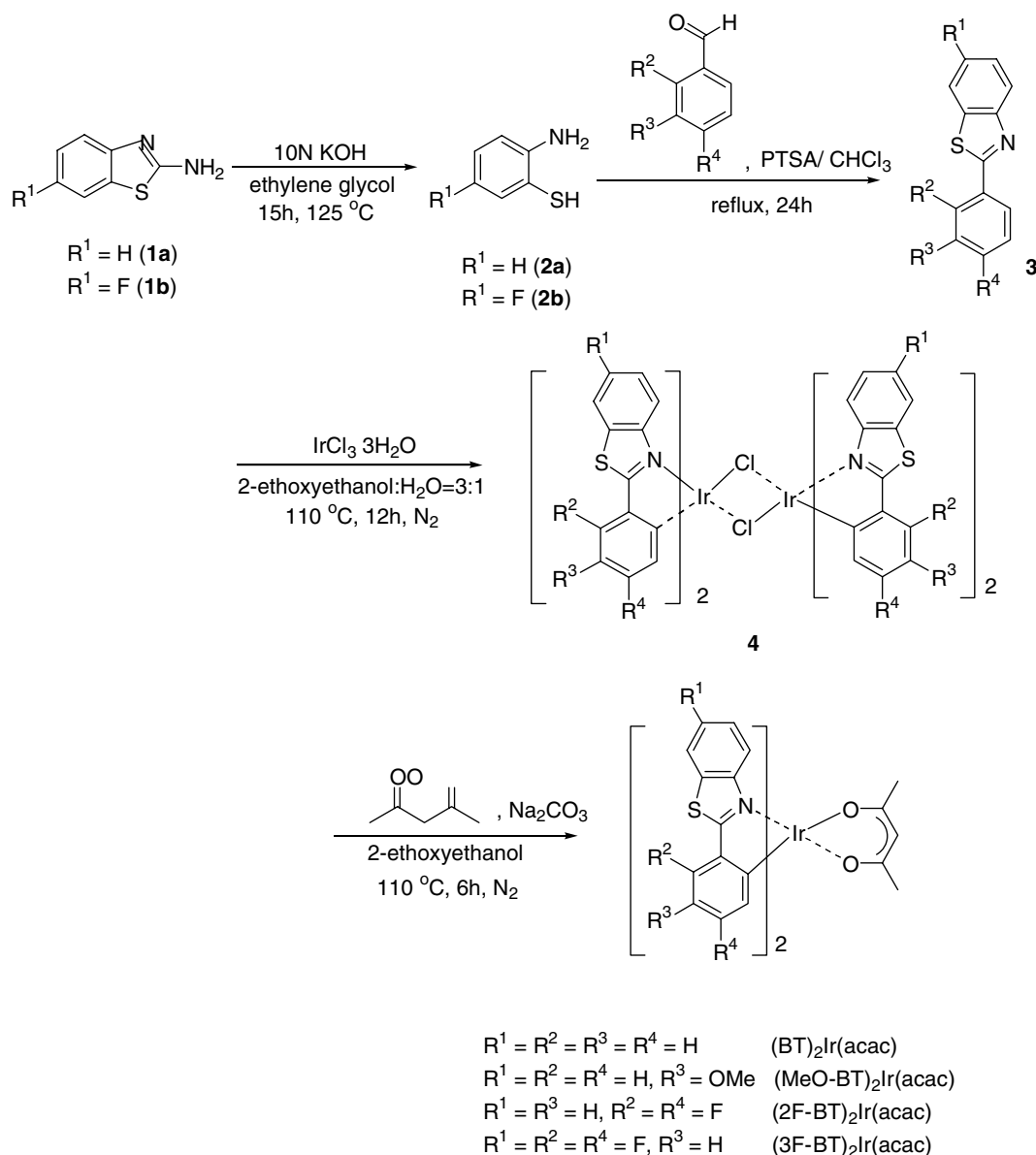
2. Experimental details

2.1. Synthesis of iridium complexes

The synthetic protocol for the cyclometallated iridium(III) complexes is essentially identical to that reported previously [14] and outlined in Scheme 1.

Synthesis of 2-aminothiophenol: 2-Aminobenzothiazole **1a** (27.8 mmol) and 10 N KOH were refluxed in ethylene glycol (6.0 ml) under nitrogen at 125 °C for 15 h. The reaction mixture was then cooled to room temperature, and neutralized with 37.8 wt% hydrochloric acid (1 g). The reaction mixture was extracted with ethyl acetate and dried over Na₂SO₄ prior to concentration in vacuum. The resulting solid was recrystallized in methanol to give the desired yellow solid yellow **2a** (yield = 78%).

Synthesis of 2-phenylbenzothiazole (3a): 2-Aminothiophenol **2a** (16 mmol), benzaldehyde (16 mmol) and *p*-toluenesulfonic acid monohydrate (PTSA) (1.6 mmol) were refluxed in chloroform (20 ml) under nitrogen for 24 h. After cooling, the mixture was extracted with water as well as ether and dried with Na₂SO₄. After



removal of solvent, the crude product was recrystallized with methanol to give a yellow solid **3a**.

Synthesis of μ -chloro-bridged iridium dimer (4a**):** 2-Phenylbenzothiazole **3a** (2.2 mmol), iridium trichloride hydrate (1.0 mmol), 2-methoxyethanol/water solution (v:v = 3:1) were heated and stirred at 110 °C for 12 h under nitrogen. After cooling to room temperature, the crude solution was filtrated to give an orange–yellow precipitate. Then the precipitate was washed with ethanol and hexane for several times. After dried in vacuum, a cyclometalated Ir(III) μ -chloro-bridged dimer (**4a**) was obtained.

Synthesis of iridium acetylacetonate complex: Dimer **4a** (0.78 mmol), 2,4-pentanedione (2.0 mmol), and Na_2CO_3 (5 mmol) were refluxed in the presence of 2-methoxyethanol under nitrogen for 6 h. After cooling to room temperature, the crude product was filtrated to give an orange–yellow precipitate. Then the precipitate was washed with water, ethanol, and hexane for several times. Finally, the crude product was purified by column chromatography (silica, dichloromethane) and dried to give the desired iridium complex $(\text{BT})_2\text{Ir}(\text{acac})$ (yield = 72%).

The same procedure was adopted for the preparation of $(\text{MeO-BT})_2\text{Ir}(\text{acac})$, $(2\text{F-BT})_2\text{Ir}(\text{acac})$, and $(3\text{F-BT})_2\text{Ir}(\text{acac})$. The yields of $(\text{MeO-BT})_2\text{Ir}(\text{acac})$, $(2\text{F-BT})_2\text{Ir}(\text{acac})$, and $(3\text{F-BT})_2\text{Ir}(\text{acac})$ were 64%, 60%, and 58%, respectively. All the Ir complexes were sublimed at 280–300 °C. The spectral data, yields and elemental analytical data of these iridium complexes are listed below.

Iridium(III)bis(2-phenylbenzothiazolato- $\text{N},\text{C}^{2'}$)-acetylacetonate, $(\text{BT})_2\text{Ir}(\text{acac})$: Yield: 72%. ^1H NMR (500 MHz, CDCl_3) δ = 1.73 (s, 6H), 5.11 (s, 1H), 6.38 (d, J = 7.5 Hz, 2H), 6.61 (td, J = 1.5 Hz, J = 8.0 Hz, 2H), 6.83 (td, J = 1.5 Hz, J = 8.0 Hz), 7.39–7.42 (m, 4H), 7.62 (dd, J = 1.0 Hz, J = 7.5 Hz, 2H), 7.87–7.89 (m, 2H), 8.06–8.08 (m, 2H); GC-MS, m/z : 711; $\text{C}_{31}\text{H}_{23}\text{N}_2\text{S}_2\text{O}_2\text{Ir}$. Elemental analysis: Found: C, 52.45%; H, 3.74%; N, 3.97%. Calc. C, 52.30%; H, 3.23%; N, 3.94%.

Iridium(III)bis[2-(3-methoxyphenyl)-1,3-benzothiazolato- $\text{N},\text{C}^{2'}$]-acetylacetonate, $(\text{MeO-BT})_2\text{Ir}(\text{acac})$: Yield: 64%. ^1H NMR (500 MHz, CDCl_3) δ = 1.74 (s, 6H), 3.70 (s, 6H), 5.10 (s, 1H), 6.25 (d, J = 9.0 Hz, 2H), 6.35 (d, J = 7.0 Hz, 2H), 7.18 (s, 2H), 7.40–7.41 (m, 4H), 7.87–7.88 (m, 2H), 8.05–8.07 (m, 2H); GC-MS, m/z : 771; $\text{C}_{33}\text{H}_{27}\text{N}_2\text{S}_2\text{O}_4\text{Ir}$. Elemental analysis: Found: C, 51.06%; H, 3.63%; N, 3.39%. Calc. C, 51.26%; H, 3.50%; N, 3.62%.

Iridium(III)bis[2-(2,4-difluorophenyl)-1,3-benzothiazolato- $\text{N},\text{C}^{2'}$]-acetylacetonate, $(2\text{F-BT})_2\text{Ir}(\text{acac})$: Yield: 60%. ^1H NMR (500 MHz, CDCl_3) δ = 1.76 (s, 6H), 5.13 (s, 1H), 5.76 (d, J = 1.5 Hz, 9.5 Hz, 2H), 6.38 (t, J = 7.5 Hz, 2H), 7.43–7.48 (m, 4H), 7.92–7.93 (m, 2H), 8.01–8.02 (m, 2H); GC-MS, m/z : 784;

$\text{C}_{31}\text{H}_{19}\text{F}_2\text{N}_2\text{S}_2\text{O}_2\text{Ir}$. Elemental analysis: Found: C, 47.90%; H, 2.97%; N, 3.63%. Calc. C, 47.42%; H, 2.42%; N, 3.57%.

Iridium(III)bis[2-(2,4-difluorophenyl)-6-fluoro-1,3-benzothiazolato- $\text{N},\text{C}^{2'}$]-acetylacetonate $(3\text{F-BT})_2\text{Ir}(\text{acac})$: Yield: 58%. ^1H NMR (500 MHz, CDCl_3) δ = 1.76 (s, 6H), 5.15 (s, 1H), 5.74 (dd, J = 1.5 Hz, J = 9.0 Hz), 6.37–6.42 (m, 2H), 7.16–7.20 (m, 2H), 7.62 (dd, J = 2.5 Hz, J = 7.5 Hz, 2H), 7.95 (dd, J = 1.5 Hz, J = 8.0 Hz, 2H); GC-MS, m/z : 819; $\text{C}_{31}\text{H}_{17}\text{F}_6\text{N}_2\text{S}_2\text{O}_2\text{Ir}$. Elemental analysis: Found: C, 45.23%; H, 2.01%; N, 3.34%. Calc. C, 45.41%; H, 2.07%; N, 3.42%.

2.2. Physical measurements and PHOLED fabrication

UV–Vis absorption spectra were recorded using a Hitachi U-3300 spectrophotometer. Photoluminescent

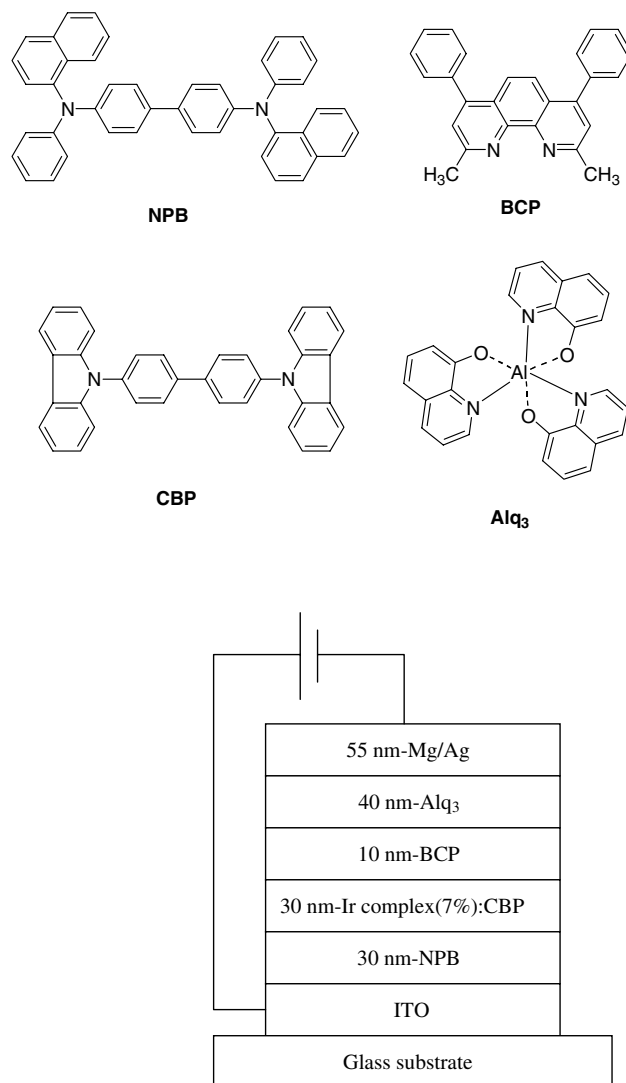


Fig. 1. The general structure for PHOLEDs and the molecular structures of the compounds used in these devices.

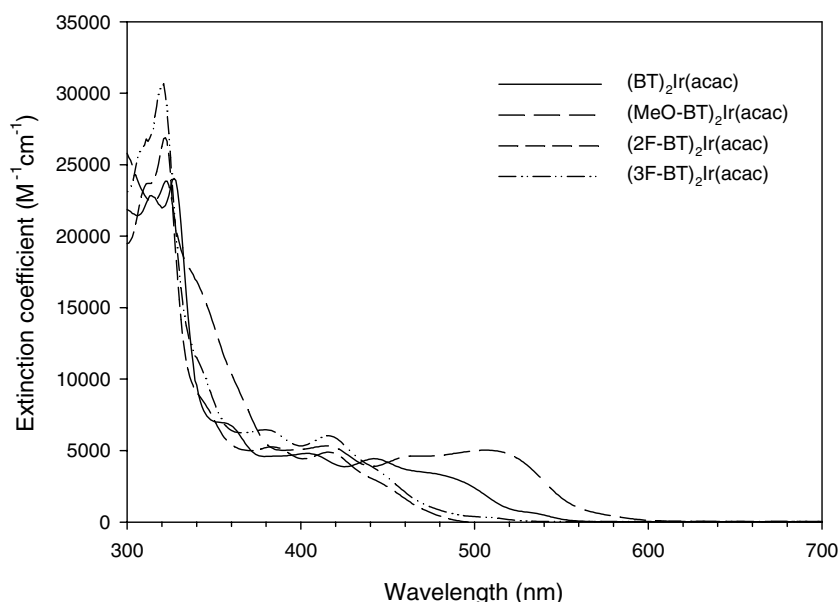


Fig. 2. The UV-Vis absorption spectra of iridium complexes in CH_2Cl_2 (concentration = 1×10^{-4}).

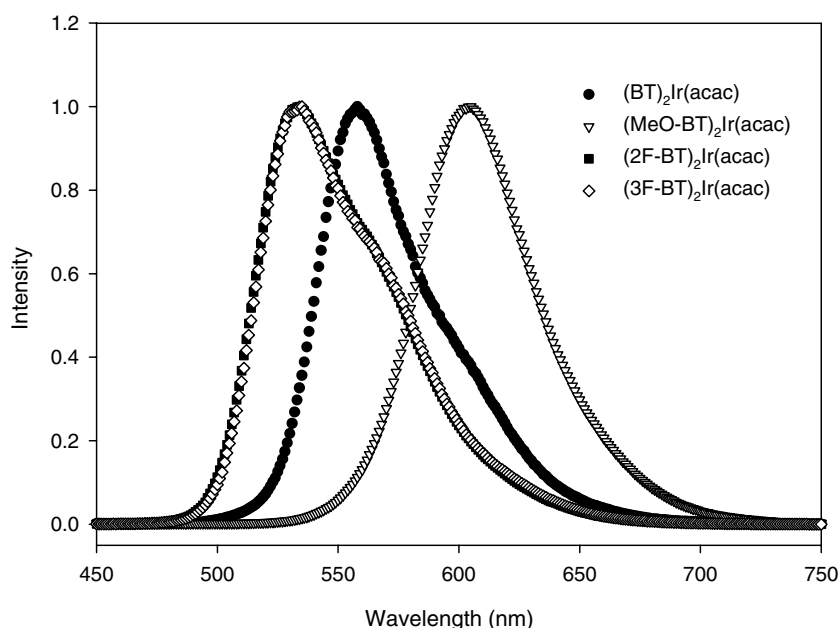


Fig. 3. The photoluminescent spectra of iridium complexes in CH_2Cl_2 (concentration = 1×10^{-4}).

(PL) and electroluminescent (EL) spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer.

The PHOLEDs were fabricated by vacuum deposition of the materials at 10^{-6} Torr onto a clean glass that was pre-coated with a layer of indium tin oxide with a sheet resistance of $25 \Omega \text{ square}^{-1}$. Fig. 1 shows the general structure for PHOLEDs and the molecular structures of the compounds used in these devices. NPB (4,4-bis[N-(1-naphthyl)-N-phenylamino]biphenyl) was used as a hole transporter and was first deposited

on the ITO glass. A layer of CBP doped with 7% Ir complex followed the NPB layer. Layers of BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) to serve as the hole blocker, Alq (tris[8-hydroxyquinoline]) as the electron transporter and Mg:Ag/Ag as the cathode were successively then deposited. Current, voltage, and light-intensity measurements were made simultaneously using a Keithley 2400 source meter and a Newport 1835-C optical meter equipped with a Newport 818-ST silicon photodiode. All chemicals

Table 1
Performance of PHOLEDs^a

Dopant phosphor	Turn on voltage (V) ^b	η_{ext} (% V)	L (cd/m ² , V)	η_c (cd/A, V)	η_p (lm/W, V)	CIE, 8V [X, Y]	Emissive wavelength (λ_{max})
(BT) ₂ Ir(acac)	3.8	9.28, 9.5	101643, 14.5	34.0, 9.5	11.4, 9	(0.47, 0.52)	560
(MeO-BT) ₂ Ir(acac)	3.2	6.50, 8.5	37876, 14	11.0, 8.5	4.32, 8	(0.63, 0.37)	610
(2F-BT) ₂ Ir(acac)	4.0	11.2, 10.5	96317, 15	45.0, 9.0	13.9, 10	(0.37, 0.60)	530
(3F-BT) ₂ Ir(acac)	4.2	12.4, 10	125348, 15	50.3, 10.5	16.0, 9.5	(0.37, 0.61)	530

^a The data for external quantum efficiency (η_{ext}), brightness (L), current efficiency (η_c), and power efficiency (η_p) are the maximum values of the device.

^b Brightness = 1 cd/m².

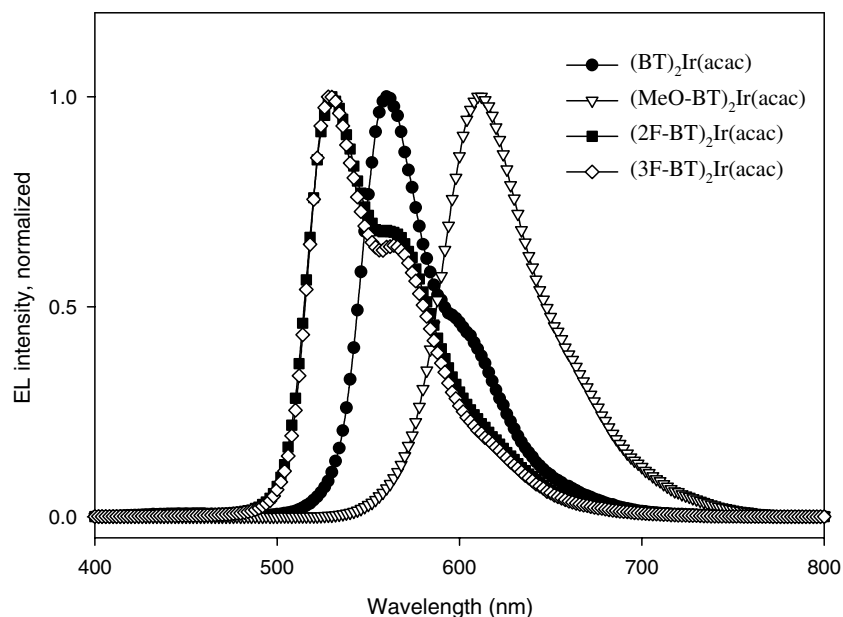


Fig. 4. The electroluminescent spectra of PHOLEDs.

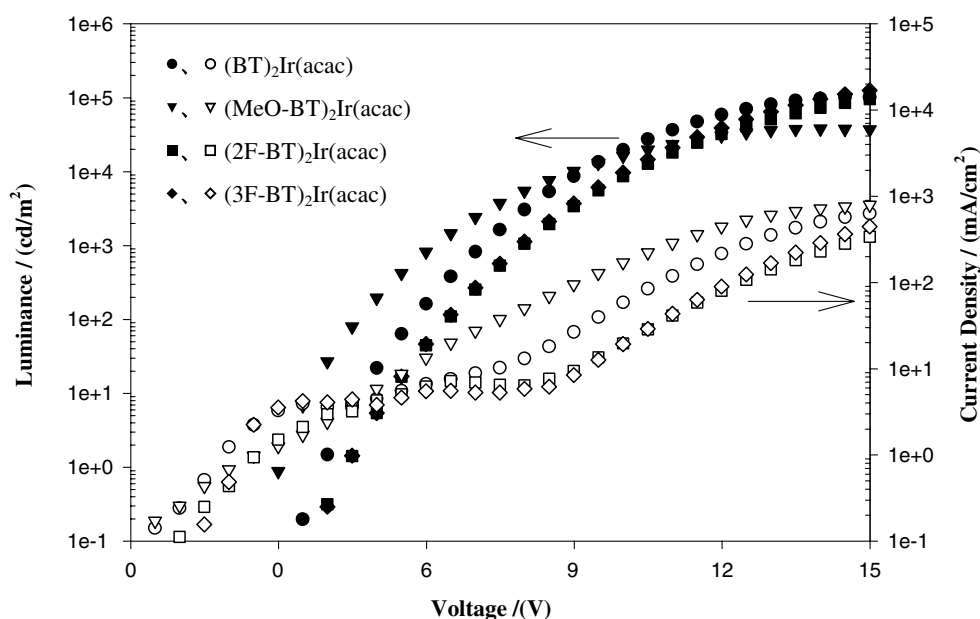


Fig. 5. The current-voltage-luminance (I - V - L) characteristics of PHOLEDs.

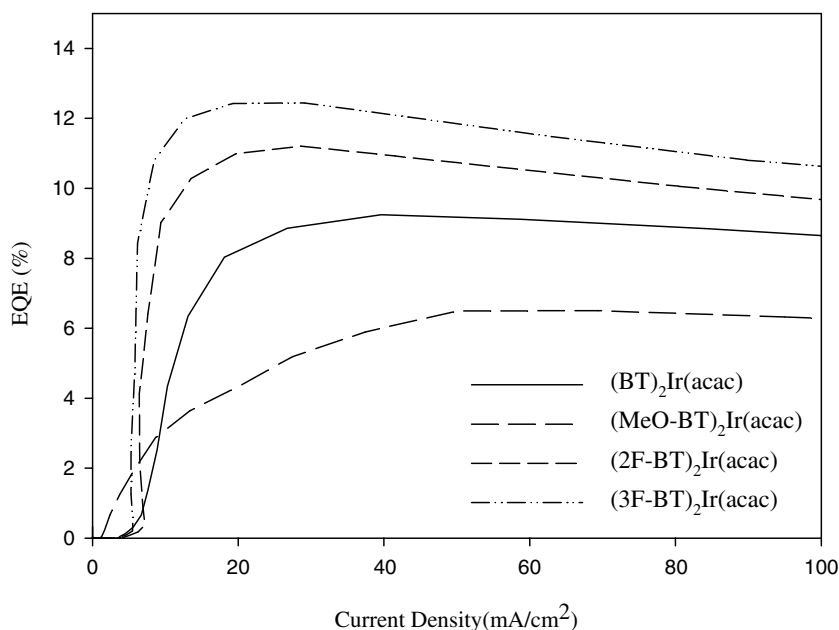


Fig. 6. The external quantum efficiency of PHOLEDs.

used for PHOLEDs were sublimed in vacuum before use.

3. Results and discussion

3.1. UV–Vis absorption and photoluminescence

The UV–Vis absorption and PL spectra of iridium complexes are shown in Figs. 2 and 3. The characteristic absorption peaks of all the complexes are as follows: (BT)₂Ir(acac) at 314, 327, 403, 442 nm, (MeO-BT)₂Ir(acac) at 323, 420, 522 nm, (2F-BT)₂Ir(acac) at 321, 384, 415 nm, and (3F-BT)₂Ir(acac) at 321, 380, 416 nm. The intense absorptions of 320–325 nm for iridium complexes are assigned to the ligand-based π – π^* transitions, whereas the other absorptions come from singlet and triplet metal to ligand charge transfer (¹MLCT and ³MLCT) transition. The absorptions at 442, 522, 415, and 416 nm for (BT)₂Ir(acac), (MeO-BT)₂Ir(acac), (2F-BT)₂Ir(acac), and (3F-BT)₂Ir(acac), respectively, were assigned as the ³MLCT bands for the iridium complexes.

These iridium complexes showed strong photoluminescence in the green to orange region. For example, irradiation of (BT)₂Ir(acac) with 320-nm light gives strong photoluminescence in dichloromethane at 557 nm (Table 1). Similarly, irradiation of dichloromethane solutions of (MeO-BT)₂Ir(acac), (2F-BT)₂Ir(acac) and (3F-BT)₂Ir(acac) led to strong photoluminescence at 605, 530, and 530 nm, respectively. The PL results show that the presence of electron-donating group such as OMe caused red shift whereas electron-withdrawing substituents such as F on the cyclometalated benzothiazole group of the Ir complex cause blue-shift of their PL spectra.

3.2. Electroluminescence

As shown in Fig. 4, PHOLEDs based on (BT)₂Ir(acac), (MeO-BT)₂Ir(acac), (2F-BT)₂Ir(acac), and (3F-BT)₂Ir(acac) emit yellow light ($\lambda_{\text{max}} = 560$ nm), orange-red ($\lambda_{\text{max}} = 610$ nm), yellow-green ($\lambda_{\text{max}} = 530$ nm), and yellow-green ($\lambda_{\text{max}} = 530$ nm), respectively. Moreover, their EL spectra are very close to their PL spectra, as shown in Figs. 3 and 4. The substituent on benzothiazole group of the iridium complexes shows substantial effect on their PL value. The emissive wavelength of PHOLEDs with the iridium complexes can be tuned from 530 to 610 nm by the change of substituents. In case of (MeO-BT)₂Ir(acac) and (2F-BT)₂Ir(acac), their substitution effect leads to 45 nm red-shift and 35 nm blue-shift, respectively with respect to (BT)₂Ir(acac), which exhibits yellow EL ($\lambda_{\text{max}} = 560$ nm).

The current–voltage–luminance (*I*–*V*–*L*) characteristics of PHOLEDs with iridium complexes and their device performances are shown in Fig. 5 and Table 1, respectively. Among the iridium complexes, (3F-BT)₂Ir(acac) has the highest brightness (125348 cd/m² at 15 V). Furthermore, fluorinated iridium complexes (2F-BT)₂Ir(acac) and (3F-BT)₂Ir(acac) exhibit higher quantum efficiency (η_{ext} , η_{c} , and η_{p}) compared with (BT)₂Ir(acac) as shown in Fig. 6 and Table 1, and their turn on voltages are comparable.

4. Conclusion

We have successfully synthesized four kinds of iridium complexes ((BT)₂Ir(acac), (MeO-BT)₂Ir(acac),

(2F-BT)₂Ir(acac) and (3F-BT)₂Ir(acac)) and fabricated the PHOLEDs with them as the emissive layers. The experimental results show that the emissive colors of the PHOLEDs iridium complexes can be modulated by the nature of substituents and their performances are better than that of iridium complex without substituents. Among them, (3F-BT)₂Ir(acac) exhibits the highest brightness of 125348 cd/m² at 15 V and a maximum external quantum efficiency of 12.4% at 10 V.

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