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Dibenzofuran-based Iridium Complexes as Green Emitters: Realizing PhOLEDs with High Power Efficiency and Extremely Low Efficiency Roll-off

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Abstract

In this work, a series of novel iridium (III) cyclometallated complexes **BF-Ir1**, **BF-Ir2** and **BF-Ir3** is developed by introducing a dibenzofuran moiety into the main ligand. The photophysical, thermal, and electroluminescent properties of these iridium (III) complexes are systematically investigated. Notably, the phosphorescent organic light-emitting diodes (PhOLEDs) with **BF-Ir1**, **BF-Ir2** and **BF-Ir3** as the green emitters displayed the maximum EQEs of 15.1%, 23.7% and 21.5%, respectively. In addition, an impressively high PE up to 96.8 lm W⁻¹ is achieved in the device based on **BF-Ir3**. When the luminance reached 1000 and 10000 cd m⁻², the corresponding EQE values of **BF-Ir3**-based PhOLEDs could be maintained at 20.7% and 18.5%. These results clearly demonstrate that dibenzofuran-based iridium (III) complexes have great potential for their application as green emitters in PhOLEDs to realize both high EQE and PE as well as low efficiency roll-off.

Keywords

Dibenzofuran; Power efficiency; Iridium complexes; PhOLEDs

1 Introduction

Since the first demonstration by Ching Tang and Vanslyke in 1987 [1], organic light-emitting diodes (OLEDs) have attracted great attention due to their excellent advantages, such as great color quality, low cost, flexibility and streachability [2, 3]. During the past several decades, tremendous endeavors have been devoted to improve the performance of OLEDs, including efficiency [4-8], stability [9, 10], lifetime and so forth [11, 12]. So far, OLEDs have been widely applied in mobile display market [13], large-area color displays and solid-state lighting sources [14].

In order to improve the efficiency of OLEDs, phosphorescence is appraised as a potential process since it can harvest both singlet and triplet excitons through spin-orbit coupling thereby realizing 100% of the theoretical internal quantum efficiency (IQE), whereas, fluorescence-based OLEDs exhibit only 25% of the IQE [15]. Several kinds of phosphors have been developed, among them, iridium (III) complexes are considered as the most outstanding candidates for high performance OLEDs because of their good stability and high photoluminescence quantum yield (PLQY) [16, 17]. Owing to the

excellent features offered by iridium (III) complexes, they have attained increasing attention in electroluminescent devices.

Recently, Zheng et al. [18] designed and synthesized green emitting iridium (III) complexes containing 4-phenyl-4*H*-1,2,4-triazole unit, and demonstrated phosphorescent OLEDs (PhOLEDs) with a maximum external quantum efficiency (EQE) and a power efficiency (PE) of 31.4% and 57.1 lm W⁻¹, respectively. Kim et al. [19] reported a blue-emitting PhOLED with an EQE of 31.9% and a PE of 52.9 lm W⁻¹. Though, the high EQEs have been achieved in PhOLEDs, the PE, a crucial criterion for the evaluation of energy consumption, still needs to be improved for the commercialization of PhOLEDs [20-22]. Thus, there still remains a challenge to develop a new class of iridium (III) complexes to realize PhOLEDs with both high EQE and PE.

The charge balance in PhOLEDs is considered as a crucial factor for achieving high performance, however, electron mobility of electron-transporting materials is far behind the hole mobility of hole-transporting materials [23, 24]. With regard to iridium (III) complexes, extensive studies have been conducted for the modification of 2-phenylpyridine (ppy) ligands to improve the electron transport property during the past few years [25, 26]. The introduction of electron-withdrawing group has been considered as an effective approach to enhance the electron mobility, which leads to balanced charge transport in PhOLEDs [18, 27-29].

As a well-known moiety, dibenzofuran group possesses oxygen linkage in the molecular structure, and has been widely utilized in electron-transport-type host materials due to their high triplet energy level [30, 31]. Furthermore, many dibenzofuran-based materials exhibit decent performance in OLEDs, thanks to its good thermal stability and high PLQY [32-35]. For instance, Kido et al. [31] reported a series of dibenzofuran-based n-type exciplex host materials and realized OLEDs with high-efficiency and long life time. Zhang et al. [36] introduced dibenzofuran group into thermally activated delayed fluorescence (TADF) emitters and obtained the maximum EQE of 25.1%.

Herein, inspired by the excellent features of dibenzofuran, we designed and synthesized a series of iridium (III) complexes by introducing a dibenzofuran unit into the main ligand. The difference of ancillary ligands resulted in tunable emission colors with peaks in the range of 500-540 nm. All of the three iridium (III) complexes developed in this study, referred as **BF-Ir1**, **BF-Ir2** and **BF-Ir3**, displayed high PLQYs of 0.76–0.80 in doped films. PhOLEDs containing our newly synthesized, well-optimized iridium (III) complexes as green emitters exhibited the maximum EQE of 23.7% and impressively high PE of 96.8 lm W⁻¹ with extremely low efficiency roll-off.

2 Experimental Section

2.1 Instruments and Methods

¹H NMR spectra were obtained on a Bruker AVANCE 500 MHz NMR spectrometer. UV-Vis spectra were recorded on a PerkinElmer Lambda 750 spectrophotometer. Fluorescence and

phosphorescence spectra at 298 K and 77 K were collected by a Horiba Fluorolog-3 in chromatographically pure methylene chloride. Transient photoluminescence decay lifetimes and absolute quantum yields were also carried out using Horiba Fluorolog-3. Thermo-gravimetric analysis (TGA) was conducted on TA2950 TGA system at a heating rate of 10 $^{\circ}$ C min⁻¹ with a nitrogen flow rate of 60 cm³ min⁻¹. Cyclic voltammetry measurements were performed using a conventional three-electrode configuration where a glass carbon was used as the working electrode, a platinum wire as the counter electrode, Ag/AgNO₃ (0.1 M) in CH₃CN as the reference electrode, Bu₄NPF₆ (0.1 M) as the supporting electrolyte, and Fc/Fc⁺ as the internal standard. Density functional theory (DFT) calculations were performed with the PBE0 functional using the SDD basis set for iridium atom and using the 6-31g(d,p) basis set for the other atoms with Gaussian 09 package.

2.2 Device Fabrication

Prior to the device fabrication, ITO glasses were ultrasonically cleaned with acetone, deionized water and isopropanol three times. Both organic and metal layers were deposited by vacuum evaporation under vacuum level lower than 10^{-6} torr. The thickness of each layer was measured by quartz crystal monitors and the emitting area of each pixel is 16 mm². The fabricated PhOLEDs were characterized by Keithley 2400 with BM-7AS luminance colorimeter in F-Star Optical Measurement System. The electroluminescence spectra and CIE coordinates were further measured by PR-788 photometer. The forward viewing external quantum efficiency (η_{ext}) was calculated based upon the electroluminescent performance and electroluminescence spectra.

2.3 General Synthesis of Ligands and Complexes



Scheme 1. Synthetic routes of Iridium Complexes BF-Ir1, BF-Ir2, and BF-Ir3

Scheme 1 depicts the overall synthetic procedures of the ligands and three Ir(III) complexes, **BF-Ir1**, **BF-Ir2**, and **BF-Ir3**. All reactions were carried out under nitrogen atmosphere, and solvents were purified by distillation before further use. 4-(2'-pyridyl)dibenzofuran (pyBf) was synthesized by Suzuki coupling with dibenzofuran-4-boronic acid and 2-bromopyridine. Three Ir(III) complexes, **BF-Ir1**, **BF-Ir2** and **BF-Ir3**, were prepared by reacting Ir(III) chloro-bridge intermediates with N-heterocyclic carbene (nhc), 2-picolinic acid (pic), and acetylacetone (acac), respectively.

Synthesis of 4-(2'-pyridyl)dibenzofuran (pyBf). Dibenzofuran-4-boronic acid (12.0 mmol, 2.54 g), 2-bromopyridine (10.0 mmol, 1.58 g) and aliquat₃₃₆ (5 drops) were dissolved in toluene (100 mL) and potassium carbonate aqueous (2.0 M, 15 mL) successively. The mixture solution was degassed by purging with nitrogen for 15 min, and then Pd(PPh₃)₄ (0.3 mmol, 0.35 g) was added. After that the solution was heated for 24 h at 105 °C under nitrogen. The resulting residue was purified by silica gel column chromatography, which produced a white powder (2.01 g, 82%) [37]. ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.78 (d, J = 4.6 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.23 (q, J = 7.7 Hz, 3H), 8.02 (t, J = 7.7 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.55 (q, J = 7.6, 7.0 Hz, 2H), 7.44 (t, J = 6.6 Hz, 2H).

Synthesis of N-heterocyclic Carbene (nhc). A mixture of 1-bromo-3-(trifluoromethyl)benzene (10.0 mmol, 1.17 g) and benzimidazole(10.0 mmol, 2.24 g), K_2CO_3 (20.0 mmol, 1.38 g), CuI (1.0 mmol, 0.19 g), 18-crown-6 (0.10 g), and DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidin- one, 6 mL) was heated at 190 °C for 24 h in a sealed round-bottom flask under nitrogen. The mixture was extracted with ethyl acetate (EA), and the intermediate product was obtained by column chromatography. Then, the intermediate product and the same molar quantity of CH₃I were dissolved in 15 mL of tetrahydrofuran (THF) and stirred at 80 °C for 12 h. The crude product was filtered and washed with THF and EA, giving the product as white powder (1.62 g, 40%) [38]. ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.20 (s, 1H), 8.26 (s, 1H), 8.17 (dd, J = 7.9, 5.1 Hz, 2H), 8.11 (d, J = 7.6 Hz, 1H), 8.00 (t, J = 7.9 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.83 – 7.70 (m, 2H), 4.18 (s, 3H).

General Procedure for the Synthesis of the Ir Complexes. A round bottom flask was charged with pyBf (4.0 mmol, 0.98 g), IrCl₃•3H₂O (1.5 mmol, 0.53 g), 2-ethoxyethanol (36 mL) and H₂O (12 mL). After heated at 85 °C in nitrogen for 24 h, the mixture was cooled, then directly filtered and washed with water and methanol. The obtained dimer was dried in vacuum and used for the next step without further purification. A mixture of the above dimer (0.2 mmol), ancillary ligand (1.0 mmol, nhc, pic or acac), Na₂CO₃ (1.0 mmol, Ag₂O was used for the synthesis of **BF-Ir1**) and THF (10 mL) was heated at 100 °C for 24 h in a sealed tube under nitrogen. The mixture was extracted with EA and further purified by column chromatography to give the yellow solids in the yields of 50-70%.

BF-Ir1. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.90 (dd, J = 8.9, 1.5 Hz, 1H), 8.82 (d, J = 7.4 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 5.4 Hz, 1H), 8.08 (s, 1H), 8.02 – 7.95 (m, 3H), 7.91 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.61 – 7.56 (m, 3H), 7.51 – 7.39 (m, 4H), 7.32 (tt, J = 7.5, 1.3 Hz, 2H), 7.12 (td, J = 7.1, 6.5, 1.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.83 (d, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.03 (dd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 7.01 (d, J =

7.4 Hz, 1H), 6.60 (d, J = 7.7 Hz, 1H), 6.23 (d, J = 7.7 Hz, 1H), 3.38 (s, 3H). HRMS (ESI), m/z calculated for C₄₉H₃₀F₃IrN₄O₂ [M + H]⁺: 957.2028. Found: 957.2019. (0.21 g, 54%)

BF-Ir2. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.92 (d, J = 7.9 Hz, 1H), 8.85 (d, J = 8.0 Hz, 1H), 8.68 (d, J = 5.2 Hz, 1H), 8.23 - 8.09 (m, 4H), 7.95 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 2.5 Hz, 1H), 7.76 (d, J = 2.5 Hz, 1H), 7.73 (d, J = 5.8 Hz, 1H), 7.69 (d, J = 5.1 Hz, 1H), 7.61 - 7.43 (m, 6H), 7.39 - 7.30 (m, 3H), 6.32 (d, J = 7.9 Hz, 1H), 6.13 (d, J = 7.9 Hz, 1H). HRMS (ESI), *m/z* calculated for C₄₀H₂₄IrN₃O₄ [M + H]⁺: 804.1474. Found: 804.1511. (0.22 g, 68%)

BF-Ir3. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.83 (d, J = 8.0 Hz, 2H), 8.57 (d, J = 5.0 Hz, 2H), 8.20 (td, J = 8.2, 1.5 Hz, 2H), 7.88 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.54 (ddd, J = 7.3, 5.6, 1.5 Hz, 2H), 7.43 (ddd, J = 8.5, 7.3, 1.4 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 6.14 (d, J = 7.9 Hz, 2H), 5.33 (s, 1H), 1.75 (s, 6H). HRMS (ESI), *m*/*z* calculated for C₃₉H₂₇IrN₂O₄ [M + Na]⁺: 803.1498. Found: 803.1538. (0.20 g, 63%)

3 Results and discussion

3.1 Synthesis and Thermal Properties

Scheme 1 shows the synthetic routes and chemical structures of **BF-Ir1**, **BF-Ir2** and **BF-Ir3**. The main ligand, pyBf, was obtained through Suzuki coupling reaction with dibenzofuran-4-boronic acid and 2-bromopyridine. Excessive pyBf was first reacted with IrCl₃•3H₂O to give the chloride-bridged iridium dimer. The dimer was then reacted with different ancillary ligands to obtain **BF-Ir1**, **BF-Ir2** and **BF-Ir3**. All these iridium (III) complexes are soluble in common chlorinated hydrocarbons solvent and could be purified by column chromatography. The chemical structures were unequivocally confirmed by NMR spectroscopy and high-resolution mass spectra (HRMS).

The thermal properties of **BF-Ir1**, **BF-Ir2** and **BF-Ir3** were measured by TGA. The 5% degradation temperature ($\Delta T_{5\%}$) of these compounds was measured to be: 420 °C for **BF-Ir1**, 372 °C for **BF-Ir2** and 399 °C for **BF-Ir3** (Fig. S4). All the complexes possess a $\Delta T_{5\%}$ higher than 350 °C, indicating good thermal stability, which is essential for enhancing the stability of PhOLEDs at high processing temperature.

3.2 Photophysical Properties

Moreover, under photoexcitation, these three compounds exhibit strong emission at 506–536 nm and an invisible shoulder at 535–567 nm with rather narrow full width at half maximum (FWHM) of ~60 nm (Fig. 1a, lines with symbols). Meanwhile, **BF-Ir1**, **BF-Ir2** and **BF-Ir3** show emission with the peaks (shoulder) at 515 nm (544 nm), 533 nm (564 nm) and 536 nm (567 nm), respectively, at 77 K (Fig. 1b) exhibiting pronounced vibronic structures. The triplet energies for **BF-Ir1** (2.62 eV), **BF-Ir2** (2.45 eV) and **BF-Ir3** (2.55 eV) were determined from the onsets in the spectra recorded at 77 K.



Figure 1. (a) UV-Vis (solid line, in film) and PL spectra (line with symbols, in methylene chloride) of **BF-Ir1**, **BF-Ir2** and **BF-Ir3** at room temperature. (b) PL spectra of **BF-Ir1**, **BF-Ir2** and **BF-Ir3** in methylene chloride at 77K.

Complex	λ_{ab}^{a} (nm)	$\lambda_{em}^{\ b}$ (nm)	λ_{em}^{c} (nm)	$egin{array}{c} \Phi_{em}^{\ d} \ (\%) \end{array}$	Ф _{ет} е (%)	$ au_{em}^{ m f}$ (µs)	$k_{r}^{g}, k_{nr}^{h} imes 10^{-5}$ (s ⁻¹)	HOMO ⁱ / LUMO ^j (eV)
BF-Ir1	311, <mark>361, 405,</mark> 443	506, 535	515, 544	46	76	3.22	1.43 / 1.68	-5.16 / <mark>-2.43</mark>
BF-Ir2	311, <mark>367, 414,</mark> 468	526, 557	533, 564	60	78	2.90	2.07 / 1.38	-5.28 / <mark>-2.55</mark>
BF-Ir3	317, <mark>368, 420,</mark> 488	536, 567	540, 567	78	80	1.63	4.78 / 1.35	-5.15 / <mark>-2.36</mark>

^a Measured in thin film. ^b Measured in methylene chloride at room temperature and ^c 77 K. ^d Absolute photoluminescence quantum yields measured in methylene chloride and ^e co-deposited films of Ir complex: DMIC-TRZ: DMIC-CZ (1:10:10) using an integrating sphere. ^f Photoluminescence decay lifetime obtained in methylene chloride. ^g Radiative rate constants. ^h Nonradiative rate constants. ⁱ Calculated from cyclic voltammetry analysis.

To reveal the photoluminescent characteristics of our newly developed green emitters in PhOLED devices, the doped films of **BF-Ir1**, **BF-Ir2** and **BF-Ir3** in DMIC-TRZ/DMIC-CZ (the host utilized in our PhOLED devices) were fabricated. All the emission spectra exhibit pure peaks, with the emission maxima at 511, 533 and 542 nm for **BF-Ir1**, **BF-Ir2** and **BF-Ir3**, respectively (Fig. S5). The emission spectra measured in doped films fit well with their corresponding emissions in solutions, indicating efficient energy transfer from hosts to these three emitters.

To further elucidate the photophysical properties of **BF-Ir1**, **BF-Ir2** and **BF-Ir3**, the photoluminescence quantum yields (Φ_{em}) were measured in methylene chloride by integrating sphere ($\Phi_{em} = 0.46-0.78$, Table 1). For doped films of **BF-Ir1**, **BF-Ir2** and **BF-Ir3** in DMIC-TRZ / DMIC-CZ, the PLQYs are much higher than their corresponding values measured in solution, with 0.76, 0.78 and 0.80, respectively. The PLQYs of **BF-Ir1** and **BF-Ir2** in films were substantially higher than those in

solution, indicating stronger interaction with solvents in the solution state for **BF-Ir1** and **BF-Ir2** than **BF-Ir3**. The PLQYs of films better reflect the actual photophysical properties of the devices and all these three compounds possess high PLQY values in films.

Furthermore, the transient PL decay lifetimes of these three compounds in methylene chloride were investigated. As shown in Fig. S6, the estimated lifetime (τ) is 3.22 µs for **BF-Ir1**, 2.90 µs for **BF-Ir2** and 1.63 µs for **BF-Ir3**. Among them, **BF-Ir3** exhibits relatively short phosphorescence lifetime, which can decrease the triplet-triplet annihilation and triplet-polaron annihilation processes, and thus is beneficial to realize high-performance PhOLEDs with low efficiency roll-off. Moreover, the radiative rate constant $k_{\rm r}$ and nonradiative rate constant $k_{\rm nr}$ can be calculated by the following equations:

$$k_{\rm r} = \Phi_{\rm em} / \tau_{\rm em} \tag{1}$$

$$\boldsymbol{\varphi}_{\rm em} = \boldsymbol{k}_{\rm r} / \left(\boldsymbol{k}_{\rm r} + \boldsymbol{k}_{\rm nr} \right) \tag{2}$$

3.3 Electrochemical Properties and Theoretical Computations

To study the redox properties of **BF-Ir1**, **BF-Ir2** and **BF-Ir3**, cyclic voltammetry was adopted to reveal the influence of ancillary ligand on frontier orbital energies. Fig. S7 overlays the cyclic voltammograms of ferrocene, **BF-Ir1**, **BF-Ir2** and **BF-Ir3**, measured in N,N-Dimethylformamide (DMF) with 0.1 M Bu₄NPF₆ electrolyte. Based on the onset of oxidation potential, the highest occupied molecular orbital (E_{HOMO}) energy level are estimated as -5.16, -5.28 and -5.15 eV (assuming the ferrocene $E_{HOMO} = -4.8$ eV vs. vacuum) for **BF-Ir1**, **BF-Ir2** and **BF-Ir3**. Subsequently, the lowest unoccupied molecular orbital (E_{LUMO}) energy levels can also be estimated from cyclic voltammetry data using the equation: $E_{LUMO} = [E_{red} - E_{(Fc/Fc')} + 4.8]$ (eV). All the data of photophysical and electrochemical properties are summarized in Table 1 and Table S1.

To obtain deep insight into the photophysical and electrochemical properties of these iridium (III) complexes, theoretical computations of their electronic structures were carried out by density functional theory (DFT). As depicted in Fig. 2, the HOMO energy levels of the **BF-Ir1**, **BF-Ir2** and **BF-Ir3** were mainly located on the main ligands (57%, 68% and 60%, respectively) together with the d-orbitals of the iridium atom (34%, 30% and 34%, respectively), while the LUMO were mostly distributed over the π^* orbitals of the main ligands (97%, 65% and 94%, respectively). A large-scale distribution of electron clouds on the iridium atom indicates an efficient MLCT transition, resulting in high PLQY.



Figure 2. Molecular orbital diagram for the HOMO / LUMO levels and the energy levels of **BF-Ir1**, **BF-Ir2** and **BF-Ir3**.

3.4

OLED Performances



Figure 3. (a) Device energy-level diagram. (b) Device configuration and molecule structures of each constituent layer.

To evaluate the electroluminescent properties, PhOLEDs were fabricated with a configuration of ITO / HATCN (5 nm) / Spiro-4-BPF (20 nm) / Spiro-3-BPF (5 nm) / DMIC-TRZ: DMIC-CZ: Ir complex (10:10:1) (30 nm) / ANT-BIZ (30 nm) / Liq (1 nm) / Al (100 nm). Herein, Spiro-4-BPF (N-([1,1'-biphenyl]-2-yl)-N-(9,9-dimethyl-9*H*- fluoren-2-yl)-9,9'-Spirobi[9*H*-fluoren]-4-amine) and ANT- BIZ (1-(4-(10-([1,1'-biphenyl]-4-yl)anthracen-9-yl)phenyl)-2-ethyl-1*H*-benzo[d]-imidazole) act

as the hole-transporting material (HTM) and electron-transporting material (ETM), respectively; Spiro-3-BPF (N-([1,1'-biphenyl]-2-yl)-N-(9,9dimethyl-9*H*-fluoren-2-yl)-9,9'-Spirobi[9*H*-fluoren]-4-amine) is used as a buffer material (BM) to facilitate the hole injection from HTL to the emitting layer (EML); and Ir complexes are doped into DMIC-TRZ (5-(3'-(4,6-Diphenyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-3-yl)-7,7-dimethyl-5,7-dihydroindeno[2,1-b] carbazole) and DMIC-CZ (2-(9-phenyl-9*H*-carbazol-3-yl)-5-phenyl-7,7-dimethyl-5,7-dihydro-indeno[2,1-b]carbazole) hosts to

form the EML. The doping ratio of DMIC-TRZ: DMIC-CZ: Ir complex was 10:10:1, i.e. the doping concentration is about 5 wt% for **BF-Ir1**, **BF-Ir2** and **BF-Ir3**. The electroluminescent properties, including current efficiency (CE), PE and EQE versus luminance, current density and luminance versus voltage, as well as the emission spectra, are shown in Fig.4 and the key parameters are summarized in Table 2.

Material	$V_{\mathrm{on}}^{\mathrm{a}}(\mathbf{V})$	L_{\max}^{b} (cd m ⁻²)	$\mathbf{CE}^{\circ} (\mathbf{cd} \mathbf{A}^{-1})$	\mathbf{PE}° (Im \mathbf{W}^{-1})	EQE° (%)	CIE ^d (x,y)
BF-Ir1	2.4	25840	52.1 / 43.9 / 31.1	62.8 / 38.3 / 16.8	15.1 / 12.8 / 9.0	(0.30,0.61)
BF-Ir2	2.4	34920	87.1 / 66.6 / 54.0	91.2 / 58.2 / 31.4	23.7 / 18.2 / 14.7	(0.40,0.58)
BF-Ir3	2.4	94160	79.3 / 76.2 / 68.1	96.8 / 79.8 / 48.6	21.5 / 20.7 / 18.5	(0.42,0.57)
<mark>Ir(ppy)₂acac</mark>	<mark>2.4</mark>	<mark>169000</mark>	<mark>57.1 / 56.6 / 55.1</mark>	<mark>63.0 / 55.6 / 36.0</mark>	15.5 / 15.4 / 15.0	<mark>(0.34,0.61)</mark>

Table 2. Summary of the Device Performance

^a Turn-on voltage at ca. 1.0 cd m⁻². ^b The maximum luminance recorded at 8.0 V. ^c In the order of the peak value / at 1000 cd m⁻² / at 10000 cd m⁻². ^d CIE coordinates at 1000 cd m⁻².



Figure 4. (a) Electroluminescence spectra recorded at 4.0 V. (b) Current density-voltage curve (left axis) and luminance-voltage curves (right axis). (c) Current efficiency-luminance curves (left axis) and power efficiency-luminance curves (right axis). (d) External quantum efficiency-luminance curves.

As shown in Fig. 4 (a), the devices based on **BF-Ir1**, **BF-Ir2** and **BF-Ir3** exhibit green emissions at 510, 541 and 545 nm, respectively, and the CIE coordinates of **BF-Ir1** are (0.30, 0.61), approaching closely to the s-RGB (standard Red Green Blue) standard for green color (0.30, 0.60). However, the introduction of the N-heterocyclic carbene on the ancillary ligand resulted in a lower PLQY and thus led to a slightly declined EQE of **BF-Ir1**-based device.

Compared to **BF-Ir1**, the device with **BF-Ir2** displayed better L_{max} , CE, PE and EQE of 34920 cd m⁻², 87.1 cd A⁻¹, 91.2 lm W⁻¹ and 23.7%, respectively. The device with **BF-Ir3** also showed good EL performance with L_{max} of 94160 cd m⁻², a peak CE of 79.3 cd A⁻¹, a peak PE of 96.8 lm W⁻¹ and a maximum EQE of 21.5%. To further figure out the merits of dibenzofuran-based iridium (III) complexes, Ir(ppy)₂acac (bis[2-(2-pyridinyl-N)phenyl-C](acetylacetonato)iridium(III)), a common green dopant utilized in PhOLEDs, was applied in above mentioned PhOLED structure for comparison purpose. The maximum EQE and PE exhibited by the device with Ir(ppy)₂acac were only 15.5% and 63.0 lm W⁻¹, respectively (Fig. S8), far behind the corresponding values of **BF-Ir2**- and **BF-Ir3**-based PhOLEDs.

These results indicate that high EQE of above 20% and PE of above 90 Im W^{-1} can be achieved in the devices with our newly developed dibenzofuran-based iridium (III) complexes. The high PE value is a crucial factor for low energy consumption and commercialization of PhOLEDs.

It is noteworthy that the device based on **BF-Ir3** displayed high L_{max} of almost 10⁵ cd m⁻² and extremely low efficiency roll-off. Low efficiency roll-off values of 3.9% at 1000 cd m⁻² and 14.1% at 10000 cd m⁻² were achieved, owing to the relatively short lifetime of **BF-Ir3**. Furthermore, thanks to the low hole/electron-injecting barriers, all the devices with **BF-Ir1**, **BF-Ir2** and **BF-Ir3** showed low turn-on voltage of 2.4 V, which is much lower than that of green PhOLED reported previously [16, 18, 27, 29, 32]. Based on the above results, it is evident that the dibenzofuran-based iridium complexes demonstrate a great potential as green emitters for PhOLEDs with both high EQE and PE.

4 Conclusions

In summary, a series of dibenzofuran-based iridium (III) complexes, **BF-Ir1**, **BF-Ir2** and **BF-Ir3** is successfully designed and synthesized. The characteristics of these complexes as green emitters in PhOLEDs were systematically investigated. The PhOLEDs with these emitters displayed the maximum EQE of 15.1% for **BF-Ir1**, 23.7% for **BF-Ir2** and 21.5% for **BF-Ir3**, respectively, as well as exhibited a high PE of up to 96.8 lm W⁻¹ for the device with **BF-Ir3**. When the luminance reached 1000 and 10000 cd m⁻², the corresponding EQE values of **BF-Ir3**-based device could be maintained at 20.7% and 18.5%. This study suggest that the dibenzofuran-based iridium (III) complexes have great potential

as green emitters to realize PhOLEDs with both high EQE and PE as well as extremely low efficiency roll-off.

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Conflicts of Interest

The authors declare that they have no conflict of interest.

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Supporting Information

Dibenzofuran-based Iridium Complexes as Green Emitters: Realizing PhOLEDs with High Power Efficiency and Extremely Low Efficiency Roll-off

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3.





Figure S4. TGA curves of BF-Ir1, BF-Ir2 and BF-Ir3



Figure S5. PL spectra of BF-Ir1, BF-Ir2 and BF-Ir3 doped in DMIC-TRZ/DMIC-CZ film

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Figure S6. Transition PL decay curves of BF-Ir1, BF-Ir2 and BF-Ir3

7.



Figure S7. Cyclic voltammetry curves of BF-Ir1, BF-Ir2 and BF-Ir3

Table S1. Electrochemical properties of Ir (III) Complexes BF-Ir1, BF-Ir2 and BF-Ir3							
Compounda		CV	UV				
Compounds	$E_{\text{HOMO}}^{a}(\text{eV})$	$E_{\text{HOMO}}^{a}(\text{eV}) = E_{\text{LUMO}}^{b}(\text{eV})$		$\lambda_{\text{onset}}^{d}$ (nm) E_{g}^{e} (e)			
BF-Ir1	-5.16	-2.43	2.73	489	2.54		
BF-Ir2	-5.28	-2.55	2.73	501	2.48		
BF-Ir3	-5.15	-2.36	2.79	515	2.41		

^a Estimated from cyclic voltammetry data using equation: $E_{\text{HOMO}} = [E_{\text{ox}} - E_{(\text{Fc/Fc+})} + 4.8]$ (eV).

^b Estimated from cyclic voltammetry data using equation: $E_{\text{LUMO}} = [E_{\text{red}} - E_{(\text{Fc/Fc+})} + 4.8]$ (eV). ^c Calculated from E_{HOMO} and E_{LUMO} using equation: $E_{\text{g}} = (E_{\text{LUMO}} - E_{\text{HOMO}})$.

^d Estimated from absorption spectra of thin films.

^e Calculated from the λ_{onset} using equation: $E_{\text{g}} = 1240 / \lambda_{\text{onset}}$.



Figure S8. (a) Electroluminescence spectrum of Ir(ppy)₂acac recorded at 4.0 V. (b) Current density-voltage curve (left axis) and luminance-voltage curve (right axis). (c) Current efficiency-luminance curve (left axis) and power efficiency-luminance curve (right axis). (d) External quantum efficiency-luminance curve.

Dibenzofuran-based Iridium Complexes as Green Emitters: Realizing PhOLEDs with High Power Efficiency and Extremely Low Efficiency Roll-off

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Highlights

- **1.** A series of novel iridium (III) complexes with dibenzofuran moiety are synthesized through a facile synthetic route.
- **2.** All of our newly developed iridium (III) complexes displayed great thermal stability and high photoluminescence quantum yields.
- 3. PhOLEDs with dibenzofuran-based iridium (III) complexes as green emitters exhibited the maximum EQE of 23.7% and impressively high PE of 96.7 Im W^{-1} .
- **4.** Moreover, our fabricated PhOLEDs showed extremely low efficiency roll-off at high luminance.

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Conflict of Interest

The authors declare that they have no conflict of interest to this work.

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