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Efficient organic light-emitting diodes with low efficiency roll-off at high brightness using iridium emitters based on 2-(4-trifluoromethyl-6-fluoro phenyl)pyridine and tetraphenylimidodiphosphinate derivatives



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ABSTRACT

Using 2-(4-trifluoromethyl-6-fluorophenyl)pyridine (tfmfppy) as the cyclometalated ligand and tetraphenylimidodiphosphinate (tpip) derivatives as ancillary ligands, three iridium complexes (**1**: Ir(tfmfppy)₂tpip; **2**: Ir(tfmfppy)₂ftpip, ftpip = tetra(4-fluorophenyl)imidodiphosphinate; **3**: Ir(tfmfppy)₂tfmtpip, tfmtpip = tetra(4-trifluoromethylphenyl)imidodiphosphinate) showing phosphorescence at 514, 513 and 508 nm in CH₂Cl₂ were synthesized, respectively. By using these complexes as emitters, the organic light emitting diodes with the concise configuration of indium tin oxides/1,1-bis(4-(di-*p*-tolyl-amino)phenyl) cyclohexane (60 nm)/**1** or **2** or **3**: bis[3,5-di(9*H*-carbazol-9-yl)phenyl]di-phenyl silane (8 wt%, 30 nm)/ 1,3,5-tri(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl (90 nm)/lithium fluoride (1 nm)/aluminium (100 nm) showed bright green light with maximum luminance higher than 40 000 cd m⁻². The maximum current efficiency (η_c) values for **1**, **2** and **3** based devices (**GIr1**, **GIr2** and **GIr3**) were 77.49, 66.57, and 53.26 cd A⁻¹ at relatively high brightness of 8025, 5286 and 5169 cd m⁻², respectively. In addition, the efficiency roll-off ratios from the peak efficiency to the brightness of 10 000 cd m⁻² are less than 10% for all the devices. We believe that the good electron mobilities of the phosphorescent emitters lead to the high devices efficiency and low efficiency roll-off. The results suggest that these complexes have potential application in organic light emitting diodes.

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1. Introduction

Phosphorescent iridium complexes play an important part in efficient organic light emitting diodes (OLEDs) due to their high quantum efficiency and short lifetime of triplet excited states [1–16]. The strong spin-orbit coupling (SOC) introduced by the central heavy atom can promote the triplet to singlet radiative transition, resulting unusually high phosphorescence quantum yields at room temperature. On the other hand, since the phosphorescence of iridium complexes primarily originates from the metal-to-ligand charge transfers (MLCT) and the ligand-centered (LC) transitions [17], the energy level of the excited state can be controlled by

* Corresponding author. E-mail address: yxzheng@nju.edu.cn (Y.-X. Zheng). tuning the energy levels of the ligands through substituent effects, which leads to a wide flexible emission color range.

In pursuit of efficient Ir(III) complexes, many heteroleptic complexes, Ir(CN)₂LX, have been developed, where CN is a monoanionic cyclometalated ligand (*e.g.*, 2-phenylpyridine (ppy), 2-(4trifluoromethylphenyl)pyridine (tfmppy)) and LX stands for a bidentate ancillary ligand (*e.g.*, acetylacetonate (acac), picolinate (pic)) [18,19]. According to the density functional theory calculations, the highest occupied molecular orbital (HOMO) is basically centered on the Ir(III) metal while the lowest unoccupied molecular orbital (LUMO) is generally localized on the cyclometalated ones. Although most ancillary ligands do not make contribution to the lowest excited state directly, they indeed alter the energy levels of the excited states by modifying the electron density at the metal center. Thus, the photophysical property and carrier mobility of iridium complexes can be tuned trough functional substitutes on both cyclometalated and ancillary ligands.

In our previous work, we have reported some high efficient OLEDs based on bis-cyclometalated iridium complexes with tetraphenylimidodiphosphinate (tpip) derivatives as the ancillary ligands [20–24]. The high efficiencies can be explained by more balanced injection and transport of electrons and holes in(to) the emitting layers (EML) due to the good electron mobility of Ir(III) complexes by using the tpip derivatives as ancillary ligands [25]. Therefore, further investigation of the substituted Ir(CN)₂tpip complexes with new tpip derivatives is possible to prepare more efficient organic light emitting materials and devices.

Fluorination can enhance the electron mobility and result in a better balance of charge injection and transfer, lower vibrational frequency of C-F bond can reduce the rate of radiationless deactivation and the bulky trifluoromethyl substituents can affect the molecular packing and suppress the self-quenching behavior [26]. In this article, a modification was made to ppy by introducing of F/ CF₃ trifluoromethyl groups into phenyl ring at the ortho- and paraposition, as well as each phenyl ring of tpip at the *para*-position. Thus, herein, we report the syntheses, photoluminescence (PL) and electroluminescence (EL) of three novel bis-cyclometalated iridium complexes of $Ir(tfmfppy)_2$ tpip (1, tfmfppy = 2-(4-trifluoromethyl-6-fluorophenyl)pyridine), $Ir(tfmfppy)_2 ftpip$ (**2**, ftpip = tetra(4fluorophenyl)imidodiphosphinate) and Ir(tfmfppy)₂tfmtpip (**3**, tfmtpip = tetra(4-trifluoromethylphenyl)imidodiphosphinate) (Scheme 1).

2. Experimental section

2.1. General information

Commercially available reagents were used without further purification unless otherwise stated. ¹H and ³¹P NMR spectra were recorded using a Bruker spectrometer at 500 MHz using TMS as an internal standard. Chemical shifts were recorded by ppm. Multiplicity was denoted by s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet). Coupling constants (1) were in hertz (Hz). Mass spectra (MS) were obtained with ESI (Electrospray Ionization, Thermo Fisher Scientific) or MALDI-TOF (Matrix-Assisted Laser Desorption-Ionization Time of Flight, Bruker Daltonic Inc.). Absorption and PL spectra were recorded with a Shimazu UV-3600 and a Hitachi F-4600 spectrometer, respectively. PL lifetime measurements were performed with an Edinburgh FLS-920 spectrometer. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard aerated aqueous solution of [Ru(bpy)₃]Cl₂ and the iridium complexes in CH_2Cl_2 solutions according to the equ. (1) [27].

$$\Phi_{\rm unk} = \Phi_{\rm std} \left(\frac{I_{\rm unk}}{I_{\rm std}} \right) \left(\frac{A_{\rm std}}{A_{\rm unk}} \right) \left(\frac{\eta_{\rm unk}}{\eta_{\rm std}} \right)^2 \tag{1}$$

where Φ_{unk} and Φ_{std} are the luminescence quantum yields of the iridium complexes and $[Ru(bpy)_3]Cl_2$ solutions, respectively. The I_{unk} and I_{std} are the integrated emission intensities of the iridium complexes and $[Ru(bpy)_3]Cl_2$ solutions, respectively. The A_{unk} and



Scheme 1. Synthetic routes of ligands and complexes. (i) Pd(PPh₃)₄, K₂CO₃,THF/H₂O, 80 °C, 24 h; (ii) lrCl₃.3H₂O, 2-EtOCH₂CH₂OH/H₂O, reflux, 24 h; (iii) Anhydrous toluene, 105 °C, 6 h; (iv) H₂O₂, THF; (v) KOH, methanol; (vi) 2-EtOCH₂CH₂OH, 120 °C, 24 h.

 A_{std} are the absorbance of the iridium complexes and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ solutions at their excitation wavelengths (A < 0.1), respectively. The η_{unk} and η_{std} terms represent the refractive indices of the corresponding solvents (pure solvents were assumed). The Φ_{std} of the aerated aqueous solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ has been revalued to be 2.8% [28].

Cyclic voltammetry (CV) was performed on an IM6ex (Zahner) electrochemistry working station using platinum electrode, Ag/AgNO₃ in saturated KCl (aq.) and a platinum wire as working electrode, reference electrode and counter electrode, respectively. All CV measurements were carried out at a scan rate of 100 mV s⁻¹ in anhydrous CH₂Cl₂ containing 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte, purging with argon prior to conduct the experiment. Each oxidation potential was calibrate with ferrocene as a reference.

2.2. X-ray crystallography

Diffraction data for **2** were collected on a Bruker SMART CCD diffractometer using monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software, and SAINT [29] program was used to reduce the highly redundant data sets. Lorentz and polarization effects were corrected. Absorption corrections were performed with SADABS [30] supplied by Bruker. Data were collected using a narrow-frame method with a scan width of 0.30° in ω and an exposure time of 4 s frame⁻¹.

The molecular structure was solved by direct methods and refined by full-matrix least squares on F^2 using the program SHELXL-97 [31]. The positions of the metal atoms and their conjoint coordination atoms were located from direct methods on E-maps; other non-H atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles. All non-H atoms were treated anisotropically. H atoms were fixed in calculated positions and they were allowed to ride on their parent C atoms and refined with a uniform value of U_{iso} .

2.3. OLEDs fabrication and characterization

All OLEDs with the emission area of 0.1 cm² were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω sq⁻¹. Substrate was cleaned by ultrasonic in organic solvents followed by ozone treatment for 20 min. The 60 nm hole transport material of 1,1-bis(4-(di-p-tolyl-amino) phenyl)cyclohexane (TAPC) film was first deposited on the ITO glass substrate. The phosphor (x wt%) and host (SimCP2, bis(3,5di(9H-carbazol-9-yl)phenyl)diphenylsilane) were co-evaporated to form 30 nm emitting layer from two separate sources. Successivelv. 1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi, 90 nm) as electron transport material. LiF (1 nm) as electron injection material, and Al (100 nm) as the cathode were evaporated. The vacuum was about 8 \times 10⁻⁵ Pa during all materials deposition. The EL spectra were measured with a Hitachi F-4600 photoluminescence spectrophotometer. The luminancevoltage (L-V) characteristics and current efficiency versus current density (η_c –J), power efficiency versus current density (η_p – J) curves of the devices were measured with a computer controlled Keithley 2400 source meter with a calibrated silicon diode in air without device encapsulation.

2.4. Syntheses procedure

Htpip, tfmfppy, $[(tfmfppy)_2Ir(\mu-Cl)]_2$ and $Ir(tfmfppy)_2tpip$ (1), $Ir(tfmfppy)_2fpip$ (2), $Ir(tfmfppy)_2tfmtpip$ (3) were synthesized according to previous published literature procedures (Scheme 1)

[20–24,32]. Pure iridium complexes were obtained from the vacuum sublimation after silica column chromatography.

2.4.1. Synthesis of 2-(2-fluoro-4-(trifluoromethyl)phenyl) pyridine (tfinfppy)

2-Bromopyridine (2.39 mL, 25.0 mmol), 2-(2-fluoro-4-trifluoromethyl)-phenylboronic acid (5.77 g, 30.0 mmol), palladium(II) acetate (0.068 g, 0.303 mmol) and K₂CO₃ (5.53 g, 40 mmol) were refluxed for 24 h in 60 mL solution of THF : water (3:2, v/v). After that, the cooled solution was poured into water, extracted with CH₂Cl₂ (50 mL × 3 times) and then dried over anhydrous magnesium sulfate. Finally, silica column purification (petroleum ether:dichloromethane = 10:1 as eluant) gave yellow color liquid in 39% yield (2.36 g, 9.79 mmol). ¹H NMR (500 MHz, CDCl₃) δ 8.73–8.52 (m, 1H), 8.01–7.82 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.71–7.48 (m, 2H), 7.46–7.22 (m, 1H). MS (MALDI-TOF) Calcd: 241.0515 [M⁺]. Found: *m*/z 241.3121 [M⁺].

2.4.2. Synthesis of $[(tfmfppy)_2Ir(\mu-Cl)]_2$

IrCl₃•2H₂O (0.80 g, 2.50 mmol) and tfmfppy (2.41 g, 10.00 mmol) in 30 mL 2-EtOCH₂CH₂OH: H₂O (3:1, v/v) were refluxed at 140 °C for 24 h. After cooling down, yellow precipitate was filtered and washed with ethanol, acetone, respectively. The product was dried under vacuum with a 43% yield (0.76 g, 0.54 mmol). MS (MALDI-TOF) Calcd: *m/z* 1416.047 [M⁺]. Found: *m/z* 1416.542 [M⁺].

2.4.3. General synthesis procedure of

tetraphenylimidodiphosphinate acid derivatives (R-Htpip)

A solution of chlorodiphenylphosphine derivatives (5 mmol) and hexamethyldisilazane (2.5 mmol) in anhydrous toluene (10 mL) was refluxed for 3 h, after which the byproduct Me₃SiCl was distilled off. The mixture was then cooled in an ice bath and a solution of H₂O₂ (0.5 mL, 30 wt% in H₂O) in THF (4 mL) was added dropwise. This solution was added to diethyl ether (15 mL) and the white precipitate was washed several times with water and recrystallized from methanol to give the desired ancillary ligands. Tetraphenylimidodiphosphinate acid (Htpip, 0.45 g, 1.08 mmol, yield: 43%). ³¹P NMR (500 MHz, CDCl₃) δ 19.34 ppm (s). MS (ESI) Calcd: *m*/*z* 416.10 [M⁻]. Found: *m*/*z* 416.12 [M⁻]. Tetra(4fluorophenyl)imidodiphosphinate acid (Hftpip, 0.62 g, 1.28 mmol, yield: 51%). MS (ESI) Calcd: m/z 489.07 [M⁻]. Found: m/z 489.10 [M⁻]. Tetra(4-trifluoromethylphenyl)imidodiphosphinate acid (Htfmtpip, 0.63 g, 0.93 mmol, yield: 37%). MS (ESI) Calcd: m/z 689.05 [M⁻]. Found: *m*/*z* 689.08 [M⁻].

2.4.4. General synthesis procedure of Ir(tfmfppy)₂R-tpip (1–3)

 $[(tfmfppy)_2Ir(\mu-Cl)]_2$ (0.20 mmol) and 2.5 equivalent R-Htpip (0.5 mmol) and K₂CO₃ (0.07 g, 0.5 mmol) were dissolved in 5 mL of 2-EtOCH₂CH₂OH. After degassed, the solution was maintained at 140 °C for 12 h under nitrogen. After cooling, the crude compounds were filtered and dried under vacuum. Further purification was taken by gradient sublimation in vacuum to give products **1–3**.

Ir(tfmfppy)₂tpip (**1**, 0.19 g, 0.18 mmol, yield: 44%). ¹H NMR (500 MHz, CDCl₃) δ 9.09 (d, *J* = 5.5 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.76 (dd, *J* = 10.5, 8.5 Hz, 4H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.39–7.31 (m, 10H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.00 (dt, *J* = 7.5, 2.5 Hz, 4H), 6.81 (d, *J* = 10.5 Hz, 2H), 6.74 (t, *J* = 7.0 Hz, 2H), 6.02 (s, 2H). MS (MALDI-TOF) Calcd: *m/z* 1089.151 [M⁺]. Found: *m/z* 1090.342 [M⁺+1]. Anal. calcd for C₄₈H₃₂IrF₈N₃O₂P₂: C 52.94, N 3.86, H 2.96. Found: C 52.88, N 3.79, H 3.01.

Ir(tfmfppy)₂ftpip (**2**, 0.25 g, 0.21 mmol, yield: 53%). ¹H NMR (500 MHz, CDCl₃) δ 9.01 (d, *J* = 6.0 Hz, 2H), 8.23 (d, *J* = 8.0 Hz, 2H), 7.75 (td, *J* = 7.5,5.0 Hz, 4H), 7.64 (t, *J* = 7.8 Hz, 2H), 7.30–7.25 (m,

4H), 7.07 (t, J = 8.5 Hz, 4H), 6.84–6.80 (m, 4H), 6.70 (t, J = 8.5 Hz, 4H), 6.03 (s, 2H). MS (MALDI-TOF) Calcd: m/z 1161.114 for [M⁺]. Found: m/z 669.987 [M⁺-ftpip]. Anal. calcd for C₄₈H₂₈IrF₁₂N₃O₂P₂: C 49.66, N 3.62, H 2.43. Found: C 49.59, N 3.58, H 2.47.

Ir(tfmfppy)₂tfmtpip (**3**, 0.22 g, 0.16 mmol, yield: 41%). ¹H NMR (500 MHz, CDCl₃) δ 8.88 (d, *J* = 5.5 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 2H), 7.99–7.96 (m, 4H), 7.70 (d, *J* = 8.0 Hz, 4H), 7.57 (t, *J* = 10.5 Hz, 2H), 7.46–7.42 (m, 4H), 7.30–7.28 (m, 4H), 6.87 (d, *J* = 12.0 Hz, 2H), 6.69 (t, *J* = 6.5 Hz, 2H), 6.01 (s, 2H). MS (MALDI-TOF) Calcd: *m/z* 1361.104 for [M⁺]. Found: *m/z* 636.521 [M⁺-tfmtpip]. Anal. calcd for C₅₂H₂₈IrF₂₀N₃O₂P₂: C 45.89, N 3.09, H 2.07. Found: C 45.82, N 3.05, H 2.10.

3. Results and discussion

3.1. X-ray crystallography

Selected parameters of the single crystal of $Ir(tfmfppy)_2$ ftpip (**2**) and tables of atomic coordinates are listed in Fig. 1 and collected in the Table S1, and bond lengths and bond angles are given in the Table S2 (Supporting Information). Fig. 1 shows the Oak Ridge Thermal Ellipsoidal plot (ORTEP) diagrams given by X-ray analysis of the complex **2**, which is crystallized in triclinic space group *P*_L. The iridium center adopts a distorted coordination geometry with two CN cyclometalated ligands and a novel ancillary ligand ftpip (*cis*-C,C and *trans*-N,N disposition). The Ir(1)-O(1) (2.216(5) Å), Ir(1)-O(2) (2.229(5) Å), Ir–N (2.082(6) Å) and Ir(1)-C(11) (2.001(8) Å), Ir(1)-C(23) (2.003(3) Å) bond lengths are in agreement with corresponding parameters described for other similarly constituted complexes. It should be noted that the sterically crowded ligands result in large deformation with regard to the phenyl rings in the complex. The deformation is caused by steric hindrance originating



Fig. 1. ORTEP diagram of Ir(tfmfppy)₂ftpip (**2**). The thermal ellipsoids were drawn at the 50% probability level. Crystallographic data (CCDC 923700): $M_w = 1127.04$, triclinic space group *P*-1, *a* = 12.0840(13), *b* = 13.5660(11), *c* = 14.2380(12) Å, $\alpha = 101.076(2)$, $\beta = 92.994(3)$, $\gamma = 100.549(2)^\circ$, $V = 2218.2(4) Å^3$, Z = 1, T = 296(2) K, calculated density $\rho_{calcd} = 1.745$ g/cm³, μ (Mo K α) = 3.177 mm⁻¹, 8661 reflections measured, of which 6254 were unique ($R_{int} = 0.0556$). Final *wR* = 0.1316 for 6254 observed reflections with I > 2 sigma(*I*).

from the repulsion between fluoro/trifluoromethyl groups located on the phenyl rings.

3.2. Photophysical property

The absorption spectra (CH₂Cl₂ solution) and emission spectra (CH₂Cl₂ solution and solid state) of the three complexes **1–3** are recorded at room temperature (Fig. 2), and the pertinent data are summarized in Table 1. Like other 2-phenylpyridine-type heteroleptic iridium complexes, **1–3** exhibit two major absorption regions (Fig. 2(a)). The intense bands in the range before 380 nm can be assigned to the spin-allowed 1π - π * transition of the ligand centered (¹LC) states localized on tfmfppy and tpip derivatives. In the range of lower energy (390 < λ < 520 nm), the relatively weak absorption bands show subtle variations, which can be assigned to the mixing of ¹MLCT and ³MLCT (metal-to-ligand charge-transfer) states, or LLCT (ligand-to-ligand charge-transfer) transition through strong spin-orbit coupling of iridium atom [33], suggesting that the electronic structures of the frontier orbitals are almost the same in all the complexes (see Table 1).

The Ir(III) complexes emit efficient and characteristic emission of phosphorescence from MLCT state both in CH₂Cl₂ solution and solid state. The emissions of 1, 2 and 3 show the broad and structureless emission maxima at 514 nm (x = 0.26, y = 0.64), 513 nm (x = 0.26, y = 0.63) and 508 nm (x = 0.24, y = 0.60) with the quantum efficiencies of 11%, 32% and 19%, respectively (Fig. 2(b)). All the complexes exhibit emissions peaked at 551 nm (x = 0.40, y = 0.58), 549 nm (x = 0.37, y = 0.60) and 531 nm (x = 0.29, y = 0.63) in solid state (Fig. 2(c)), respectively, which are substantially red-shifted compared with their corresponding solution emissions. These low-energy emissions can be ascribed to excimer formation arising from π - π stacking interactions in solid state, which will lead to a broad and featureless red-shifted luminescence compared with that in dilute solution [19,34]. The results indicate that these ancillary ligands do not affect the electronic structures of the frontier orbitals that engaged in the emission process significantly, and the change of the ancillary ligand leads to a really subtle shift in the emission color.

As we know, the phosphorescence lifetime (τ_p) is the crucial factor influencing the rate of triplet—triplet annihilation in the OLEDs. Long τ_p of the material usually causes the great triplet—triplet annihilation [35]. The lifetimes of complexes **1**, **2**, **3** are in the range of microseconds (1.78–1.95 µs in CH₂Cl₂ solution and 2.17–2.79 µs in solid state) at room temperature (Table 1, Fig. S1), which are indicative of the phosphorescent origin for the excited states in each case.

3.3. Electrochemistry

The HOMO and LUMO energy levels are important for the design of the device structure. To obtain the HOMO/LUMO energy levels of the Ir(III) complexes 1, 2 and 3, the electrochemical properties were investigated by cyclic voltammetry at room temperature (Fig. S2 and Table 1). Both quasi-reversible oxidation and reduction process were observed in CH₂Cl₂ solution indicating 1, 2 and 3 possess both hole- and electron-transporting characteristics. The HOMO levels of the compounds were calculated from the oxidation potentials using the ferrocene as a reference (4.8 eV) and the LUMO levels were calculated from the HOMO and bandgap obtained from UV-vis spectra [36-38]. As listed in Table 1, the HOMO/LUMO levels of **1**, **2** and **3** are -5.66/-3.26 eV, -5.44/-3.08 eV, and -5.68/ -3.26 eV, respectively. And the HOMO and LUMO levels are all lowered by 0.2–0.5 eV compared with that of Ir(tfmppy)tpip (tfmppy = 2-(4-trifluoromethylphenyl)pyridine) reported in our previous work [20] due to the introduction of the



Fig. 2. The absorption ((a), 1×10^{-5} mol/L) and emission ((b): CH₂Cl₂ solution, 1×10^{-5} mol/L; (c): solid state) spectra of complexes Ir(tfmfppy)₂tpip, Ir(tfmfppy)₂tpip and Ir(tfmfppy)₂tfmtpip.

electrowithdrawing fluro- and trifluoromethyl groups in 2phenylpyridine and tetraphenylimidodiphosphinate.

3.4. OLEDs performances

With the aim of evaluation the EL performances of the novel Ir(III) emitters, OLEDs were fabricated with the structure of ITO/ TAPC (60 nm)/iridium complexes (8 wt%) : SimCP2 (30 nm)/TPBi (90 nm)/LiF (1 nm)/Al (100 nm). The energy level diagrams of HOMO and LUMO levels (relative to vacuum level) and molecular structures for materials investigated in this work were shown in Scheme 2. The devices using **1**, **2** and **3** emitters were named **GIr1**, **GIr2** and **GIr3**, respectively. SimCP2 was used as the host material due to its bipolar properties which can balance the electron—hole transport [39], and the optimized doping concentrations were determined to be 8 wt%. By monitoring the EL performances with increasing the thickness of the layers, the thicknesses of TAPC, iridium complexes doped SimCP2 and TPBi layers were optimized to be 60, 30 and 90 nm, respectively.

The EL spectra, current density–current efficiency $(J-\eta_c)$, current density–power efficiency $(J-\eta_p)$ and luminance–voltage (L-V) characteristics of each device are shown in Fig. 3. The key EL

data are summarized in Table 2. All of the devices exhibit typical emission of the Ir(III) complexes **1** (**GIr1**), **2** (**GIr2**) and **3** (**GIr3**) in CH₂Cl₂ solution with the maximum peak at 534, 512 and 509 nm, respectively. The CIE color coordinates are x = 0.36, y = 0.60 for device **GIr1**, x = 0.27, y = 0.64 for device **GIr2**, and x = 0.24, y = 0.63 for device **GIr3**, respectively, corresponding to the green region. But it cannot be ignored that there are little residual emissions from the host SimCP2 at 381 nm [39] for each device, which indicates that the energy transfer from the host excited state to the guest emitters is incomplete upon electrical excitation.

And all of the devices have low turn-on voltages of 3.5– 3.6 V. It can be observed that the maximum luminance value of 40 000 cd m⁻² retained during a driving voltage range, suggesting that they exceed our measurement limitation under examined conditions. For the Ir(tfmfppy)₂tpip based device **Gir1**, the maximum current efficiency and power efficiency are 77.5 cd A⁻¹ (7.6 V) and 37.5 lm W⁻¹ (6.4 V), respectively. The driving voltages needed to reach the practical brightness of 100 and 1000 cd m⁻² are 4.5 and 5.8 V, respectively. The performances of device **Gir2** based on Ir(tfmfppy)₂tpip are little inferior to device **Gir1**, with the maximum η_c and η_p of

Table 1

Physical properties of complexes Ir(tfmfppy)₂tpip, Ir(tfmfppy)₂ftpip and Ir(tfmfppy)₂tfmtpip.

Compounds	$\lambda_{abs, CH_2Cl_2} nm$	$\lambda_{em, CH_2Cl_2} nm$	λ _{em, solid} nm	Φ^{a} %	τ^{b} µs	HOMO/LUMO ^c eV
Ir(tfmfppy) ₂ tpip	345/408/462	514	551	11	1.78/2.17	-5.97/-3.56
Ir(tfmfppy) ₂ ftpip	348/409/467	513	549	32	1.84/2.78	-5.60/-3.14
Ir(tfmfppy) ₂ tfmtpip	347/410/461	508	531	19	1.95/2.79	-5.68/-3.26

^a Φ : emission quantum yield reference to an aerated aqueous solution of [Ru(bpy)₃]Cl₂ (Φ = 2.8%) as the standard solution.

^b Measured at room temperature in solutions and solid powders.

^c HOMO/LUMO calculated based on the cyclovoltammety (CV) diagram with using ferrocene as the internal standard and UV–Vis spectra in dichloromethane.



Scheme 2. Energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this work and their molecular structures.

66.6 cd A⁻¹ (7.1 V) and 35.4 lm W⁻¹ (5.1 V), respectively. The driving voltages needed to reach the brightness of 100 and 1000 cd m⁻² are 4.4 and 5.5 V, respectively. The efficiencies of Ir(tfmfppy)₂tfmtpip-based OLED device **GIr3** are furthermore

degraded to a maximum η_c and η_p of 53.3 cd A⁻¹ (7.5 V) and 25.1 lm W⁻¹ (6.6 V), respectively. The driving voltages needed to reach the brightness of 100 and 1000 cd m⁻² are 4.7 and 6.0 V, respectively.



Fig. 3. Characteristics of device **GIr1** to **GIr3**: (a) EL spectra and (b) power efficiency as a function of current density, (c) current efficiency as a function of current density, and (d) *J*-*V*-*B*, current density and brightness versus voltage for **GIr1** to **GIr3**.

Device	$V_{on}\left(V ight)$	$\lambda_{em,max} (nm)$	$CIE(x, y)^{a}$	Max.	Current efficiency (cd A ⁻¹) voltage (V), luminance (cd m ⁻²)			Max. Power efficiency
				Luminance (cd m ⁻²)	Max.	$10\ 000\ cd\ m^{-2}$	$20\ 000\ cd\ m^{-2}$	(Voltage, V) (lm W ⁻¹)
GIr1	3.5	534	0.36, 0.60	>40 000	77.5 (7.6, 8025)	73.5	66.4	37.5 (6.4)
GIr2	3.5	512	0.27, 0.64	>40 000	66.6 (7.1, 5286)	65.8	60.0	35.4 (5.1)
GIr3	3.6	509	0.24, 0.63	>40 000	53.3 (7.5, 5169)	50.0	43.1	25.1 (6.6)

 Table 2

 EL properties of OLEDs based on lr(tfmfppy)₂tpip, lr(tfmfppy)₂ftpip and lr(tfmfppy)₂tfmtpip.

^a Commission Internationale de L'Eclairage coordinates.

With current density increasing, the EL efficiency increases until it reaches the maximum. Then, the EL efficiency decreases gradually with current density further increasing. This phenomenon is called EL efficiency roll-off effect due to the triplet-triplet annihilation (TTA) of the phosphor-bound excitons increasing [36–38] and field-induced quenching effects [40,41]. For device **GIr1**, the η_c at the practical luminance of 100 and 1000 cd m⁻² is 35.4 and $67.4 \text{ cd } \text{A}^{-1}$, respectively, and it reaches the maximum current efficiency (77.5 cd A⁻¹) at 8025 cd m⁻². The η_c at the high luminance of 10 000 and 20 000 cd m^{-2} is 73.5 and 66.4 cd A^{-1} , respectively. The roll-off ratios of efficiency from the peak value (77.5 cd A^{-1}) to that at the brightness of 10 000 cd m^{-2} and from the brightness of 10 000 to 20 000 cd m^{-2} are as low as 5.12% and 9.73%, respectively. For device **GIr2**, the η_c at the practical luminance of 100 and 1000 cd m^{-2} is 36.31 and 59.58 cd A^{-1} , respectively, and it reaches the maximum current efficiency (66.6 cd A^{-1}) at 5286 cd m^{-2} . The η_c at the high luminance of 10 000 and 20 000 cd m⁻² is 65.8 and 60.0 cd A^{-1} , respectively. The roll-off ratios of efficiency from the peak value (66.6 cd A^{-1}) to that at the brightness of 10 000 cd m^{-2} and from the brightness of 10 000 to 20 000 cd m^{-2} are as low as 1.14% and 8.83%, respectively. For device **GIr3**, the η_c at the practical luminance of 100 and 1000 cd m^{-2} is 16.60 and 41.08 cd A^{-1} , respectively, and it reaches the maximum current efficiency (53.3 cdA^{-1}) at 5169 cd m⁻². The η_c at the high luminance of 10 000 and 20 000 cd m⁻² is 50.0 and 43.1 cd A⁻¹, respectively. The roll-off ratios of efficiency from the peak value $(53.26 \text{ cd } \text{A}^{-1})$ to that at the brightness of 10 000 cd m^{-2} and from the brightness of 10 000 to 20 000 cd m^{-2} are 6.16% and 13.73%, respectively. All the devices maintain high efficiencies at relative high brightness suggesting they are useful for practical application, especially for lighting.

3.5. Electron mobility

The high efficiency of devices at high brightness and low efficiency roll-off effects can be interpreted by the more balanced injection and transport of carriers in(to) the emitting layer, due to the more balanced hole and electron mobility of the SimCP2 and the good electron transport ability of Ir(III) complexes. The respective hole (μ_h) and electron mobility (μ_e) of the SimCP2 are $\mu_h = 6.4 \times 10^{-4}$ and $\mu_e = 4.6 \times 10^{-4}$ cm² V⁻¹ s⁻¹, which are higher than that of the popular host of mCP (1,3-bis(carbazol-9-yl)benzene, $\mu_h = 3.2 \times 10^{-4}$, $\mu_e = 2.0 \times 10^{-4}$ cm² V⁻¹ s⁻¹) [39,42]. Meanwhile, the electron mobilities of Ir(tfmfppy)₂tpip (1) and Ir(tfmfppy)₂ftpip (**2**) were measured by the transient EL method based on the device structure of ITO/TAPC (50 nm)/1 or 2 (60 nm)/ LiF (1 nm)/Al (100 nm). The TAPC is the hole-transport layer while 1 and **2** perform as both emissive and electron-transport layers. The experimental setup and the process for transient EL measurements were listed in Fig. S3. Due to the serious TTA effect of the Ir(tfmfppy)₂tfmtpip (3), the EL intensity of ITO/TAPC (50 nm)/3 (60 nm)/LiF (1 nm)/Al (100 nm) was too weak to calculate the electron mobility. Because the hole mobility of TAPC ($\sim 1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [43] is much higher than the electron mobility of **1** and **2**, the voltage drop across the TAPC layer and the built-in electric field between organic/organic interface is negligible. Bearing this in mind, the electron mobility can be roughly calculated with the equation of

$$\mu_e = d^2 (t_d \cdot V)^{-1} \tag{2}$$

where *d* is the thickness of the emitting layer, *V* is the driving voltage and t_d is the delay time. We chose the popular electron transport material Alq₃ (tri(8-hydroxyquinoline)aluminum) as the reference because its electron mobility was reported (Fig. S4) [44]. The transient EL signals for Ir(tfmfppy)₂tpip-based, Ir(tfmfppy)₂ft-pip-based devices and electric field dependence of charge electron mobilities in the thin films of Ir(tfmfppy)₂tpip, Ir(tfmfppy)₂ftpip and Alq₃ were shown in Fig. 4.

The experimental results showed that the 60 nm Ir(tfmfppy)₂tpip and Ir(tfmfppy)₂ftpip layers have good electron mobilities between $2.71-3.18 \times 10^{-6}$ cm² V⁻¹ s⁻¹ and 2.47- $2.71 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under electric field from 1150 (V cm⁻¹)^{1/2} to 1300 (V cm⁻¹)^{1/2}, a litter lower than those of Alq₃ (4.74–4.86 × 10⁻⁶ cm² V⁻¹ s⁻¹ vs 1150–1300 (V cm⁻¹)^{1/2}). In the OLEDs, the dopants act as the hole and electron traps to retard the motion of both types of carriers. The lower LUMO levels of the dopants are particularly important for the reason that the hole mobility of the TAPC is high than the electron mobility of the SimCP2 and TPBi in OLEDs [45], the excitons accumulation is expected in hole blocking layer (TPBi) near the interface of emitting layer (Ir complexes (x wt %) : SimCP2)/TPBi due to the energy barrier between TPBi and SimCP2 [46]. The accumulation of excitons is expected to cause the serious TTA and triplet-polaron annihilation (TPA) of the iridium complexes, and high efficiency roll-off consequently. Therefore, the excitation lifetime of OLEDs relies on the capability of electron transport. In our case, the good electron mobility of the phosphorescent emitters would facilitate the injection and transport of electrons, which broaden the recombination zone, balance the distribution of holes and electrons and reduce leakage current, particularly for the high doping concentration, leading to the suppressed the TTA, TPA effects [47,48], improved recombination probability and high device efficiency, low efficiency roll-off.

4. Conclusion

Three Ir(III) complexes using 2-(4-trifluoromethyl-6-fluorophenyl)pyridine as a cyclometalated ligand and tetraphenylimidodiphosphinate derivatives as ancillary ligands were synthesized. The complexes emit green phosphorescence at 514, 513 and 508 nm in CH₂Cl₂ solution, respectively. The OLEDs with these Ir(III) complexes doped SimCP2 as missive layers exhibited high EL efficiency at high brightness with the maximum current efficiency (η_c) value of 77.49 cd A⁻¹ at relatively high brightness of 8025 cd m⁻². In addition, the efficiency roll-off ratios from the peak efficiency to the brightness of 10 000 cd m⁻² are less than 10% for all the devices. We have utilized the transient EL method to measure the electron mobilities in Ir(tfmfppy)₂tpip and Ir(tfmfppy)₂ftpip films directly, which are a little lower than that in Alq₃. We believe that the good



Fig. 4. The transient EL signals for the devices based on Ir(tfmfppy)₂tpip (a), Ir(tfmfppy)₂ftpip (b) and electric field dependence of charge electron mobilities in the thin films of Ir(tfmfppy)₂tpip, Ir(tfmfppy)₂tpip and Alq₃.

electron mobility of the phosphorescent emitter leads to the high devices efficiency and low efficiency roll-off effect. All the devices maintain high efficiencies at relative high brightness suggesting they are useful for practical application, especially for lighting.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.01.033.

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