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# Synthesis, photoluminescence and electroluminescence of one iridium complex with 2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyrimidine and tetraphenylimidodiphosphinate ligands

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Abstract: Using 2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyrimidine as main ligand and tetraphenylimidodiphosphinate as ancillary ligand, one iridium complex was synthesized. This complex shows a green emission peaking at 543 nm with a quantum efficiency yield as 48% in deareated  $CH_2Cl_2$  solution. It also has good thermal stability with a decomposition temperature of 351 °C. Using this material as emitter, the organic light-emitting diode shows good performances with a maximum luminance 42 898 cd/m<sup>2</sup>, a maximum current efficiency up to 54.29 cd/A with low efficiency roll-off. At the luminance of 5000 and 10 000 cd/m<sup>2</sup>, the current efficiencies are still kept at 46.70 and 40.63 cd/A, respectively.

*Keywords*: pyrimidine; tetraphenylimidodiphosphinate; organic light-emitting diode; efficiency; efficiency roll-off

# **1. Introduction**

Organic light-emitting diodes (OLEDs) have attracted enormous interest in last decades as are expected to be used in large-size, flexible-panel display technologies and solid-state lighting [1-16] Notably, iridium(III) complexes are the most widely

investigated phosphorescent emitting materials for highly efficient OLEDs owing to their encouraging properties including thermal stability, flexible color tunability, short excited lifetime and high quantum yields [17-21]. Furthermore, the phosphorescence of Ir(III) complexes originates from the metal-to-ligand charge transfers (MLCT) and ligand-centered (LC) transition [17-21], so that the energy level of the excited state can be controlled by tuning the energy levels of the ligands through substituent effects, resulting a wide flexible emission color range.

However, for many OLEDs based on Ir(III) complexes, the device efficiency roll-off ratios are serious, which can mainly be attributed to the deterioration of charge carrier balance and the increase of nonradioactive quenching processes, including triplet-triplet annihilation (TTA), triplet-polaron annihilation (TPA), and electric field induced dissociation of excitons at high current density. At present, because the hole mobility of most hole transport materials is roughly 2-3 orders of magnitude higher than the electron mobility of the electron transport materials and most hosts are also hole transport materials, the efficiency and efficiency roll-off of OLEDs rely on the capability of electron transport. Thus, it is necessary to use the ambipolar host materials and synthesize Ir(III) dopants with outstanding electron mobility to obtain phosphorescent OLEDs with low efficiency roll-off.

In this work. we synthesized а green Ir(III) complexes using 2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyrimidine (dfptfmpm) as the main ligand with two fluorine atoms substituted on phenyl ring and trifluoromethyl on pyrimidine. Fluorination can enhance the electron mobility of the complexes resulting in a better balance of charge injection and transfer, and the lower vibrational frequency of C-F bond can reduce the rate of nonradiative deactivation and the bulky CF3 substituents can affect the molecular packing and the steric protection around the metal can suppress the self-quenching behavior [23-26]. In addition, nitrogen heterocycle will increase the electron affinity and a more negative framework of ligand C^N may improve the electron mobility. Furthermore, Htpip (tetraphenylimidodiphosphinate acid) derivatives reported by our group previously were introduced as ancillary ligands, which have two diphenyl phosphoryl (Ph<sub>2</sub>P=O) groups [27-32]. Thus, not only the electron transport ability of the complex be improved, the four bulky phenyl groups also lead to a larger spatial separation of the neighboring molecules of the complexes [24-27], resulting high device efficiency and low efficiency roll-off.

#### 2. Experimental Section

#### 2.1 General Information

High resolution mass spectra (HR EI-MS) were recorded from Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS. TGA measurements were carried out on STA 449F3 (NETZSCH). Absorption and emission spectra were measured on a Shimadzu UV-3100 and a Hitachi F-4600 luminescence spectrophotometer, respectively. The thermogravimetric analysis (TGA) curve of the complex was carried out with an STA 449F3 instrument (NETZSCH) under nitrogen with a temperature increasing rate of 10 °C/min. Cyclic Volta metric experiments were carried out with an CHI 600E system (Chenhua, Shanghai) using three electrode cell assemblies in deaerated dichloromethane solution with tetrabutylammoniumperchlorate as supporting electrolyte at a scan rate of 100 mV/s. Each oxidation potential was calibrated with ferrocene as a reference.

#### 2.2 Synthesis of dfptfmpm and Ir(dfptfmpm)<sub>2</sub>tpip complex

All reactions were performed under nitrogen. Solvents were carefully dried and distilled from appropriate drying agents prior to use for syntheses of ligands. Tetraphenylimidodiphosphinate (tpip) and its potassium (Ktpip) were synthesized according to our former publications.

2-Chloro-4-(trifluoromethyl)pyrimidine (20 mmol), 2,4-difluorophenylboronic acid (30 mmol), Na<sub>2</sub>CO<sub>3</sub> (36 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.20 mmol) were dissolved in toluene : ethanol : water (30 mL, 2 : 1 : 2, v / v). The mixture was refluxed for 24 h and extracted twice with CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The mixed organic solution was washed with brine and the solid obtained was purified with column chromatography on SiO<sub>2</sub> using ethyl acetate and petroleum ether (v : v = 10: 1) as eluant to afford white solid 2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyrimidine (dfptfmpm, yield:

75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.01 (d, *J* = 5.0 Hz, 1H), 8.14 (td, *J* = 8.7, 6.6 Hz, 1H), 7.48 (d, *J* = 5.0 Hz, 1H), 6.98 – 6.83 (m, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -70.12 (s, 3F), -105.06 (d, *J* = 11.0 Hz, 1F), -108.14 (d, *J* = 11.0 Hz, 1F). MS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>5</sub>F<sub>5</sub>N<sub>2</sub>H [M+H]: 261.05, found: 260.95.

A mixture of  $IrCl_3 \cdot 3H_2O$  (1.8 mmol) and dfptfmpm (4 mmol) in 2-ethoxyethanol and water (6 mL, 3 : 1, v / v) was refluxed for 24 h. After cooling, the yellow solid precipitate was filtered to give the crude cyclometalated Ir(III) chloro-bridged dimer. MS (ESI) *m/z* calcd for C<sub>44</sub>H<sub>16</sub>Cl<sub>2</sub>F<sub>20</sub>Ir<sub>2</sub>N<sub>8</sub>H [M+H]: 1492.99, found: 1492.95.

Then, the slurry of crude chloro-bridged dimer (0.5 mmol) and Ktpip (1.4 mmol) in 2-ethoxyethanol (6 mL) was refluxed for 24 h. The solvent was evaporated at low pressure and the crude product was washed with water, and then chromatographed with CH<sub>2</sub>Cl<sub>2</sub> gave complex Ir(dfptfmpm)<sub>2</sub>tpip, which were further purified by sublimation in vacuum (yield: 56%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.25 (d, *J* = 6.0 Hz, 2H), 7.83 (ddd, *J* = 12.4, 7.6, 1.7 Hz, 4H), 7.48 – 7.30 (m, 10H), 7.25 – 7.18 (m, 2H), 7.04 (td, *J* = 7.7, 3.1 Hz, 4H), 6.71 (d, *J* = 6.0 Hz, 2H), 6.45 (ddd, *J* = 11.4, 9.5, 2.2 Hz, 2H), 5.51 (dd, *J* = 8.6, 2.2 Hz, 2H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -69.77 (s, 3F), -103.00 (d, *J* = 13.1 Hz, 1F), -105.19 (d, *J* = 13.1 Hz, 1F). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  24.32 (s). MS (ESI) *m*/*z* calcd for C<sub>46</sub>H<sub>28</sub>F<sub>10</sub>IrN<sub>5</sub>O<sub>2</sub>P<sub>2</sub>H [M+H]: 1128.13, found: 1128.00. HR-MS (*m*/*z*) Calcd for C<sub>46</sub>H<sub>28</sub>F<sub>10</sub>IrN<sub>5</sub>O<sub>2</sub>P<sub>2</sub>H [M+H]: 1128.1261. Found: 1128.1260 [M+H]<sup>+</sup>.

# 2.3 OLEDs fabrication and measurement

OLEDs with the emission area of 0.1 cm<sup>2</sup> were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15  $\Omega$  sq<sup>-1</sup>. Substrate was cleaned by ultrasonic in organic solvents followed by ozone treatment for 20 min. All materials used for EL devices were sublimed in vacuum (2.2 × 10<sup>-4</sup> Pa) prior to use. The 40 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 (10 wt%) and host (mCP, *N*,*N*'-dicarbazolyl-3,5-benzene) were co-evaporated to form 20 nm emitting layer from two separate sources. Successively,

1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB, 30 nm) as electron transport material, LiF (1 nm) as electron injection material, and Al (100 nm) as the cathode were evaporated. The vacuum was less than  $1 \times 10^{-5}$  Pa during all materials deposition. The device characteristics were measured with a computer controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. The electroluminescence (EL) spectra were measured with a Hitachi F-4600 photoluminescence spectrophotometer. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra Scan PR650 spectrophotometer.

#### 3. Results and discussion

#### 3.1 Thermal stability

The thermal stability of emitter is very important for efficient OLEDs. If a complex is suitable for application, the decomposition temperature ( $T_d$ ) should be high enough to guarantee that the complex could be deposited onto the solid face without any decomposition on sublimation. The thermogravimetric analysis (TGA) curve of Ir(dfptfmpm)<sub>2</sub>tpip is listed in Figure 2. It can be observed that the decomposition temperature (5% loss of weight) is 351 °C, indicating that the complex is suitable for application in OLEDs.

#### 3.2 Photophysical property

The absorption spectrum of Ir(dfptfmpm)<sub>2</sub>tpip complex was recorded at room temperature in CH<sub>2</sub>Cl<sub>2</sub> at  $1 \times 10^{-5}$  mol/L (Fig. 3). Like other heteroleptic iridium complexes, this complex exhibits two major absorption regions. The intense band at high energy before 300 nm is assigned to the spin-allowed ligand-centered ( $\pi \rightarrow \pi^*$ ) transition of dfptfmpm and tpip ligands. The relatively weak absorption bands in the range 350 - 450 nm are due to the mixing of <sup>1</sup>MLCT and <sup>3</sup>MLCT (metal-to-ligand charge-transfer) states, or LLCT (ligand-to-ligand charge-transfer) transition through strong spin-orbit coupling of iridium atom. [17-33].

For phosphorescent emitters used in OLEDs, significant mixing of the lowest triplet and higher-lying singlet excited states caused by efficient SOC favors high phosphorescent quantum efficiency. At room temperature,  $Ir(dfptfmpm)_2tpip$  complex shows broad emission spectrum in deareated CH<sub>2</sub>Cl<sub>2</sub> solution with maxima at 543 nm, generated by the electronic 0-0 transition between the lowest triplet excited state and the ground state, which makes it green phosphors. In general, the emission band from MLCT states are broad and featureless, while the highly structured emission band mainly originates from the  ${}^{3}\pi$ - $\pi$ \* state. Accordingly, the complex emit sfrom a mixture of MLCT states and the dominant ligand-based  ${}^{3}\pi$ - $\pi$ \* state. The emission quantum efficiency yield of Ir(dfptfmpm)<sub>2</sub>tpip complex is 48%, referenced to *fac*-(Ir(ppy)<sub>3</sub>) ( $\Phi_p$ = 0.4) [33]. Furthermore, the phosphorescence excited state lifetime  $\tau_p$  of an Ir(III) complex is a crucial factor that determines the rate of TTA and TPA in OLEDs. The lifetime of Ir(dfptfmpm)<sub>2</sub>tpip complex is 2.66 µs measured in degassed CH<sub>2</sub>Cl<sub>2</sub> with excitation at 370 nm at room temperature, is indicative of a phosphorescent origin of the excited state.

#### 3.3 Theoretical and Electrochemical Property

The frontier molecular orbitals, especially the HOMO and LUMO, are crucial for the photophysical properties and also important in designing the structure of OLEDs. To determine the HOMO and LUMO energy levels, cyclic voltammetry (CV) and theoretical calculations were carried out.

To calculate the HOMO and LUMO energy levels of the  $Ir(dfptfmpm)_2tpip$  complex, cyclic voltammetry experiment was carried out using ferrocene as the internal standard (Figure 4). During the anodic scan in CH<sub>3</sub>CN, the complex exhibited an obvious oxide peak with oxidation potential attributed to the metal-centered Ir(III)/Ir(IV) oxide couple in accordance with reported cyclometallated Ir(III) systems. The HOMO level of the complex was calculated from the oxidation potential and the LUMO level was estimated from the HOMO and the band gap obtain from UV-vis absorption spectrum [34]. Therefore, HOMO/LUMO energy levels of the Ir(dfptfmpm)<sub>2</sub>tpip complex can be estimated as -5.55/-3.21 eV, from the empirical

formulas  $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.8)$  and  $E_{\text{LUMO}} = E_{\text{HOMO}} + Eg$  [34].

In the theoretical calculation, the density functional theory (DFT) calculations for Ir(III) complexes are conducted to gain insights into the electronictates and the orbital distribution employing the Gaussian09 software12 with B3LYP functional; the accurate energy and location of HOMO/LUMO were calculated with QMForge program [35-37]. The basis set used for C, H, O, N, F and P atoms was 6-31G(d,p), while the LanL2DZ basis set were employed for Ir atoms [38]. According to the Figure 4, it is obvious that the HOMO is mainly located on dfptfmpm main ligand (38.07%) and the *d* orditals of iridium atom (55.14%), while the LUMO is mainly located on the cyclometalated main ligands (91.73%). Both HOMO and LUMO are rarely located on ancillary ligand, which are only 6.79% and 2.29%, respectively.

#### 3.4 OLEDs Performance

To investigate the possibility of Ir(dfptfmpm)<sub>2</sub>tpip as emitter, PhOLED with the structure of TAPC (1,1-bis[4-(di-*p*-tolylamino)phenyl]cyclohexane, 40 nm) / Ir(dfptfmpm)<sub>2</sub>tpip (10 wt%): mCP (1,3-bis(9*H*-carbazol-9-yl)benzene, 20 nm) / TmPyPB (1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene, 30 nm) / LiF (1 nm) / Al (100 nm) was fabricated. The molecule structures and energy level diagrams of the materials and devices are shown in Figure 5. TAPC and TmPyPB were used as the hole and electron transport materials due to their good carrier mobility [39,40], respectively, and mCP was used as the host material. Apparently, the HOMO/LUMO levels of the Ir(III) complex are within those of mCP, thus, carriers are expected to transport easily between layers and excellent carrier trapping would be the main mechanism in the devices. Notably, carriers would be well confined and recombined within the EML and the TTA/TPA effects would be effectively avoided. The EL spectra, luminance-voltage, current efficiency-luminance and power efficiency-luminance characteristics of all the devices are shown in Fig. 6.

The device exhibits typical emission with the peak maxima at 536 nm in accordance with the PL spectrum of  $Ir(dfptfmpm)_2$ tpip in CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. 2) indicating that the EL emissions of the devices originate from the triplet excited states

of the phosphors. The Commission Internationale de 1'Eclairage (CIE) color coordinates operated at 8 V are (0.35, 0.62), corresponding to the green region. And the emission spectra are almost invariant of the current density and also do not show any concentration dependence. No emission from TAPC, mCP and TmPyPB suggested that the exciton was only formed in the emissive layer and the complete energy transfer from host to dopant.

The device shows good performances with a maximum luminance 42 898 cd/m<sup>2</sup> at 13.0 V. And the maximum current efficiency, external quantum efficiency and power efficiency are up to 54.29 cd/A, 14% and 25.44 lm/W, respectively, at a luminance of 1186 cd/m<sup>2</sup>. Furthermore, the device efficiency roll-off is not serious. For example, at the luminance of 5000 cd/m<sup>2</sup>, the current efficiency is 46.70 cd/A. Even at the luminance of 10 000 cd/m<sup>2</sup>, the current efficiency is still remain as 40.63 cd/A. From the good device performances it can be conclude that the introduction of 2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyrimidine and tetraphenylimidodiphosphinate ligands has definitely improved the electron mobility of the iridium complex. As a result, the recombination chance of electrons and holes has been strengthened, which is beneficial to the improvement of OLEDs' performances.

#### 4. Conclusion.

In conclusion, one iridium complex with 2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyrimidine as main ligand and tetraphenylimidodiphosphinate as ancillary ligand was reported. This green material has an emission peak at 543 nm with a quantum efficiency yield as 48% in deareated  $CH_2Cl_2$  solution. The OLED using this complex as emitter shows good performances with a maximum luminance 42 898 cd/m<sup>2</sup>, a maximum current efficiency up to 54.29 cd/A with low efficiency roll-off. At the luminance of 5000 and 10 000 cd/m<sup>2</sup>, the current efficiencies are still kept at 46.70 and 40.63 cd/A, respectively.

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# **Figure captions**

Fig. 1. The synthetic route of the ligands and Ir(dfptfmpm)<sub>2</sub>tpip complex.

Fig. 2. The TGA curve of Ir(dfptfmpm)<sub>2</sub>tpip complex.

Fig. 3. The absorption and emission spectra of  $Ir(dfptfmpm)_2tpip$  complex in  $CH_2Cl_2$  at  $1 \times 10^{-5}$  mol/L at room temperature.

**Fig. 4.** The Cyclic voltammogram in  $CH_3CN$  and spatial distributions of the HOMO/LUMO levels of the Ir(dfptfmpm)<sub>2</sub>tpip complex.

**Fig. 5.** Energy level diagrams of HOMO/LUMO levels (relative to vacuum level) for device and molecular structures of materials investigated in this study.

**Fig. 6.** Device characteristics: (a) normalized EL spectra at 8 V; (b) luminance-voltage (*L*-*V*), (c) current efficiency-luminance ( $\eta_c$ -*L*) and (d) power efficiency-luminance ( $\eta_p$ -*L*) curves.





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Fig. 2. The TGA curve of  $Ir(dfptfmpm)_2tpip$  complex.



Fig. 3. (a) The normalized absorption spectra of the complex  $Ir(dfptfmpm)_2tpip$  and ligands dfptfmpm, tpip; (b) the absorption (with molar extinction coefficient) and emission spectra of complex  $Ir(dfptfmpm)_2tpip$  in  $CH_2Cl_2$  at  $1 \times 10^{-5}$  mol/L at room temperature.



**Fig. 4**. The Cyclic voltammogram in CH<sub>3</sub>CN and spatial distributions of the HOMO/LUMO levels of the Ir(dfptfmpm)<sub>2</sub>tpip complex.

CP CP



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CER (E)



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# Highlights

- One efficient green iridium(III) complex was synthesized.
- The complex shows good thermal stability.
- The OLED based on this complex displays maximum current efficiency of 54.29

cd/A.

• The device shows low efficiency roll-off.