



# Efficient bluish-green phosphorescent iridium complex for both solution-processed and vacuum-deposited organic light-emitting diodes



Lijun Deng, Wei Li, Jiuyan Li\*

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China

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## ABSTRACT

Iridium(III)bis(4,6-(difluorophenyl)pyridinato-N,C<sup>2'</sup>)picolate (Firpic) is one typical bluish-green phosphor widely used in phosphorescent organic light-emitting diodes (PhOLEDs). In order to optimize its electroluminescent performance, 3,6-(di-*tert*-butyl)carbazolyl was introduced into the pyridine ring of the 2,4-difluorophenyl-pyridine ligand via a non-conjugated CH<sub>2</sub> linkage. The generated 3,6-di-*tert*-butyl-9-((6-(2,4-difluorophenyl)pyridine-3-yl)methyl)-9H-carbazole (Cz-CH<sub>2</sub>-dfppy) was used as cyclometalating ligand to prepare iridium complex **1**, (Cz-CH<sub>2</sub>-dfppy)<sub>2</sub>Ir(pic). In comparison with the case to attach carbazole directly on pyridine, this non-conjugated CH<sub>2</sub> linking strategy avoids the unwanted bathochromic shift of the phosphorescence and improves the solubility of the iridium complex. (Cz-CH<sub>2</sub>-dfppy)<sub>2</sub>Ir(pic) (**1**) was used as doped emitter to fabricate OLEDs by both spin-coating and vacuum evaporation methods. Efficient bluish-green electrophosphorescence was obtained with maximum luminance efficiency of 22 cd/A (14 lm/W, 8.7%) and 26 cd/A (12 lm/W, 9.5%) for the solution-processed and vacuum-deposited devices, respectively, which far exceed those of the parent Firpic based device. The improved performance for (Cz-CH<sub>2</sub>-dfppy)<sub>2</sub>Ir(pic) was interpreted in terms of improved charge balance brought by the presence of the carbazole groups in the ligands.

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## 1. Introduction

Electrophosphorescent devices that contain transition-metal complexes have attracted much attention in recent years, as they can harvest both singlet and triplet excitons to realize a theoretical internal quantum efficiency of 100% [1–3]. In particular, cyclometalated Ir(III) complexes show high phosphorescent efficiencies and are one of the most important classes of phosphorescent dyes [4,5]. In order to reduce concentration quenching and triplet–triplet annihilation effects, the host–guest strategy is implemented by dispersing the guest into a suitable host at a relatively low concentration [6,7]. Over the past decade, the vacuum-deposited devices have attracted a great deal of attention for extremely high external efficiencies [8,9]. Recently, solution-processed PhOLEDs provided an economically attractive alternative to vacuum-deposited ones, which benefited from using large and bulky molecules or polymers as host or guest materials [10,11]. In the large molecular materials such as phosphorescent dendrimers, the surface groups and/or the dendrons control the processing and intermolecular interactions of the cores, which is responsible for the emission of light [12,13]. Nonetheless, the incorporation of the phosphorescent emitter with decorating groups through conjugated approaches usually causes a

red shift in emission spectrum [14]. In order to keep the emission energy and wavelength, non-conjugated linkage between the emissive core and the decorating group is believed to be an ideal strategy that may have the advantage of being solution processable and to tune the optoelectronic properties of the target materials.

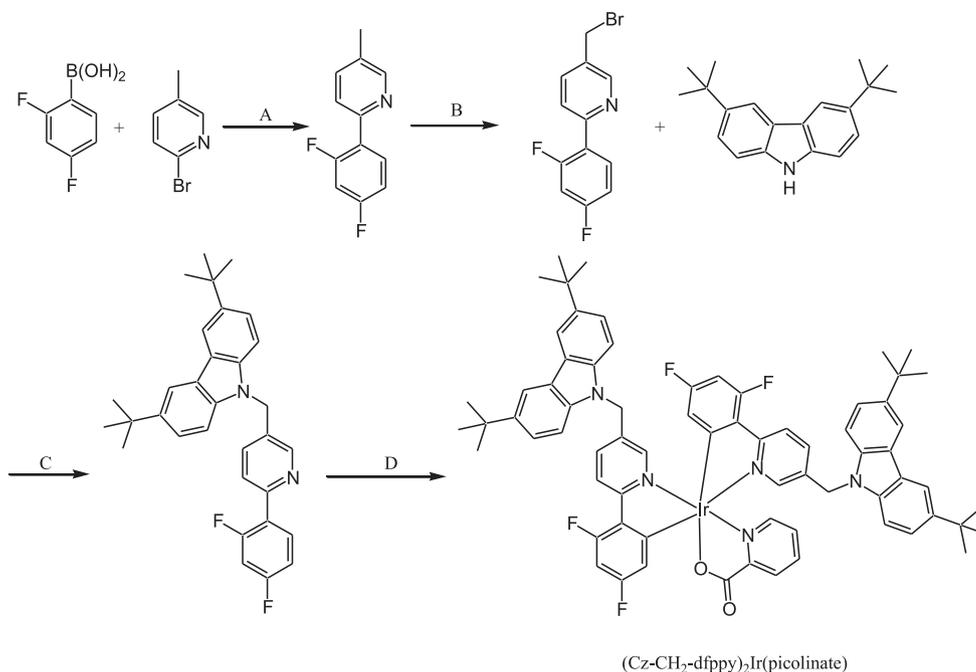
In this work, we report the synthesis and properties of the novel derivative of Firpic, (Cz-CH<sub>2</sub>-dfppy)<sub>2</sub>Ir(pic) complex (**1**). *tert*-Butylcarbazolyl was introduced via non-conjugated CH<sub>2</sub> linkage [15] into the pyridyl ring in the difluorophenylpyridine (dfppy) ligand to tune the optical and electronic behavior of the resultant iridium complex **1**. The electrochemical, photophysical properties of the complex **1** was investigated. Particularly, complex **1** was used as doped emitter to fabricate OLEDs by both spin-coating and vacuum evaporation methods, and the Firpic-based devices with identical architectures also fabricated for comparison. The maximum luminance efficiency of 22 cd/A (14 lm/W, 8.7%) and 26 cd/A (12 lm/W, 9.5%) were realized for solution-processed and vacuum-deposited devices of (Cz-CH<sub>2</sub>-dfppy)<sub>2</sub>Ir(pic), respectively, which far exceed those of the parent Firpic based device.

## 2. Experimental

The synthetic route of the complex **1** is shown in Scheme 1. First, the reaction of 2,4-difluorophenyl boronic acid with 2-bromo-4-methylpyridine in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst

\* Corresponding author. Tel.: +86 411 84986233.

E-mail address: [jiuyanli@dlut.edu.cn](mailto:jiuyanli@dlut.edu.cn) (J. Li).



**Scheme 1.** Chemical structure and synthetic route for complex (Cz-CH<sub>2</sub>-dfppy)<sub>2</sub>Ir(pic) (**1**). Conditions and reagents; (A) Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 M aq Na<sub>2</sub>CO<sub>3</sub>, EtOH, toluene, heat, N<sub>2</sub>. (B) NBS, AIBN, CCl<sub>4</sub>, heat. (C) NaH, DMF, 3,6-di-*tert*-butylcarbazole, rt. (D) IrCl<sub>3</sub>·3H<sub>2</sub>O, 2-ethoxyethanol, water, heat, N<sub>2</sub>, and then K<sub>2</sub>CO<sub>3</sub>, picolinate, 2-ethoxyethanol, heat, N<sub>2</sub>.

[16] produced the intermediate 2-(2,4-difluorophenyl)-4-methylpyridine, which was brominated with N-bromosuccinimide (NBS) in the presence of azodiisobutyronitrile (AIBN) in CCl<sub>4</sub> to give the 2-(2,4-difluorophenyl)-4-(bromomethyl)pyridine. Then 2-(2,4-difluorophenyl)-4-(bromomethyl)pyridine was then added dropwise into the solution of sodium hydride and 3,6-ditertbutylcarbazole in dimethylformamide [17] to form the ligand 2-(2,4-difluorophenyl)-4-(ditertbutylcarbazolyl-methyl)pyridine. Next the target iridium complex was prepared following the standard two step procedure, i.e. the ligand first reacted with chloride trihydrate in 2-ethoxyethanol at high temperature and then the dichloro dimer intermediate was treated with picolinic acid in the presence of potassium carbonate in the 2-ethoxyethanol to give the final iridium complex **1** [18].

2-(2,4-Difluorophenyl)-4-(ditertbutylcarbazolyl-methyl)pyridine Ligand: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.66 (s, 1H), 8.13 (s, 2H), 7.98–7.92 (m, 1H), 7.60–7.57 (d, 1H), 7.50–7.48 (d, 2H), 7.43–7.40 (d, 1H), 7.29–7.25 (d, 2H), 6.99–6.94 (m, 1H), 6.89–6.83 (m, 1H), 5.50 (s, 2H), 1.45 (s, 18H). TOF-MS-EI (m/z): 482.25 [M]<sup>+</sup>.

(Cz-CH<sub>2</sub>-dfppy)<sub>2</sub>Ir(pic) (**1**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.85 (s, 1H), 8.36–8.29 (m, 1H), 8.05–8.01 (m, 6H), 7.87–7.74 (m, 5H), 7.48–7.42 (m, 6H), 7.22–7.15 (m, 4H), 7.01–6.99 (d, 3H), 5.59–5.55 (m, 4H), 1.46–1.42 (d, 36H). MALDI-TOF-MS (m/z): 1300.6 [M + Na]<sup>+</sup>, 1278.5 [M + H]<sup>+</sup>. Anal. Calcd. for C<sub>70</sub>H<sub>66</sub>F<sub>4</sub>IrN<sub>5</sub>O<sub>2</sub>: C, 65.81; H, 5.21; N, 5.48. Found: C, 65.73; H, 5.25; N, 5.52.

The UV–vis absorption and photoluminescence (PL) spectra of the complex **1** was measured in CH<sub>2</sub>Cl<sub>2</sub> solution. The absorption and photoluminescence spectrum of Firpic was also measured for comparison. The electrochemical behaviors of the complex **1** and Firpic were measured in deoxygenated CH<sub>2</sub>Cl<sub>2</sub> solutions containing 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as supporting electrolyte by cyclic voltammetry.

The organic light-emitting diodes (OLEDs) were made and measured in the following way. The pre-cleaned ITO glass substrates with a sheet resistance of 30 Ω square<sup>-1</sup> were treated by UV-ozone for 20 min. Then 40 nm thick PEDOT:PSS film was first deposited on the ITO glass substrates, and baked at 120 °C for 30 min in air. For the solution-processed devices (device I), the emitting layer

was obtained by spin-coating a chlorobenzene solution of iridium complex dopant and a certain host at a doping concentration of 10 wt%. Then, the substrate was transferred to the vacuum chamber for organic and metal deposition. For the evaporated devices (device II), all the organic layers were deposited by vacuum evaporation in the vacuum chamber with a base pressure less than 10<sup>-6</sup> torr. The type I devices have the following configuration: ITO/PEDOT:PSS (40 nm)/H1 (60 wt%): OXD-7 (30 wt%): **1** or Firpic (10 wt%) (30 nm)/TPBI (60 nm)/LiF (1 nm)/Al (200 nm). The type II devices have the configuration of ITO/PEDOT:PSS (40 nm)/NPB (20 nm)/mCP: **1** or Firpic (10 wt%) (30 nm)/TPBI (60 nm)/LiF (1 nm)/Al (200 nm). Particularly, the host H1 employed in solution-processed devices was previously reported by Wang et al. [19]. These multi-layer devices and chemical structures of materials are shown in Fig. 1. The emitting area of each pixel was determined by the overlap of both anode and cathode as 9 mm<sup>2</sup>. The EL spectra, CIE coordinates and current density–voltage–luminance (*J*–*V*–*L*) characteristics of the devices were measured with PR705 photometer and a source–measure–unit Keithley 236 under ambient conditions. The forward viewing external quantum efficiency ( $\eta_{\text{ext}}$ ) was calculated using the luminance efficiency, EL spectra and human photopic sensitivity.

### 3. Results and discussion

Fig. 2 illustrates the absorption and photoluminescence (PL) spectra of complexes **1** and Firpic. The absorption spectrum of the ligand was also measured for comparison in Fig. 2. Both the exhibit two major absorption bands in their absorption spectra. The intense absorption bands in the higher energy region (<400 nm) are assigned to the spin-allowed ligand-centered <sup>1</sup>π–π\* transitions. The weak absorption bands tailing from 400 to 460 nm should correspond to the excitations to the <sup>1</sup>MLCT and <sup>3</sup>MLCT, and the spin-orbit coupling enhanced <sup>3</sup>π–π\* states. Firpic shows intense room-temperature phosphorescence with emission maximum at 472 nm. The phosphorescence of complex **1** is bluish-green with emission peak at 480 nm, which is red shifted by 8 nm relative to

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