

Phosphorescent organic light-emitting devices (PhOLEDs) based on heteroleptic *bis*-cyclometalated complexes using acetylacetonate as the ancillary ligand

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ABSTRACT

A series of four heteroleptic iridium (III) complexes comprising acetylacetonate as the ancillary ligand is synthesized and tested as phosphorescent dopants in OLEDs. It was found that the substitution pattern of the cyclometalated ligand strongly influences the device performance. Notably, reduced device performances were observed for the fluorinated complexes as a result of poor exciton confinement in the guest molecules.

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1. Introduction

During the past decade, intense research efforts have been devoted to develop highly emissive dopants for organic light-emitting devices (OLEDs). In this aim, phosphorescent emitters have attracted the attention of researchers as these emitters grant superior advantages over fluorescent materials. Notably and as the most appealing feature of these emitters, both triplet and singlet excitons can be both advantageously harvested for light emission. Phosphorescent materials are generally based on heavy metal complexes and the most efficient complexes are undoubtedly those based on iridium (III) [1]. Homoleptic and heteroleptic complexes have been both successfully utilized in OLEDs [2–10]. Over the years, a wide range of cyclometalated ligands have also been used to design these different iridium-based emitters. However, although photochemical properties of numerous complexes have been examined and reported, some of them have never been

used or tested in devices. For example, the heteroleptic complex $\text{Ir}(\text{tpy})_2(\text{acac})$ **C1** where tpy stands for 2-(*p*-tolyl)pyridine (**L1**) is one of those. Although Li et al. [11] reported this complex and its photophysical properties in 2004, to the best of our knowledge, this complex has never been tested in OLEDs. $\text{Ir}(\text{dfppy})_2(\text{acac})$ **C2** (with dfppy = 2-(2,4-difluorophenyl)pyridine) **L2** also named Firacac is a second example of complex studied from a theoretical standpoint in at least four publications, yet has never been tested in devices [12–15]. Similarly, $\text{Ir}(\text{fppy})_2(\text{acac})$ **C3** (with fppy = 2-(4-difluorophenyl)pyridine) **L3** with only one fluorine atom per ligand is yet another example [16]. Therefore, these three complexes have been studied in this report for the first time as emitters in OLEDs. To evaluate the electroluminescence properties of the three emitters, a well-known dopant, namely $\text{Ir}(\text{ppy})_2(\text{acac})$ **C4** [17,18], has been studied for comparison. The chemical structures of the four emitters (i.e. **C1–C4**) are presented in Fig. 1.

2. Experimental

2.1. General informations

¹H and ¹³C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer

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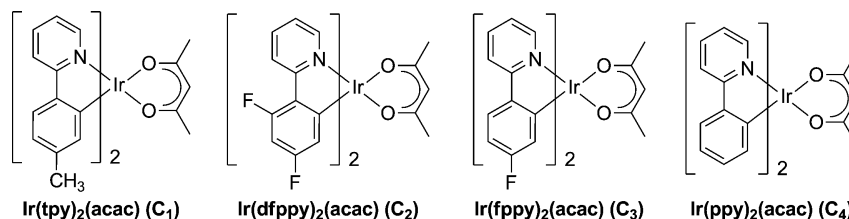


Fig. 1. Structures of the four heteroleptic bis-cyclometalated complexes **C1–C4** investigated in this study.

equipped with a QNP probe head: ^1H (300 MHz) and ^{13}C (75 MHz). The ^1H chemical shifts were referenced to the solvent peak: CDCl_3 (7.26 ppm), and the ^{13}C chemical shifts were referenced to the solvent peak: CDCl_3 (77.0 ppm). All starting materials and solvents were purchased from Aldrich or Lumtec and used as supplied commercially. 2-(4-Fluorophenyl)pyridine **L3** [19] and 2-(4-methylphenyl)pyridine **L4** [20] were prepared according to procedures previously reported in the literature. Cyclometalated iridium dimers were synthesized under inert atmosphere according to the Nonoyama route by refluxing $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with 2–2.5 equiv. of cyclometalating ligand in a 3:1 mixture of 2-ethoxyethanol and water [21]. $\text{Ir}(\text{tpy})_2(\text{acac})$ **C1** [22] and $\text{Ir}(\text{fppy})_2(\text{acac})$ **C3** [23] were synthesized according to procedures previously reported in the literature, without modification and in similar yields.

2.1.1. Synthesis of the dimer precursors $\text{Ir}_2(\text{L})_4\text{Cl}_2$ D1–D4

To a suspension of **LH** (3.5 mmol) in 2-ethoxyethanol/water (75:25, 40 mL) was added $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.344 g, 1.0 mmol). The reaction mixture was stirred at reflux for 24 h. Then, water (50 mL) was added and the product was filtered, washed, with ethanol and diethyl ether. The product was then isolated as a powder.

$[(\text{tpy})_2\text{Ir}(\mu\text{-Cl})_2]$ **D1**. Yellow powder, 89%. NMR characterizations were consistent with those previously reported [24]. ^1H NMR (300 MHz, CDCl_3 , ppm): 9.18 (d, $^3J=5.1$ Hz, 4H), 7.82 (d, $^3J=8.1$ Hz, 4H), 7.71 (t, $^3J=8.1$ Hz, 4H), 7.38 (d, $^3J=8.1$ Hz, 4H), 6.73 (t, $^3J=6.3$ Hz, 4H), 6.57 (d, $^3J=7.5$ Hz, 4H), 5.76 (s, 4H), 1.94 (s, 12H).

$[(\text{dfppy})_2\text{Ir}(\mu\text{-Cl})_2]$ **D2**. Yellow powder, 93%. NMR characterizations were consistent with those previously reported [25]. ^1H NMR (300 MHz, CDCl_3 , ppm): 9.15 (d, $^3J=6.0$ Hz, $^4J=1.5$ Hz, 4H), 8.32 (d, $^3J=8.4$ Hz, 4H), 7.85 (dt, $^3J=7.8$ Hz, $^4J=0.9$ Hz, 4H), 6.84 (m, 4H), 6.35 (m, 4H), 5.30 (d, $^3J=9.0$ Hz, $^4J=2.1$ Hz, 4H).

$[(\text{fppy})_2\text{Ir}(\mu\text{-Cl})_2]$ **D3**. Yellow powder, 97%. NMR characterizations were consistent with those previously reported [26]. ^1H NMR (300 MHz, CDCl_3 , ppm): 9.14 (d, $^3J=5.7$ Hz, 4H), 7.80 (m, 8H), 7.52 (dd, $^3J=8.4$ Hz, $^3J=5.7$ Hz, 4H), 6.81 (m, 4H), 6.53 (dt, $^3J=8.4$ Hz, $^4J=2.4$ Hz, 4H), 5.54 (dd, $^3J=9.9$ Hz, $^4J=2.4$ Hz, 4H).

$[(\text{ppy})_2\text{Ir}(\mu\text{-Cl})_2]$ **D4**. Yellow powder, 99%. NMR characterizations were consistent with those previously reported [27,28]. ^1H NMR (300 MHz, CDCl_3 , ppm): 9.25 (d, $^3J=5.4$ Hz, 4H), 7.88 (d, $^3J=8.1$ Hz, 4H), 7.75 (dt, $^3J=7.2$ Hz, $^4J=1.5$ Hz, 4H), 7.50 (dd, $^3J=7.8$ Hz, $^4J=1.2$ Hz, 4H), 6.77 (m, 8H), 6.57 (dt, $^3J=7.8$ Hz, $^4J=0.9$ Hz, 4H), 5.94 (d, $^3J=7.5$ Hz, 4H).

2.1.2. Synthesis of $\text{Ir}(\text{L})_2(\text{acac})$ C1–C4

To a suspension of the dimer $[(\text{L})_2\text{Ir}(\mu\text{-Cl})_2]$ (0.2 mmol) in 2-ethoxyethanol (30 mL) was added acetylacetone (60 mg, 0.6 mmol) and sodium carbonate (0.212 g, 2.0 mmol). The reaction mixture was stirred at reflux for 15 h. Then, water (50 mL) was added and the product was filtered and purified by chromatography on silica gel to be isolated as a powder.

$\text{Ir}(\text{tpy})_2(\text{acac})$ **C1**. Yellow powder (153 mg, 61%). NMR characterizations were consistent with those previously reported [29]. ^1H NMR (300 MHz, CDCl_3 , ppm): 8.49 (d, $^3J=5.4$ Hz, 2H), 7.81 (d,

$^3J=7.8$ Hz, 2H), 7.71 (t, $^3J=7.5$ Hz, 2H), 7.45 (d, $^3J=8.1$ Hz, 2H), 7.10 (m, 2H), 6.64 (d, $^3J=7.8$ Hz, 2H), 6.08 (s, 2H), 5.21 (s, 1H), 2.06 (s, 6H), 1.79 (s, 6H). HRMS (ESI) m/z : $[\text{M}]^+$. calcd for $\text{C}_{29}\text{H}_{27}\text{IrN}_2\text{O}_2$ 628.1702; found 628.1704.

$\text{Ir}(\text{dfppy})_2(\text{acac})$ **C2**. Yellow powder (135 mg, 51%). NMR characterizations were consistent with those previously reported [30]. ^1H NMR (300 MHz, CDCl_3 , ppm): 8.45 (d, $^3J=5.4$ Hz, 2H), 8.26 (d, $^3J=8.4$ Hz, 2H), 7.81 (dt, $^3J=7.8$ Hz, $^4J=1.2$ Hz, 2H), 7.20 (m, 2H), 6.34 (m, 2H), 5.67 (dd, $^3J=9.0$ Hz, $^4J=2.4$ Hz, 2H), 5.27 (s, 1H), 1.83 (s, 6H). HRMS (ESI) m/z : $[\text{M}]^+$. calcd for $\text{C}_{27}\text{H}_{19}\text{F}_4\text{IrN}_2\text{O}_2$ 672.10; found 672.1046.

$\text{Ir}(\text{fppy})_2(\text{acac})$ **C3**. Yellow powder (173 mg, 72%). Yellow powder (135 mg, 51%). NMR characterizations were consistent with those previously reported [16]. ^1H NMR (300 MHz, CDCl_3 , ppm): 8.45 (d, $^3J=6.0$ Hz, 2H), 7.78 (m, 4H), 7.55 (dd, $^3J=6.0$ Hz, $^3J=8.7$ Hz, 2H), 7.17 (m, 2H), 6.55 (dt, $^3J=9.0$ Hz, $^4J=2.4$ Hz, 2H), 5.87 (dd, $^3J=9.6$ Hz, $^4J=2.4$ Hz, 2H), 5.24 (s, 1H), 1.81 (s, 6H). HRMS (ESI) m/z : $[\text{M}]^+$. calcd for $\text{C}_{27}\text{H}_{21}\text{F}_4\text{IrN}_2\text{O}_2$ 636.1200; found 636.1207.

$\text{Ir}(\text{ppy})_2(\text{acac})$ **C4**. Yellow powder (154 mg, 64%). NMR characterizations were consistent with those previously reported [31,32]. ^1H NMR (300 MHz, CDCl_3 , ppm): 8.52 (d, $^3J=5.8$ Hz, 2H), 7.86 (d, $^3J=8.0$ Hz, 2H), 7.74 (dt, $^3J=7.4$ Hz, $^4J=1.4$ Hz, 2H), 7.56 (dd, $^3J=7.6$ Hz, $^4J=1.0$ Hz, 2H), 7.15 (dt, $^3J=5.8$ Hz, $^4J=1.4$ Hz, 2H), 6.82 (dt, $^3J=7.4$ Hz, $^4J=1.0$ Hz, 2H), 6.70 (dt, $^3J=7.4$ Hz, $^4J=1.8$ Hz, 2H), 6.28 (dd, $^3J=7.4$ Hz, $^4J=1.2$ Hz, 4H), 5.23 (s, 1H), 1.80 (s, 6H). HRMS (ESI) m/z : $[\text{M}]^+$. calcd for $\text{C}_{27}\text{H}_{23}\text{IrN}_2\text{O}_2$ 600.14; found 600.1412.

2.2. OLEDs fabrication and measurements

OLEDs were fabricated onto cleaned indium tin oxide (ITO) glass substrates with sheet resistance of 10–12 Ω/sq . Prior to organic layer deposition, the ITO substrates were successively washed with acetone and isopropanol in an ultrasonic bath for 10 min. Organic layers were then sequentially deposited onto the ITO substrate at a rate of 2–4 $\text{\AA}/\text{s}$ and a base pressure below 5×10^{-6} Torr. Aluminum cathode was formed with a shadow mask by thermal evaporation. Devices have the following general structure (see Fig. 3): ITO was used as a transparent anode electrode, MoO_3 (5 nm) as a hole injecting material/CBP (4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl) (35 nm) as a hole transporting layer/CBP doped with the iridium complexes as the emission layer (EML) (10 nm), TPBI (1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene) (40 nm) as an electron transporting material, LiF (0.6 nm) as an electron injecting material, and Al (80 nm) as a cathode electrode material. Doped layers were made by co-evaporation from carefully temperature controlled organic sources. All materials except the emitters used in the devices were purchased from Lumtec with the best purity available and used as received. Current density–Voltage–Luminance (J – V – L) measurements were carried out using Agilent 4156C and Minolta Chroma Meter CS-100. Devices were stored and characterized under nitrogen without encapsulation. Fig. 1 shows the schematic structure of the devices.

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