# A highly fluorinated iridium complex as a blue-green emitting component for white electroluminescence

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## ARTICLE INFO

## ABSTRACT

A novel perfluorinated heteroleptic iridium complex, namely iridium(III)bis[2-(2,5,2′,3′,4′,5′,6′-heptafluoro-biphenyl-4-yl)-pyridinato-N,C2′][3-(pentafluorophenyl)-pyridin-2-yl-1,2,4-triazolate] (Ir-F19), has been synthesized and characterized both in solution and in the solid state. The compound displays blue-green photoluminescence, with emission peaks at 480 and 512 nm and 68% quantum yield, in degassed acetonitrile solution. The use of this phosphor in blue and white organic light emitting devices (WOLEDs) has been investigated. Current efficiency of 8.3 cd/A at 100 cd/m$^2$ has been recorded for the blue emitting device whereas white electroluminescence with good color rendering index (CRI = 76) and CIE coordinates (0.43, 0.42) have been observed for a WOLED made of two stacked layers based on Ir-F19 and the commercial orange Ir(MDQ)$_2$(acac) [bis(2-methyldibenzo[f,h]quinoxaline)(acetylacetonate)iridium(III)]. WOLED luminous efficiency of 10.5 cd/A at 100 cd/m$^2$, almost constant (10.1 cd/A) up to 1000 cd/m$^2$, indicates that Ir-F19 is a promising blue-green emitting component for white electroluminescence.

## 1. Introduction

Heteroleptic iridium complexes [(CˆN)$_2$Ir(LX)] bearing two 2-aryl-pyridinate (CˆN) and one ancillary (LX) ligands are among the most promising phosphorescent emitters for optoelectronics and lighting applications [1–4]. They combine high quantum efficiencies, due to the strong spin-orbit coupling of heavy metal phosphors [5,6], with easier synthetic accessibility versus their homoleptic Ir(CˆN)$_3$ counterparts [7,8], as well as tunable emission wavelength by proper chemical design and functionalization of the organic ligands [9–13]. In particular, fluorinated iridium complexes attract attention as effective and not so numerous blue phosphors for fabrication of blue and white organic light emitting devices (OLEDs). In fact, fluorination is a suitable functionalization to blue-shift light emission, to increase volatility favouring vapour deposition, to enhance electron mobility, and to prevent close packing that can cause electroluminescence self-quenching of molecular active materials in devices [14–16]. Moreover, fluorine atoms bound to ancillary ligands can be effective tools to afford iridium emitters with good performances in devices [17,18].

White electroluminescence in OLEDs can result from simultaneous emission of three (red, green and blue) or two (most commonly blue and orange) emitting components blended in a single host material or confined in different stacked layers. An advantage of white OLED (WOLED) architectures based on emitters confined in different layers consists in (i) inhibition of complete energy transfer, which is a major issue in electroluminescence from blends, eventually leading to the emission from the sole low energy (orange/red) emitter, and (ii) good control of white colour emission by individually optimizing the thickness and the emitter concentration in each of the stacked layer. Nevertheless, stacked white OLEDs manufacture is more complex than solution processing of blends of different emitters. On this ground, the use of two layers with complementary (blue and orange) emission colours is desirable versus stacking three layers emitting fundamental colours. Examples of WOLEDs based on vacuum deposited stacked layers of two iridium complexes emitting complementary colours (blue and orange) are quite limited. For example, white electroluminescence was obtained by Yu et al., with a maximum current efficiency of 11.08 cd/A, using the sky-blue iridium(III)[bis(4,6-difluorophenyl)-

pyridinato-N,C$^{2\prime}$]picolinate complex (FIrpic) and the yellow complex bis[2-(4-tertbutylphenyl)benzothiazolato-N,C$^{2\prime}$]iridium(acetylaceto-nate) in a two stacked layer device architecture [19]. Deng et al. also used the same approach to fabricate a white OLED with FIrpic and a tailored orange diphenylphosphorylpyridine-iridium complex, achieving an efficiency of 23.9 cd/A with CIE coordinates (0.29, 0.43) [20]. However, apart from few exceptions [21], most devices based on two stacked emitting layers suffer from colour rendering index values (CRI < 70) lower than those of three layer devices [22]. Moreover, their luminous efficiency generally rolls off by increasing brightness and current density, as a combined effect of field-induced quenching and triplet–triplet annihilation [23,24]. Among exceptions, high current efficiency of 54.8 cd/A at high brightness (5000 cd/m$^2$) were reported by Wang et al. for a device based on two stacked emitting layers of FIrpic and an orange iridium complex with trifluoromethyl substituted 2-phenylbenzothiazole ligands [25]. Sasabe et al. recorded a CRI of 73 for a two-color WOLED using a blue emitting cyclometalated carbene iridium complex and the yellow emitter bis(2-phenylbenzothia-zolato)(acetylacetonate)iridium(III) [26].

Here we report the synthesis and the photophysical characterization of a new heteroleptic iridium complex (Ir-F19 in Fig. 1), bearing highly fluorinated cyclometalating ligands and acting as an efficient blue/green phosphor. A two-color based stacked WOLED with CRI of 76, CIE coordinates (0.43, 0.42) and 10.5 cd/A luminous efficiency at 100 cd/m$^2$, almost constant (10.1 cd/A) up to 1000 cd/m$^2$, has been constructed using Ir-F19 as the blue component in combination with the commercial orange emitter bis(2-methyldibenzo[f,h]quinoxaline)(acet-ylacetonate)iridium [Ir(MDQ)$_2$(acac), Fig. 1].

## 2. Experimental

### 2.1. Synthesis of Ir-F19

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran, 1,4-dioxane and toluene were distilled immediately prior to use from sodium and benzophenone. All reagents and catalysts were purchased at the highest commercial purity degree from Sigma Aldrich. The ancillary ligand 4 was prepared according to the literature [27]. Column chromatography was carried out on silica gel 60, (40–63 μm) from Merck, whereas Merck silica gel 60 F254 aluminum sheets were used for thin layer chromatography. The products were characterized by high resolution mass spectrometry, FT-IR, $^1$H-, $^{13}$C-, and $^{19}$F NMR spectroscopies. Mass spectrometry was carried out by a Shimadzu high performance liquid chromatography-ion trap-time of flight mass spectrometer (LCMS-IT-TOF). FT-IR spectroscopy was performed by a Perkin–Elmer Spectrum BX spectrophotometer with dry KBr pellets. $^1$H-, $^{13}$C- and $^{19}$F NMR spectra were recorded at 400, 100 and 376 MHz, respectively, by Varian Inova 400 and Agilent Technologies 500/54 Premium Shielded spectrometers. The residual proton signals of CDCl$_3$ and CD$_2$Cl$_2$ at $\delta$ = 7.26 and 5.36 ppm, respectively, were used as references for the $^1$H NMR spectra, while the signals of CDCl$_3$ and CD$_2$Cl$_2$ at $\delta$ = 77.0 and 53.8 ppm were used as

references for the $^{13}$C NMR spectra. The $^{19}$F signal of trichlorofluor-omethane was used as the internal standard at $\delta$ = 0.0 ppm for the $^{19}$F NMR spectra. Melting points were determined on a Stuart Scientific Apparatus SMP3 (UK).

### 2.1.1. Synthesis of 2-(4-bromo-2,5-difluoro-phenyl)-pyridine (1)

In a 100 mL three-necked round bottom flask, the catalyst Pd (AsPh$_3$)$_4$ was prepared *in situ* by suspending Pd$_2$(dba)$_3$ (0.400 g, 0.44 mmol) and triphenylarsine (1.080 g, 3.52 mmol) in toluene (45 mL) at room temperature, under a nitrogen atmosphere. After few minutes, 1,4-dibromo-2,5-difluorobenzene (4.000 g, 14.70 mmol) and a solution of tributyl(pyridin-2-yl)stannane (5.960 g, 16.20 mmol) in toluene (15 mL) were added in sequence, under a nitrogen atmosphere. The resulting reaction mixture was stirred for 12 h at 90 °C. After cooling to room temperature, the solvent was distilled under vacuum. Then water (30 mL) was added and the crude product was extracted three times with diethyl ether (3 × 30 mL). The combined organic extracts were concentrated to a final volume of 30 mL by vacuum distillation and, after addition of a solution of KF (4 g) in distilled water (10 mL), solid organotin by-products were filtered off. The organic solution was dried with anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The product **1** was isolated in 45% yield by column chromatography over silica gel, using a mixture of hexane and ethyl acetate (volume ratio 95:5) as the eluent. Mp: 87 − 88 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29 (ddd, $J$ = 7.3, 4.8, 1.3 Hz, 1H), 7.39 (dd, $^3J_{HF}$ = 10.0, $^4J_{HF}$ = 5.5 Hz, 1H), 7.77 (td, $J$ = 7.3, 1.8 Hz, 1H), 7.79–7.83 (m, 1H), 7.88 (dd, $^3J_{HF}$ = 9.3, $^4J_{HF}$ = 6.7 Hz, 1H), 8.71 (ddd, $J$ = 4.8, 1.8, 1.0 Hz, 1H) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 109.50 (dd, $^2J_{CF}$ = 23.9, $^3J_{CF}$ = 10.2 Hz), 117.51 (dd, $^2J_{CF}$ = 26.1, $^3J_{CF} \sim$ 3.9 Hz), 121.05 (d, $^2J_{CF}$ = 28.7 Hz), 123.15, 124.28 (d, $^4J_{CF}$ = 11.0 Hz), 127.95 (dd, $^2J_{CF}$ = 13.7, $^3J_{CF}$ = 6.7 Hz), 136.65, 149.88, 151.22 (dd, $^3J_{CF}$ = 3.3, $^4J_{CF}$ = 1.4 Hz), 155.88 (dd, $^1J_{CF}$ = 243.9, $^4J_{CF}$ = 2.7 Hz), 155.91 (dd, $^1J_{CF}$ = 250.1, $^4J_{CF}$ = 2.7 Hz) ppm. $^{19}$F NMR (500 MHz, CDCl$_3$): $\delta$ −121.12 ÷ −121.02 (m, 1F), −113.75 ÷ −113.63 (m, 1F) ppm. FTIR (KBr): $\nu$ = 3029, 1767, 1620, 1593, 1572, 1490, 1463, 1439, 1390, 1290, 1174, 1159, 1070, 993, 891, 797, 781, 741, 723, 697, 619 cm$^{-1}$. HRMS: [M + H]$^+$ $m/z$ calcd 269.9724, found 269.9701.

### 2.1.2. Synthesis of 2-(2,5,2′,3′,4′,5′,6′-heptafluoro-biphenyl-4-yl)-pyridine (2)

In a 250 mL three-necked round bottom flask, magnesium powder (0.600 g, 24.7 mmol) was suspended in dry THF (35 mL) and activated by adding one little grain of iodine, under a nitrogen atmosphere. Then, the suspension was heated to reflux and a solution of bromopenta-fluorobenzene (5.080 g, 20.6 mmol) in dry THF (5 mL) was added dropwise by a dropping funnel. The reaction mixture was stirred at 90 °C for two hours and the complete conversion of bromopentafluor-obenzene into pentafluorophenyl magnesium bromide was confirmed via GC/MS analysis observing the presence of deuteropentafluoroben-zene after quenching a small sample of the mixture with deuterium oxide. After cooling to room temperature, sequential additions of CuBr (5.900 g, 41.1 mmol), dry 1,4-dioxane (20 mL) and a solution of **1** (1.390 g, 5.14 mmol) in dry toluene (40 mL) were respectively carried out, under a nitrogen atmosphere, waiting one hour between each addition. Then, the system was heated overnight at 90 °C. The complete disappearance of **1** was confirmed after 12 h via TLC. After cooling to room temperature, the organic solvents were distilled at reduced pressure and the crude product dissolved into diethyl ether (50 mL). The solution was filtered to remove inorganic salts, washed with water (30 mL) and then dried with anhydrous sodium sulphate. After the distillation of the solvent at reduced pressure, the organic ligand **2** was isolated in 84% yield by column chromatography, using a mixture of hexane and dichloromethane (volume ratio 30: 70) as the eluent.

Yield: 84%. Mp: 149–150 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.20 (dd, $^3J_{HF}$ = 10.5, $^4J_{HF}$ = 5.5 Hz, 1H), 7.34 (ddd, $J$ = 7.5, 4.8, 1.2 Hz, 1H),
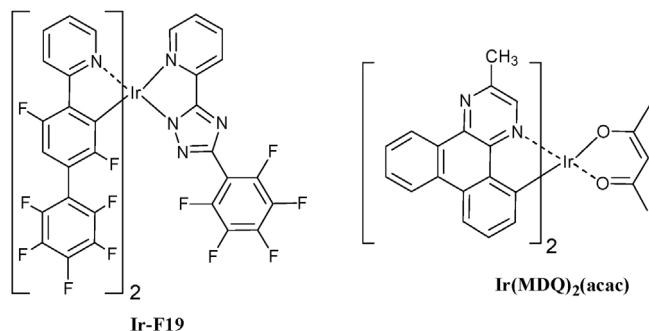


**Fig. 1.** Chemical structures of Ir-F19 and Ir(MDQ)$_2$(acac) emitters.