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Heteroleptic iridium (III) complexes with three different ligands: Unusual triplet emitters for light-emitting electrochemical cells



Marc Lepeltier ^a, Bernadette Graff ^b, Jacques Lalevée ^b, Guillaume Wantz ^{c, d}, Malika Ibrahim-Ouali ^e, Didier Gigmes ^f, Frédéric Dumur ^{d, f, *}

^a Institut Lavoisier de Versailles, UMR 8180 CNRS, Université de Versailles Saint-Quentin en Yvelines, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France

^b Institut de Science des Matériaux de Mulhouse IS2M, UMR 7361 CNRS, Université de Haute Alsace, 15 rue Jean Starcky, 68057 Mulhouse Cedex, France

^c Bordeaux INP, Univ. Bordeaux, CNRS, IMS, UMR 5218, F-33400 Talence, France

^d CNRS, IMS, UMR 5218, F-33400 Talence, France

^e Aix Marseille Université, Centrale Marseille, ISm2 UMR 7313, 13397 Marseille, France

^f Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire ICR, UMR 7273, F-13397 Marseille, France

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ABSTRACT

Two cationic iridium (III) complexes **[Ir(dfppy)(tpy)(bpy)](PF6)** and **[Ir(dfppy)(tpy)(phen)](PF6)** bearing three different ligands were tested as triplet emitters for Light-Emitting Electrochemical Cells (LECs). These two phosphorescent materials only constitute the third and fourth examples of triple heteroleptic cationic iridium complexes to be tested in electroluminescent devices. LECs fabricated with this almost unknown class of iridium complex furnished green-emitting devices. Parallel to investigations devoted to electroluminescent properties, photophysical and electrochemical properties of the two new complexes were examined. Density functional theory calculations were also performed to provide insight into the electronic structure of the two emitters.

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1. Introduction

During the past decade, light-emitting electrochemical cells (LECs) have aroused great interest as promising candidates for next generation solid-state light sources [1–6]. LECs possess many advantages over the traditional organic light-emitting diodes (OLEDs) including simple architecture, solution processing and air-stable electrodes [7–9]. Compared to polymer-based LECs that require a light-emitting material, a polymer electrolyte and an inorganic salt, ionic transition metal complexes (iTMCs)-based LECs are simpler to fabricate than the polymer ones [10–13]. Typically and due to the intrinsic charge transport ability of ionic complexes, no additional polymer electrolyte or inorganic salts are required and the emissive layer of iTMCs-based LECs can only be composed of a neat film of complex [14–16]. However, to accelerate the doping process at both

E-mail address: frederic.dumur@univ-amu.fr (F. Dumur).

electrodes, an ionic liquid is often admixed with the metal complex [17,18]. Beyond the simple easiness of fabrication, iTMC-based LECs comprise a phosphorescent emitter with which both singlet and triplet excitons can be harvested for light emission, enabling to achieve 100% internal quantum efficiency [19]. Therefore, from the performance point of view, iTMC-based LECs can reach higher performances and luminances than their polymeric analogues by harvesting both types of excitons. Among all iTMCs-based LECs, those based on iridium have been the most widely studied [20,21]. As appealing features, emission color of iridium complexes can be easily tuned from blue [22,23] to red [24–26] with all intermediate colors such as green [27,28], yellow [29-32] and orange [33,34]. Cationic iridium complexes can also be synthesized in high yields contrarily to the neutral tris-cyclometalated iridium complexes that are the most stable for OLED applications but that can only be prepared with reaction yields ranging from 10 to 25% [35–39].

To date, iridium complexes bearing three different ligands are extremely rare and only 13 complexes have been reported in the literature [40–45]. More precisely, among them, only two *tris*-heteroleptic cationic complexes with two different cyclometalated

^{*} Corresponding author. Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire ICR, UMR 7273, F-13397 Marseille, France.

ligands are known (see Fig. 1), the eleven others being neutral complexes [41,42]. This new and as yet unknown class of cationic complexes still suffers from the low availability of synthetic procedures to access to these structures. Typically, the third ligand of iridium complexes is introduced by a bridge-splitting and substitution reaction of the μ -dichloride-bridged iridium dimer, this latter being itself prepared by mixing one equivalent of iridium trichloride hydrate with two equivalents of the same ligand (see Scheme 1) [46–49]. Using this approach, the synthesis of *bis*-heteroleptic iridium complexes is thus limited to two steps.

On the opposite, synthesis of *tris*-heteroleptic iridium complexes requires more steps and a higher level of sophistication. These complexes can only be prepared in four steps, as exemplified by the synthetic procedure depicted in the Scheme 2. The key point of this strategy is the convenient choice of the two cyclometalated ligands C^{\n} and C'^{\n'}. Indeed, mixing these two ligands with IrCl₃·3H₂O gives a statistical mixture of six different dimers (see Scheme 2, step 1). This inseparable mixture is then engaged in reaction with acetylacetone (acac) to furnish after reaction three different complexes (step 2). At this stage, the two homoleptic complexes Ir(C^{\n})₂(acac) and Ir(C'^{\n'})₂(acac) must have a sufficient difference of polarity with the targeted heteroleptic complex Ir(C^{\n})(C'^{\n'})(acac) to be separable by simple chromatography on silica gel [42,44]. The second key point is the regeneration of the pure [Ir(C^{\n}N)(C'^{\n'})µ-Cl]₂ dimer under acidic conditions (step 3).

Finally, bridge splitting and substitution reaction with the cyclometalated ancillary ligand N^N furnish the desired cationic *tris*-heteroleptic complex $Ir(C^N)(C^N)(N^N)^+$ (step 4). If at first sight, examination of such sophisticated complexes in devices can seem counter-intuitive, tris-heteroleptic complexes allow a high control of the emission wavelength without taking recourse to fluorination of the cyclometalated ligands. Indeed, since the pioneer works on iridium-based emitters, fluorination of the cyclometalated ligands has been extensively used and proved to be an effective tool to blue-shift the emission of complexes with a precision of 5–10 nm [50]. However, numerous works have recently evidenced the limitations of this strategy, defluorination of ligands occurring during complex synthesis [51–53] or during device operation [54,55]. Parallel to this, a correlation between device lifetime and fluorine content of the emitters has recently been established, with a significant reduction of the device lifetime with increasing the fluorine content of the emitters [56]. A 4-fold decrease in the lifetime was notably observed upon doubling the number of fluorine atoms per complex [57]. Face to defluorination and with aim at still maintaining a high control on the emission wavelength without sacrificing the device stability, alternatives

F + (V + V) +

Fig. 1. Cationic *tris*-heteroleptic *bis*-cyclometalated iridium (III) complexes reported in the literature.





Scheme 1. Synthetic route to cationic bis-heteroleptic complexes.

enabling to lower the fluorine content per complex have been searched [58], as exemplified with ionic triple heteroleptic complexes. Notably, recent works have evidenced the phosphorescence maximum of triple heteroleptic complexes $Ir(C^N)(C'^N')(N^N)^+$ to lie between those of the corresponding *bis*-heteroleptic complexes $Ir(C^N)_2(N^N)^+$ and $Ir(C'^N')_2(N^N)^+$ [43]. Therefore, without taking recourse to time-consuming theoretical calculations and prior to any synthesis, emission maximum of a triple heteroleptic complex can be anticipated with a precision of 3-5 nm, knowing the structure of the two cyclometalated ligands and the ancillary ligand that will be used to synthesize the complex. In this context, two new tris-heteroleptic cationic complexes [Ir(dfppy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆) differing by their N^N ligands have been synthesized and tested as light-emitting materials in LECs (see Fig. 2). Noticeably, [Ir(dfppy)(tpy)(phen)](PF₆) that bears the most rigid N^N ligand gave the best performances. The two complexes were also characterized by UV-visible absorption and photoluminescence spectroscopy as well as cyclic voltammetry. TD-DFT calculations were also carried out.

2. Experimental details

2.1. General information

¹H and ¹³C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer equipped with a QNP probe head: ¹H (300 MHz) and ¹³C (75 MHz). The ¹H chemical shifts were referenced to the solvent peak: CDCl₃ (7.26 ppm), and the 13 C chemical shifts were referenced to the solvent peak: CDCl₃ (77.0 ppm). All starting materials and solvents were purchased from Aldrich or Lumtec and used as received commercially. Absorption and emission spectra were recorded with a UV MC2 spectrophotometer from the SAFAS Monaco Society and a Photon Technology International spectrofluorimeter. Absolute fluorescence quantum yields in solution and in the solid state were measured by a Hamamatsu Photonics Quantaurus QY at room temperature. Cyclic voltammetry (CV) was performed using an EG & G 273 A driven by a PC with the M270 software at a scan rate of 100 mV/s, at room temperature in dichloromethane solution (10^{-3} M) , with tetrabutylammonium hexafluorophosphate at 0.1 M concentration as the supporting electrolyte. All measurements were carried out in a nitrogen filled glovebox (O2 and $H_2O < 0.1$ ppm). The working and the counter electrodes were a Pt disc and a Pt wire respectively, whereas Ag wire was used as a



Scheme 2. Synthetic route to cationic tris-heteroleptic complexes.

pseudo-reference electrode. Ferrocene was used as the internal standard material.

isolated as a yellow powder (1.2 g, 75% yield).

2.2. Synthetic procedures

2.2.1. Mixture of dimers

To a solution (50 mL) of 2-(2,4-difluorophenyl)pyridine (0.521 g, 2.73 mmol) and 2-(4-methylphenyl)pyridine (0.461 g, 2.73 mmol) in a mixture 2-ethoxyethanol/water (80: 20) was added IrCl₃·xH₂O (0.94 g, 2.73 mmol). The reaction mixture was stirred at reflux for 24 h. Then water (50 mL) was added and the precipitate was filtrated off, washed with water and ethanol. The mixture of dimers is

2.2.2. $Ir(C^N)_2(acac)$

To a solution of the mixture of dimers (1.2 g, 1.02 mmol) in 2ethoxyethanol (50 mL) was added acetylacetone (0.512 g, 5.12 mmol) and sodium carbonate (1.08 g, 10.2 mmol). The reaction mixture was refluxed for 15 h. Then, water (50 mL) was added and the precipitate was filtered off and washed with ethanol. The three different products were then separated by chromatography on silica gel with a gradient of petroleum ether and dichloromethane as eluent from (50:50) to (0:100). The products were isolated as yellow powders.



Fig. 2. Structures of the two complexes investigated in this study.

2.2.2.1. $Ir(dfppy)_2(acac)$. (0.24 g, 18%): ¹H NMR (300 MHz, CDCl₃, 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). MS (ESI) Calcd for C₂₇H₁₉F₄IrN₂O₂ 672.1012; Found 672.1046.

2.2.2.2. Ir(dfppy)(tpy)(acac). (0.414 g, 31%): ¹H NMR (300 MHz, CDCl₃, ppm): 8.53 (d, ⁴J = 5.1 Hz, 1H), 8.41 (dd, ³J = 6.0 Hz, ⁴J = 1.2 Hz, 1H), 8.25 (dd, ³J = 8.7 Hz, ⁴J = 2.7 Hz, 1H), 7.78 (m, 3H), 7.47 (d, ³J = 7.5 Hz, 1H), 7.15 (m, 2H), 6.69 (d, ³J = 7.8 Hz, 1H), 6.29 (d, ³J = 7.8 Hz, 1H), 6.01 (s, 1H), 5.72 (dd, ³J = 8.7 Hz, ⁴J = 2.7 Hz, 1H), 5.23 (s, 1H), 2.08 (s, 3H), 1.81 (s, 3H), 1.79 (s, 3H). MS (ESI) Calcd for C₂₈H₂₃F₂IrN₂O₂ 650.1357; Found 650.1352.

2.2.2.3. $Ir(tpy)_2(acac)$. (0.28 g, 22%): ¹H NMR (300 MHz, CDCl₃, 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). MS (ESI) Calcd for C₂₉H₂₇IrN₂O₂ 628.1702; Found 628.1704.

2.2.3. $Ir(C^N)_2Cl_2Ir(C^N)_2$

To a suspension of *HC*^N (3.5 mmol) (2-(2,4-difluorophenyl) pyridine or 2-(4-methylphenyl)pyridine) in 2-ethoxyethanol/water (75: 25, 40 mL) was added IrCl₃·3H₂O (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 yellow powders.

2.2.3.1. $Ir(dfppy)_2Cl_2Ir(dfppy)_2$. (0.53 g, 93%). ¹H NMR (300 MHz, CDCl₃, ppm): 9.15 (d, ³*J* = 6.0 Hz, ⁴*J* = 1.5 Hz, 4H), 8.32 (d, ³*J* = 8.4 Hz, 4H), 7.85 (dt, ³*J* = 7.8 Hz, ⁴*J* = 0.9 Hz, 4H), 6.84 (m, 4H), 6.35 (m, 4H), 5.30 (d, ³*J* = 9.0 Hz, ⁴*J* = 2.1 Hz, 4H). MS (ESI) Calcd for C₄₄H₂₄Cl₂F₈Ir₂N₄ 1216.0509; Found 1216.0514.

2.2.3.2. $Ir(tpy)_2Cl_2Ir(tpy)_2$. (0.5 g, 89%). ¹H NMR (300 MHz, CDCl₃, 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, 12 H). MS (ESI) Calcd for C₄₈H₄₀Cl₂Ir₂N₄ 1128.1889; Found 1128.1906.

2.2.4. *Ir(dfppy)(tpy)Cl₂Ir(dfppy)(tpy)*

To a solution of Ir(dfppy)(tpy)(acac) (0.4 g, 0.615 mmol) in dichloromethane (20 mL) was added at 0 °C a solution of HCl in diethyl ether (1.2 mol L⁻¹, 10 mL). The reaction mixture was stirred for 1 h. Then, methanol (30 mL) was added and the dichloromethane was evaporated. The methanol solution was then filtered off and the product was isolated as a yellow powder (0.306 g, 85% yield). ¹H NMR (300 MHz, CDCl₃, ppm): 9.21 (m, 1H), 9.11 (m, 1H), 8.29 (m, 1H), 7.82 (m, 3H), 7.42 (m, 1H), 6.81 (m, 2H), 6.65 (m, 1H),

6.31 (m, 1H), 5.68 (m, 1H), 5.38 (m, 1H), 1.97 (s, 3H). MS (ESI) Calcd for C₄₆H₃₂Cl₂F₄Ir₂N₄ 1172.1199; Found 1172.1204.

2.2.5. $[Ir(C^N)_2(N^N)](PF_6)$

To a solution of the dimer $Ir(C^N)_2Cl_2Ir(C^N)_2$ (0.128 mmol) $(Ir(dfppy)_2Cl_2Ir(dfppy)_2, Ir(tpy)_2Cl_2Ir(tpy)_2 or Ir(dfppy)(tpy)Cl_2Ir(dfp$ $py)(tpy)) in 1,2-dichloroethane (20 mL) was added the N^N ligand$ (0.32 mmol) (2,2'-bipyridine or 1,10-phenanthroline). The reactionmixture was refluxed for 2 h. Then, a saturated solution of sodiumhexafluorophosphate in methanol (5 mL) was added. The reactionmixture was stirred at room temperature for 30 min. Then thesolvent was evaporated and dichloromethane (50 mL) was added.The solution was filtered, the solvent was reduced and the productwas precipitated by addition of diethyl ether (50 mL). The productwas then filtered and purified by flash chromatography on silica gelusing a gradient of dichloromethane and methanol from (100:0) to(90:10) as eluent. The product was isolated as a yellow powder.

2.2.5.1. $[Ir(dfppy)(tpy)(bpy)](PF_6)$. (0.18 g, 82%), ¹H NMR (300 MHz, CDCl₃, ppm): 9.53 (d, ³*J* = 7.8 Hz, 2H), 8.29 (m, 3H), 7.83 (m, 5H), 7.60 (d, ³*J* = 8.1 Hz, 1H), 7.47 (m, 3H), 7.39 (d, ³*J* = 5.4 Hz, 1H), 7.06 (t, ³*J* = 6.0 Hz, 1H), 6.98 (td, ³*J* = 7.2 Hz, ⁴*J* = 0.9 Hz, 1H), 6.90 (dd, ³*J* = 8.1 Hz, ⁴*J* = 6.9 Hz, 1H), 6.52 (m, 1H), 6.01 (s, 1H), 5.76 (dd, ³*J* = 8.7 Hz, ⁴*J* = 2.4 Hz, 1H), 2.16 (s, 3H). MS (ESI) Calcd for $[C_{33}H_{24}F_{2}IrN_{4}]^{+}$ 707.1600 Found 707.1595. Anal. calcd for $C_{33}H_{24}F_{8}IrN_{4}P$: C 46.53, H 2.84, N 6.58, Anal. found: C 46.36, H 3.04, N 6.75.

2.2.5.2. $[Ir(dfppy)(tpy)(phen)](PF_6)$. (0.185 g, 82%), ¹H NMR (300 MHz, CDCl₃, ppm): 9.05 (d, ³*J* = 7.8 Hz, 1H), 8.99 (d, ³*J* = 8.1 Hz, 1H), 8.51 (m, 2H), 8.32 (m, 2H), 8.24 (d, ³*J* = 4.8 Hz, 1H), 7.97 (m, 2H), 7.90 (d, ³*J* = 7.8 Hz, 1H), 7.75 (m, 2H), 7.65 (d, ³*J* = 7.8 Hz, 1H), 7.38 (d, ³*J* = 5.7 Hz, 1H), 7.24 (d, ³*J* = 5.7 Hz, 1H), 6.97 (m, 2H), 6.88 (t, ³*J* = 6.6 Hz, 1H), 6.59 (m, 1H), 6.13 (s, 1H), 5.88 (dd, ³*J* = 8.1 Hz, ⁴*J* = 2.4 Hz, 1H), 2.22 (s, 3H). MS (ESI) Calcd for $[C_{35}H_{24}F_{2}IrN_{4}]^{+}$ 731.1600; Found 731.1613. Anal. calcd for $C_{35}H_{24}F_{8}IrN_{4}P$: C 48.00, H 2.76, N 6.40, Anal. found: C 47.94, H 2.86, N 6.45.

2.2.5.3. $[Ir(dfppy)_2(bpy)](PF_6)$. (0.17 g, 77%). ¹H NMR (300 MHz, CDCl₃, ppm): 8.34 (m, 4H), 7.87 (m, 6H), 7.50 (m, 4H), 7.10 (m, 2H), 6.60 (m, 2H), 5.71 (d, ³J = 8.4 Hz, 2H). MS (ESI) Calcd for $[C_{32}H_{20}F_4IrN_4]^+$ 729.1248; Found 729.1245.

2.2.5.4. $[lr(tpy)_2(bpy)](PF_6)$. (0.18 g, 86%).¹H NMR (300 MHz, CDCl₃, ppm): 9.61 (m, 2H), 8.26 (m, 2H), 7.87 (m, 4H), 7.74 (t, ³*J* = 7.5 Hz), 7.59 (d, ³*J* = 8.1 Hz, 2H), 7.42 (m, 4H), 6.95 (m, 2H), 6.86 (d, ³*J* = 7.8 Hz), 6.10 (s, 2H), 2.15 (s, 6H). MS (ESI) Calcd for $[C_{34}H_{28}IrN_4]^+$ 685.1938; Found 685.1941.

2.2.5.5. $[Ir(dfppy)_2(phen)](PF_6)$. (0.2 g, 88%) ¹H NMR (300 MHz, CDCl₃, ppm): 8.79 (d, ³*J* = 8.4 Hz, 2H), 8.32 (m, 6H), 7.92 (m, 2H), 7.78 (t, ³*J* = 7.5 Hz, 2H), 7.35 (d, ³*J* = 5.4 Hz, 2H), 6.98 (t, ³*J* = 6.9 Hz, 2H), 6.40 (m, 2H), 5.80 (dd, ³*J* = 8.4 Hz, ⁴*J* = 1.8 Hz, 2H). MS (ESI) Calcd for $[C_{34}H_{20}F_4IrN_4]^+$ 753.1248; Found 753.1247.

2.2.5.6. $[Ir(tpy)2(phen)](PF_6)$. (0.14 g, 64%). ¹H NMR (300 MHz, CDCl₃, ppm): 8.75 (m, 2H), 8.28 (m, 4H), 7.88 (m, 4H), 7.71 (m, 2H), 7.63 (d, ³*J* = 7.2 Hz, 2H), 7.32 (m, 2H), 6.92 (d, ³*J* = 7.2 Hz, 2H), 6.87 (m, 2H), 6.22 (s, 2H), 2.19 (s, 6H). MS (ESI) Calcd for $[C_{36}H_{28}IrN_4]^+$ 709.1945; Found 709.1937.

2.3. LECs fabrication and measurements

All materials used for the device fabrication were purchased from Lumtec with the best purity available and used as received. LECs 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, ethanol and isopropanol in an ultrasonic bath for 10 min before surface treatment with UV-ozone plasma for 20 min. This was followed by coating a 40 nm thick layer of poly(ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) on the treated ITO sheets at 4000 rpm for 60 s. The film was baked at 120 °C for 30 min under reduced pressure and the substrates were loaded in a glove box. The solutions of complexes ([Ir(dfppy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆), 20 mg/mL) and ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM.PF₆, 20 mg/mL) in chloroform (mixture in a 1:1 v/v ratio) were spin coated onto the substrate at 500 rpm for 60 s and then the light emitting layer was baked at 80 °C under inter atmosphere for 2 h 30. The substrates were transferred into a metal evaporating chamber and let for 60 h under secondary vacuum $(P < 4 \cdot 10^{-7} \text{ mbar})$ to remove all traces of water and solvents. Finally, an aluminum cathode (80 nm) was evaporated under secondary vacuum. The EL spectra, CIE coordinates, current-voltage and brightness-voltage characteristics of the devices were recorded with an External Quantum Efficiency Measurement System (model C9920-12) of Hamamatsu Photonics K.K. The device configuration is presented in the Fig. 3.

2.4. Theoretical calculations

Molecular orbitals calculations were carried out using the Gaussian 03 suite of programs [59,60]. The electronic absorption spectra for the different compounds were calculated with the time dependent density functional theory at B3LYP/LANL2DZ level on the relaxed geometries calculated at B3LYP/LANL2DZ level. The geometries were frequency checked (no imaginary frequencies).

3. Results and discussion

3.1. Synthesis of [Ir(dfppy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆)

The complexes [Ir(dfppy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆) were synthesized by the classical procedure by reacting the dimer $Ir(dfppy)(tpy)Cl_2Ir(dfppy)(tpy)$ with two equivalents of the corresponding N^N ligand (2,2'-bipyridine or phenanthroline) with good yield (82% each). The pure mixed dimer was obtained in 3 steps following the established procedure (see Scheme 3). The full assignation of the proton signals remains a real challenge. The ¹H NMR signals were attributed only for one complex i.e. **[Ir(dfppy)(tpy)(bpy)](PF_6)** with the combination of multiple NMR analysis (¹H, ¹³C, HSQC, COSY ¹H-¹H and HMBC) as shown on Fig. 4. It hasn't been possible to distinguish the pyridine rings E and F of the bpy ligand but they are not equivalent. The same difficulty was observed for the pyridine ring A and D of the ligands dfppy and tpy. No assignment was possible for the second complex **[Ir(dfppy)(tpy)(phen)](PF_6)** as a result of more NMR signals overlapping each other.

3.2. Photophysical properties

Fig. 5 shows the UV-visible absorption and photoluminescence emission spectra of the two complexes in dichloromethane solutions at room temperature. The UV-visible absorption spectra of the two complexes displays broad and intense absorption bands in the UV region centered on 300 nm assigned to the spin-allowed ligand centered (LC) ${}^{1}\pi-\pi$ transitions on cyclometalated ligands. Along with these high intense LC bands, less intense absorption bands are observed from 320 nm to 500 nm which correspond to spin-allowed metal-to-ligand charge-transfer (¹MLCT), spinforbidden metal-to-ligand charge-transfer (³MLCT), ligand-toligand charge-transfer (³LLCT and ¹LLCT) and ligand-centered (LC) ${}^{3}\pi-\pi$ transitions. Excitation at 350 nm produces a broad and structureless emission centered at 544 and 556 nm for [Ir(dfppy)(tpy)(phen)](PF₆) and [Ir(dfppy)(tpy)(bpy)](PF₆) respectively (See Table 1). These featureless emission peaks are indicative of the emissive excited states to have ³MLCT or ³LLCT characters rather than a LC ${}^{3}\pi-\pi$ character [61,62]. While comparing their respective photoluminescence quantum yields and luminescence lifetimes, almost similar values were determined for the two complexes (0.97 μ s and $\phi = 0.63$ for **[Ir(dfppy)(tpy)(bpy)](PF₆)**, 0.66 μ s and $\phi = 0.66$ for **[Ir(dfppy)(tpy)(phen)](PF₆)** respectively). These results are consistent with their similarity of structures and unsurprisingly to photophysical properties previously reported in the similar complexes, as exemplified literature for bv



Fig. 3. Device structure and energy levels of the materials employed in this work.



Scheme 3. Syntheses of [Ir(dfppy)(tpy)(bpy)](PF6) and [Ir(dfppy)(tpy)(phen)](PF6).

[Ir(dfppy)(ppy)(tert-bpy)]PF₆ (tert-bpy = 4,4'-di-tert-butyl-2,2'bipyridine) (0.99 µs and φ = 0.59) which exhibits a closely related structure [43]. Finally, investigation of the photophysical properties of the two complexes in thin films with 1-butyl-3methylimidazolium hexafluorophosphate (1:1 ratio) showed the emission maxima in thin films to superimpose those measured in solution. Only a slight reduction of the photoluminescence quantum yields in thin films compared to solution was determined and this result is consistent with the presence of well-separated complexes in thin films resulting from the high amount of 1-butyl-3methylimidazolium hexafluorophosphate (1:1 ratio). In the introduction section, we mentioned that the emission wavelengths of triple heteroleptic complexes could be anticipated prior to synthesis knowing the structure of the two cyclometalated ligands as well as the ancillary ligand [43]. This point was verified with **[Ir(dfppy)(tpy)(bpy)](PF₆)** and **[Ir(dfppy)(tpy)(phen)](PF₆)**. Fig. 6 shows the photoluminescence spectra of both series of compounds recorded in dichloromethane solutions. As attended, emission maximum of **[Ir(dfppy)(tpy)(bpy)](PF₆)** ($\lambda_{em} = 556$ nm) lies between those of **[Ir(dfppy)₂(bpy)](PF₆)** ($\lambda_{em} = 517$ nm) and those of **[Ir(dfppy)(tpy)(phen)](PF₆)** ($\lambda_{em} = 544$ nm) stands between those of **[Ir(dfppy)₂(phen)](PF₆)** ($\lambda_{em} = 509$ nm) and **[Ir(tpy)₂(phen)](PF₆)** ($\lambda_{em} = 581$ nm). The emission maxima are summarized in Table 2. The hypsochromic effect of 10 nm in average of the emission wavelength by changing the N[^]N ligand bpy for phen can be confidently to the extension of the π-system of this N[^]N ligand stabilizing the HOMO level.



Fig. 4. Aromatic region of the 300 MHz ¹H NMR spectrum of [Ir(dfppy)(tpy)(bpy)](PF₆) (top) and [Ir(dfppy)(tpy)(phen)](PF₆) (bottom) recorded in CDCl₃ solution at room temperature.



Fig. 5. UV-visible absorption (solid line) and photoluminescence (dashed line) spectra of [Ir(dfppy)(tpy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆) recorded in chloroform solutions.

3.3. Electrochemical properties

The electrochemical properties of the two complexes were investigated by cyclic voltammetry. The redox potentials calibrated against Ferrocene/Ferrocenium⁺ (Fc/Fc⁺) as the internal reference are summarized in Table 1. Data are reported versus SCE. Fig. 7 depicts the cyclic voltammograms of the two complexes in chloroform solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAF.PF₆) as the supporting electrolyte. As shown in Fig. 7, the two complexes exhibited quasi-reversible oxidation and reduction peaks. Similarity of the oxidation potentials for the two complexes clearly evidences the oxidation process to be largely metal-centered. Considering that the pure metal-centered oxidation is assumed to be reversible, loss of electrochemical reversibility arises from a contribution of the cyclometalated phenyl fragment to the highest occupied molecular orbital (HOMO) level. These results are consistent with the literature [63-65]. On the opposite, the reduction was ascribed to the addition of an electron on the diimine ligand and this electrochemical process proved to be almost insensitive to the conjugated length of this latter. The above discussion thus suggests the lowest unoccupied molecular orbital (LUMO) to be located on the diimine ligands. These different assignments are consistent with the DFT calculations done on the two complexes. On the basis of the onset potentials of oxidation and reduction, HOMO and LUMO energy levels of [Ir(dfppy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆) could be estimated with regard to the energy level of ferrocene (4.8 eV below vacuum) and determined as being 5.51 eV and 5.56 eV for the HOMO levels and

Table 1

Photophysical and electrochemical properties of [Ir(dfppy)(tpy)(bpy)](PF6) and [Ir(dfppy)(tpy)(phen)](PF6) and electronic energy levels.

Iridium (III) complex	$\lambda_{abs} \left(nm \right)$	λ _{em} a (nm)	τ ^b (μs)	φ ^c	λ _{em} d (nm)	ϕ^d	E _p (Ox) (V)	E _p (Red) (V)	E(Ox) ^{onset} (V)	E(Red) ^{onset} (V)	HOMO (eV)	LUMO (eV)	ΔE (eV)	ΔE (eV) ^e
[Ir(dfppy)(tpy) (bpy)](PF ₆)	311, 363, 402, 454	556	0.97	0.63	562	0.57	1.02	-1.93	0.71	-1.60	5.51	3.20	2.31	2.72
[Ir(dfppy)(tpy) (phen)](PF ₆)	302, 366, 402, 454	544	0.99	0.66	552	0.62	2 1.03	-1.96	0.76	-1.62	5.56	3.18	2.38	2.78

^a Measured in chloroform solutions at $C = 1 \cdot 10^{-6}$ M upon excitation at 350 nm.

^b Fluorescence lifetime under nitrogen in acetonitrile.

^c φ Absolute photoluminescence quantum yield.

^d Thin film of complex with 1-butyl-3-methylimidazolium hexafluorophosphate (1:1 ratio).

^e Determined by theoretical calculations.



Fig. 6. Photoluminescence spectra of [Ir(C^N)₂(bpy)](PF₆) and [Ir(C^N)₂(phen)](PF₆) recorded in dichloromethane solutions.

Table 2 Photoluminescence emission maxima of [Ir(C^N)₂(bpy)](PF₆) and [Ir(C^N)₂(phen)](PF₆) recorded in dichloromethane solutions.



Fig. 7. Cyclic voltammogram of **[Ir(dfppy)(tpy)(bpy)](PF_6)** (black curve) and **[Ir(dfp-py)(tpy)(phen)](PF_6)** (orange curve) in chloroform solutions (10^{-3} M) with tetrabutylammonium hexafluorophosphate NBu₄·PF₆ (0.1 M) as the supporting electrolyte. Scan rate: 100 mV/s. Potentials were recorded versus SCE. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.20 eV and 3.18 eV for the LUMO levels respectively (see Table 1) [66,67].

3.4. Theoretical calculations

Theoretical calculations were carried out to get a deeper insight into the energetic ordering of the frontier orbitals. TD-DFT calculations were performed for the two complexes at the B3LYP/ LANL2DZ level without symmetry restrictions using the Gaussian software suite. Energy gaps and features of the frontier orbitals and the different values for the two complexes are depicted in the Fig. 8. As anticipated, no major differences can be found between the two complexes. As previously reported in the literature for cationic heteroleptic iridium complexes [68–70], the highest occupied molecular orbital (HOMO) is an admixture of Ir(III) d_{π} orbitals (t_{2g})



Fig. 8. Representations of the frontier molecular orbitals for the optimized geometry of the two complexes (isovalue = 0.04).

and phenyl π orbitals of the cyclometalated ligands. In our case, the two complexes bear two different cyclometalated ligands and from the contour plot of the HOMO and HOMO-1 orbitals, a non-

equivalent contribution of the two ligands to these orbitals can be evidenced. Notably, a larger contribution of the tpy ligand to the HOMO and to a larger extent to the HOMO-1 as compared to that of the dfppy ligand can be detected. On the opposite and as classically observed for heteroleptic complexes, the lowest occupied molecular orbital (LUMO) is exclusively located on the ancillary ligand. Replacement of the bpy ligand of **[Ir(dfppy)(tpy)(bpy)](PF_6)** by the phen ligand of [Ir(dfppy)(tpy)(phen)](PF₆) let the energy levels of the different orbitals almost unaffected, excepted for the LUMO+1 orbital that benefited from the larger stabilizing effect of the phen ancillary ligand. First unoccupied orbital of [Ir(dfppy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆) are mostly localized over the ancillary ligand with a contribution of the metal center. On the opposite, LUMO+2 of the two complexes are mostly centered on the dfppy ligand, with an increased contribution from this ligand in [Ir(dfppy)(tpy)(phen)](PF₆) than in [Ir(dfppy)(tpy)(bpy)](PF₆). Based on previous works on triple heteroleptic complexes, these observations suggest the first electronic triplet states to be likely formed by transfer of one electron from a 5d(Ir) orbital to the phen/ bpy ligand or from a 5d(Ir) orbital to dfppy [44]. Finally, the theoretical HOMO-LUMO gaps followed the same trend than that determined experimentally, with a wider energy gap for [Ir(dfppy)(tpy)(phen)](PF₆). A good agreement between the theoretical and the experimental values of HOMO-LUMO gap can thus be evidenced. Finally, nitrogen-iridium bond lengths between the metal cation and the ancillary ligand were theoretically determined. Interestingly, longer bond lengths were determined in $[Ir(dfppy)(tpy)(phen)](PF_6)$ (d = 2.17 and 2.18 Å) than in [Ir(dfp**py)(tpy)(bpy)](PF₆)** (d = 2.16 and 2.17 Å), consistent with a lower internal cohesion.

3.5. Electroluminescence performances

Electroluminescence properties of the two complexes were evaluated by employing these triplet emitters as the active materials in LECs. The key performance parameters are listed in Table 3. It has to be noticed that the two complexes were perfectly soluble in organic solvents, thanks to a metathesis step using KPF₆ as the salt. Even if the procedure we used is standard, presence of remaining chloride ions can't be excluded, lowering device performances [71]. Besides, a comparison with previous results reported in the literature is still possible, emitters being purified in the same conditions than ours. Devices were prepared by spincoating a thin layer (40 nm) of poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) PEDOT:PSS on top of a patterned indium tin oxide (ITO)-coated glass substrate, followed by the active layer consisting of a mixture of each complex with the ionic liquid 1-butyl-3-methylimidazolium (IL)hexafluorophosphate (BMIM.PF₆) in a 1:1 w/w ratio. Notably, the ionic liquid was added to the emissive layer to increase the amount of ionic species and thus allow higher mobilities while reducing the turn-on time of device [20,21]. Finally, an aluminum layer was evaporated as the top electrode onto the emitting layer through a shadow mask. More details concerning the device preparation can be found in the experimental section. The two complexes yielded electroluminescent devices of appreciable brightness and stability.

Electroluminescence (EL) spectra of **[Ir(dfppy)(tpy)(bpy)](PF₆)** and **[Ir(dfppy)(tpy)(phen)](PF₆)** are presented in the Fig. 9. The EL emission maximum of **[Ir(dfppy)(tpy)(bpy)](PF₆)** and **[Ir(dfp-py)(tpy)(phen)](PF₆)** are 561 nm and 552 nm respectively, closely matching their photoluminescence spectra. Commission Internationale de l'Éclairage (CIE) coordinates of (0.401, 0.547) for **[Ir(dfppy)(tpy)(bpy)](PF₆)** and (0.416, 0.545) for **[Ir(dfppy)(tpy)(phen)](PF₆)** are indicative of a green electroluminescence (see Table 2). The luminance versus time characteristics of LECs employing **[Ir(dfppy)(tpy)(bpy)](PF₆)** and **[Ir(dfppy)(tpy)(-phen)](PF₆)** as triplet emitters under the constant driving voltage of 6 V are given in the Fig. 10. Considering the presence of ionic liquid within the active layer, devices showed relatively long turn-on times that correspond to the time needed to reach the maximum luminance under a constant applied voltage.



Fig. 9. Electroluminescence spectra of LECs fabricated with **[Ir(dfppy)(tpy)(bpy)](PF_6)** (a) and **[Ir(dfppy)(tpy)(phen)](PF_6)** (b) recorded by scanning the applied voltage up to a maximum value of 9 V with incremental steps of 0.2 V.

Table 3

Device characteristics of LECs fabricated with [Ir(dfppy)(tpy)(bpy)](PF6) and [Ir(dfppy)(tpy)(phen)](PF6).

Complex	V _{turn-on} ^a	CIE (x,y) ^b	$\lambda_{EL}\left(nm ight)$	$\lambda_{\text{EM}}\left(nm ight)$	$L(cd/m^2)$	Max. current eff. (cd/A)	Max. power eff. (lm/W)	EQE (%)
[Ir(dfppy)(tpy)(bpy)](PF ₆)	5.3	0.401, 0.547	561	564	4486 (8.9 V)	7.11	2.49	1.91
[Ir(dfppy)(tpy)(phen)](PF ₆)	5.1	0.416, 0.545	552	554	5238 (9.2 V)	9.81	3.55	2.99

^a Turn-on voltage at a brightness of 1 cd/m².

^b Determined upon applying a driving voltage of 6 V.



Fig. 10. Lifetimes of devices fabricated with **[Ir(dfppy)(tpy)(bpy)](PF**₆) and **[Ir(dfppy)(tpy)(phen)](PF**₆) upon applying a driving voltage of 6 V. Inset: Variation of the chromaticity coordinates over time.

[Ir(dfppy)(tpy)(bpy)](PF6)-based devices reached the maximum luminance of 300 cd/m² in 99 min, while [Ir(dfppy)(tpy)(**phen**)](PF₆)-based devices achieved 360 cd/m² in 81 min. However, these values are consistent with those previously reported in the literature since LECs with turn-on times of several hours were even reported in the literature [72,73]. The half-lifetime of LECs which is defined as the time for the brightness to decay from the maximum to half of the maximum were respectively of 10 h for [Ir(dfppy)(tpy)(bpy)](PF₆)-based devices and 7 h for [Ir(dfppy)(tpy)(phen)](PF₆)-based devices. Therefore, from these experiments, it can be concluded that [Ir(dfppy)(tpy)(phen)](PF₆) exhibit a higher maximum luminance than Ir(dfppy)(tpy)(bpy)](PF₆) but a lower stability in devices. These differences can be tentatively assigned to non-equivalent doping abilities of the two materials and the lower stability of [Ir(dfppy)(tpy)(phen)](PF₆)-based devices to the higher electron-donating ability and rigidity of the phenanthroline ligand compared to its bipyridine counterpart that weaken the carbon-iridium bond. Indeed, the rigidity of the phenanthroline ligand can contribute to reduce the electron density accepted by the metal cation as a result of a less favorable orientation of the two pyridine units, impeding the formation of strong π interactions [74]. This explanation is notably supported by the theoretical calculations that established longer nitrogen-iridium bond lengths for the complex comprising a phenanthroline as the ancillary ligand. While examining the variation of the CIE coordinates over time, no significant changes could be detected, excepted during the initial doping step. This color variation was more pronounced for [Ir(dfppy)(tpy)(phen)](PF₆) than [Ir(dfppy)(tpy)(bpy)](PF₆), as shown in the inset of Fig. 10. Such a color shift during the dynamic doping step is frequently observed in LECs and is directly related to a modification of the location of the emission zone with ions propagation [75]. Finally, LECs were operated as classical OLEDs (see Fig. 11). In this approach, ions motion is strongly accelerated by the increasing voltage sweep, profoundly modifying the dynamic of electrochemical doping. Indeed, it is well-established that the doping front propagation is governed by the speed of ionic migration within the emissive layer. By rapidly increasing the operating voltage, a strong acceleration of the dynamic response of LECs is obtained [76]. Timescale at which the voltage sweep is applied also drastically influences the EL characteristics. Therefore, even if this characterization constitutes a less conventional way to investigate LECs and that parameters such



Fig. 11. V-L curves of LECs fabricated with [Ir(dfppy)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆) and operated as a classical OLED.

as the sweep rate or the measurement time can modify the *V-L* response, it can however furnish an idea of the range of maximum luminance that can reach LECs. As observed in the Fig. 11, brightness increased sharply beyond 8 V and reached the maximum brightness of 4486 cd/m² at 8.9 V and 5238 cd/m² at 9.2 V for [Ir(dfp-py)(tpy)(bpy)](PF₆) and [Ir(dfppy)(tpy)(phen)](PF₆) respectively. Best device characteristics were obtained for [Ir(dfppy)(tpy)(-phen)](PF₆), which led to efficiency values of 9.81 cd/A, 3.55 lm/W and an EQE of 2.99% (see Table 2).

4. Conclusions

To conclude, two highly luminescent heteroleptic iridium complexes with three different ligands were synthesized and investigated as triplet emitters for light-emitting electrochemical cells. The two cationic complexes that differ by their ancillary ligands exhibit a pure green emission around 560 nm. LECs fabricated with these complexes were studied at constant voltage and upon voltage sweep. Device performances obtained with **[Ir(dfp-py)(tpy)(phen)](PF_6)** were clearly enhanced as compared to those obtained with **[Ir(dfppy)(tpy)(bpy)](PF_6)** and these differences are tentatively assigned to inequal doping and charge transport abilities of the two materials. Once again, these results highlight the dramatic influence of the ligand effects on EL performances.

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