



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 Gimes ^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

ARTICLE INFO

Article history:

Received 6 April 2016

Received in revised form

8 June 2016

Accepted 10 June 2016

Available online 21 June 2016

Keywords:

Iridium complex

Lifetime

Ionic liquid

Electroluminescence

Light-emitting electrochemical cells

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.

© 2016 Elsevier B.V. All rights reserved.

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

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

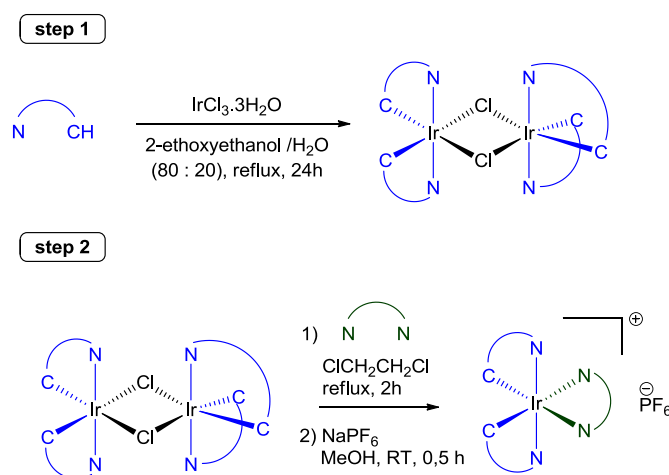
* Corresponding author. Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire ICR, UMR 7273, F-13397 Marseille, France.

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

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 $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ gives a statistical mixture of six different dimers (see Scheme 2, step 1). This inseparable mixture is then engaged in reaction with acetylacetonate (acac) to furnish after reaction three different complexes (step 2). At this stage, the two homoleptic complexes $\text{Ir}(\text{C}'\text{N})_2(\text{acac})$ and $\text{Ir}(\text{C}''\text{N}')_2(\text{acac})$ must have a sufficient difference of polarity with the targeted heteroleptic complex $\text{Ir}(\text{C}'\text{N})(\text{C}''\text{N}')(\text{acac})$ to be separable by simple chromatography on silica gel [42,44]. The second key point is the regeneration of the pure $[\text{Ir}(\text{C}'\text{N})(\text{C}''\text{N}')\mu\text{-Cl}]_2$ 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 $\text{Ir}(\text{C}'\text{N})(\text{C}''\text{N}')(\text{N}'\text{N})^+$ (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



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 $\text{Ir}(\text{C}'\text{N})(\text{C}''\text{N}')(\text{N}'\text{N})^+$ to lie between those of the corresponding *bis*-heteroleptic complexes $\text{Ir}(\text{C}'\text{N})_2(\text{N}'\text{N})^+$ and $\text{Ir}(\text{C}''\text{N}')_2(\text{N}'\text{N})^+$ [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 $[\text{Ir}(\text{dfppy})(\text{tpy})(\text{b-ppy})](\text{PF}_6)$ and $[\text{Ir}(\text{dfppy})(\text{tpy})(\text{phen})](\text{PF}_6)$ differing by their N'N ligands have been synthesized and tested as light-emitting materials in LECs (see Fig. 2). Noticeably, $[\text{Ir}(\text{dfppy})(\text{tpy})(\text{phen})](\text{PF}_6)$ 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 ^{13}C 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 ^{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 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 Quantaaurus 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 (O_2 and $\text{H}_2\text{O} < 0.1$ ppm). The working and the counter electrodes were a Pt disc and a Pt wire respectively, whereas Ag wire was used as a

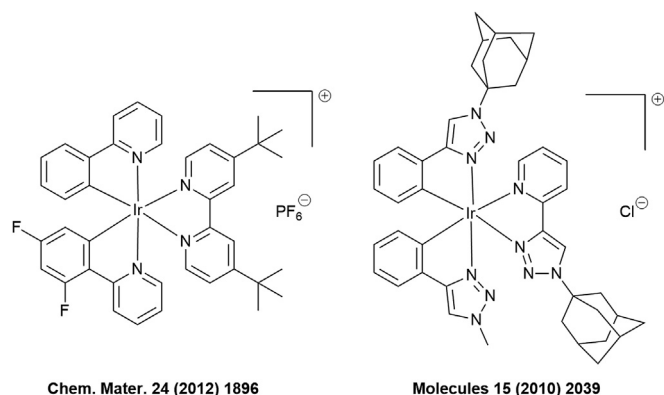


Fig. 1. Cationic *tris*-heteroleptic *bis*-cyclometalated iridium (III) complexes reported in the literature.

Download English Version:

<https://daneshyari.com/en/article/1264652>

Download Persian Version:

<https://daneshyari.com/article/1264652>

[Daneshyari.com](https://daneshyari.com)