ANOMALOUS BEHAVIOR OF Ir(III) CYCLOMETALATED COMPLEXES. APPLICATION IN LIGHT-EMITTING ELECTROCHEMICAL CELLS

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ABSTRACT

The cationic Ir(III) complex with 7,8-benzoquinoline (bzq) as cyclometalating ligand and 4,4'-diterbutyl-2,2'-bipyridine (tBuB) as ancillary ligand, [Ir(bzq)₂(tBuB)](PF₆) (**1**), was utilized in the fabrication of a light-emitting electrochemical cell (LEC). The photophysical properties and the characterization of the LEC device with this complex was compared with literature data for the analogous complex with 2-phenylpyridine (ppy), [Ir(ppy)₂(tBuB)](PF₆) (**2**). Complex **1** showed blue shifted emission compared to complex **2**. Surprisingly, complex **1** shows lower luminance, efficiency and stability in regard to **2**. This behavior correlated well with the low values of quantum yield and lifetime, registered for complex **1** in solution. The performance observed is unexpected, taking into account the emission wavelengths recorded for each complex, and the lesser non radiative deactivation processes expected for a complex with a more rigid ligand as bzq. A possible explanation of this behavior is given in terms of the predominance of a fluorescent emission in the case of the complex **1** instead of a phosphorescent emission, as observed for complex **2**.

Keywords: light-emitting electrochemical cell, cyclometalated complexes, phosphorescence, fluorescence.

INTRODUCTION

Solid state light-emitting electrochemical cells (LECs) are a sort of luminescent devices based on a thin film of an ionic material confined between two electrodes.^{1,2} According to the architecture and cost of the lighting devices, LECs are a promising alternative to the organic light-emitting diode (OLED).³ The luminescent materials used in LEC devices can be conjugated light-emitting polymers together with an inorganic salt (PLECs)¹ or ionic transition metal complexes (iTMC).^{4,7} In the case of iTMC, the fabrication consist in the deposition of a single layer of the iTMC material by spin coating onto ITO (Indium Tin Oxide) followed by a metallic cathode deposited by evaporation under vacuum.⁸ In the case of the OLED devices, the fabrication consists in a multilayer architecture, including the emitter layer (neutral molecule or polymer), sandwiched between two electrodes. Organic layers are added to promote the electron and hole injection into the light emissive layer. Some of these layers can only be prepared by evaporation under high vacuum conditions.^{9,10} As electron injection layers, low work function metals are commonly used as cathodes, for example barium or calcium, but the problem is the instability in air of these metals, and for this reason a rigorous encapsulation is needed in order to prevent degradation.¹¹ In the case of LEC devices, it is possible to use air stable cathodes, for example gold and silver, due to only a film of the ionic complex is needed to promote the electric charge injection into emissive layer independent of the metallic electrode employed.¹²

Representative iTMCs utilized in the development of LEC devices are the polypyridinic ruthenium (II) complexes.¹³⁻¹⁵ These materials are characterized by emission processes of orange to deep-red light at low voltages.¹⁴⁻¹⁶ However, Ru(II) complexes have a limited color tuning capability, therefore, their potential applications in lighting technologies is restricted.¹⁶ In this context, the possibility to improve the performance of LECs can be achieved using cyclometalated complexes of Ir(III). This sort of complexes are characterized by high spin-orbit coupling leading to efficient intersystem crossing from singlet to triplet excited states, showing high emission quantum efficiencies.¹⁷ Also, these complexes allow to extend the variability of the emission colors, according to the substituents on the periphery of the ligands, covering a broad gamma of colors from blue to red.¹⁸ Bis-cyclometalated Ir(III) complexes are typical examples of complexes utilized in diverse applications due to their special emission properties.¹⁹ Commonly, the third ligand (ancillary ligand) bonded to Ir(III) center, for LEC applications, are phenanthroline (phen), bipyridine (bpy) and 2-(1H-pyrazol-1-yl)pyridine (pzpy). By incorporation of adequate substituent on these ligands it is possible to control the emission color. In some cases, the blue color has been achieved, which opens the possibility to obtain a full range of colors.²⁰

Some years ago, our group reported the synthesis and, electrochemical and spectroscopic characterization of a new bis-cyclometalated Ir(III) complex, of general formula [Ir(bzq)₂(tBuB)](PF₆), where bzq = 7,8-benzoquinoline and

tBuB = 4,4'-diterbutyl-2,2'-bipyridine.²¹ In this work, the fabrication of a LEC device with this complex, and the evaluation of the electroluminescent properties are reported and discussed in comparison with the analogue complex with 2-phenylpyridine (ppy).

RESULTS

Electrochemical and photophysical properties

The schematic structures of the complexes analyzed in this work are shown in Figure 1.

Figure 1. Schematic structures of the cyclometalated complexes of Ir(III) studied in this work: [Ir(bzq)₂(tBuB)](PF₆) **1** and [Ir(ppy)₂(tBuB)](PF₆) **2**.

The electrochemical and electronic spectroscopy properties of complex **1** were reported in a previous work.²¹ Table 1 summarizes the corresponding data, as well as the equivalent information for complex **2** taken from literature.^{22,23} In both cases, all data were obtained from measurements at room temperature in acetonitrile (ACN) solutions.

Table 1. Electronic spectroscopy and electrochemical properties of Ir(III) complexes at 25°C in ACN.

Complex	E (Ir ^{3+/4+})/V	E (red)/V	λ_{em}/nm	QY	τ/ns	k_r 24,25 (10 ⁶ s)	k_{nr} 24,25 (10 ⁶ s)
[Ir(bzq) ₂ (tBuB)](PF ₆) 1	0.91 ²¹	-1.40 ²¹	559 ²¹	0.071 ²¹	60 ²¹	1.18	15.48
[Ir(ppy) ₂ (tBuB)](PF ₆) 2	0.85 ²²	-1.87 ²²	581 ²³	0.235 ²³	557 ²³	0.42	1.37

$$k_r = QY/\tau \text{ and } k_{nr} = 1/\tau - k_r^{24,25}$$

In Table 1 the electrochemical data are reported vs the Fc^+/Fc couple and correspond to the oxidation process of $\text{Ir}^{3+/4+}$, at positive potentials, and the reduction process of the ancillary ligand, at negative potential, as can be observed for another d^6 low spin complexes.²⁶ These values can be related with the energies of the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO).²⁷ As it has already been reported, in this type of compounds the HOMO is composed of a mixture of Ir(III) $d\pi$ orbitals and phenyl π orbitals of the cyclometalating ligands, and the LUMO correspond to the π^* orbitals of the ancillary tBuB ligand.²¹⁻²³ The electrochemical gaps obtained from Table 1 are 2.31 V (**1**) and 2.72 V (**2**). According to these data, it would be expected that the photoluminescent maximum of complex **1** to appear red shifted in comparison with the spectrum of complex **2**. However, the data are inverted. The exhibited experimental behavior is somewhat unexpected, for the reason given above, and, taking into account, for example, studies developed by Lamansky *et al.*^{28,29} with Ir(III) complexes with the same ancillary ligand (acac: acetylacetonate, instead of tBuB) and different cyclometalating ligand (ppy vs bzq), which that show emission spectra registered in 2-methyl-tetrahydrofuran solutions with a maximum at 548 nm for the complex with the bzq ligand and at 516 nm for the complex with ppy ligand.

At first glance, the behavior observed in this work would be indicative of an effective intersystem crossing (ISC) process in the case of the complex **2**, obtaining mainly phosphorescent emission from the triplet excited state. In the opposite case, for complex **1**, the ISC would not be efficient and consequently the emission process would correspond to fluorescence from the singlet excited state. The notoriously different emission lifetime values for complex **1** and **2** shown in the Table 1, support this explanation. Also, the values of the quantum yield (QY) are consistent. In addition, with the experimental data of Table 1 the radiative rate constant (k_r) and non-radiative rate constant (k_{nr}) were calculated.^{24,25} Complex **1** shows a high value of k_{nr} , which is consistent with the low QY and electrochemical gaps but, according to the energy gap law, is inconsistent with the higher energy of emission.^{30,31,7} Consequently, it is possible to consider the possibility of a non-emitting state of lower energy, that the same time would be preventing the ISC.

Emission spectroscopy in solid film

On the other hand, in this work are showing the absorption and emission spectrum of the complex **1** obtained from thin solid film prepared with solution of 5% weight of the complex in poly(methylmethacrylate) (PMMA) (Figure 2). Using spin coating technique, the solid films of the complex was deposited on quartz surfaces (details are described in the experimental section). The PMMA polymer was utilized as a strategy to keep the immobilized molecules and separated from each other with the purpose to decrease the non-radiative decays.³²

Figure 2. Absorption (solid line) and emission (dot line) spectra of $[\text{Ir}(\text{bzq})_2\text{tBuB}](\text{PF}_6)$ of a thin film containing 5% of Ir(III) complex and 95% of PMMA.

The comparison of the emission spectrum in solution and in thin film indicates that in the latter the emission maxima (546 nm) are shifted to higher energy as a consequence of different environment. Similar behavior has been observed with the analogous complex with ppy ligand, with a wavelength emission at 558 nm.²³ Also, the QY obtaining in solid film for the complex **1** (0.43) is higher than in solution and this behavior is due to that the molecules

are very diluted in the PMMA film thus reducing the molecular interactions that affect the non-radiative decay. According to literature, the mixture of the luminescent material with a polymer is a good strategy in order to prevent aggregate or excimer formation of the emitting molecules. Therefore, the emission maxima are shifted to blue.³³

Electroluminescent properties

The LEC device with complex **1** was obtained by spin-coating on patterned indium tin oxide (ITO) covered glass substrate. Prior to the deposition of the emitting layer, a film of poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) was deposited onto the ITO anode with the objective of increasing the yield and reproducibility of the working devices. The emitting layer was prepared by dissolving the corresponding complex in acetonitrile. An aluminum layer was used as the top electrode contact. The LEC device was driven using pulsed current methods with an average current density of 100 Am^{-2} using a duty cycle of 50%.³⁴ Details of the device preparation are explained in the Experimental section.

Figure 3 shows the electroluminescent spectrum from ITO/PEDOT:PSS/complex **1**/Al device.

Figure 3. Normalized electroluminescent spectra of ITO/PEDOT:PSS/complex **1**/Al LEC device driven at a pulsed current with an average current density of 100 Am^{-2} , using a block wave at a frequency of 1000 Hz and a duty cycle of 50%.

The wavelength of the electroluminescence spectrum is located around 580 nm. This spectrum is strongly red shifted with respect to the emission spectra in solution and in thin solid film (with PMMA). This behavior has already been observed in other LEC devices and should be ascribed to a polarization effect due to electrical excitation.^{32,35} The CIE (International Commission on Illumination) coordinates determined from the electroluminescent spectrum for complex **1** are (0.51, 0.48).

The graphic of the luminance and average voltage versus operation time is shown in Figure 4 for the ITO/PEDOT:PSS/complex **1**/Al LEC, where the maximum luminance is faster reach at 8 second (t_{on} : turn on time).

The parameters determined by the measurement of the performance of the LEC device fabricated with complex **1** are shown in Table 2, and are compared with the parameters obtained from literature²² for the performance of the LEC device fabricated with complex **2** in similar conditions.

As can be observed in Table 2, the luminance reached for the device with complex **1** is lower than the maximum luminance of the LEC with complex **2**. In addition, in the LEC built with complex **1**, the luminance response decreases faster and the $t_{1/2}$ (time need to reach 50% of the peak) is shorter compared with the performance of the LEC with complex **2**. The response observed in ITO/PEDOT:PSS/complex **1**/Al LEC reflects low stability of the device, which relates to the poor emission process of this complex observed in solution. Nevertheless, it is important to note that the t_{on} in the case of the complex **1**, is around 10% faster than complex **2**, being a noteworthy feature of this device, in considering their application in lighting systems.

Figure 4. Luminance (open circle) and average voltage (solid line) for ITO/PEDOT:PSS/complex 1/Al LEC device driven at a pulsed current with an average current density of 100 A m^{-2} , using a blockwave at a frequency of 1000 Hz and a duty cycle of 50%.

Table 2. Performance of LEC devices with the complex **1** and **2**.

Complex	t_{on}/s	Luminance _{max} / cd m^{-2}	$t_{1/2}/\text{h}$	Efficacy/ cd A^{-1}	Power efficiency/ lm W^{-1}	%EQE
[Ir(bzq) ₂ (tBuB)](PF ₆), 1	8.2	74	1.57	0.68	0.3	0.27
[Ir(ppy) ₂ (tBuB)](PF ₆), 2 ²²	9.0	1083	370	10.8	6.1	3.49

CONCLUSIONS

In this work, two cyclometalated complexes of Ir(III), with similar ancillary ligand and different cyclometalating ligands have been compared in terms of the photophysical and electrochemical properties. The data of the electrochemical characterization are in concordance with the QY and k_{nr} values, but the emission spectra maxima are inverted according to the behavior expected. The life time and quantum yield determined are lower in the case of complex **1**.

Since complex **1** emits light shifted to blue, it was considered that it might be a good candidate as LEC device, opening the possibilities for a wide range of emission colors.

However, the evaluation of the complex **1** in LEC device shows poor characteristic in comparison with the LEC devices characterization of the complex **2** (using literature data). According to experimental data of lifetime, quantum yield and radiative and non-radiative constants, we proposed an explanation of the behavior observed in terms of the predominant fluorescent process in the case of the complex **1**, while that in the complex **2**, the main process is phosphorescent, considering that the fluorescent emission are characterized by lifetime shorter than the emission phosphorescent.

Considering that one of the main disadvantages of the LEC devices are long t_{on} ,^{16,36} the fast turn on time of complex **1** is highlighted. Although the difference between the values of the t_{on} between **1** and **2** (0.8 s) is not a large magnitude, it can be considered a transcendent value taking in account a lighting system.

Experimental Section

Materials

All the reagents and solvents were at least of analytical grade and were used without further purification.

Electrochemical and photophysical properties

Data of the cyclic voltammetry were obtained from reference 21 and 23, and in both case, the experiment were developed in inert atmosphere using solutions of the complexes in anhydrous acetonitrile with 0.1 M TBAPF₆ as the electrolyte. The electrochemical potentials are reported vs ferrocenium/ferrocene and the scan rate applied was 100 mV s^{-1} . Data of the photophysical measurement were obtained from reference 21 and 23, and in both report using acetonitrile solutions of the complexes deaerated with nitrogen. The emission

quantum yields were measured relative to [Ru(bpy)₃](PF₆)₂. The emission spectrum and quantum yields of complex **1** in thin film of 5% in weight of the complex mixed with 95% in weight of PMMA was measured with a Hamamatsu C9920-02 Absolute PL Quantum Yield Measurement System. The system is made up of an excitation light source, consisting of a xenon lamp linked to a monochromator, an integration sphere and a multi-channel spectrometer. The thin film was obtained by spinning from acetonitrile solutions at 1000 rpm for 20 s.

Electroluminescent properties

The solvents were supplied by Aldrich. The thickness of the film was determined with an Ambios XP-1 profilometer. Indium tin oxide ITO-coated glass plate ($15 \Omega^{-1}$) was patterned by conventional photolithography (Naranjo Substrates). The substrate was cleaned by sonication in water-soap, water, and 2-propanol baths, in that order. After drying, the substrate was placed in a UV-ozone cleaner (Jelight 42-220) for 20 min.

The electroluminescence device was made as follows. First, a 100 nm layer of PEDOT:PSS (CLEVIOSTTM P VP Al 4083, aqueous dispersion, 1.3–1.7% solid content, Heraeus) was spin-coated on the ITO glass substrate to improve the reproducibility of the device and to prevent the formation of pinholes. Then, 80 nm transparent film of the complex was spin-coated from 20 mg mL^{-1} acetonitrile solution at 1000 rpm for 20 s. The solution was filtered using a 0.1 μm PTFE-filter and spin-coated on top of the PEDOT:PSS layer. The device was transferred in an inert atmosphere glovebox ($< 0.1 \text{ ppm O}_2$ and H_2O , M. Braun). The Al electrode (70 nm) was thermally vapor deposited using a shadow mask under a vacuum ($< 10^{-6} \text{ mbar}$) with an Edwards Auto500 evaporator integrated in the glovebox. The area of the device was 6.5 mm^2 . The device was not encapsulated and was characterized inside the glovebox at room temperature. Lifetime data was obtained by applying pulsed current and monitoring the voltage and, simultaneously, the luminance by a True Colour Sensor MAZEt (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System. An Avantes luminance spectrometer was used to measure the electroluminescent spectrum.

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