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Ionic luminescent cyclometalated Ir(III) complexes with polypyridine co-ligands

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Abstract

Two novel ligands containing a functionalized $N \wedge N$ chelating moiety (pbpy-OBut and tpy-COOH, respectively) were treated with $[Ir(ppy)_2(\mu-Cl)]_2$ (ppy = 2-(2-pyridyl)phenyl), leading to the cationic cyclometalated complexes $[Ir(ppy)_2(pbpy-OBut)]^+$ (2) (pbpy-OBut = 4-{4'-(4-phenyloxy)-6'-phenyl-2,2'-bipyridyl}butene) and $[Ir(ppy)_2(tpy-COOH)]^+$ (3) (tpy-COOH = 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine). Complexes 2 and 3 exhibit intense room temperature luminescence both in solution and as solid films. Assignment of the emissive behavior to a ³LLCT (ppy-to-N \wedge N) excited state is proposed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Iridium; Cyclometalated complexes; Luminescent complexes

1. Introduction

The study of the photophysical properties and potential applications of luminescent cyclometalated Ir(III) complexes had become very important in the last decade. Applications in the field of organic electronics [1-3], labeling of biomolecules [4], and photoinduced hydrogen production [5] are currently exploited, while further use in medical, chemical, and environmental analysis is envisioned [6–8].

Investigation of cyclometalated Ir(III) complexes with superior photo- and electroluminescent properties is directed mainly toward tris(cyclometalated) [Ir($C \land N$)₃] and bis(cyclometalated) [Ir($C \land N$)₂L] species, where $C \land N$ is usually a C-2 metalated 2-phenylpyridine (ppy) ligand or analogs. In both cases, and in the presence of "nonchromophoric" L ligands, it has been proposed that the luminescence mainly originates from a ligand-centered triplet

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excited state (³LC) with variable contribution from MLCT states through spin-orbit coupling [9–13]. Therefore, tuning of the emission energy may follow two different paths: (i) control of the ³LC energy through chemical substitution on the cyclometalating $C \wedge N$ moiety [14–16], or (ii) control of the LC-MLCT excited states mixing by variation of the "nonchromophoric" L ligand [17,18]. Other characteristics such as solubility, processability, morphology, and luminescence stability of the Ir luminophores are addressed by devising specific synthetic strategies [19–21].

In addition to charge-neutral tris- and bis(cyclometalated) Ir(III) complexes, we and others have developed alternative classes of charged cyclometalated Ir(III) luminophores [4,5,17,22–26]. In one major class, which contains coordinated 2,2'-bipyridines as ancillary ligands for the "Ir(ppy)₂" fragment, the good emitting properties of the parent species $[Ir(ppy)_2(bpy)]^+$ (1) (bpy = 2,2'bipyridine) [9,10,27] are combined with the phenomenal synthetic versatility of α -diimine ligands. For example, the availability of functionalized bpy ligands allows the synthesis of polymetallic luminescent species [26,28,29], while the occurrence of a charged luminophore allows its

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use as a major component in single-layer electroluminescent devices [30].



In this work, we present further examples of cationic Ir(III) cyclometalated complexes with two novel polypyridine ligands acting as $N \wedge N$ donors. The latter are designed for introducing reactive functional groups on the periphery of the donating $N \wedge N$ backbone, thus enabling a wider array of photoactive Ir(III) complexes that can be useful per se or as synthons for larger systems.

2. Experimental

2.1. Materials and methods

All reactions were performed in air. All solvents were of reagent grade and were used as received from Aldrich and Riedel-de Haën. The dimeric precursor $[Ir(ppy)_2(\mu-Cl)]_2$ was prepared as reported by Sprouse et al. [31].

¹H NMR spectra were recorded at 300.13 MHz with a Bruker AC 300 spectrometer; chemical shifts are referenced to internal tetramethylsilane. FT-IR spectra were recorded on a Perkin–Elmer 2000 spectrophotometer for KBr pellets. Elemental analyses were performed using a Perkin– Elmer 2400 microanalyzer.

Spectrofluorimetric grade solvents (Acros Organics) were used for the photophysical investigations in solution and for the preparation of spin-coated films. Absorption spectra were obtained with a Perkin-Elmer Lambda 900 spectrophotometer, while the emission spectra (all confirmed by excitation ones) were recorded with a Perkin-Elmer LS 50B or a Jobin-Yvon Fluoromax P spectrofluorimeter, both equipped with a Hamamatsu R928 photomultiplier tube. The corrected emission spectra were obtained by using a standard lamp. Emission quantum yields were determined using the optically dilute method [32a] on solutions whose absorbance at excitation wavelengths was <0.1. [Ru(bpy)₃]Cl₂ in water was used as a standard ($\Phi = 0.028$) [32b]. The emission lifetimes were measured with an Edinburgh OB900 single-photon counting equipment (nitrogen discharge; pulse width, 3 ns).

The electrochemical measurements were carried out in an argon-purged acetonitrile at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm², Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was a SCE separated with a fine glass frit. The concentration of the complexes was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte and its concentration was 0.05 M. Cyclic voltammograms were obtained at scan rates of 20, 50, 200, and 500 mV/s. For reversible processes, halfwave potentials (vs. SCE) were calculated as an average of the cathodic and anodic peaks. The criteria for reversibility were the separation between the cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. For irreversible processes, the values reported in table are the peaks estimated by differential pulse voltammetry (DPV).

Experimental uncertainties are as follows: redox potentials, $\pm 10 \text{ mV}$; absorption maxima, 2 nm; extinction coefficients, 10%; and emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%.

2.2. Synthesis and spectroscopic characterization of the ligands

2.2.1. 4-{4'-(4-phenyloxy)-6'-phenyl-2,2'-bipyridyl}butene (pbpy-OBut)

4-Bromo-1-butene (0.96 mmol) was added to a stirred suspension of 4'-(4-hydroxyphenyl)-6'-phenyl-2,2'-bipyridine (0.77 mmol), K_2CO_3 (3.85 mmol), and ΚI (0.077 mmol) in cyclohexanone (5 ml). The reaction mixture was heated under reflux conditions for 10 h. After removing the solid residue by filtration, the solid was washed with dichloromethane. The combined mother liquor and washings were taken to dryness affording a dark oil. Chromatography on silica gel (CH₂Cl₂/MeOH, 97:3) yielded the pure product as a white solid in very low yield (18%). Anal. Calc. for C₂₆H₂₂N₂O: C, 82.51; H, 5.86; N, 7.40. Found: C, 82.16; H, 5.93; N, 7.58%. ¹H NMR $(CDCl_3)$: δ (ppm) 8.70–8.65 (m, 2H, H-6 + H-3), 8.59 (d, J = 1.5 Hz, 1H, H-3' or H-5'), 8.18 (m, 2H, H-2', 6"), 7.92 (d, J = 1.5 Hz, 1H, H-5' or H-3'), 7.83 (dt, J = 7.8, 7.3, 1.5 Hz, 1H, H-4'), 7.75 (d, J = 8.9 Hz, 2H, phenyl-OBut), 7.70–7.41 (m, 3H, H-3",4", 5"), 7.31 (ddd, J = 7.3, 4.9, 1.5 Hz, 1H, H-5), 7.00 (d, J = 8.9 Hz, 2H, phenyl-OBut), 5.99-5.85 (m, 1H, OBut), 5.22-5.11 (m, 2H, OBut), 4.05 (t, J = 6.6 Hz, 2H, OBut), 2.56 (m, 2H, OBut).

2.2.2. 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine (tpy-COOH)

A suspension of 1-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (3.20 mmol), 1-(2-pyridyl)-3-(4'-carboxyphenyl) propen-1-one (3.16 mmol), and excess ammonium acetate (31.6 mmol) in methanol (15 ml) was heated under reflux for 6 h. Overnight cooling of the reaction mixture afforded a gray microcrystalline precipitate. The solid was removed by filtration, washed with cold methanol and diethyl ether and vacuum dried. Yield: 65%. *Anal.* Calc. for $C_{22}H_{15}N_3O_2$: C, 74.78; H, 4.28; N, 11.90. Found: C, 74.77; H, 4.40; N, 12.03%. IR (KBr, cm⁻¹) 1701 (v_{as} (C=O)). ¹H NMR (DMSO-d₆): δ (ppm) 8.87 (d, 2H, H-6,6", J = 5.3 Hz), 8.86 (s, 2H, H-3',5'), 8.78 (d, 2H, phenyl-COOH, J = 8.5 Hz), 8.25 (d, 2H, H-3,3", J = 7.5 Hz), 8.16 (d, 2H, phenyl-COOH, J = 8.5 Hz), 8.14 (m, 2H, H-4,4", J = 1.5 Hz), 7.65 (dd, 2H, H-5,5", J = 7.3, 4.9 Hz).

2.3. Synthesis of the complexes

2.3.1. $[Ir(ppy)_2(pbpy-OBut)]/PF_6]$ (2)

A solution of pbpy-OBut (0.046 g, 0.122 mmol) in CH₂Cl₂ (3 ml) was added to a stirred suspension of $[Ir(ppy)_2(\mu-Cl)]_2$ (0.066 g, 0.061 mmol) in MeOH (6 ml). The reaction mixture was heated under reflux for 2 h affording a clear orange solution, which was allowed to cool to room temperature. Addition of a 5-fold excess of ammonium hexafluorophosphate dissolved in MeOH (2 ml) with stirring for 30 min did not cause any further color change. The solvent was removed under reduced pressure till an orange precipitate formed. The solid was filtered off, washed with water, and redissolved with CH₂Cl₂. The filtrate was dried over Na_2SO_4 for 2 h and layered with *n*-hexane to obtain the pure product as an orange powder. Yield 0.085 g (68%). Anal. Calc. for C₄₈H₃₈F₆IrN₄OP: C, 56.30; H, 3.74; N, 5.47. Found: C, 55.86; H, 3.77; N, 5.29%. IR (KBr, cm⁻¹): 842 (ν (PF)). ¹H NMR (CD₃CN): δ (ppm) 9.24 (br d, J = 6.7 Hz, 1H), 8.86 (d, J = 8.0 Hz, 1H), 8.82 (d, J = 1.8 Hz, 1H), 8.17 (dt, J = 8.0, 9.0, 1.8 Hz, 1H), 7.92 (d, J = 8.5 Hz, 2H), 7.85 (br t, 1H), 7.80–7.69 (m, 6H), 7.53 (d, J = 1.8 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.29 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.10–7.03 (m, 3H), 6.92 (t, J = 7.3 Hz, 1H), 6.90 (t, J = 7.3 Hz, 1H), 6.80–6.70 (m, 4H), 6.58–6.53 (m, 2H), 6.36 (dt, J = 7.3, 7.2, 1.3 Hz, 1H), 5.93 (d, J = 7.9 Hz, 1H), 5.87 (m, 1H,

OBut), 5.57 (d, *J* = 7.9 Hz, 1H), 5.21–5.10 (m, 2H, OBut), 4.09 (t, *J* = 6.7 Hz, 2H, OBut), 2.55 (m, 2H, OBut).

2.3.2. $[Ir(ppy)_2(tpy-COOH)][PF_6]$ (3)

The pure product was obtained as a golden yellow microcrystalline solid through a procedure similar to that previously used for the preparation of $[Ir(ppy)_2(ttpy)][PF_6]$ (ttpy = 4'-(4-tolyl)-2,2':6',2"-terpyridine) [22]. Yield: 97%. *Anal.* Calc. for C₄₄H₃₁F₆IrN₅O₂P: C, 52.91; H, 3.13; N, 7.01. Found: C, 52.69; H, 3.49; N, 6.76%. IR (KBr, cm⁻¹): 1710 (v_{as} (C=O)), 843 (v(PF)). ¹H NMR (CD₃CN): δ (ppm) 8.84–8.74 (m, 3H), 8.21–8.17 (m, 3H), 8.04–8.00 (m, 3H), 7.97–7.78 (m, 6H), 7.70 (d, 1H, J = 7.3 Hz), 7.59 (d, 1H J = 5.0 Hz), 7.46 (br t, 1H), 7.40 (d, 1H, J = 7.3 Hz), 7.22–7.14 (m, 2H), 7.01–6.93 (m, 3H), 6.80–6.71 (m, 2H), 6.60 (t, 1H, J = 7.3 Hz), 6.32 (t, 1H, J = 7.3 Hz), 5.89 (d, 1H, J = 7.4 Hz), 5.46 (d, 1H, J = 7.3 Hz).

3. Results and discussion

3.1. Synthesis and characterization

The butenyloxy-functionalized ligand pbpy-OBut was prepared through condensation of 4'-(4-hydroxyphenyl)-6'-phenyl-2,2'-bipyridine [33] with 4-bromo-1-butene in the presence of potassium carbonate (Scheme 1). This procedure led to the alkenyl derivative in very low yield ($\geq 20\%$). The incorporation of the alkenyl function may however impart an interesting reactivity to the ligand (either as a free molecule or upon coordination to a metal), allowing the potential formation of macromolecular derivatives.

The formation of complex $[Ir(ppy)_2(pbpy-OBut)][PF_6]$ (2) was achieved via a bridge-splitting reaction of the dimer $[Ir(ppy)_2(\mu-Cl)]_2$, as outlined in Scheme 1. Our synthetic approach allows the preparation of cationic cyclometalated complexes in high yield and mild conditions [22], and it is



Scheme 1. Reagents and conditions. (i) 4-Br-1-butene, K_2CO_3 , cyclohexanone, reflux, 10 h; (ii) 0.5 [Ir(ppy)₂(μ -Cl)]₂, CH₂Cl₂/MeOH, reflux, 2 h; (iii) NH₄PF₆, room temperature.



Scheme 2. Reagents and conditions. (i) NH4OAc, MeOH, reflux, 6 h; (ii) 0.5 [Ir(ppy)2(µ-Cl]2, CH2Cl2/MeOH, reflux, 2 h; (iii) NH4PF6, room temperature.

now recognized as a standard procedure for obtaining similar heteroleptic Ir(III) systems avoiding harsh and time-consuming methods [23-26,29,34]. Spectroscopic characterization showed that complex **2** is a single isomer with cyclometalated ppy ligands in a *trans* configuration as in the parent chloro-bridged dimer. The pbpy-OBut ligand is therefore chelating through the N atoms of the bpy moiety leaving a free 6'-phenyl group (as outlined in Scheme 1). Complex **2** is an orange solid, which is highly soluble in acetonitrile and fairly soluble in acetone and chlorinated solvents.

In order to expand the range of ancillary ligands for the coordination of " $Ir(C \land N)_2$ " fragments, we have also prepared a novel terpyridine. Terpyridine ligands are increasingly used as components for luminescent and redox-active Ir(III) complexes [35], either for the preparation of bisterpyridine systems [36,37] or as bidentate co-ligands for cyclometalated complexes [34]. Indeed, we have previously prepared [Ir(ppy)₂(ttpy)][PF₆], a complex containing a (4'-tolyl)-functionalized terpy ligand [22]. Here, we present a novel terpy with a much more pronounced ability to react/interact (e.g., it could be useful for grafting, coupling, H-bonding, etc.) and that could be exploited for the construction of supramolecular architectures [38].

Tpy-COOH was prepared through a classical Kröhnke synthesis (Scheme 2), a methodology [39] which is very effective for the synthesis of oligopyridine ligands [40]. Although most terpyridines are accessible only in very low yields [41], the synthesis of tpy-COOH proceeded in good yield. A subsequent complexation reaction with $[Ir(ppy)_2(\mu-Cl)]_2$ led to the formation of $[Ir(ppy)_2(tpy-COOH)][PF_6]$ (3) in almost quantitative yield. NMR characterization confirmed the presence of the tpy-COOH ligand in an *N*,*N*-bidentate fashion. In this regard, the third free pyridine ring could be considered as a second active function of the ligand (in addition to the carboxy functional group).

3.2. Absorption spectra

The electronic absorption spectra of both complexes 2 and 3 show strong absorption bands in the UV region (Table 1). The absorptions at λ 250–325 nm are assigned to spin-allowed $\pi - \pi^*$ ligand-centered transitions. ¹LC transitions around 270 nm are characteristic of ppy-centered transitions [42], while absorption features at lower energy (280-330 nm) receive larger contributions from diiminecentered transitions. Spin-allowed CT transitions are observed with lower intensity at 350-450 nm. However, in this region the assignment is less clear-cut. Besides ¹MLCT ($d\pi(Ir) \rightarrow \pi^*(N \land N \text{ or } C \land N^-)$) transitions, here ligand-to-ligand charge transfer (¹LLCT) transitions should also be considered [42]. In the visible region, broad absorption features at 460-480 nm of much lower intensity $(\varepsilon \leq 1000 \text{ M}^{-1} \text{ cm}^{-1})$ can be assigned to spin-forbidden CT $(d\pi(Ir) \rightarrow \pi^*(N \land N))$ transitions, which are enabled through spin-orbit coupling.

3.3. Luminescence studies

Both complexes 2 and 3 display room temperature emissive behavior in fluid solutions. Luminescence data are gathered in Table 2 (which also contains data for the model

| Table 1 | |
|--|--|
| Absorption spectral data for complexes 2 and 3 | |

| - | • | ÷ | | | | |
|----------|---|--|--|--|--|--|
| Compound | Medium (298 K) | $\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm M}^{-1}~{\rm cm}^{-1})$ | | | | |
| 2 | CH ₂ Cl ₂ CH ₃ CN | 272 (49715), 325sh (32760), 365sh (15670), 390sh (9970), 470 (940) 263 (38670), 325sh (20590), 360sh (8820), 380sh (5800), 470 (1000) | | | | |
| 3 | CH ₂ Cl ₂ CH ₃ CN | 270 (48 180), 289sh (42 490), 375sh (5450), 470 (900) 267 (52 100), 283sh (44 360), 370sh (8000), | | | | |
| | | 460 (1000) | | | | |

| Compound | Medium ^a | $\lambda_{\rm em} (\rm nm)$ | τ (ns) ^b | $arPhi^{	ext{b}}$ | Redox-potentials (V vs. SCE | |
|---|--|-----------------------------|--------------------------|-------------------|-----------------------------|------------|
| | | | | | $E^0(ox)$ | E^0 (red |
| $\left[Ir(ppy)_2(bpy)\right]^+ (1)^{c,e}$ | CH ₂ Cl ₂ ^c | 606 | | 0.06 | +1.15 ^d | -1.50 |
| | CH ₃ CN ^e | 585 | 390 | 0.06 | +1.25 | -1.42 |
| $\left[Ir(ppy)_2(pbpy-OBut)\right]^+$ (2) | CH_2Cl_2 | 612 | 148 | 0.076 (0.060) | | |
| | CH ₃ CN | 622 | 140 (85) | 0.034 (0.020) | $+1.18^{f}$ | -1.38 |
| | Solid (film) | 586 | | | | |
| | 77 K ^g | 560 | 4100 | | | |
| $[Ir(ppy)_2(tpy-COOH)]^+$ (3) | CH_2Cl_2 | 626 | 52 | 0.018 (0.014) | | |
| | CH ₃ CN | 632 | 71 (60) | 0.013 (0.010) | $+1.21^{f}$ | -1.34 |
| | Solid (film) | 615 | | | | |
| | 77 K ^g | 598 | 4300 | | | |

Table 2 Photophysical and electrochemical data for complexes **1–3**

^a Data refer to 298 K deaerated solutions or to spin-coated films, unless otherwise stated. All the emission maxima are corrected for photomultiplier response.

^b The lifetimes and quantum yield values obtained in air are given in parentheses.

^c PF_6^- salt; data from Ref. [8].

^d In acetonitrile solution.

^e PF_6^- salt; data from Ref. [5].

^f Quasi reversible process.

^g In butyronitrile rigid matrix.

compound $[Ir(ppy)_2(bpy)]^+$ (1) obtained in similar conditions).

Upon excitation ($\lambda_{exc} = 390$ nm), complex **2** exhibits an intense yellow-orange luminescence (Fig. 1). The broad unstructured emission band peaks at 622 nm in acetonitrile, while a small blue-shift of the emission maximum is observed in dichloromethane solution ($\lambda_{em} = 612$ nm). The luminescence quantum yield is not very high (yet comparable to that of **1** and related compounds [5,22,23, 26,28,42]), and it increases in air-free conditions, as expected. In a previous study on Ir(III) complexes with strictly similar ligands (i.e., a bpy ligand with 6'-phenyl and *p*-X-4'-phenyl substituents [42]), we assigned the emission mainly to a ³LLCT (ppy-to-bpy) excited state, although the participation from a ³MLCT state cannot



Fig. 1. Emission spectra of compound 2 at room temperature. The spectra shown here are uncorrected; for corrected values, see Table 2.

be excluded. In particular, an active role in the stabilization of the ³LLCT state has been devised for the phenyl in *ortho* position to the chelating bpy ligand. More recently, participation of a σ -bond-to-ligand (³SBLCT, i.e., Ir(ppy)₂-tobpy) excited state has also been invoked for the emission from a series of cyclometalated [Ir(ppy)₂(L)]⁺ complexes, where L are various phenylated bipyridine ligands [43]. Very recent DFT calculations on related cationic species such as [Ir(ppz)₂(bpy)]⁺ (where ppz is the cyclometalating 1'-phenylpyrazolato anion) led to a similar conclusion, assigning the observed emission to an excited state with ³MLLCT (i.e., Ir(ppz)₂-to-bpy) character [44].

The luminescence of complex 3 in both dichloromethane and acetonitrile solutions is revealed as an unstructured intense band at a lower energy than that observed for 2, and with a similar bathochromic shift (Fig. 2 and Table 2). The assignment of the emission of 2 to a ³LLCT(ppyto-bpy) excited state receives strong support from our previous studies [22,42]. In particular, the emission properties of **2** are quite similar to those of $[Ir(ppy)_2(L1)]^+$ (where L1) is a 4'-(p-alkoxyphenyl)-6'-phenyl-2,2'-bipyridine [42]). At the same time, the emission from 3 is tentatively assigned to a similar ³LLCT (ppy-to-tpy) state. In fact, for this purpose the $N \wedge N$ bidentate tpy-COOH can be simply considered as a 6'-pyridyl-substituted bpy ligand. Strong analogies of the emission properties of 3 can be found with those of the previously studied $[Ir(ppy)_2(L2)]^+$ (where L2 is a 4'-(4-tolyl)-2,2':6',2"-terpyridine [22]). Both comparisons highlight the fact that remote substituents on the 4'-phenyl substituent of the chelating bpy fragment are less effective on the chromophore properties than the 6'-substituent, at least to a first approximation.

The luminescence spectra of both 2 and 3 are blueshifted at 77 K in comparison with the room temperature



Fig. 2. Emission spectra of compound **3** at room temperature. The spectra shown here are uncorrected; for corrected values, see Table 2.

solution spectra (see Table 2), and the luminescence lifetimes are much longer. This is a common behavior for CT emissions and further confirms our assignment.

Given the importance of testing the photophysical response of the emitters in conditions more similar to those of real light-emitting devices, we prepared solid films. The films were obtained by spin-coating acetonitrile solutions of both **2** and **3**. In both cases, and in accordance with previous data on similar systems [42], the emission energy maxima are intermediate between room-temperature solution and 77 K values (Table 2).

3.4. Redox behavior

Oxidation processes of Ir(III) cyclometalated compounds have been assigned to metal-centered orbitals and/or to sigma bond $Ir-C^-$ orbitals [45]. It is assumed that pure metal-centered oxidations are reversible, and irreversibility increases as the contribution to the HOMO of the cyclometalating phenyl(s) increases [46]. Because of the nature of the monoelectronic oxidation processes of **2** and **3** (Table 2), we suggest that in both the new complexes the oxidation involves an orbital receiving contribution from both metal- and phenyl-centered orbitals. The slight difference between the oxidation potentials of **2** and **3** is probably due to the different electronic nature of the aromatic substituent in 6'-position of the coordinating bpytype fragment (phenyl in **2** and 2-pyridyl in **3**).

The reversibility of the reduction processes (Table 2) indicates that they are ligand-based in both cases. In particular, the polypyridine ligands are involved. As for the oxidation process, the difference in the reduction potential values can be straightforwardly related to the nature of the substituents of the chelating moieties.

4. Conclusion

In summary, we have demonstrated that our approach to the synthesis of charged cyclometalated Ir(III) complexes with interesting photophysical properties can be very fruitful, and it can be successfully applied to a variety of polypyridine ligands [4,34,42,43,47]. The complexes are air-stable, soluble in common organic solvents, they can be processed as films while keeping their photophysical solution properties, and they also contain reactive functionalities that could be further derivatized.

These results are mirrored by the intense current interest for pre-functionalized luminescent bis(cyclometalated) Ir(III) complexes with chelating N \land N ligands [29,48,49]. A less traditional approach used combinatorial techniques for the preparation of a large series of cationic bis(cyclometalated) Ir(III) luminophores [50]. The aim was both synthetic (testing the effectiveness of parallel synthesis against traditional methods) and methodologic (building up a large set of photophysical data in order to choose the best luminescent materials). In all cases, the search for novel and efficient phosphorescent triplet emitters is still open, although it is only preliminary to the final goal which still remains the fabrication of affordable and versatile electroluminescent devices [51,52].

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