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Proton Sensitive Charge-Transfer Excited States in bis-Terdentate Cyclometalated Ir(III) Complexes : Spectroscopic and Theoretical Investigation

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ABSTRACT

Two bis-terdentate cyclometalated Ir(III) complexes with polypyridyl (N^N^N) and cyclometalated (C^N^C) ligands [Ir-Py]⁺ and [Ir-Py-Me]²⁺ have been synthesized and characterized. Their absorption and emission properties have been examined, more particularly in MeCN as a function of the addition of different acids. Depending on the acid strength and concentration, two distinct effects have been observed. For acetic acid at high concentration or trifluoroacetic acid (TFA) at low concentration, the pyridine moiety of [Ir-Py]⁺ is protonated; its spectroscopic behaviour is then similar to that of [Ir-Py-Me]²⁺. Moreover at higher concentration in TFA, the methoxy group of both complexes is protonated. The spectroscopic and electrochemical data as well as the DFT and TD-DFT calculations support contributions of charge-transfer excited states in absorption and emission from metal-ligand/ligand based HOMOs to ligand-based LUMOs, *i.e.* MLLCT.

KEYWORDS

Iridium - protonation - MLLCT - terdentate - photophysics

ABBREVIATIONS

 $[\mathbf{Ir}-\mathbf{Py}]^{+} = [\mathrm{Ir}(4'-\mathrm{Py}-\mathrm{tpy})(4'-\mathrm{MeO}-\mathrm{tppy})]^{+}$

 $[Ir-Py-Me]^{2+} = [Ir(4'-Me-Py-tpy)(4'-MeO-tppy]^{2+}]^{2+}$

 $[Ir-Py-H]^{2+} = [Ir(4'-H-Py-tpy)(4'-MeO-tppy]^{2+}]^{2+}$

 $[Ir-Py-H-Me]^{3+} = [Ir(4'-Me-Py-tpy)(4'-MeOH-tppy]^{3+}]^{3+}$

 $[Ir-Py-H_2]^{3+} = [Ir(4'-H-Py-tpy)(4'-MeOH-tppy]^{3+}]^{3+}$

1. INTRODUCTION

Transition metal complexes have attracted the interest of increasing numbers of researchers these past decades due to their exceptional properties.[1] Among the available transition metal ions, Ir(III) is becoming one of the most interesting elements for designing new complexes because of its strong spin-orbit coupling, its high quantum yield of luminescence with organic ligands and its fine-tunable properties by ligand modifications.[2] Therefore iridium (III) complexes are useful for the development of supramolecular devices, with photo-induced energy[3, 4] and/or electron transfer.[5-7] More recently, the incorporation of strong donor ligands has been exploited to red-shift the absorption and emission bands in transition metal complexes, such as Ru(II),[8-14] Re(I)[15] and Ir(III)[16] complexes. Generally greater effects result by using anionic cyclometalating ligands, such as derivatives of 2-phenylpyridine, that produce Ir(III) complexes like $[Ir(C^N), (N^N)]^+$ (C^N = cyclometalated ligand, N^N = polypyridine). These complexes have attracted much attention because of their potential applications in various fields such as photo-catalysis, [17-19] dye-sensitized solar cells, [20] electroluminescence and electrochemiluminescence, [21, 22] DNA sensors [23] and cellular imaging.[24, 25] Compared to cyclometalated Ir(III) tris-bidentate complexes, the bis-terdentate equivalents have been less investigated mainly due to difficulties of synthesis and purification.[26, 27] However, these compounds exhibit several important advantages. Ir(III) terpyridyl complexes derivatized on the 4'-position by suitable substituents circumvent the occurrence of geometrical isomers as with tris-bidentate arrangements. This problem has been well documented in Ru(II) chemistry of bidentate and tridendate ligands. [28] Moreover the Ir(III) complexes of tridentate ligands also allow the design of systems for linear charge separation by photo-induced intramolecular electron transfer. In the literature, cyclometalated Ir(III) complexes involving two tridentate ligands, one N^N tpy derivative (tpy = 2:2', 6':2''-terpyridine) and

one C^N^C dppy derivative (dppy = 2,6-diphenylpyridine), have been first reported by Scandola *et al.[29]* Based on computational results, the predominant emitting excited state has been attributed to a Ligand-to-Ligand charge-transfer state (LLCT) from the cyclometalated iridium fragment to the tpy ligand.[30] However, experimental proof of LLCT transitions are not always easy to obtain. Because the photo-redox properties of this type of complexes and the understanding of their origins are essential for potential applications, it has become of prime importance to design and study other Ir(III) complexes constructed with different derivatives of tridentate ligands. Such studies could allow gathering new data on the complicated photophysics of this type of complexes.

Therefore in this work, we report the synthesis and characterization of two new Ir(III) complexes obtained from the coordination of a terpyridyl ligand and a triphenylpyridyl ligand *i.e.* $[Ir(4'-Py-tpy)(4'-MeO-tppy)]^+$ (4'-Py-tpy = 4'-(4-pyridinyl)-2,2';6',2'' terpyridine and 4'-MeO-tppy = 2,6-diphenyl-4-(4'-methoxyphenyl)pyridine) and its *N*-methylated equivalent *i.e.* $[Ir(4'-Me-Py-tpy)(4'-MeO-tppy)]^{2+}$ (4'-Me-Py-tpy = 4'-(4-methyl-pyridinio)-2,2';6',2'' terpyridine) termed **[Ir-Py]^+** and **[Ir-Py-Me]^{2+}**, respectively (Figure 1). The impact of acidity on the spectroscopic properties of both complexes in MeCN is analyzed from an experimental and theoretical approach and provides arguments in favor of contributions of Metal-Ligand/Ligand to Ligand centered charge-transfer excited states.

2. EXPERIMENTAL SECTION

2.1. Synthetic procedures

4'-((4-Pyridinyl)-2,2';6',2'' terpyridine) (4'-Py-tpy) was prepared following the previously described methods from 2-acetyl-pyridine and 4-pyridinecarboxaldehyde.[31, 32] (4'-(4-Methyl-pyridinio)-2,2';6',2''-terpyridine) ([4'-Me-Py-tpy]⁺) was synthetized by a selective methylation of 4'-Py-tpy as previously described.[33] 2,6-Diphenyl-4-(4'-methoxyphenyl)pyridine) (4'-MeO-

tppy) was prepared by grinding two equivalents of acetophenone and NaOH in the presence of *p*-anisaldehyde followed by cyclization with ammonium acetate.[34]

2.2. Materials and methods

¹H NMR (300 and 500 MHz) experiments were performed in CD₂CN on a Bruker AC-300 Avance II (300 MHz) or on a Bruker AM-500 (500 MHz). The chemical shifts (given in ppm) were measured versus the residual peak of solvent as internal standard. HRMS were recorded on a Q-Extractive orbitrap from ThermoFisher. The samples were ionized by ESI (capillary temperature: 250 °C, vaporizer temperature: 250 °C, sheath gas flow rate: 20). UV-vis absorption spectra were recorded on a Shimadzu UV-1700. Room temperature fluorescence spectra were recorded on Varian Cary Eclipse. Complexes were excited at 520 nm. Luminescence lifetimes were measured with a modified Applied Photophysics laser kinetic spectrometer by exciting the samples at 355 nm with a Nd-YAG pulsed laser (Continuum NY 61-10). Emitted light as a function of time was detected with a R-928 Hamamatsu photomultiplier tube the output of which was applied to a digital oscilloscope (Hewlett-Packard HP 54200A) interfaced with a Dell Dimension DE051 computer. The signals were averaged over at least 16 shots and the baseline was corrected. Igor 6.1 software was used for the decay analysis. Transient absorption spectra were acquired using a LP920K system from Edinburgh Instruments. Excitation was carried out from the third-harmonic (355 nm) of a Brilliant-Quantel Nd:YAG Laser at 6 Hz. A Xe900 pulsed Xenon Lamp is used as probe source. The photons were dispersed using monochromator, transcripted by a R928 (Hamamatsu) photomultiplicator and recorded on a TDS3012C (Tektronix) oscilloscope. Cyclic voltammetry was carried out in a onecompartment cell, using a glassy carbon disk working electrode (approximate area = 0.03 cm^2), a platinum wire as counter electrode and an Ag/AgCl electrode as reference. The potential of the working electrode was controlled by an Autolab PGSTAT 100 potentiostat through a PC

interface. The cyclic voltammograms were recorded with a sweep rate of 100 or 400 mV s⁻¹ in dried acetonitrile (Acros, HPLC grade). Tetrabutylammonium perchlorate (0.1 M) was used as supporting electrolyte and the samples were purged by argon before each measurement. DFT calculations were performed using Gaussian 09.[35] The B3LYP method[36-38] was used to carry the DFT[39-42] and TD-DFT[43-45] calculations. The 6-31G* basis set[46] was used for H, C, N and O, and the VDZ (valence double ζ) with the SBKJC effective core potential basis set[47-50] was used for Ir. Geometry optimizations were conducted without symmetry constraints. Frequency calculations on each optimized structure confirmed that energy minima had been reached in all cases. The energy, oscillator strength, and related MO contributions for the 100 lowest singlet–singlet and 10 lowest singlet–triplet excitations were obtained from the TD-DFT/singlets and the TD-DFT/triplets output files, respectively, for the S₀-optimized geometry. GaussView3.0.9[51], GaussSum 3.0[52] and Chemissian 4.33[53] software were used for data analysis, visualization and surface plots. All calculations were performed with MeCN as solvent by use of the polarized continuum (PCM) solvation model as implemented in Gaussian 09.[54, 55]

[Ir(4'-Py-tpy)(4'-MeO-tppy)]⁺.NO₃⁻ ([Ir-Py]⁺)

(NH₄)₃IrCl₆ (100 mg, 0.21 mmol) was added to a solution of 4'-Py-tpy (65 mg, 0.21 mmol) in DMF (3 mL). The mixture was heated at 120°C for 6h. The dark red precipitate was isolated and washed with water (twice), EtOH and CHCl₃. The crude [(4'-Py-tpy)-IrCl₃] (100 mg, 0.16 mmol), 4'-MeO-tppy (55 mg, 0.16 mmol) and AgNO₃ (136 mg, 0.80 mmol) were refluxed in degassed ethylene glycol (4 mL) in the dark and under Ar for 16h. On cooling, the mixture was filtered through Celite to remove AgCl. The Celite plug was washed with MeOH, which was subsequently evaporated. Water was added and the aqueous layer was extracted with CHCl₃ (3 times). The organic solutions were combined and evaporated to dryness. The crude product was

purified by column chromatography on SiO₂ (MeCN/saturated aqueous KNO₃ (10/1)). The first eluted orange band was recovered and the solvent evaporated. The red powder was washed with water and dried under vacuum to afford [**Ir-Py**]⁺ (55 mg, 29 %). ¹H NMR (CD₃CN, 300 MHz) : $\overline{\mathbf{0}}$ (ppm), 8.99 (s, 2H, H₃, and H₃, of tpy-C₆H₃N), 8.93 (d, 2H, H₄ of tpy-C₆H₅N, J_{Ha-Hb} = 6.1 Hz), 8.66 (d, 2H, H₃ of tpy-C₆H₃N, J_{H3-H4} = 7.6 Hz), 8.27 (s, 2H, H₃, and H₃ of tppy-OMe), 8.11-8.07 (m, 4H, H_b of tpy-C₆H₃N and H₃ of tppy-OMe), 8.01-7.95 (m, 4H, H_b of tppy-OMe and H₄ tpy-C₆H₅N), 7.88 (d, 2H, H₆ of tpy-C₆H₅N, J_{H6-H5} = 5.8 Hz), 7.30-7.25 (m, 2H₄, H₅ of tpy-C₆H₅N), 7.24 (d, 2H, H_a of tppy-OMe, J_{H6-H5} = 8.8 Hz), 6.99 (td, 2H, H₄ of tppy-OMe, J_{H4-H5 (H5)} = 7.3 Hz, J_{H4-H6} = 1.0 Hz), 6.75 (td, 2H, H₅ of tppy-OMe, J_{H5-H4} = 1.0 Hz), 3.95 (s, 3H, OMe). ¹³C NMR (CD₃CN, 125 MHz) : $\overline{\mathbf{0}}$ (ppm), 167.0, 165.2, 158.3, 153.6, 153.4, 151.7, 151.5, 148.3, 138.9, 134.9, 131.3, 130.7, 130.6, 128.8, 127.3, 126.4, 125.4, 123.6, 118.7, 116.0, 115.1, 56.7. HRMS (ESI): m/z calculated for [C₄₄H₃₁N₅O₁¹⁹³Ir - NO₃₁⁺, 838.2152; found: 838.2146. Elem. Anal. Calcd for [C₄₄H₃₁N₅OIr]PF₆: C, 53.77; H, 3.18; N, 7.12. Found: C, 53.94; H, 2.97; N, 7.30.

[Ir(4'-Me-Py-tpy)IrCl₃]⁺.I⁺

 $[4' - Me - Py - tpy]^{+}$.I (50 mg, 0.11 mmol) and $(NH_{4})_{3}$ IrCl₆ (53 mg, 0.11 mmol) were heated at 120°C for 6h in DMF (3 mL). The dark red precipitate was isolated and washed with water (twice), MeCN and Et₂O. Yield: 34 mg (42%). ¹H NMR (DMSO-d₆, 300 MHz) : δ (ppm), 9.51 (s, 2H, H_{3'} and H_{5'}), 9.34 (d, 2H, H_a, J_{Ha-Hb} = 6.6 Hz), 9.23 (dd, 2H, H6, J_{H6-H5} = 5.6 Hz, J_{H6-H4} = 1.2 Hz), 9.01 (d, 2H, H_b, J_{Hb-Ha} = 6.6 Hz), 8.98 (d, 2H, H₃, J_{H3-H4} = 7.9 Hz), 8.38 (td, 2H, H₄, J_{H4-H3(H5)}) = 8.0 Hz, J_{H4-H6} = 1.2 Hz), 8.03 (m, 2H, H₅), 4.45 (s, 3H, Me). MS (ESI): m/z calculated for $[C_{21}H_{17}N_4Cl_3^{193}Ir - I]^{+}$, 623.01; found: 622.92.

[Ir(4'-Me-Py-tpy)(4'-MeO-tppy]²⁺.2NO₃⁻ ([Ir-Py-Me]²⁺)

This complex was prepared using the same procedure as that used for complex (**[Ir-Py**]⁺) except that [Ir(4'-Me-Py-tpy)IrCl₃]^{*}.I^{*} was used instead of [(4'-Py-tpy)-IrCl₃]. Yield: 10 mg (25%). ¹H NMR (CD₃CN, 500 MHz) : $\overline{\mathbf{0}}$ (ppm), 9.16 (s, 2H, H₃, and H₃, of tpy-C₆H₃N-Me), 8.96 (d, 2H, H₄ of tpy-C₆H₃N-Me, J_{Ha-Hb} = 6.7 Hz), 8.78 (d, 2H, H₅ of tpy-C₆H₅N-Me, J_{Hb-Ha} = 6.8 Hz), 8.75 (d, 2H, H₃ of tppy-OMe, J_{Ha-Ha} = 8.0 Hz), 8.29 (s, 2H, H₃ and H₃, of tppy-OMe), 8.10 (d, 2H, H_b of tppy-C₆H₃N-Me, J_{Hb-Ha} = 8.8 Hz), 8.04-8.00 (m, 4H, H₄ and H₃ tpy-C₆H₃N-Me), 7.91 (dd, 2H, H₆ of tpy-C₆H₃N-Me, J_{H5-Ha} = 5.8 Hz, J_{H6-H4} = 1.1 Hz), 7.31 (ddd, 2H, H₅ of tpy-C₆H₃N-Me, J_{H5-Ha} = 7.3 Hz, J_{H5-H6} = 5.8 Hz, J_{H5-H6} = 1.1 Hz), 6.75 (td, 2H, H₄ of tpy)-OMe, J_{H5-H6} = 7.3 Hz, J_{H5-H6} = 7.3 Hz, J_{H5-H6} = 1.1 Hz), 6.75 (td, 2H, H₄ of tppy-OMe, J_{H5-H6} = 7.3 Hz, J_{H5-H6} = 1.1 Hz), 6.75 (td, 2H, H₄ of tppy-OMe, J_{H5-H6} = 7.3 Hz, J_{H5-H6} = 1.1 Hz), 6.21 (dd, 2H, H₆ of tppy-OMe, J_{H6-H5} = 7.3 Hz, J_{H6-H5} = 7.3 Hz, J_{H6-H5} = 7.3 Hz, J_{H6-H6} = 7.3 Hz), 151.2, 147.8, 147.3, 139.0, 134.7, 131.1, 130.3, 128.7, 127.1, 126.9, 126.4, 125.3, 124.0, 115.7, 114.9, 56.4, 49.2. HRMS (ESI): m/z calculated for [C₄₅H₄₄N₆O₄¹⁹³Ir - NO₃]⁺, 915.2265; found: 915.2273, m/z calculated for [C₄₅H₃₄N₃O¹⁹³Ir - 2NO₃]^{2²}, 426.6191; found: 426.6192. Elem. Anal. Calcd for [C₄₅H₃₄N₃OIr]P₂F_B: C, 47.29; H, 3.00; N, 6.12. Found: C, 48.27; H, 3.05; N, 5.54.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization

The synthesis of the two Ir(III) complexes (Figure 1) was achieved in two steps from the Ir(III) chloride salt according to methodologies previously described;[29, 30] they were purified by column chromatography (see experimental section). Both complexes were unambiguously characterized by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectrometry (HRMS) (see experimental section).



Figure 1. Structures of $[Ir(4'-Py-tpy)(4'-MeO-tppy)]^+([Ir-Py]^+)$ and $[Ir(4'-Me-Py-tpy)(4'-MeO-tppy)]^{2+}([Ir-Py-Me]^{2+})$.

The redox potentials of the two complexes have been determined from cyclic voltammetry in order to obtain more information on the relative energy of their HOMO and LUMO levels. The data are gathered in Table 1. Both complexes display one reversible oxidation wave at + 1.16/1.19 V vs. Ag/AgCl (Figures S1-S2). These similar oxidation potentials are in agreement with a similar oxidation process, which indicates that the HOMOs have a similar energy level in the two compounds. The potential values are also in a range similar to those of other cyclometalated complexes[29, 30]. The oxidation process most likely involves the cyclometalated iridium fragment (Ir-tppy) as also proposed in the literature for the non-substituted carbometalated Ir compound.[30]

At negative potentials, there are two reduction waves for $[Ir-Py-Me]^{2+}$, the first one at -0.71 V vs. Ag/AgCl (Figure 2) is ascribed to the reduction of the *N*-methyl-pyridinium substituent

similar to the attribution of the first reduction wave of $[Pt(4'-Me-Py-tpy)(Cl)](ClO_4)_2$.H₂O (-0.45 *vs.* Ag/AgCl).[33] As the potential of this first wave can be related to the LUMO level of the complex, this means that the LUMO of $[Ir-Py-Me]^{2+}$ is much more stabilized than that of $[Ir-Py]^+$. The second reduction wave of $[Ir-Py-Me]^{2+}$ at -1.14 V *vs.* Ag/AgCl is ascribed to the reduction of the tpy motif, as for $[Ir-Py]^+$, with only a weak effect caused by the substituent (Table 1 and Figures 2 and S3).



Figure 2. Reduction voltammogram of $[Ir-Py-Me]^{2+}(10^5 \text{ M})$ in MeCN (0.1 V/s) with Bu₄NClO₄ 0.1 M as supporting electrolyte.

3.2. Absorption and emission spectroscopy

The absorption and emission spectra in MeCN are shown in Figure 3. The data are gathered in Table 1 for MeCN. Intense absorption bands between 280-330 nm are ascribed to Ligand Centered transitions (LC), based on previous studies of cyclometalated Ir(III) complexes[29]; as shown in Table 1, they are not affected upon methylation of the pyridine substituent.

Table 1. Electrochemical and spectroscopic data for the complexes [Ir-Py]⁺ and [Ir-Py-Me]²⁺.

Complexes	$[Ir-Py]^+$	[Ir-Py-Me] ²⁺
E _{ox} ^a (V vs.Ag/AgCl)	1.16 (r, $\Delta E_p = 70 \text{ mV}$)	$1.19 (r, \Delta E_p = 62 mV)$
E _{red} ^a (V	-1.16 (r, $\Delta E_p = 72 \text{ mV}$)	-0.71 (r, ΔE_{p} = 73 mV);

vs.Ag/AgCl)		-1.14 (r, ΔE_{p} = 71 mV)
$λ_{\max abs}, nm^{b}$ (ε, x 10 ⁻³ M ⁻¹ cm ⁻¹)	514 (5.5), 445 (9.1), 324 (41.6), 283 (53.6)	540 (6.7), 476 (9.3), 327 (31.8), 281 (42.2)
$\lambda_{\max Em}$ under air at 298 K	705	<u>-</u> °
$\lambda_{\max Em}$ at 77 K	673	720
τ (μs) under air at 298 K	0.22	<u>-</u>
τ (μs) under argon at 298 K	1.05	<u>-</u> °
ф(Air)	0.0009	- C
ф(Ar)	0.0041	<u>-</u> °
$k_r (x \ 10^{-3} \ s^{-1})^e$	3.9	- ^c

^aElectrochemical data were recorded at room temperature in MeCN ([Complex] = 10⁻⁵ M) with Bu₄NClO₄ 0.1 M as supporting electrolyte; (r) = reversible, (ΔE_p) (peak-to-peak difference). ^bMeasured in MeCN. ^cNon emissive. ^dQuantum yield was measured under air and argon using [Ru(bpy)₃]²⁺ as reference $\Phi_{mr} = 0.018$, $\Phi_{mrgon} = 0.094$ in MeCN,[56] $\lambda_{Exc} = 450$ nm, 293 K. ^cRadiative rate constant under argon at 298 K (k_r= Φ r).

PCC



Figure 3. Absorption spectra of $[Ir-Py]^+$ (green) and $[Ir-Py-Me]^{2+}$ (red) in MeCN; emission of $[Ir-Py]^+$ (dotted green line) under air at room temperature and excitation at 520 nm. Inset: emission spectra at 77 K of $[Ir-Py]^+$ (green), $[Ir-Py-Me]^{2+}$ (red) and $[Ir-Py-H]^{2+}$ (blue) in a mixture EtOH/MeOH (4/1)($\lambda_{exc} = 520$ nm).

Absorption bands also appear in the visible. In contrast to the LC transitions in the UV, these bands are affected by methylation of the pyridine substituent. Thus, a red shift of *ca.* 30 nm is observed upon methylation of **[Ir-Py]**⁺ into **[Ir-Py-Me]**²⁺ (Figure 3). Regarding the luminescence properties at 298 K, only the **[Ir-Py]**⁺ is emissive (Figure 3). A shoulder in the emission spectrum might indicate the contribution of more than one excited state. At 77 K, the luminescence of **[Ir-Py]**⁺ in MeOH/EtOH is shifted to the blue (Figure 3, inset). For **[Ir-Py-Me]**²⁺ in MeOH/EtOH at 77K a weak emission with a maximum around 725 nm can be detected (Figure 3, inset). Pulsed laser induced transient absorption spectra of **[Ir-Py]**⁺ have also been recorded in MeCN under Ar (Figure S4). Transient absorption (TA) is observed around 700 nm, concomitant with the bleaching of the ground state. The associated lifetime of the excited state obtained from the TA measurements is 216 ns, in good agreement with that of the emission lifetime (Table 1). Strikingly, the transient absorption is reminiscent of the reduced methyl

viologen absorption[57]. All these observations lead to different conclusions. (i) For [**Ir-Py**]⁺, the unstructured room temperature emission, which is blue-shifted at 77 K, is characteristic of a CT emission. (ii) The fact that a very weak emission for [**Ir-Py-Me**]²⁺ can be detected at 77 K around 725 nm (Figure 3, inset) indicates also the participation of a luminescent excited state for the methylated compound. This excited state is however affected by important radiationless deactivation at 298 K, probably caused by an important stabilization of this state and thus governed by the energy gap law[58], (iii) An emission lifetime of the order of 1 μ s with k_r values of *ca*. 10⁴ s⁻¹ for [**Ir-Py**]⁺ is compatible with CT excited state lifetimes.[59]

The spectroscopy in absorption and emission is thus compatible with the attribution of the lowest energy transitions to CT transitions for both Ir complexes. Based on the electrochemistry, the transient absorption results and data in the literature[29], the CT would take place from the whole fragment C-N-C-Ir towards the tpy ligand with possibly participation of more than one CT for [**Ir-Py**]⁺.

3.3. Acid-base titration studies

In order to check further the CT characteristics in absorption and emission of $[Ir-Py]^+$, acidbase titration experiments were performed with this complex. Indeed, if MLLCT/LLCT transitions are predominant, the corresponding absorption and emission energy should be greatly affected by protonation of the pyridine group of the tpy. In contrast no protonation effect should be observed with $[Ir-Py-Me]^{2+}$. Therefore acid-base titrations experiments were also carried out with the methylated complex for comparison purposes. MeCN was used as solvent in both cases, with two acids that have different pKa values, acetic acid (pKa = 23.51)[60] and trifluoroacetic acid (TFA) (pKa = 12.65).[61]

3.4. Spectroscopic behaviour upon addition of acetic acid or TFA at low concentration *(i.e.* in the mM range in TFA)

Modifications of absorption and emission bands are shown in Figure 4 for **[Ir-Py]**⁺ upon addition of acetic acid in MeCN. For **[Ir-Py-Me]**²⁺ (Figure S5) in the same conditions, no change is observed, as expected for the methylated compound. For **[Ir-Py]**⁺, there is a clear bathochromic shift of the visible band upon addition of acetic acid. The presence of isosbestic points (387 nm, 455 nm) indicates at least the existence of two species in equilibrium. No shift is noticed for the higher energy absorption bands (283 nm and 324 nm) but the absorbance slightly decreases. The emission of **[Ir-Py]**⁺ dramatically decreases with the addition of acetic acid. These absorption and emission modifications are due to the gradual protonation of the pyridine substituent of **[Ir-Py]**⁺, which once protonated, becomes a better acceptor in the CT transition with a concomitant decrease in the LUMO energy. No further change by supplementary addition of acetic acid can be observed with the exception of slight solvatochromic effects caused by a too large amount of acid in MeCN.



Figure 4. Absorption and emission (inset) spectral changes for a 2.2 x 10⁻⁵ M solution of **[Ir-Py]**⁺ in MeCN for increasing concentrations of acetic acid (0.5 M, 0.9 M, 1.4 M, 1.8 M , 2.2 M, 2.6 M, 2.9 M, 3.3 M, 3.6 M).

The addition of low concentrations of TFA (mM range) induces similar changes in the **[Ir-Py]**⁺ spectrum as those observed with acetic acid in absorption (with the same isosbestic points) and decreases the emission of **[Ir-Py]**⁺ (Figures 4 and 5). Moreover, as in the case of acetic acid, these low TFA concentrations have no effect on the absorption of **[Ir-Py-Me]**²⁺ (Figure S6) as expected. The effect of a stronger acid in mM concentration range is thus the same as with the acetic acid.

The spectroscopic properties of protonated **[Ir-Py]**⁺ (with acetic acid or TFA in the mM range) look very much like those of the methylated complex, *i.e.* a bathochromic shift in absorption (Figure S7) and disappearance of emission in MeCN at RT. At 77 K in EtOH/MeOH in strong acidic conditions (100 % protonation with TFA) a slight emission (Figure 3, inset) exists with the same emission maximum as **[Ir-Py-Me]**²⁺. These similar properties with a very poor emission can be attributed to the important stabilization of the excited state and to a decrease of emission due to the energy gap law effect[58].

From the absorption and emission changes of $[Ir-Py]^+$ with the TFA addition in mM range of concentration, an association constant K_{a1} between TFA (Figure 5, insets) and the complex (reaction 1) could be determined by the Benesi-Hildebrand method[62] (equation 1):

$$[\mathbf{Ir} - \mathbf{Py}]^{+} + \mathbf{CF}_{3}\mathbf{COOH} \xrightarrow{\mathbf{K}_{a1}} [\mathbf{Ir} - \mathbf{Py} - \mathbf{H}]^{2+} + \mathbf{CF}_{3}\mathbf{COO^{-}}$$
(1)

Accepter

where A_0 is the absorbance of the $[Ir-Py]^+$ without acid, A is the absorbance at different TFA concentrations at 525 nm, K_{a1} is the association constant, and $\Delta [Ir-Py]^+$ is the difference between the molar extinction coefficient of $[Ir-Py]^+$ and its associated form with TFA. The adjustment to a linear plot obtained by the Benesi-Hildebrand relation (Figure 5, insets) is in agreement with a 1:1 binding stoichiometry (reaction 1). The corresponding values of K_{a1} calculated from the absorption and emission data are 1400 ± 200 M⁻¹ and 1530 ± 75 M⁻¹, respectively. These similar values indicate that the red-shift of the absorption and loss of emission correspond to the appearance of the red-absorbing and non-luminescent protonated $[Ir-Py]^+$ form, *i.e.* $[Ir-Py-H]^{2+}$.



Figure 5. Absorption (A) and emission (B) changes for a 2.6 x 10^{-5} M solution of [**Ir-Py**]⁺ in MeCN at low and increasing concentrations of trifluoroacetic acid (0.24 mM, 0.47 mM, 0.69 mM, 0.89 mM, 1.09 mM, 1.27 mM, 1.45 mM, 1.62 mM). Inset: Corresponding Benesi-Hildebrand plot with CF₃COOH when monitoring absorbance changes at 525 nm (A) and emission changes at 704 nm (B).

3.5. Spectroscopic behaviour upon addition of TFA at higher concentrations

When higher concentrations of TFA (from 0.1 M range till 0.6 M) are used, both absorption spectra, *i.e.* that of $[Ir-Py]^+$ and $[Ir-Py-Me]^{2+}$ (Figure 6), seem to be modified with the addition of TFA. An absorption band appears at ca. 360 nm and there is a hypochromic effect in the visible. The spectral modification of both complexes could be attributed to protonation of the common fragment, *i.e.* the 4'-MeO-tppy. At such high proton concentrations, the MeO group of the ligand 4'-MeO-tppy can indeed be protonated. We have checked by ¹H NMR analysis that for these high TFA concentrations, the complex does not decompose (see Supporting Information). The modifications of absorption introduced by biprotonation are in agreement with the attribution of the lowest energy transitions to a mixture of different CT transitions. Indeed, the protonation of the MeO group induces a stabilization of the HOMO orbital centered on this fragment and a clear hypsochromic shift of the visible band to form a new absorption band at *ca*. 360 nm. However, if the HOMO was exclusively centered on the ligand 4'-MeO-tppy, the complete protonation of the MeO group should induce a total disappearance of the absorption bands in the 400-600 nm region. But, as shown on Figure 6B, some absorption remains in the visible, *i.e.* at 430 nm (Figure 6B, inset). These transitions should be probably attributed to other CT transitions from the fragment C-N-C-Ir without the participation of the MeO group towards the tpy ligand.

DFT and TD-DFT calculations were performed with **[Ir-Py]**⁺ and **[Ir-Py-Me]**²⁺ in order to better understand the nature of the different lowest energy transitions in the protonated and unprotonated forms.



Figure 6. Absorption changes for a 2.6 x 10^{-5} M solution of $[Ir-Py]^+$ (A) and a 3.6 x 10^{-5} M solution of $[Ir-Py-Me]^{2+}$ (B) in MeCN with increasing concentrations of TFA (0.10 M, 0.19 M, 0.28 M, 0.37 M, 0.45 M, 0.53 M, 0.60 M). Inset for 6B: titration curve by monitoring the absorbance at 430 nm.

3.6. Computational studies

The ground and vertical excited state electronic structures were investigated by the means of DFT/TD-DFT calculations using the B3LYP method[36-38], the 6-31G* basis set[46] for H, C, N and O and the VDZ (valence double ζ) with the SBKJC effective core potential basis set[47-50] for Ir. Solvent (MeCN) was included by a polarizable continuum model. The computed

HOMO, HOMO-1, HOMO-2, LUMO and LUMO+1 for $[Ir-Py]^+$, $[Ir-Py-H]^{2+}$, $[Ir-Py-Me]^{2+}$, $[Ir-Py-H_2]^{3+}$ and $[Ir-Py-H-Me]^{3+}$ are depicted in Table 2 while further details on electronic and geometrical structure can be found in Tables S1-S15. Figure 7 compares the energy levels of selected occupied and unoccupied molecular orbitals (MOs) of the S₀ state. The contributions of the Ir(III) as well as those of the two types of ligands are represented with different colors and the percentages of these contributions can be found in Tables S1-S5. The calculated lowest energy transitions follow the trend observed in the electrochemical measurements as well as in the absorption spectra, with $[Ir-Py]^+$ exhibiting a larger energy gap than $[Ir-Py-Me]^{2+}$. Methylation stabilizes the LUMO levels, as suggested by the higher reduction potential of [Ir- $Py-Me]^{2+}$, while the HOMO levels are almost unaffected.

As also summarized in Figures S8, S9 and Tables S6, S8, the TD-DFT results show that the lowest energy transitions should have a charge transfer characteristic as they correspond to transitions involving orbitals centered on the Ir-tppy fragment to an orbital centered on the tpy ligand.

It is difficult to clearly define these CT transitions as pure Metal-Ligand to Ligand (MLLCT), due to the participation of the Ir and carbometalated ligand, or as Ligand to Ligand (LLCT), because the % of participation of the carbometalated ligand is higher than that of the Ir. These cases are more aptly seen as being of mixed origins and are due to the fact that there are different CT transitions of very close energy for [Ir-Py]⁺. Although the LUMOs are clearly tpy centered, there is a slight difference between [Ir-Py]⁺ and the methylated derivative in the electron accepting tpy. For [Ir-Py]⁺ the LUMO and LUMO+1 participating in the lowest energy transition are mainly tpy type, whereas for [Ir-Py-Me]²⁺ and [Ir-Py-H]⁺, the participating LUMO is localized not only on the tpy but also on the pyridinium group as suggested by the presence of two reduction waves in the voltamogram of [Ir-Py-Me]²⁺.

computational studies performed with the protonated $[Ir-Py]^+$ complex show the same characteristics in the results as with the methylated $[Ir-Py]^+$ (see the comparisons in Figure 7 and Tables 2 and S1-S15), *i.e.* a bathochromic shift of absorption as compared to $[Ir-Py]^+$ and also a more important participation of the pyridinium group in the LUMO (Table 2) of the tpy ligand in the CT transition.

These conclusions from computational calculations agree very well with the electrochemical data and spectroscopic behavior before and after the first protonation.

For further understanding of the system, the protonated forms of [**Ir-Py-Me**]²⁺ and [**Ir-Py-H**]²⁺, namely [**Ir-Py-H-Me**]³⁺ and [**Ir-Py-H**₂]³⁺ were also studied by DFT/ TD-DFT. The energy levels of selected occupied and unoccupied molecular orbitals (MOs) of the S₀ state are presented on Figure 7. As a consequence of the protonation of the MeO-tppy ligand, the HOMO and HOMO-1 levels are slightly stabilized. This stabilization leads to a small increase in the band gap thus, as observed in TD-DFT studies (Figure 7, Table S1-15), a blue-shift of the low energy MLLCT absorption band. The situation is however more dramatic for the HOMO-2 levels that are clearly strongly stabilized (Figure 7 and Table 2). Thus, the transitions involving this level are shifted to higher energy leading to the hypochromic effect and the appearance of a band in near-UV at high concentrations of TFA. These observations from computational calculations bring further evidence that absorption bands in the visible for [**Ir-Py**]⁺ and [**Ir-Py-Me**]²⁺ involve a mixture of CT transitions from the cyclometalated iridium fragment (Ir-tppy) towards the tpy ligand.

Table 2. Representation of the molecular orbitals from HOMO-2 through LUMO+1 for [Ir-Py]⁺[Ir-Py-H]²⁺[Ir-Py-Me]²⁺[Ir-Py-H2]³⁺and [Ir-Py-Me-H]³⁺

	$[Ir-Py]^{+}$ $[Ir-Py-H]^{2+}$ $[Ir-Py-Me]^{2+}$ $[Ir-Py-H_2]^{3+}$ $[Ir$	r-Py-H-Me] ³⁺
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LUMO+1 (-2.5 eV)	LUMO+1 (-2.7 eV)	LUMO+1 (-2.68 eV)	LUMO+1 (-2.68 eV)	LUMO+1 (-2.74 eV)
The states	The Me	The second	THE REAL PROPERTY IN THE REAL PROPERTY INTO THE REAL PR	Station of the second s
LUMO (-2.63 eV)	LUMO (-3.33 eV)	LUMO (-3.27 eV)	LUMO (-3.38 eV)	LUMO (-3.33 eV)
		The states	A AREA .	A REAL
HOMO (-5.78 eV)	HOMO (-5.9 eV)	HOMO (-5.89 eV)	HOMO (-6.01 eV)	HOMO (-6 eV)
	The second second			THE REAL
HOMO-1 (-5.79 eV)	HOMO-1 (-5.94 eV)	HOMO-1 (-5.93 eV)	HOMO-1 (-6.02 eV)	HOMO-1 (-6.01 eV)
	A CARLER OF CONTRACT	- Aller	A REAL PROPERTY AND A REAL	A A A A A A A A A A A A A A A A A A A
HOMO-2 (-6.06 eV)	HOMO-2 (-6.11 eV)	HOMO-2 (-6.1 eV)	HOMO-2 (-6.62 eV)	HOMO-2 (-6.61 eV)
in the second	in the second	Sold and a sold		THE REAL
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Figure 7. Energy diagram for **[Ir-Py]**⁺, **[Ir-Py-H]**²⁺, **[Ir-Py-Me]**²⁺, **[Ir-Py-H**₂]³⁺ and **[Ir-Py-H**-**Me]**³⁺. The contribution of **Ir** (red), **tppy** (green) and **tpy** (blue) are presented for each orbital.

4. CONCLUSION

The electrochemical and spectroscopic data for $[Ir-Py]^+$ and $[Ir-Py-Me]^{2+}$ are in full agreement with the computational results which indicate that the lowest transitions correspond to CT transitions. Moreover the effect of mono- and bi-protonation observed on the absorption and emission behavior of the two complexes also corroborates the theoretical data.

However it is difficult from the experimental and theoretical results to describe more specifically the type of CT transition occurring in these complexes, *i.e.* a metal-ligand to ligand (MLLCT) or ligand to ligand (LLCT) charge transfer transition. Based on the calculations, it might be possible that for $[Ir-Py]^+$, at least two transitions or more participate to the absorption and emission processes *i.e.* (i) a CT from the HOMO and HOMO-1 (almost isoenergetic) to the typ ligand or the pyridine moiety of the typ ligand and (ii) a CT involving the HOMO-2 level. The situation should be different for the methylated complex in which the CT excitation would correspond better to an electron transfer from the cyclometalated fragment to the pyridinium moiety.

The first protonation of **[Ir-Py]**⁺ on the pyridine substituent stabilizes the LUMO level and this stabilization is similar to the one due to the methylation of 4'-Py-tpy in [Ir-Py-Me]²⁺. Therefore, the absorption band of [Ir-Py-H]²⁺, shifted to the red with respect to [Ir-Py]⁺, becomes quite similar to that of [Ir-Py-Me]²⁺. After the second protonation of [Ir-Py]⁺, or first protonation of [Ir-Py-Me]²⁺, on the methoxy group of both complexes, the corresponding HOMO levels are stabilized, resulting in a large hypochromic effect and hypsochromic shift of the lowest energy absorption of both complexes. The experimental results of this work show also that the HOMO of the two Ir complexes are not purely Ir centred as is the case, for example, for MLCT transitions in Ru(II) complexes, but it is characteristic of the whole fragment (Ir-tppy-MeO) and could thus be termed MLLCT (Metal-Ligand fragment to Ligand Charge Transfer) as referenced by Williams et al. for other cyclometalated bis-terdentate Ir(III) complexes.[63, 64] The attribution of MLLCT to the lowest energy absorption and emission (at 298 K and 77 K) for [Ir-**Py**]⁺, protonated [**Ir-Py-H**]⁺, and [**Ir-Py-Me**]²⁺ in MeCN is also in perfect agreement with the conclusions from theoretical calculations reported by Scandola et al. for other cyclometalated Ir(III) complexes.[29]

ASSOCIATED CONTENT

Supporting Information. Cyclic voltammograms, ¹H NMR spectra and HRMS data for complexes $[Ir-Py]^+$ and $[Ir-Py-Me]^{2+}$. Absorption changes for $[Ir-Py-Me]^{2+}$ in the presence of acetic acid and low TFA concentrations. Comparison of absorption spectra of $[Ir-Py]^+$ upon addition of 0.1 M in TFA and $[Ir-Py-Me]^{2+}$. Spectral absorption changes for $[Ir-Py-Me]^{2+}$ upon addition of TFA in H₂O. Computational studies details: geometrical and electronic structure, detailed TD-DFT results.

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HIGHLIGHTS

- Proton sensitive cyclometalated Ir(III) complexes
- Acceleration

