**Dipyridylketone as a Versatile Ligand Precursor for New Cationic Heteroleptic Cyclometalated Iridium Complexes†**

Giorgio Volpi,‡ Claudio Garino,‡ Emanuele Breuza, Roberto Gobetto\* and Carlo Nervi\*

*Department of Chemistry IFM, University of Turin, Via P. Giuria 7,10125, Turin, Italy. Fax: +39 011 670 7855; Tel: +39 011 670 7507; E-mail: carlo.nervi@unito.it*

**Abstract**

Three new bis-cyclometalated iridium(III) complexes, of general formula [Ir(2-phenylpyridine)2(L)]+, are reported. The compounds contain a dipyridine-type ligand (L) derived from di-2-pyridylketone (dipyridin-2-ylmethanol, 2,2'-(hydrazonomethylene)dipyridine, and 3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile) and were synthesized through two different reaction pathways. The alternative synthetic pathway herein proposed, namely the direct reactions on the complex [Ir(2-phenylpyridine)2(2,2’-dipyridylketone)]+, overcame the inconveniences encountered with the standard reaction between the dimeric precursor [Ir(2-phenylpyridine)2(µ-Cl)]2 and the ancillary ligands (L). The photophysical characterization of the iridium complexes reveals that modifications on the ancillary ligand introduce large changes in the photophysical behaviour of the complexes. High emission quantum yield is associated to the presence of a saturated carbon between the two pyridyl moieties: [Ir(2-phenylpyridine)2(2,2’-dipyridylketone)]+ and [Ir(2-phenylpyridine)2(2,2'-(hydrazonomethylene)dipyridine)]+ are extremely low emissive, while [Ir(2-phenylpyridine)2(dipyridin-2-ylmethanol)]+ and [Ir(2-phenylpyridine)2(3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile)]+ are good photoemitters. DFT and TD-DFT calculations confirmed the mixed LC/MLCT character of the excited states involved in the absorption and emission processes and highlighted the role of the π-conjugation between the two subunits of the ancillary ligand in determining the nature of the LUMO.

Introduction

Second- and third-row transition-metal complexes have attracted significant attention due to their outstanding luminescence properties.1, 2 Among them, cyclometalated iridium(III) complexes exhibit highly desirable features in terms of thermal- and photo-stability, emission quantum yields and lifetime, and emission wavelength that can be tuned to cover a full range of visible colours.3, 4 All these features make iridium(III) complexes highly promising for various optical applications, in particular as phosphors in multicolor organic light-emitting devices (OLEDs) and in light-emitting electrochemical cells (LECs), but also as biological labelling agents, as photocatalysts for CO2 reduction and water-splitting, and as singlet oxygen sensitizers.5-10

The general structure of a cyclometalated Iridium(III) complex is characterized by an octahedral coordination arrangement with strong Ir–C bonds between the metal ion and the cyclometalating ligands. This compact framework guarantees a good thermal- and photo-stability, together with a strong electronic interaction between the d orbitals of the metal and the p orbitals of the ligands, increasing the d-d energy gap and preventing the radiationless quenching. Furthermore, the large spin–orbit coupling effect of the Ir atom assures efficient room temperature phosphorescence.11, 12

Cationic bis-cyclometalated iridium(III) complexes combine promising photophysical properties with good solubility in polar solvents.6, 13 In these systems, the HOMO (highest occupied molecular orbital) is generally centred over the Ir atom and the cyclometalating ligands, while the LUMO (lowest unoccupied molecular orbital) is preferentially localized on ligands. For this reason the photophysical properties of Ir(III) complexes can be readily perturbed modifying the cyclometalating ligand with proper substituents, as well as accurately choosing the ancillary ligand.11, 14 However, if metal and ligand orbitals do not mix efficiently, ligand-based 3π–π\* or 3LLCT states can be obtained, and the emission efficiency decreases resulting in lower quantum yields and longer lifetimes.15

The use of certain type of dipyridine ligands can lead to the formation of six-membered chelated metal complexes and sometimes has the advantage to break the crosstalk between the pyridine rings, allowing in principle to shift the HOMO and LUMO energies independently.16, 17 However, if dipyridine type ligands are characterized by the presence of multiple coordinating sites, they provide a variety of structural motifs and coordination modes. For example, 2,2’-dipyridylimines (2,2’-dipyridyl-N-methylimine or 2,2'-dipyridylmethylideneaniline) or di-2-pyridylmethanamine can act as tridentate ligands18, 19 or behave as bidentate ligands.20 They may form a six-membered chelate ring by using the two pyridinic nitrogen or may coordinate to the metal by the iminic/aminic nitrogen and just one pyridinic nitrogen, forming a five-membered chelate ring. This variety of coordination modes may lead to the formation of several compounds, preventing the synthesis or lowering the reaction yield of the desired complex. Furthermore, the standard synthesis of cationic heteroleptic cyclometalated Ir(III) complexes is generally accomplished by reacting a chloride-bridged Ir(III) dimer (containing four cyclometalating ligands) with an appropriate organic ligand. This approach can not always be pursued, because in some cases the ancillary ligand contains reactive units or embeds σ-coordinating groups that interact with the metal precursor, preventing the synthesis of the desired complex. This is also the major drawback of ligands containing sensitive functionality that cannot necessarily tolerate harsh synthetic conditions.

In our previous work, we studied the complex [Ir(ppy)2(di-2-pyridylketone)]+ (**IrL1**) where ppy = 2-phenylpyridine.21 This compound is extremely low emissive but we predicted that the replacement of C=O by a non electroreducible conjugated group should lead to complexes having high quantum yields, analogously to what observed for the dipyridylamine Ir complex. 22

Herein we extend those studies and explore the possibility of carrying out new synthetic strategies in order to obtain mononuclear complexes via clean reactions, at low temperature, and with good reaction yield. The syntheses and the photophysical characterization of new phosphorescent bis-cyclometalated iridium(III) phenylpyridinato complexes [Ir(ppy)2(L)]+, where L (**L2**–**L4**) is a ligand derived from the di-2-pyridylketone (**L1**) carrying two pyridines separated by a single atom spacer (Scheme 1), are reported. The usual synthetic procedure of reacting the chloride-bridged Ir(III) dimer [Ir(ppy)2(μ-Cl)]2 with an appropriate ancillary ligand (L) was substituted by exploiting the wide



**Scheme 1**

and versatile reactivity of the carbonyl group of the [Ir(ppy)2(2,2’-dipyridylketone)]+ (**IrL1**) complex (Scheme 2 and 3). The reduction of the carbonyl group with NaBH4 on **IrL1** afforded [Ir(ppy)2(dipyridin-2-ylmethanol)]+ (**IrL2**), whereas [Ir(ppy)2(2,2'-(hydrazonomethylene)dipyridine)]+ (**IrL3**) and [Ir(ppy)2(3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile)]+ (**IrL4**) were obtained by nucleophilic addition of hydrazine (in methanol) and acetonitrile (activated by potassium hydroxide), respectively. All the complexes were obtained in reasonable or almost quantitative yields. It is worth noting that modification of the ketone moiety introduces relatively large changes in the photophysical behaviour of the iridium complexes. A similar phenomenon has been previously reported by Lehn and coworkers in a ruthenium bipyridyl complex containing a quinone group.23 In its oxidized form the quinone selectively quenches the luminescence whereas the luminescence is not quenched in the hydroquinone form.



**Scheme 2** Sketch of the synthetic pathways to **IrL2**



**Scheme 3** Sketch of the synthetic pathways to **IrL3**

Ligands and related iridium complexes were fully characterized by NMR, UV-vis absorption and emission spectroscopy, mass spectrometry, and electrochemical measurements. DFT (density functional theory) and TD-DFT (time-dependent density functional theory) studies were undertaken to rationalize the key role of the ketone group –and its modifications to form non-conjugated ancillary ligands– on the photophysical properties of these closely related iridium(III) complexes.

Results and discussion

Common ancillary ligands incorporate 2,2’-bipyridine subunits and coordinate the metal forming a stable ﬁve-membered chelate rings. Much less attention has been dedicated to the study of ligands containing two pyridines linked by a spacer. The simplest of these ligands is the di-2-pyridylmethane while the most studied is probably the di-2-pyridylketone. [Ir(ppy)2(di-2-pyridylketone)]+ (**IrL1**) can be easily obtained in good yield using the same synthesis employed for the complex [Ir(ppy)2(bipyridine)]+.24 The bipyridine derivative shows good photophysical properties but lacks of functional groups easy to modify; conversely, [Ir(ppy)2(di-2-pyridylketone)]+ bears a carbonyl group that is widely versatile from the synthetic point of view.

*Synthesis*

The classical synthesis of bis-cyclometalated iridium(III) phenylpyridinato complexes [Ir(ppy)2(L)]+ has been followed to get the complex **IrL1**, i.e. by refluxing a mixture of [Ir(ppy)2(μ-Cl)]2 and 2,2’-dipyridylketone (**L1**) in CH3OH/CH2Cl2 solution for 2 h. This procedure affords **IrL1** as pure product in good yield (91%), as published before.21 However, the same synthetic approach was not effective when we tried to synthesize **IrL2**, **IrL3**, and **IrL4** by reacting [Ir(ppy)2(μ-Cl)]2 with dipyridin-2-ylmethanol (**L2**), 2,2'-(hydrazonomethylene)dipyridine (**L3**), and 3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile (**L4**), respectively.

Employing the ligand **L2**, obtained from the reduction of **L1** with NaBH4 in methanol (Scheme 2a), only a very low amount of **IrL2** was obtained (reaction yield 10%) with the concomitant formation of several side products. To avoid this drawback, the reaction strategy has been changed by performing the carbonyl group reduction directly on **IrL1** (Scheme 2b). The reaction of **IrL1** with NaBH4 in methanol afforded **IrL2** as pure product in high yield (97%).

By using the same reaction strategy employed to synthesize **IrL2**, we set up a nucleophilic addition between hydrazine and **IrL1** in methanol (Scheme 3a). This approach afforded a good amount of **IrL3** that was easily purified by thin layer chromatography (yield 43%).

We also obtained **IrL3** as unexpected side product from the reaction of [Ir(ppy)2Cl]2 with di-2-pyridylketoneazine (1,2-bis(dipyridin-2-ylmethylene)hydrazine) performed in order to obtain the corresponding dinuclear complex (Scheme 3b).25-28 In our case the reaction of di-2-pyridylketoneazine with [Ir(ppy)2Cl]2 in refluxing MeOH/CH2Cl2 did not produced the expected corresponding dinuclear complex, but afforded a plethora of compounds, where **IrL3** was isolated only as a minor product (yield <5%).

The free ligand **L4** (3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile) can be obtained by introducing a cyanomethyl group on **L1**; the synthesis is straightforward and was performed by reacting **L1** with potassium hydroxide in acetonitrile (see Scheme ESI1 in the electronic supplementary information).

The same reaction, performed on benzophenone affords the dehydratation product (3,3-diphenylacrylonitrile).29 By using di-2-pyridylketone(**L1**) the elimination reaction was not observed and we obtained the stable β-hydroxy-nitrile intermediate, as confirmed by ESI mass spectrometry (molecular peak at m/z 226.3 [M+H]+) and by NMR spectroscopy (hydroxyl signal at 6.70 ppm and methylene signal at 3.60 ppm in [D6]acetone).

Several attempts to react **L4** with the iridium dimeric precursor [Ir(ppy)2(μ-Cl)]2 at reflux in different solvents (CH2Cl2/CH3OH, CH3CH2OH, and CH3CH2OH/CH3COOH) failed. In all the conditions the two reagents did not give the expected product nor any other compounds. The problem was solved by introducing the cyanomethyl group directly on the di-2-pyridylketone unit of **IrL1**. The reaction of **IrL1** in acetonitrile with potassium hydroxide at reflux afforded the complex **IrL4** in high yield (40%), after chromatographic purification.

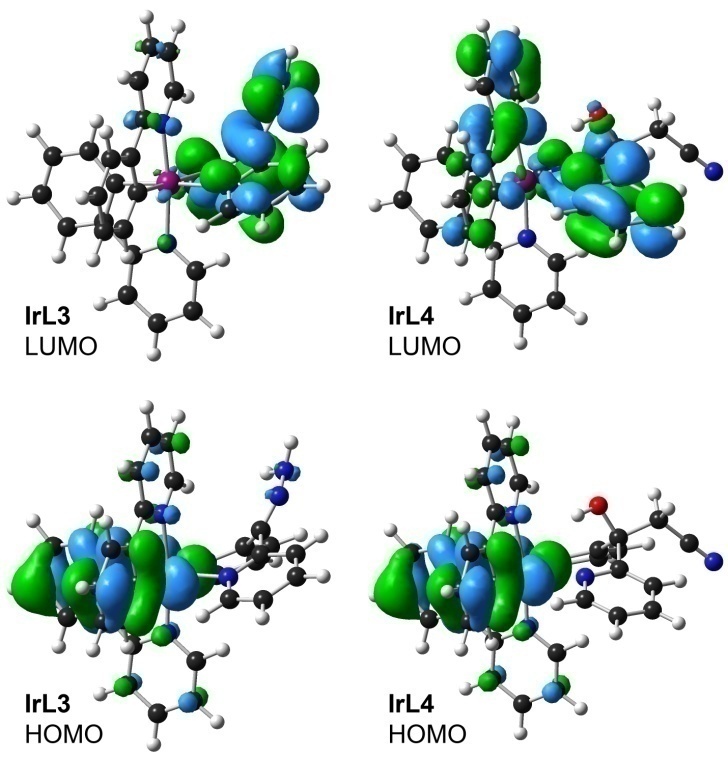
*Computed geometries and electronic structures*

Geometry optimization of the singlet ground state (S0) of the complexes **IrL1**–**IrL4** was performed in gas phase using the B3LYP method, as described in the Computational details section. The main optimized geometrical parameters are reported in Table 1. All the complexes have a pseudo-octahedral coordination structure; the Ir–N(ppy), Ir–C(ppy), and Ir–N(L) bond lengths are in the range 2.085–2.099, 2.021–2.024, and 2.249–2.352 Å, respectively. In the case of **IrL1**, for which X-ray data are available,21 the bond lengths and angles obtained by DFT calculations are in excellent agreement with experimental data. For complexes **IrL2**–**IrL4**, we were not able to get suitable crystals for X-ray diffraction analysis. In all optimized geometries, N–Ir–C and N–Ir–N angles are found to be very similar. The bite angle of the ppy ligands (N1–Ir–C1 and N2–Ir–C2) is relatively small, close to 80°, whereas the bite angle of the L ligands (N3–Ir–N4) spans from 84.48° to 86.67°. The main geometrical parameters of **IrL1**–**IrL4** in the lowest-lying triplet state (T1) are also calculated and results are given in Table 1. Compared to the data of the ground state, there are some variations. In particular, the Ir–N3/N4 bond lengths are shortened in **IrL1** (0.021 and 0.040 Å) and **IrL3** (0.024 and 0.021 Å) and are lengthened in **IrL2** (0.028 and 0.029 Å) and **IrL4** (0.048 and 0.018 Å). With the exception of **IrL3**, the Ir–C1/C2 bond lengths are shortened for all the complexes, while the Ir–N1/N2 bond lengths remain unaltered. It is worth noting that, in the triplet state of **IrL1** and **IrL3**, the double C=O (**L1**) and C=N (**L3**) bonds are significantly lengthened. With respect to the ground state, the two bonds are 0.045 Å and 0.106 Å longer, in agreement with the population of orbitals with antibonding features along the C=O and the C=N bonds.

**Table 1** Selected bond lengths [Å] and angles (°) of **IrL1**–**IrL4** on calculated ground state (S0) and lowest-lying triplet state (T1) geometries, and X-ray crystallography

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Complex | | Ir–N1 | Ir–C1 | Ir–N2 | Ir–C2 | Ir–N3 | Ir–N4 | N1–Ir–C1 | N2–Ir–C2 | N3–Ir–N4 |
| **IrL1** | X-ray | 2.039 | 2.007 | 2.041 | 2.015 | 2.179 | 2.153 | 80.45 | 80.96 | 86.96 |
|  | S0 | 2.090 | 2.024 | 2.085 | 2.023 | 2.264 | 2.249 | 79.99 | 80.12 | 85.67 |
|  | T1 | 2.093 | 2.005 | 2.082 | 1.997 | 2.243 | 2.209 | 80.65 | 80.67 | 83.32 |
| **IrL2** | S0 | 2.087 | 2.022 | 2.092 | 2.023 | 2.287 | 2.266 | 79.90 | 80.14 | 86.67 |
|  | T1 | 2.075 | 1.990 | 2.090 | 1.985 | 2.315 | 2.295 | 80.89 | 81.15 | 82.90 |
| **IrL3** | S0 | 2.085 | 2.022 | 2.086 | 2.022 | 2.276 | 2.259 | 79.97 | 80.17 | 85.25 |
|  | T1 | 2.086 | 2.024 | 2.081 | 2.024 | 2.252 | 2.238 | 79.94 | 80.15 | 85.47 |
| **IrL4** | S0 | 2.098 | 2.021 | 2.099 | 2.023 | 2.352 | 2.307 | 79.81 | 80.16 | 84.48 |
|  | T1 | 2.068 | 1.980 | 2.113 | 2.018 | 2.400 | 2.325 | 81.49 | 80.17 | 83.37 |

To provide insight into the electronic structure of **IrL1**–**IrL4**, we performed single-point calculations on the optimized geometries, taking into account the solvent effect (acetonitrile). The complexes have common orbital features. For all complexes, the highest occupied molecular orbital (HOMO) is an antibonding combination of Ir(d) and ppy(π) orbitals, centred on the Ir atom and on the two phenyl groups of the ppy ligands (Fig. 1 and Fig ESI1 in electronic supplementary information). The HOMO is followed, at lower energy (0.5 –0.7 eV below), by five or six combinations of Ir (d) and ppy and/or **L** (π) orbitals. These orbitals are very close in energy (within 0.464–0.470 eV) and are followed by the π-bonding framework of the **L** ligand (0.8–0.9 eV below). The lowest unoccupied molecular orbital (LUMO) of **IrL1**–**IrL4** is preferentially localized on the ligands (Fig. 1 and Fig ESI1 in electronic supplementary information). The LUMO of **IrL1** and **IrL3** is a π\* orbital localized on the whole **L** ligand, with antibonding features along the double C=O and C=N bonds, respectively. As in the case of most Ir(III) complexes, the LUMO of **IrL2** resides on the cyclometalating ligands, being a π\* orbital delocalized on one ppy. In a different way, the LUMO of **IrL4** is a π\* orbital delocalized on one ppy and on the aromatic rings of **L4**, with no contribution from the aliphatic portion. The sp2 hybridized carbon atom in **L1** and **L3** is likely to promote the direct electronic crosstalk, i.e. π-conjugation, between the two pyridyl moieties. Such conjugation seems to stabilize the L-centred π\* frontier orbital; conversely the saturated carbon in **L2** and **L4** eﬀectively interrupts the π-conjugation, increasing the energy of the L-centred π\* orbital over the π\* orbital of the cyclometalating ligands. For all complexes, the LUMO is followed in energy by a series of ppy and **L** π\* orbitals.



**Fig. 1** Frontier orbitals for complexes **IrL3** and **IrL4**

*Photophysical properties*

Electronic absorption spectra of **IrL1**–**IrL4** were recorded at room temperature in acetonitrile solution. Results are summarized in Table 2.

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| **Table 2** Absorption and emission data for complexes **IrL1**–**IrL4** in deareated acetonitrile solutions | | | | |
| Complex | λabs/nm | λem/nm | Φ | τav/μs |
| **IrL1** | 262  288*a*  333*a*  376  480 | (678) | <0.005 | – |
| **IrL2** | 260  290*a*  330*a*  380  480 | 477  507  547 | 0.10 | 1.335 |
| **IrL3** | 260  300*a*  361  405*a*  465 | 480  510 | <0.005 | 2.411 |
| **IrL4** | 263  290*a*  338  390  458 | 535 | 0.49 | 1.600 |
| *a* Shoulders | | | | |

Typical Ir(III) complexes have a multitude of concurrent electronic transitions. In principle, singlet and triplet metal-to-ligand charge-transfer (1MLCT and 3MLCT) transitions and singlet and triplet ligand-centered (1LC and 3LC) transitions should be considered.

The complexes **IrL1**–**IrL3** show intense absorption bands in the range 250–300 nm, less intense features in the range 300–400 nm with tails which extend into the visible region, and no absorption above 500 nm. **IrL4** has a similar absorption spectrum, plus a pronounced shoulder at λ = 458 nm (Figure 2).

The nature of the electronic transitions responsible for the absorption bands was assigned using TD-DFT calculations. Sixty-four singlet and eight triplet excited states were computed starting from the gas-phase optimized geometry. The solvent effect was taken into account by using the CPCM method.

The high-energy absorptions are well described by TD-DFT, but for these Ir systems the efficient spin-orbit coupling make possible to experimentally observe the normally forbidden singlet-triplet absorptions.30 Triplet excited states were calculated in order to consider the contribution of the singlet–triplets transitions that dominate the low-energy portion of the spectra. Since the TD-DFT calculation used here is known to neglect the spin-orbit coupling, the singlet–triplet transitions have zero oscillator strength and are reported in Figure 2 with arbitrary intensity.

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| Fig 2 (IrL4).jpg |
| **Fig. 2** Experimental absorption (blue line) and emission (green line) spectra, calculated singlet (purple bars) and triplet (blue bars) excited state transitions, and estimated emission energy using ΔSCF (dashed green bar) and TD-DFT (solid green bar) approaches, of complex **IrL4** in acetonitrile. The vertical bar height of singlet transitions is equal to the oscillator strength, while the other bars have arbitrary intensity to indicate their position |

The absorption spectrum of **IrL1** shows an intense UV band at λ = 262 nm. This feature can be ascribed to mixed 1LC/1MLCT transitions involving all ligands; where **L1** is the unit receiving electron density. A second band (shoulder) falls at λ = 376 nm. Ir-ppy→ppy singlet transitions are responsible of such absorption. At λ = 480 nm **IrL1** has a large and weak absorption band assigned to a singlet Ir-ppy→**L1** transition, according to calculations.

The complex **IrL2** has an absorption band centred at λ = 260 nm that can be ascribed to mixed 1LC/1MLCT transitions, where **L2** is the unit receiving electron density. The two shoulders at λ = 290 nm and λ = 330 nm are essentially due to Ir-ppy→ppy-**L2** transitions, and in the case of the first shoulder a Ir-ppy→**L2** transition is also contributing. The less intense feature at 380 nm can be ascribed to a mixed 1LC/1MLCT (Ir-ppy→ppy-**L2**) transition. The weak band experimentally found at 480 nm can be related to the presence of two singlet–triplet transitions having a mixed 3LC/3MLCT character (Ir-ppy→ppy transition at 449 nm, Ir-ppy→ppy-**L2** transition at 445 nm).

In the case of **IrL3**, calculations attribute the UV band at λ = 260 nm to mixed 1LC/1MLCT transitions involving all ligands. However, **L3** is the unit receiving electron density. The shoulder falling at λ = 300 nm can be ascribed to Ir-ppy→ppy transitions. The less intense feature at 361 nm is due to mixed 1LC/1MLCT (Ir-ppy→**L3**) transitions, while the shoulder at λ = 405 nm is mainly due to an Ir-ppy→ppy transition, with a minor contribution from a Ir-ppy→**L3** transition. The weak band experimentally found at 465 nm can be related to the presence of three singlet–triplet transitions having mixed 3LC/3MLCT character (Ir-ppy→**L3** at 483 nm, Ir-ppy→ppy at 449 nm, and Ir-ppy→ppy at 447 nm).

Finally, **IrL4** displays an intense absorption band at λ = 263 nm (Ir-ppy→ppy transition), and a shoulder at λ = 290 nm (Ir-ppy→**L4** and Ir-ppy→ppy-**L4** transitions). Less intense absorptions are present at λ = 338 nm and λ = 390 nm (Ir-ppy→**L4** transition), plus a pronounced shoulder at λ = 458 nm, neglected by singlet excited state calculation. This shoulder can be ascribed to singlet–triplets transitions (452 and 444 nm) having mixed 3LC/3MLCT character (Ir-ppy→ppy-**L4** and Ir-ppy→ppy, respectively).

When excited in acetonitrile solution at room temperature, the luminescence of all complexes is strongly quenched by oxygen. **IrL1** and **IrL3** are very weak emitters, both showing emission quantum yields lower than 0.005. The former displays a wide and unresolved emission centred at 678 nm21 while the latter presents a structured emission profile with rather well defined maxima at 480 and 510 nm (τ = 2.411 μs). On the contrary, **IrL2** and **IrL4** exhibit intense emission spectra. **IrL2** shows a structured emission with prominent vibrational progression, with maximum at 477, 507, and 547 nm (Φ = 0.10, τ = 1.335 μs), while **IrL4** presents a structureless emission centred at 535 nm with an excellent quantum yield (Φ = 0.49, τ =1.600 μs).

The lowest triplet state, which is responsible for phosphorescence emission, can be either 3MLCT transition state or 3LC transition state and it is generally accepted to describe the phosphorescent state as a mix of MLCT and LC transition states.11 The emission lifetimes and the effective quenching by oxygen molecules of the luminescence quantum yields are indicative of emission properties due to triplet excited states. In terms of spectral shape, we can attribute the structureless emission of **IrL1** and **IrL4** to an emitting excited state with predominant MLCT character. On the contrary, in the case of **IrL2** and **IrL3** an increasing of the content of π–π\* character in the emitting excited state gives rise to more structured emission profile that we label as LC phosphorescence.

To gain insights into the nature of the excited states involved in the emission process, we used two different computational approaches. The first consisted on TD-DFT calculations of triplet excited states from the ground state, using the lowest-lying triplet state geometries, the second employed the DFT/UKS calculation (unrestricted Kohn–Sham) of lowest-lying triplet geometries (ΔSCF method, see the Computational details).

TD-DFT correctly estimates the emission energy of **IrL2** (experimental 477 nm, calculated 485 nm) and slightly overestimates the emission of **IrL4** (experimental 535 nm, calculated 571 nm). ΔSCF also gives satisfactory results, predicting the emission of **IrL2** at 448 nm and the emission of **IrL4** at 533 nm.

According to triplet excited state calculations obtained by TD-DFT, for both **IrL2** and **IrL4** the luminescence is due to a mixed 3LC/3MLCT (Ir-ppy→ppy) emissive state (Figure 3), confirmed by the spin density of the lowest-lying triplet-state obtained with the unrestricted Kohn–Sham formalism (Figure 4 and Figure ESI4). Due to the qualitative nature of the computational methods used to evaluate the emission, calculation are not able to discriminate between the LC or MLCT nature of the state responsible for the emission and describe it as a mix of MLCT and LC states. Although from the experimental data, it is clear that the emissive state of **IrL2** has a greater LC character while the emissive state of **IrL4** can be mainly considered as a MLCT transition state.

As already reported,21 the structureless weak emission observed in **IrL1** can be ascribed to a 3LC/3MLCT transition (Ir**-**ppy→**L1**) involving the electron withdrawing carbonyl group on **L1** (Figure ESI4); this is consistent with the quenching of the emission properties in such compound.

The very weak emission observed for **IrL3** could be related to an analogous electronic situation; both the lowest singlet and triplet absorptions have mixed 3LC/3MLCT character involving the population of the LUMO (π\* orbital localized on the **L3** ligand). Unfortunately, the ΔSCF and the TD-DFT approaches are unable to describe the emission process that takes place in the case of **IrL3**; both methods predict negative emission energy. However, the spin density obtained for the lowest-lying triplet-state shows a triplet state centred over **L3**, involving the C=N bond (Figure 4). This in agreement with the spectral shape and with the oxygen quenching of the emission observed experimentally.

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| Fig 3.jpg |
| **Fig. 3** Electron density difference maps (EDDMs) of the lowest energy singlet-triplet electronic transition of **IrL2** and **IrL4** in their lowest-lying triplet state geometries. Blue indicates a decrease in charge density, while orange indicates an increase |

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| --- |
| Fig 3.jpg |
| **Fig. 3** Contour plots of the spin density of the lowest-lying triplet-state geometry of complexes **IrL3** and **IrL4** (isovalue=0.004) |

*Electrochemistry*

Cationic [Ir(ppy)2(N–N)]+ derivatives (where N–N is a bipyridine type ligand) are known to undergo one-electron ligand-based reduction and one-electron metal-based oxidation.13, 31 These are not strict assignment, because metal and ligand orbitals are strongly mixed. Furthermore, one should consider that in some cases the presence of electro-reducible moieties, like the nitro group,21 can significantly alter the electrochemical behaviour in reduction, and sometimes, the reversible Ir(III)/Ir(IV) oxidation step can become quasi-reversible due to an increased contribution of the formal anionic ppy ligands to the HOMO.31, 32 The electrochemical behaviour in acetonitrile solutions of the complexes herein studied is similar to that of this class of cationic complexes, namely [Ir(C–N)2(N–N)]+ (where C–N is a phenyl-pyridine type ligand). In cyclic voltammetry **IrL1** undergoes an additional reversible 1e reduction centred on the carbonyl moiety at –1.26 V vs. ferrocene/ferrocinium redox couple.21 Also **IrL3** carries an electro-reducible group (C=N) that undergoes a reversible 1e reduction process, however its reduction potential, besides the Ir(ppy)2 fragment, is located at –1.72 V, a more negative value because nitrogen is less electronegative than oxygen.33 **IrL3** shows a chemical irreversible oxidation process at Ep = 1.01 V vs. Fc/Fc+, that probably involves the organic hydrazone fragment. At more negative potentials appear chemically irreversible multielectron reductions, which are very likely centred on the organic ligands.

Conclusions

In conclusion, we have synthesized and fully characterized three new cationic bis-cyclometalated Ir(III) complexes (**IrL2**–**IrL4**).

The standard synthetic strategy, i.e. the reaction of the ancillary ligands (**L2**–**L4**) with the chloride-bridged Ir(III) dimer [Ir(ppy)2(μ-Cl)]2 did not yield the related complexes. Therefore, we changed the synthetic strategy, exploiting the reactivity of the carbonyl group directly on the complex **IrL1**. The reduction with NaBH4, the nucleophilic addition of hydrazine in methanol, and the nucleophilic addition of acetonitrile activated by potassium hydroxide gave **IrL2**, **IrL3**, and **IrL4**, respectively. The modification of the carbonyl group directly on the complex **IrL1** allowed to obtain the related complexes in good yields. These examples show how to take advantage of the synthon versatility of di-2-pyridylketone moiety already coordinated to the metal.

Photophysical data reveals that slight modifications of the ketone moiety introduce relatively large changes in the photophysical behaviour of the iridium complexes. The complex **IrL3** is extremely low emissive, as well as the precursor **IrL1**. On the contrary, the complexes **IrL2** and **IrL4** are good photoemitters; in particular **IrL4** affords an emission quantum yield value of 49%.

The results of DFT and TD-DFT calculations allowed to characterize the nature of the excited states involved in the absorption and emission properties. Frontier orbital analysis highlighted the role of the π-conjugation, between the two subunits of the ancillary ligand, in determining the nature of the LUMO and thus influencing the radiationless decay through C=O and C=N units. Calculations confirmed the mixed 3LC/3MLCT character of the states responsible for the structured emission of **IrL2** and for the structureless emission of **IrL4**.

Experimental

*Materials and methods*

Di-2-pyridylketone (**L1**), 2-phenylpyridine, iridium trichloride, and all other reagents and solvents were of reagent grade and used as received without any further purification. Acetonitrile was distilled over calcium hydride just before use. All the reactions involving the metal complexes or precursor were routinely performed under nitrogen atmosphere by using standard Schlenk techniques.

Electrochemistry was performed by a PC-controlled Autolab PGSTAT302N electrochemical analyser in the usual conditions,34 using a standard three electrode cell configuration (glassy carbon working electrode, Pt counter electrode, aqueous 3 M KCl Calomel reference electrode). All measurements were carried out under Ar atmosphere, in acetonitrile solution with tetrabutylammonium hexafluorophosphate (TBAPF6) 0.1 M as supporting electrolyte, obtained as previously reported.35 Positive feedback iR compensation was applied routinely and ferrocene (Fc) was used as an internal standard (half-wave potentials are reported against the Fc(0/+1) redox couple).

NMR spectra were recorded on a JEOL EX 400 spectrometer (B0 = 9.4 T, 1H operating frequency 399.78 MHz) with chemical shifts referenced to residual protons in the solvent. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet.

UV–Vis absorption spectra were measured with a double-beam Perkin–Elmer Lambda 20 UV–Vis spectrophotometer equipped with a 1 cm quartz cell. Room temperature emission spectra as well as luminescence lifetimes were obtained using a HORIBA Jobin Yvon IBH Fluorolog–TCSPC spectrofluorimeter. Fluorescence quantum yields Φ were determined by the comparative method,36 using quinine bisulfate (0.1 N H2SO4) as standard (Φ = 0.546).37 Refractive index corrections were made to adjust for different solvents used. Five solutions with increasing concentrations (Absorbance at the excitation wavelength ranging from 0/solvent blank to 0.10) were prepared for the standard and for each sample. A graph of integrated fluorescence intensity vs. absorbance was plotted for each compound and the gradients of the graphs obtained, which are proportional to the quantum yield of the different samples,38 were used to provide the quantum yields according to the following equation:

Where the subscripts ST and X denote standard and test respectively, Φ is the fluorescence quantum yield, *Grad* the gradient from the plot of integrated fluorescence intensity vs. absorbance, and *η* the refractive index of the solvent. Luminescence lifetimes were determined by time-correlated single-photon counting. Excitation with nanosecond pulses of 297 nm light (repetition rate of 100 kHz) generated by a NanoLED pulsed diode was used. The emission data were collected using a spectral bandwidth of 2-10 nm. The data were collected into 2048 channels to 10,000 counts in the peak channel. The sample was maintained at 20 °C in an automated sample chamber (F-3004 Peltier Sample Cooler from Horiba Jobin Yvon IBH) for ambient temperature measurements. Emission decay data were analysed using the software DAS6 (TCSPC Decay Analysis Software).

Mass spectra were recorded using an XCT PLUS electrospray ionisation-ion trap (ESI–IT) mass spectrometer (Agilent Italy, Milan). In the spectra description the abbreviation [M] was used for the molecular ion. The reported values are in atomic mass units. Samples were dissolved in methanol. Scan range was 50–2000 m/z.

*Computational details*

All calculations were performed with the Gaussian 09 program package.39 Geometry optimization was performed in the gas phase, employing the DFT method for the ground state and the unrestricted Kohn–Sham formalism (UKS) for the lowest-lying triplet state. The nature of all stationary points was confirmed by normal-mode analysis. The conductor-like polarizable continuum model (CPCM)40-42 with acetonitrile as the solvent was used to calculate the electronic structure and the excited states in solution. A total of 64 singlet and 8 triplet excited states were determined with a TD-DFT43, 44 calculation, employing ground state geometries optimized in the gas phase. The emission energy was evaluated by the ∆SCF45 and TD-DFT46, 47 approaches, taking into account the solvent effect with the CPCM method. The ∆SCF approach calculates the vertical energy gap between the ground state and the lowest-lying triplet state, both evaluated at the geometry optimized for lowest-lying triplet state and both computed using unrestricted wave functions (UKS). The TD-DFT approach calculates 8 triplet excited states as electronic transitions from the ground state, evaluated with lowest-lying triplet state geometry. This TD-DFT calculation uses a restricted wave function. The program GaussSum 2.2.448 was used to simulate the electronic spectra and to visualize the excited state transitions as electron density difference maps (EDDMs).49, 50 All calculations employed the Becke three-parameter hybrid functional,51 and Lee Yang Parr’s gradient-corrected correlation functional (B3LYP).52 The LanL2DZ basis set53 and effective core potential were used for the Ir atom, and the 6-31G\*\* basis set54 was used for all other atoms.

*Synthesis*

Dipyridin-2-ylmethanol (**L2**),55 di-2-pyridylketoneazine (1,2-bis(dipyridin-2-ylmethylene)hydrazine),25 [Ir(ppy)2(μ-Cl)]2,56 and **IrL1**21 were synthesized as previously reported.

**3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile (L4).** Di-2-pyridylketone (1.000 g, 5.43 mmol) and KOH (360 mg, 6.42 mmol) were refluxed in acetonitrile (5 ml) for 20 min, under N2. After cooling at r.t., 6 ml of H2O were added and the solution stirred for 10 min, extracted 3 times with 3 ml of Et2O and the organic phase evaporated. Chromatographic purification on silica (CH2Cl2/CH3OH 98:2 v/v as eluent), gave 277 mg of **L4** (1.23 mmol, 22.6% yield).

1H NMR ([D6]acetone, 400 MHz) δ: 8.58 (d, *J* = 4.69 Hz, 2H), 7.82 (t, *J* = 7.68, 2H), 7.76 (d, *J* = 8.05 Hz, 2H), 7.34 (t, *J* = 6.22Hz, 2H), 6.70 (s, 1H), 3.60 (s, 2H). 13C NMR ([D6]acetone, 100 MHz) δ: 161.93, 148.88, 138.28, 123.94, 121.69, 118.30, 77.29, 31.32. MS (ESI+): m/z 226.1 [M+H]+.

**[Ir(ppy)2(dipyridin-2-ylmethanol)]Cl ([IrL2]Cl).** Two different reaction approaches has been carried out. In the first method, a suspension of [Ir(ppy)2(μ-Cl)]2 (150 mg, 0.140 mmol) and **L2** (65 mg, 0.350 mmol) in CH2Cl2/MeOH (20 ml, 1:1 v/v) was heated to reflux while stirring under inert atmosphere. After 2 h, the resulting yellow solution was cooled to r.t. The solution was filtered and the solvent removed. The resulting yellow solid was purified by thin layer chromatography (TLC) (CH2Cl2/MeOH 96:4 v/v). **IrL2** was the slowest yellow band out of nine (yield: 10%, 20 mg, 0.028 mmol).

In the second reaction approach, **IrL2** was prepared by reacting **IrL1** (100 mg, 0.139 mmol), dissolved in 15 ml of MeOH at 0° C, with a large excess of NaBH4 (25 mg, 5 eq.). The solution was stirred at 0° C for 1 h, evaporated under vacuum, and the obtained pale yellow solid dissolved in CH2Cl2 (5 ml) and H2O (5 ml). The resulting solution was neutralized with HCl 0.1 M and stirred for 10 min. The organic layer was washed four times with 1 ml of H2O, filtered, dried over Na2SO4 and the solvent removed under vacuum, giving a yellow solid (yield: 97%, 97 mg, 0.135 mmol).

1H NMR (CDCl3, 400 MHz) δ: 8.91 (d, *J* = 5.86 Hz, 1H), 8.39 (d, *J* = 9.09 Hz, 1H), 8.33 (d, *J* = 5.27 Hz, 1H), 8.02 (d, *J* = 7.91 Hz, 1H), 7.79-7.70 (m, 6H), 7.54 (t, *J* = 6.15 Hz, 1H), 7.49 (d, *J* = 8.20 Hz, 1H), 7.41 (d, *J* = 5.56 Hz, 1H), 7.07 (t, *J* = 6.44 Hz, 1H), 6.96 (t, *J* = 7.61 Hz, 1H), 6.90 (d, *J* = 6.15 Hz, 2H), 6.86-6.78 (m, 4H), 6.52 (s, 1H), 8.58 (d, *J* = 4.69 Hz, 2H), 6.19 (d, *J* = 7.50 Hz, 1H), 6.11 (d, *J* = 7.50 Hz, 1H). 13C NMR (CDCl3, 400 MHz) δ: 168.35, 167.65, 163.20, 162.15, 153.60, 151.60, 151.55, 149.90, 148.80, 148.30, 148.05, 144.90, 143.35, 139.15,138.90, 138.55, 138.00, 132.15, 131.55, 130.75, 130.40, 124.85, 124.60, 124.45, 124.15, 123.40, 123.05, 122.65, 122.40, 120.20, 119.40, 72.50.

MS (ESI+): m/z 687.2 [M]+, 501.1 [M–**L2**]+.

**Ir(ppy)2(2,2'-(hydrazonomethylene)dipyridine)]Cl ([IrL3]Cl).** This complex has been synthesized using two different reaction approaches. The first method was carried out in a similar way described for **IrL2**. In the second method the precursor **IrL1** (100 mg, 0.139 mmol) was dissolved in methanol (15 ml) and glacial acetic acid (0.5 ml) with hydrazine monohydrate (2 ml). The mixture was heated to reflux, stirring under inert atmosphere. After 1 h the resulting red solution was cooled to room temperature and the solvent removed under vacuum. The resulting crude product was dissolved in 3 ml of CH2Cl2 and washed 3 times with 1 ml of H2O. The orange organic solution was filtered on silica (CH2Cl2/CH3OH 94:6 v/v as eluent), and the yellow solid recovered (yield: 43%, 44 mg, 0.060 mmol).

1H NMR ([D6]acetone, 400 MHz) δ: 8.86 (d, *J* = 4.39 Hz, 1H), 8.59 (d, *J* = 5.86, 1H), 8.27 (t, *J* = 9.52 Hz, 2H), 8.15 (t, *J* = 7.91Hz, 1H), 8.08-8.00 (m, 3H), 7.96 (d, *J* = 4.98, 1H), 7.90-7.85 (m, 4H), 7.65 (d, *J* = 9.08Hz, 2H), 7.52 (t, *J* = 6.00 Hz, 1H), 7.44 (t, *J* = 6.88, 1H), 7.33 (t, *J* = 6.44 Hz, 1H), 7.04-6.97 (m, 2H), 6.92 (t, *J* = 7.18 Hz, 1H), 6.86 (t, *J* = 7.47, 1H), 6.38 (d, *J* = 7.61 Hz, 1H), 6.31 (d, *J* = 7.03Hz, 1H). 13C NMR ([D6]acetone, 100 MHz) δ: 168.76, 168.35, 157.43, 151.77, 151.14, 150.69, 150.35, 149.67, 148.49, 144.85, 139.85, 139.71, 139.31, 132.83, 132.30, 131.24, 131.14, 127.44, 126.97, 126.78, 126.42, 125.80, 125.76, 124.97, 124.87, 123.88, 123.61, 120.89, 120.83. MS (ESI+): m/z 699.2 [M]+.

**[Ir(ppy)2(3-hydroxy-3,3-di(pyridine-2-yl)propanenitrile)]Cl ([IrL4]Cl).** The precursor **IrL1** 100 mg, 0.139 mmol) and KOH (25 mg, 0.44 mmol) were refluxed in acetonitrile (10 ml) for 15 min, under nitrogen atmosphere. The resulting red solution was evaporated to dryness under vacuum, the solid dissolved in CH2Cl2 (5 ml) and washed with H2O (2 ml for 3 times). Evaporation of the organic layer gave a red solid, which resulted to be a mixture of **IrL4** and **IrL1**. The yellow solid **IrL4** (yield: 40%, 41 mg, 0.056 mmol) was obtained after TLC separation (CH2Cl2/MeOH 96:4 v/v).

1H NMR ([D6]acetone, 400 MHz) δ: 10.00 (d, *J* = 5.86 Hz, 1H), 8.23 (d, *J* = 4.69, 1H), 8.16 (d, *J* = 8.20 Hz, 1H), 8.06 (t, *J* = 7.91Hz, 1H), 8.00 (d, *J* = 7.91 Hz, 1H), 7.92 (t, *J* = 7.91, 1H), 7.85 (t, *J* = 7.91 Hz, 1H), 7.76 (d, *J* = 7.61Hz, 1H), 7.72 (d, *J* = 7.61 Hz, 1H), 7.64 (d, *J* = 4.98, 1H), 7.50 (d, *J* = 7.91 Hz, 1H), 7.35 (d, *J* = 8.20Hz, 1H), 7.28 (t, *J* = 6.44 Hz, 1H), 7.21 (t, *J* = 6.74, 1H), 7.03 (t, *J* = 7.61 Hz, 1H), 6.92 (d, *J* = 5.56Hz, 1H), 6.85 (t, *J* = 6.30Hz, 1H), 6.81 (t, *J* = 7.47 Hz, 3H), 6.68 (t, *J* = 7.61, 1H), 6.62 (t, *J* = 7.47 Hz, 1H), 6.31 (t, *J* = 6.59 Hz, 1H) 7.26 (d, *J* = 7.61Hz, 1H), 6.12 (d, *J* = 7.61 Hz, 1H). 13C NMR ([D6]acetone, 400 MHz) δ: 172.09, 150.01, 149.03, 148.79, 147.69, 136.77, 136.36, 136.26, 133.16, 132.62, 130.18, 129.60, 128.03, 125.19, 125.12, 124.59, 122.01, 121.69, 121.51, 121.06, 121.01, 119.49, 118.95, 90.13, 80.30, 54.89, 38.11. MS (ESI+): m/z 726.2 [M]+.

Acknowledgements

C.G. thanks Regione Piemonte for financial support.

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