



# Luminescent Ir Complexes

# Photophysical Properties of Oligo(phenylene ethynylene) Iridium(III) Complexes Functionalized with Metal-Anchoring Groups

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Abstract: The electrochemical and photophysical properties of a family of conjugated ligands and their iridium(III) cyclometallated complexes are described. They consist of a series of monocationic Ir<sup>III</sup> bis-2-phenylpyridine complexes with p-phenylethynyl-1,10-phenanthroline ligands of different length. The structure of these ligands includes terminal acetylthiol or pyridine groups, which can provide good electrical contacts between metal electrodes. Cyclic voltammetry, absorption and emission spectroscopy, laser flash photolysis and density functional theory calculations reveal that the high conjugation of the diimine ligand affords small energy gaps between the frontier orbitals. Nevertheless, the nature of the terminal substituents and the extent of the conjugation in the diimine ligand have little influ-

# Introduction

The field of molecular electronics has been enriched recently by the idea of using electromagnetic radiation to modulate the response of molecular junctions.<sup>[1–4]</sup> On this basis, the conductance of some single molecules contacted between metallic electrodes could be optically switched through light-triggered isomerization.<sup>[5–9]</sup> On the other hand, molecular-dipole changes have a deep influence on the electronic structures of contacted molecules.<sup>[10–12]</sup> According to this idea, light has also been proposed as a control tool of molecular conductance in systems that do not undergo photochemical reactions. In addition to some experimental work,<sup>[13-15]</sup> theoretical studies in this area support this idea.<sup>[2,16–19]</sup> For example, the effect of illumination on junctions comprising molecules of different lengths<sup>[20,21]</sup> or characterized by strong charge-transfer optical transitions<sup>[22]</sup> have been studied theoretically.

Cyclometallated iridium(III) compounds are the focus of intense research owing to their unique and tuneable photophysical properties. Their characteristic intense photoluminescence



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ence on the photophysical features at room temperature. The spectroscopic data and theoretical calculations agree that the charge-transfer nature of the emitting excited state is maintained along the series at room temperature, whereas in rigid matrices ligand-centred states also contribute to the low-temperature emission. The good conducting features of the diimine ligands, the small dependence of the HOMO-LUMO (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) gaps of these complexes on the ligands and the charge-transfer nature of the emitting excited state make these complexes promising test beds for the study of photoconducting phenomena in molecular junctions.

and high quantum yields<sup>[23]</sup> have made Ir<sup>III</sup> complexes highly attractive for a wide variety of applications, such as emitters in organic light-emitting diodes (OLEDs),<sup>[24]</sup> light-emitting electrochemical cells (LECs),<sup>[25]</sup> and oxygen sensors.<sup>[26]</sup> However, to the best of our knowledge, these phosphorescent complexes have never been implemented in single-molecule junctions.

In the prototypical complex  $[Ir(ppy)_2(N^N)]^+$  (Hppy = 2-phenylpyridine and  $N^N$  = diimine ligand), the photoluminescent emission occurs from a triplet metal-to-ligand charge-transfer (<sup>3</sup>MLCT) excited state.<sup>[27,28]</sup> The nature of the substituents on the diimine ligand has a marked influence on the luminescence of the complexes.<sup>[28,29]</sup> For example, the contribution of triplet ligand-centred (<sup>3</sup>LC) excited states to the photoluminescence increases with the conjugation length.<sup>[29-33]</sup>

In this work, we present the synthesis and characterization of a series of monocationic photoluminescent Ir<sup>III</sup> complexes (Ir1-Ir4, Figure 1), which incorporate conjugated ligands of different molecular length and are functionalized with suitable anchoring groups for their integration into metallic molecular junctions.<sup>[34,35]</sup> The new compounds result from the combination of iridium(III) bis-cyclometallated 2-phenylpyridine complexes with four different diimine  $\pi$ -conjugated ligands (1–4). Ligands 1-4 are 1,10-phenanthroline (phen) derivatives symmetrically functionalized at their 3- and 8-positions with 1-(Sacetylthio)-4-phenyl and pyridine terminal groups, which are connected to the phen core by phenylethynyl spacers of different length. The molecular conductances of some of these li-

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Figure 1. Chemical structures of iridium complexes Ir1-Ir4.

gands have been investigated already in mechanically controlled break junctions.<sup>[36]</sup> Therefore, complexes Ir**1**–Ir**4** combine the low resistance of molecular wires **1–4** with the rich photophysics of Ir<sup>III</sup> complexes.

 $[Ir(ppy)_2(N^N)]^+$  complexes functionalized with phenylethynyl groups have been reported before.<sup>[37,38]</sup> However, the interplay between the conjugation and different anchoring groups in Ir**1**–Ir**4** makes it difficult to anticipate the nature of the emitting excited state and, thus, their behaviour at illuminated molecular junctions. For the first time, this work brings together electro- and spectrochemical techniques along with theoretical calculations in the study of iridium(III) bis-cyclometallated 2-phenylpyridine complexes with phenylethynyl-substituted diimine ligands.

## **Results and Discussion**

### **Chemical Synthesis**

The synthesis of ligands **1–4** was accomplished by the sequence of Sonogashira-type cross-coupling reactions between 3,8-dibromo-1,10-phenanthrolines and substituted phenylacetylenes displayed in Scheme 1. Ethynyl derivatives **1** and **3** have been reported previously,<sup>[39,40]</sup> whereas **2** and **4** have been synthesized for the first time. The synthesis of the short molecular



Scheme 1. (a) *n*BuLi, chlorotrimethylsilane (TMSCI), THF (68 %); (b) Pd(PPh<sub>3</sub>)Cl<sub>2</sub>, Cul, THF, *i*Pr<sub>2</sub>NH (74 % for **7**, 50 % for **8**); (c) K<sub>2</sub>CO<sub>3</sub>, MeOH (97 % for **9**, 91 % for **10**); (d) **11** (2 equiv.), Pd(dba)<sub>2</sub>, PPh<sub>3</sub>, Cul, THF, DIEA (40 % for **1**, 63 % for **2**); (e) 4-iodopyridine (2 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub>, Cul, THF, DIEA (84 % for **3**); (f) 4-iodopyridine (2 equiv.), Pd(dba)<sub>2</sub>, PPh<sub>3</sub>, Cul, THF, DIEA (96 % for **4**). DIEA = *N*,*N*-diisopropylethylamine, dba = dibenzylideneacetone.

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wires 1 and 3 was accomplished by coupling 3,8-dibromo-1,10phenanthroline (5)<sup>[41]</sup> with commercial ethynyltrimethylsilane to afford 7 in good yield. For the longer ligands 2 and 4, 5 was coupled with [(4-ethynylphenyl)ethynyl]trimethylsilane (6), which had been previously prepared by a reported procedure,<sup>[42]</sup> that is, the reaction of 1,4-diethynylbenzene with *n*BuLi in tetrahydrofuran (THF) and the subsequent addition of chlorotrimethylsilane. The desilylation of 7 and 8 under basic conditions (K<sub>2</sub>CO<sub>3</sub> in methanol) afforded diethynyl derivatives 9 and 10, respectively, in high yield.<sup>[43]</sup> These diethynyl-terminated phenanthrolines were then coupled under Sonogashira conditions with 2 equiv. of 1-(S-acetylthio)-4-iodobenzene (11) to afford 1 and 2 or with commercially available 4-iodopyridine to afford 3 and 4. Derivative 11 was prepared in high yield by the reduction of 4-iodobenzenesulfonyl chloride.[44] Alternatively, 2 was synthesized in 24 % yield by following the procedure described in the Supporting Information and shown in Scheme S1.

Complexes Ir1–Ir4 were prepared from the dichloridobridged Ir<sup>III</sup> dimer [Ir(ppy)<sub>2</sub>Cl]<sub>2</sub>.<sup>[45]</sup> The treatment of this salt with 1 equiv. of ligands 1–4 in dichloromethane/methanol mixtures under reflux under inert conditions and the subsequent treatment with an excess of KPF<sub>6</sub> afforded monocationic [Ir(ppy)<sub>2</sub>(L)][PF<sub>6</sub>] (L = 1–4) complexes in reasonable yields (Scheme 2). In the <sup>1</sup>H NMR spectra of all of the complexes (see Supporting Information), the ppy ligands present one set of eight signals, each one of which integrates to two protons. This equivalency is consistent with the selective formation of the isomer in which the Ir–C<sub>ppy</sub> bonds are *trans* to the Ir–N<sub>phen</sub> bonds according to the so-called "*trans* effect".<sup>[23]</sup>



Scheme 2. Synthesis of Ir1-Ir4: (a)  $CH_2CI_2/MeOH$  (2:1), reflux; (b) excess  $KPF_6$  (54 % for Ir1, 35 % for Ir2, 40 % for Ir3, 41 % for Ir4).

#### **Electrochemical Characterization**

The cyclic voltammograms of Ir**1**–Ir**4** are displayed in Figure S1, and relevant electrochemical data are collected in Table 1. The electrochemical measurements revealed oxidation and reduction half-wave potentials more than 1.8 V apart and the high redox stability of the complexes. All of the complexes display an oxidation process centred at 1.40 V. This oxidation process has been observed previously for other bis-cyclometallated Ir<sup>III</sup> complexes<sup>[28–31,46,47]</sup> such as [Ir(ppy)<sub>2</sub>(phen)]<sup>+</sup> [1.36 V vs. saturated calomel electrode (SCE)]<sup>[28]</sup> and has been associated with the bis-cyclometallated Ir(III/IV) oxidation. In agreement with this assignment, the oxidation potential presents minor variations along the Ir**1**–Ir**4** series. The irreversibility of this process denotes the participation of the ppy moiety in the redox process, as supported by previous reports and our theoretical calculations (see below).<sup>[48,49]</sup> Although the oxidation is more irre-



versible for the acetylthiol-terminated compounds Ir1 and Ir2 than for the pyridine-terminated derivatives Ir3 and Ir4, this may only reflect the different tendency of the acetylthiol derivatives to become adsorbed on the electrodes following the redox process.<sup>[36]</sup>

Table 1. Oxidation and reduction	potentials versus SCE for Ir1-Ir4
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	$E_{\rm c}^{\rm red}$ [V]	$E_{\rm a}^{\rm ox}$ [V]	Electrochemical gap <sup>[a]</sup> [V]
lr <b>1</b>	-0.96	+1.39	2.35
lr <b>2</b>	-1.03	+1.39	2.42
lr3	-0.94	+1.42	2.36
lr <b>4</b>	-0.95	+1.40	2.35
fac-Ir(ppy) <sub>3</sub>	-2.26 <sup>[b]</sup>	+0.75 <sup>[b]</sup>	

[a] The electrochemical gaps were obtained as the differences between the cathodic peak of the reduction process ( $E_c^{red}$ ) and the anodic peak of the oxidation process ( $E_a^{ox}$ ). [b] The  $E_{1/2}^{red}$  and  $E_{1/2}^{ox}$  values of fac-lr(ppy)<sub>3</sub> from ref.<sup>[50]</sup> have been added for comparison. The electrochemical measurements were performed in anhydrous dimethylformamide.

At negative potentials, a single reduction process is visible between –1.03 and –0.96 V, and the ratio between the cathodic and anodic peaks is again far from one for Ir**1** and Ir**2**. The potential of the reduction process, particularly for the pyridine-terminated derivatives, is far higher than that described for the parent complex [Ir(ppy)<sub>2</sub>(phen)][PF<sub>6</sub>] ( $E_{1/2} = -1.28$  V vs. SCE).<sup>[28]</sup> This suggests that the reduction processes for Ir**1**–Ir**4** are centred on the N<sup>^</sup>N ligand, as mentioned in previous reports<sup>[28–31]</sup> and discussed below.

#### **Photophysical Properties**

The absorption spectra of ligands 1-4 and their iridium complexes Ir1-Ir4 in dichloromethane are shown in Figure 2, and the corresponding absorption maxima and molar extinction coefficients are listed in Table 2. The short ligands 1 and 3 exhibited two strong absorption bands, the first at  $\lambda = 289$  and 283 nm ( $\varepsilon \approx 55000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and the second at  $\lambda = 351$  and 340 nm ( $\varepsilon \approx 60000 \text{ M}^{-1} \text{ cm}^{-1}$ ), respectively. These maxima are significantly shifted to lower energies as the conjugation length increases (ligands 2 and 4), and the bathochromic effect is higher for the pyridine-terminated molecular backbones. As for related ligands, we assign the lower- and higher-energy bands to long- and short-axis polarized  $\pi \rightarrow \pi^*$  transitions, respectively.<sup>[37,38,51]</sup> The absorption bands of Ir1-Ir4 are broader than those of the bare ligands 1-4 (Figure 2, bottom). The spectra show an intense band ( $\varepsilon > 5 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$ ) below  $\lambda = 350 \text{ nm}$ and a less-intense band ( $\varepsilon > 4 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$ ) in the  $\lambda = 350$ – 450 nm range. On the basis of previous reports, [28-31,33,37] we assign the first band to  $\pi \rightarrow \pi^*$  transitions centred on the ppy and phen ligands. The second broad band is the result of the overlap of  $\pi \rightarrow \pi^*$  LC transitions with spin-allowed <sup>1</sup>MLCT transitions. For Ir3, the latter transitions are distinguishable as a separate band at  $\lambda \approx 400$  nm. The redshift (up to 30 nm) of the bands into the  $\lambda$  = 360–390 nm range compared with those observed for 1-4 is in part attributed to the stabilization of the  $\pi$ -electron system of the phen chromophore as a result of the coordination to the cationic Ir<sup>III</sup> centre (see below).<sup>[51,52]</sup>





Tabla 2	Photophysical	properties of	f ligands 1_A	and com	nlovos Ir <b>1</b> _IrA	in dichlorome	thang and	othanol	colutions [a]
Table 2.	Photophysical	properties of	i liyanus <b>i-4</b>	and com	piexes ir i-ir4	In alchioronie	inane anu	ethanoi	solutions.

	$\lambda_{\rm max} \ {\rm CH_2Cl_2} \ {\rm [nm]} \ (\epsilon, \ 10^3 \ {\rm m^{-1} \ cm^{-1}})$	λ <sub>em</sub> <sup>[b]</sup> CH <sub>2</sub> Cl <sub>2</sub> 278 K [nm]	λ <sub>em</sub> <sup>[b]</sup> EtOH 278 K [nm]	λ <sub>em</sub> <sup>[b,c]</sup> EtOH 77 K [nm]	<i>E</i> <sub>T</sub> <sup>[b,d]</sup> CH <sub>2</sub> Cl <sub>2</sub> 278 K [eV]	$\phi_{ m air}$ CH $_2$ Cl $_2$ 278 K	$\phi_{ m Ar}$ CH <sub>2</sub> Cl <sub>2</sub> 278 K	τ <sup>[e]</sup> CH <sub>2</sub> Cl <sub>2</sub> 278 K [ns]	τ <sup>[f]</sup> EtOH 77 K [μs]	k <sub>r</sub> <sup>[g]</sup> CH <sub>2</sub> Cl <sub>2</sub> 278 K [10 <sup>6</sup> s <sup>-1</sup> ]	<i>k</i> <sub>nr</sub> <sup>[g]</sup> CH <sub>2</sub> Cl <sub>2</sub> 278 K [10 s <sup>-1</sup> ]
1	289 (55), 351 (62)	384		561	2.48	0.76	0.79	<1			
2	305 (45), 367 (74)	403		568	2.37	0.83	0.84	<1			
3	283 (57), 340 (60)	384		511	2.56	0.12	0.15	<1			
4	300 (39), 367 (64)	394		564	2.35	0.90	0.93	<1			
lr <b>1</b>	272 (69), 380 (46)	638	644	562 (552)	2.22	0.097	0.151	502	5.7, 18.8	0.30	1.7
lr <b>2</b>	314 (66), 395 (51)	638	644	563 (563)	2.21	0.113	0.179	564	4.5, 15.1	0.32	1.5
lr <b>3</b>	290 (56), 362 (38)	648	658	588 (512)	2.13	0.057	0.073	202	6.7, 18.2	0.36	4.6
lr <b>4</b>	301 (53), 389 (51)	640	646	566 (566)	2.19	0.049	0.073	460	6.8, 20.6	0.16	2.0
fac-lr(ppy)3 <sup>[h]</sup>	244 (45), 283 (45)		492 <sup>[h]</sup>	510 <sup>[h]</sup>			0.4	1900	3.6	0.21	0.32

[a] The concentrations were  $3 \times 10^{-6}$  M.  $\lambda_{max}$  = absorption maximum,  $\varepsilon$  = molar attenuation coefficient,  $\lambda_{em}$  = emission maximum,  $E_{T}$  = triplet energy,  $\phi$  = fluorescence quantum yield,  $\tau$  = luminescence lifetime,  $k_{r}$  = radiative emission constant, and  $k_{nr}$  = nonradiative emission constant. [b]  $\lambda_{exc}$  (1-4) = 300 nm,  $\lambda_{exc}$  (lr1–lr4) = 375 nm. [c] The emission maxima were registered with delays of 50 µs for 1–4 and 5 (50) µs for lr1–lr4. [d] Determined in deaerated dichloromethane from the 10% increase phosphorescence spectra. [e] Measurements in deaerated dichloromethane solution at the emission maximum ( $\lambda_{exc}$  = 375 nm); the lifetimes for 1–4 are shorter than 1 ns and could not be resolved by our system. [f] Measurements in deaerated ethanol solid matrix at 560 nm ( $\lambda_{exc}$  = 355 nm), the lifetimes correspond to biexponential fits. [g]  $k_r$  and  $k_{nr}$  in dichloromethane solution were calculated according to the equations:  $k_r = \phi_{Ar}/\tau$  and  $k_{nr} = (1 - \phi_{Ar})/\tau$ . [h] The data for *fac*-lr(ppy)<sub>3</sub> from ref.<sup>[50]</sup> have been added for comparison. In this case, the emission and lifetime measurements were performed in 2-methyltetrahydrofuran.



Figure 2. Normalized absorption spectra of ligands **1–4** (top) and complexes Ir**1**–Ir**4** (bottom) in dichloromethane.

The photoluminescence spectra of ligands **1–4** in dichloromethane at 298 K ( $\lambda_{exc} = 300$  nm) are shown in Figure 3. The emissions are centred in the  $\lambda = 380-400$  nm range and show relatively high quantum yields ( $\phi$ ), which are essentially unaffected by the presence of oxygen and evidence the fluorescence character of the emission (Table 2). The enhancement of the  $\pi$  conjugation results in higher  $\phi$  values and the stabilization of the lower-energy transitions. The fluorescence lifetimes ( $\tau$ ) of **1–4** were less than 1 ns and could not be resolved by our experimental setup.



Figure 3. Normalized photoluminescence spectra of ligands 1–4 ( $\lambda_{exc}$  = 300 nm) and complexes Ir1–Ir4 ( $\lambda_{exc}$  = 375 nm) in dichloromethane at 298 K.

The photoluminescence spectra of lr1-lr4 at room temperature are shown in Figure 3 (right), and their photophysical properties are summarized in Table 2. The emission quantum yields of the complexes are much lower than those observed for the bare ligands and are significantly affected by the presence of oxygen. The emission lifetimes of lr1-lr4 at room temperature range in the sub-microsecond time scale and are more than two orders of magnitude longer than those found for 1-4( $\tau < 1$  ns). All of these features are consistent with the triplet nature of the emissive excited state for all of the lr complexes.<sup>[53]</sup>

In contrast to those observed for 1-4, the emission shapes for Ir1–Ir4 in dichloromethane solution at 298 K are broad and unstructured (Figure 3, right), as is typical for emissions from MLCT excited states,<sup>[54]</sup> and the emission shifts by 6–10 nm towards longer wavelengths in more polar ethanol (Table 2).

The emissions of Ir**1** and Ir**3** appear redshifted compared with that of  $[Ir(ppy)_2(phen)]^+$  (575 nm).<sup>[28]</sup> Therefore, the emission is most likely localized in the N<sup>^</sup>N unit. However, in contrast to the observations for ligands **1–4** and previous re-



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ports,<sup>[37,38,51,55]</sup> a further increase in the conjugation of the diimine ligand does not lead to an energy decrease of the emission (compare Ir**2** and Ir**4** with Ir**1** and Ir**3**, respectively, in Table 2).

The photoluminescence decay traces of lr1-lr4 in dichloromethane, measured at the emission maxima, can be accurately fitted to single exponential functions. The lifetimes from these fits range from 0.20 to 0.56 µs and are longer for the acetylthiol compounds than for the pyridine-terminated derivatives (Table 2). The increase of the conjugation length of the diimine ligand also leads to an increase of the lifetime. The quantum yields are higher for the acetylthiol-terminated derivatives than for the pyridine-terminated derivatives, and all of them are in the range reported for other  $[lr(ppy)_2(N^N)]^+$  complexes with MLCT emissive excited states.<sup>[30,33,46]</sup>

Interestingly, compared with those observed at room temperature, the low-temperature phosphorescence decay curves measured at  $\lambda = 560$  nm for Ir1–Ir4 show biexponential decays with lifetimes for the two component differing by ca. 10 µs (Table 2). The emission spectra of Ir3 recorded in ethanol glass at different delay times (5 and 50 µs) are shown in Figure 4. In this case, the two components of the emission are well-separated in energy and could be clearly resolved. The short-lived (6.7  $\mu$ s) emission that peaks at  $\lambda \approx 600$  nm is unstructured and appears blueshifted by 1800 cm<sup>-1</sup> compared with the roomtemperature emission. This behaviour is typical of MLCT emitters and originates from the rigidochromic effect.<sup>[54]</sup> The longlived emission (18.2 µs) is structured and peaks at the same energy (512 nm) as that measured for 3 under equivalent experimental conditions (Table 2). Similarly, the emission spectra of Ir1, Ir2 and Ir4 shows structured bands with maxima that are close to those found for the low-temperature emissions of the corresponding ligands (Figure S2). However, in this case, both components peak at similar wavelengths, and the different contribution to the emission could not be time-resolved. At low temperature, <sup>3</sup>MLCT states increase in energy, and <sup>3</sup>LC states can increase their contribution to the emission.[55] Thereby, at 77 K, Ir1-Ir4 show dual emission from two different triplet



Figure 4. Normalized luminescence spectra at  $\lambda_{exc}$  = 375 nm of ligand **3** and complex Ir**3** in dichloromethane (300 K) and in ethanol glass (77 K) measured at different delays.

states, which, according to their lifetime, energy and shape are assigned to  ${}^{3}MLCT$  and  ${}^{3}LC$  states.

#### **Transient Absorption**

Laser flash photolysis (LFP) measurements were performed at room temperature with samples in deaerated dichloromethane at  $\lambda_{exc}$  = 355 nm. The LFP of **1–4** affords long-lived absorption species that are highly quenched by oxygen and low-energy triplet acceptors such as  $\beta$ -carotene ( $E_{T}$  = 1.00 eV). Therefore, they are assigned to triplet  ${}^{3}\pi \rightarrow \pi^{*}$  excited states. The transient absorption spectra of **1–4** are shown in Figure S3 and are characterized by a broad absorption band throughout the visible region, which extends to the near-infrared, with triplet lifetimes of 9.3–16.5 µs (see Table S1).

The transient absorption spectra of Ir1-Ir4 (Figure 5) contrast with those obtained for ligands 1–4. The negative signal at  $\lambda \approx$ 400 nm is assigned to ground-state bleaching, according to the absorption spectra (Table 2). The absorption species with  $\lambda_{max}$  $\approx$  510 nm are largely quenched by oxygen with rate constants of ca.  $6 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$  (see Figure 5, b and d) and by low-energy triplet acceptors such as  $\beta$ -carotene; as for related Ir<sup>III</sup> complexes, they are assigned to <sup>3</sup>MLCT excited states.<sup>[37,38,55]</sup> Additionally, the decay traces of Ir1–Ir4 at  $\lambda$  = 510 nm can be accurately fitted with a first-order exponential function. The lifetimes range from 0.24 to 0.54 µs and are very close to the photoluminescence decay components detected by emission spectroscopy (Table 2). Finally, the bleaching observed at  $\lambda \approx 640$  nm is assigned to the photoluminescence detected in the emission spectra measured in deaerated dichloromethane solution at room temperature (see Table 2).



Figure 5. Transient absorption spectra of (a) Ir**2** and (c) Ir**4** in deaerated dichloromethane solution recorded 0.01 (circles), 0.1 (squares), 0.3 (triangles), and 1 µs (inverted triangles) after the laser pulse. The arrows show the evolution of the absorption band with time. Decay traces of (b) Ir**2** and (d) Ir**4** monitored at  $\lambda = 510$  nm in N<sub>2</sub> (dot), air (solid), and O<sub>2</sub> (dash). The insets show the Stern–Volmer plots for quenching by oxygen. All measurements were performed at 298 K,  $\lambda_{exc} = 355$  nm.

#### **Theoretical Calculations**

Density functional theory (DFT) calculations were performed at the B3LYP/(6-31G\*\*+LANL2DZ) level for cationic complexes Ir1–



Ir4 in the presence of dichloromethane (see Computational Details). The isolated phenanthroline-based ligands 1-4 were also computed at the B3LYP/6-31G\*\* level for comparison. The calculations of the electronic ground states (S<sub>0</sub>) correctly predict near-octahedral coordination geometries for the Ir centres and provide geometrical parameters in good agreement with the experimental data for similar Ir-based complexes. The optimized values calculated for the bond lengths and bond angles that define the coordination spheres of the iridium centres of all of the complexes are collected in Table S2.

The energies calculated for the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the phenanthroline-based ligands 1-4 and complexes Ir1-Ir4 are shown in Figure 6, and the isovalue contours computed for the frontier molecular orbitals of Ir1 and Ir3 are shown in Figure 7 as representative examples. The topologies of the molecular orbitals of Ir2 and Ir4 (Figure S4) are identical to those of Ir1. Similarly to those of related ppy-based cyclometallated Ir complexes,<sup>[31-33]</sup> the HOMO is composed of a mixture of Ir<sup>III</sup> d $\pi$  orbitals (t<sub>2a</sub>) and phenyl  $\pi$  orbitals with little contribution from the pyridine rings of the cyclometallated ligands. As the family of complexes Ir1-Ir4 only differs in the diimine ligand, the energy of the HOMO remains almost constant along the series and is slightly more stable for Ir3 and Ir4 (Figure 6, b). Therefore, the theoretical calculations support the participation of the ppy ligands in the first oxidation process and fully justify the small variation of the oxidation potentials observed from Ir1 (+1.39 V) and Ir2 (+1.39 V) to Ir3 (+1.42 V) and Ir4 (+1.40 V). In contrast to the HOMO, the LUMO is completely localized over the diimine ligands and is mainly centred on the phenanthroline core. Compared with the LUMO of the parent  $[lr(ppy)_2(phen)]^+$  complex with an energy of -2.35 eV,<sup>[28]</sup> the LUMO is stabilized by the attachment of phenylethynylene groups at the 3- and 8-positions of the phen ligand, and the HOMO-LUMO gap decreases from 3.18 eV in [lr(ppy)<sub>2</sub>(phen)]<sup>+</sup> to ca. 2.75 eV in Ir1 and Ir3. However, the attachment of an additional phenylethynylene unit in Ir2 and Ir4 does not lead to a further stabilization of the LUMO; thus, the HOMO-LUMO gap is similar for all the complexes, in agreement with the electrochemical data.

A wider inspection of the energy positions along with the atomic orbital compositions at the optimized ground-state geometry of the frontier molecular orbitals (Figures 7 and S4) can provide qualitative information about the nature of the lowlying triplet excited states. The lowest-energy triplet electronic





Figure 7. Schematic representation showing the isovalue contours ( $\pm$ 0.03 a.u.) and the energy values [eV] calculated for the HOMOs and LUMOs of Ir1 (left) and Ir3 (right).

transitions from HOMO $\rightarrow$ LUMO excitation have an MLCT nature mixed with some ligand-to-ligand charge-transfer (LLCT) character for all of the complexes. Additionally, for Ir1, Ir2 and Ir4, the HOMO-1 is located on the diimine ligands; thus, a <sup>3</sup>LC excited state described by the HOMO-1 $\rightarrow$ LUMO one-electron promotion can appear close in energy to the <sup>3</sup>MLCT state. This effect is more likely for the more conjugated Ir2 and Ir4 (Figure S4), for which both the HOMO-1 and HOMO-2 spread over the diimine ligand and are closer in energy to the HOMO. In contrast, the HOMO-1 of Ir3 is localized on the Ir-ppy environment; and the HOMO-2 and HOMO-3, which show some contribution from the diimine skeleton, are significantly stabilized (Figure 7).

Thus, <sup>3</sup>LC excited states for Ir**3** are expected to appear at higher energies than those of Ir**1**, Ir**2** and Ir**4**. This analysis of the frontier molecular orbitals supports the well-separated emission from the <sup>3</sup>LC and <sup>3</sup>MLCT states observed experimentally for Ir**3** at low temperature.

To characterize the nature of the emitting excited states in more detail, the molecular structures of the lowest triplet excited states (T<sub>1</sub>) were optimized by using the spin-unrestricted UB3LYP approach. After full-geometry relaxation, the T<sub>1</sub> state is computed to lie in the range 1.89–2.05 eV above S<sub>0</sub> (adiabatic energy differences,  $\Delta E$  in Figure 8), in reasonable agreement with the triplet energies experimentally registered from the onset of the phosphorescence (Table 2). As illustrated in Figure 8



Figure 6. Energy diagram for the HOMOs and LUMOs of (a) ligands 1-4 and (b) complexes Ir1-Ir4.





(b and c), the unpaired-electron spin-density distributions calculated for Ir1 and Ir3 (Ir: 0.48 e, ppy: 0.50 e, **2**: 1.02 e) perfectly match the topology of the HOMO $\rightarrow$ LUMO excitation (Figure 7). Similar spin-density distributions are found for Ir2 and Ir4. Therefore, the calculations clearly indicate that the emitting T<sub>1</sub> state at room temperature mainly results from the HO-MO $\rightarrow$ LUMO monoexcitation and implies an electron transfer from the Ir–ppy environment to the conjugated diimine ligand for Ir1–Ir4. Therefore, T<sub>1</sub> has <sup>3</sup>MLCT character with some LLCT contribution, in good concordance with the spectroscopic and electrochemical data at room temperature.



Figure 8. (a) Schematic energy diagram showing the adiabatic energy difference ( $\Delta E$ ) between the S<sub>0</sub> and T<sub>1</sub> states and the emission energy ( $E_{em}$ ) from T<sub>1</sub> calculated for Ir**1**–Ir**4**. Unpaired-electron spin-density contours (0.003 a.u.) calculated for the fully relaxed T<sub>1</sub> state of (b) Ir**1** and (c) Ir**3**.

To estimate the phosphorescence emission energies, the vertical energy differences between  $T_1$  and  $S_0$  were computed by performing single-point calculations of  $S_0$  at the optimized minimum-energy geometries of  $T_1$  ( $E_{em}$  in Figure 8). The theoretical emission energies follow the same trend as the maximum vertical emission of the emission bands observed at room temperature; Ir1, Ir2 and Ir4 emit at almost the same energy, and Ir3 emits at slightly lower energies (Table 2).

### Conclusions

The syntheses of a family of highly conjugated, phenanthrolinebased diimine ligands, functionalized with suitable terminal groups to anchor them to metal electrodes, and their corresponding cyclometallated monocationic Ir<sup>III</sup> complexes have been described. In these complexes, the energy of the LUMO, centred on the diimine ligand, is greatly stabilized by the increased conjugation of ligands 1-4 with respect to that of the bare phen ligand. Accordingly, the electrochemical and photophysical features of Ir1-Ir4 show lower HOMO-LUMO gaps than that of the reference complex  $[Ir(ppy)_2(phen)][PF_6]$ . However, the HOMO-LUMO gap does not follow the expected trend with the extension of the conjugation of the diimine ligand observed in other monocationic Ir<sup>III</sup> complexes and remains almost unchanged from Ir1 and Ir3 to the more conjugated Ir2 and Ir4. As a result, the emission wavelength remains almost invariable along the series, except for Ir3, the emission of which is slightly redshifted with respect to those of the other complexes. The spectroscopic measurements and DFT calculations suggest that the room-temperature emission of the iridium complexes can be unambiguously assigned to <sup>3</sup>MLCT excited states in all cases. Nevertheless, the contributions of <sup>3</sup>LC states to the emission increase in rigid matrices at low temperature. This could be clearly observed in the low-temperature emission of Ir**3**, for which the long-lived component of emission perfectly matches the emission of ligand **3** at room temperature. According to DFT calculations, this behaviour arises from the different distribution of the HOMO of Ir**3** compared with those of Ir**1**, Ir**2** and Ir**4**.

Induced dipolar moments are a pursued feature in molecular electronics. The charge-transfer nature of the emitting excited states of Ir1–Ir4, together with the small dependence of the HOMO–LUMO gap on the molecular length and the substituents (anchoring groups) of the diimine 1–4 ligands and the good conducting features reported for ligands 1 and 3 makes the complexes reported herein promising test beds for the study of photoconducting phenomena in molecular junctions. This work represents a first stage of the construction of nano-scale optoelectronic devices with metallic complexes.

# **Experimental Section**

**Chemical Synthesis:** All of the chemicals and solvents used were purchased from commercial sources and used without further purification, unless mentioned. The starting chlorido-bridged iridium dimer [ $Ir(ppy)_2CI$ ]<sub>2</sub> was prepared according to the literature procedure.<sup>[45]</sup>

**Instrumentation:** The <sup>1</sup>H NMR spectra were acquired with a Bruker AVANCE DRX 300 spectrometer. The spectra were referenced to the residual proton resonances of the solvent. Electrospray (ES) mass spectra were obtained with a Waters Micromass ZQ spectrometer in the positive-ion mode. The absorption spectra of samples in  $3 \times 10^{-6}$  M dichloromethane solutions were recorded with a Shimadzu UV-2501PC spectrophotometer with 1 cm path-length quartz cuvettes. The electrochemical measurements were performed under nitrogen in a glovebox with an Autolab PGSTAT 128N potentiostat and a three-electrode electrochemical cell consisting of a glassy carbon working electrode, a platinum wire counter electrode and a silver wire pseudoreference electrode.

Detailed synthetic procedures can be found in the Supporting Information.

**Laser Flash Photolysis Measurements:** A pulsed Nd:YAG SL404G-10 laser (Spectron Laser Systems) was used at the excitation wavelength of 355 nm. The single pulses were ca. 10 ns in duration, and the energy was less than 15 mJ/pulse. The detecting light source was a pulsed Lo255 Oriel xenon lamp. The laser flash photolysis system consisted of a pulsed laser, a Xe lamp, a 77200 Oriel monochromator, an Oriel photomultiplier tube (PMT) system made up of a 77348 side-on PMT tube, a 70680 PMT housing, and a 70705 PMT power supply. A Tektronix TDS-640A oscilloscope was used. The output signal from the oscilloscope was transferred to a personal computer. All transient measurements were recorded in dichloromethane or ethanol by employing  $10 \times 10 \text{ mm}^2 4 \text{ mL}$  quartz cells, which were purged with nitrogen or oxygen for at least 10 min before acquisition. All of the experiments were performed at room temperature.

**Phosphorescence Measurements:** The phosphorescence spectra were obtained with a Photon Technology International TimeMaster





TM-2/2003 spectrofluorometer equipped with a pulsed Xe lamp. The instrument was operated in time-resolved mode with a variable delay time. The compounds were dissolved in ethanol in a quartz tube (5 mm of diameter) and cooled to 77 K. The absorbance of the samples was 0.3 at the excitation wavelength (355 nm).

**Fluorescence Measurements:** The fluorescence decay traces were recorded with an EasyLife X system from OBB with a PTI lifetime detector. The solutions were purged with N<sub>2</sub> for at least 10 min. The experiments were performed at room temperature ( $\lambda_{exc}$  = 375 nm).

Computational Details: DFT calculations were performed with the D.01 revision of the Gaussian 09 program package<sup>[56]</sup> with the Becke three-parameter B3LYP exchange-correlation functional<sup>[57]</sup> together with the 6-31G\*\* basis set for C, H, N, O, and S<sup>[58]</sup> and the "double-5" guality LANL2DZ basis set for Ir.[59] The geometries of the singlet ground state  $(S_0)$  and the lowest-energy triplet state  $(T_1)$ were optimized within the  $C_2$  symmetry group. The geometry of the first triplet state was calculated at the spin-unrestricted UB3LYP level with a spin multiplicity of three. All calculations were performed in the presence of the solvent (dichloromethane). Solvent effects were considered within the self-consistent reaction field (SCRF) theory by using the SMD keyword that performs a polarized continuum model (PCM)<sup>[60-62]</sup> calculation by using the solvation model of Truhlar et al.<sup>[63]</sup> The SMD solvation model is based on the polarized continuous quantum chemical charge density of the solute (the "D" in the name stands for "density").

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