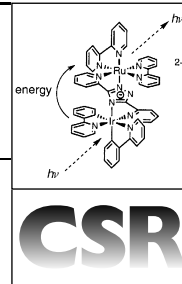


A family of luminescent coordination compounds: iridium(III) polyimine complexes



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Received 15th June 2000

First published as an Advance Article on the web 28th September 2000

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Francesco Barigelletti was born in 1944 and got his "Laurea" in Chemistry in 1971. He joined the National Research Council of Italy, at FRAE, Bologna in 1973. His work is concerned mostly with the spectroscopy of photoinduced energy and electron transfer processes in molecular and supramolecular species based on various photoactive and electroactive metal complexes. The assemblies (mostly arranged to constitute molecular wires) are useful models for the study of directional energy transport, conversion and storage and may operate as light driven molecular devices.



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30 years of Ir^{III} coordination chemistry with polyimine-type ligands are summarized. Over the years, milder reaction conditions have been used for their synthesis, allowing the incorporation of various functional substituents. Complexes are described with bidentate and terdentate ligands, with both N- and C-donor sites. All complexes are luminescent, with predominantly charge-transfer or ligand-centred emissive states depending on the charge density donated from the ligands to the metal. Ir^{III} excited state lifetimes range from nanoseconds to microseconds. A wide range of properties are obtained: [IrN₆]³⁺ complexes are strong photooxidants while tris-cyclometallated [IrN₃C₃] complexes are strong photoreductants.

1 Introduction

As far as inorganic photochemistry is concerned, several distinct eras can be identified.¹ 30 years ago, chemical transformation of complexes by irradiation was predominant, with the reign of chromium(III) among other metals. The mid 70's saw the emergence of "solar" photochemistry. Excited states were regarded as electron transfer reagents, of which Ru(bpy)₃²⁺† was the indisputable champion.² In recent years, several research groups have tried to broaden the family of compounds with excited states capable of acting as interesting redox reagents, and transition metals such as Os^{II}, Re^I, Cu^I, Rh^{III}, Ir^{III}, Pt^{II} and Pd^{II} have turned out to be promising.¹

Generally, iridium is regarded as a "catalytic" metal or as a useful metal centre for reactivity and model studies related to homogeneous catalysis. We will show in the present review article that iridium is more than that. In particular, some of its complexes display promising photochemical properties. Our aim is to provide an overview of iridium(III) polyimine complexes, since the 1970's. The very first papers will briefly be mentioned, but no applications and few characterizations were available at that time. For selected Ir^{III} polyimine complexes, this review will be concerned with the outline of synthetic procedures. Relevant photophysical and photochemical properties of some of the examined complexes will be discussed.

2 Families of Ir^{III} polyimine complexes

As a third-row transition metal, iridium(III) is characterized by the great inertness of its coordination sphere, requiring harsh reaction conditions to substitute the classical chlorine ligands of the starting iridium salts. It is noteworthy that iridium(III) is capable of forming a large range of complexes, including mono-, bis- and tris-cyclometallated complexes (the last is a unique feature among all polyimine complexes of transition metals),^{3,4} and that many more complexes are known with bidentate ligands than with terdentate ligands.

Two classes of complexes can be distinguished, depending on the extent to which the ligands contribute to the electron density at the metal centre.^{3,4} When some ligands are anionic (chloride, cyclometallating ligand), the emitting excited states have metal-to-ligand charge transfer (MLCT) character and there is sufficient charge compensation for the metal-centred

oxidation to proceed. In contrast, when the ligands are neutral and donate less charge density to the metal, emission is ligand centred (LC) and no metal-based oxidation is observed. For both classes of complexes for which reduction processes have been investigated, these are exclusively ligand centred.

3 [IrL₂Cl₂]ⁿ⁺ complexes (L = bidentate ligand) and related polymetallic species

From the literature it is clear that phenanthroline has been used much more often than bipyridine. This may be a result of the greater difficulty of obtaining pure samples of complexes with bpy ligands.

3.1 (N,N) species

In 1969 DeSimone *et al.* reported the preparation of [Ir(bpy)₂Cl₂]Cl by fusing K₃IrCl₆·3H₂O and bpy at 270 °C for 15 min,⁵ and unambiguously demonstrated the *cis*-configuration of the complex using NMR spectroscopy.

cis-[Ir(phen)₂Cl₂]Cl was first described in 1964 by Chiswell *et al.*,⁶ prepared in 27% yield by heating K₃IrCl₆ with 1,10-phenanthroline at 220 °C for 14 h. In 1971 Broomhead *et al.* reported a different synthesis.⁷ In a first step [Ir(phen)-Cl₄]⁻[phenH]⁺ was prepared in 90% yield from (NH₄)₃IrCl₆·2H₂O and phen by reflux in acidic water for 2 h. The second step consisted of heating the phenanthroline salt in refluxing glycerol for 1 min, and gave *cis*-[Ir(phen)₂Cl₂]Cl as a yellow solid in 85% yield. These early examples reflect the synthetic difficulties usually encountered when preparing simple iridium(III) complexes.

In 1990 Brewer *et al.* reported the preparation of various complexes of the type *cis*-[IrL₂Cl₂]⁺ (L = bidentate chelate, Fig. 1) following a slightly modified procedure.⁸ IrCl₃·3H₂O

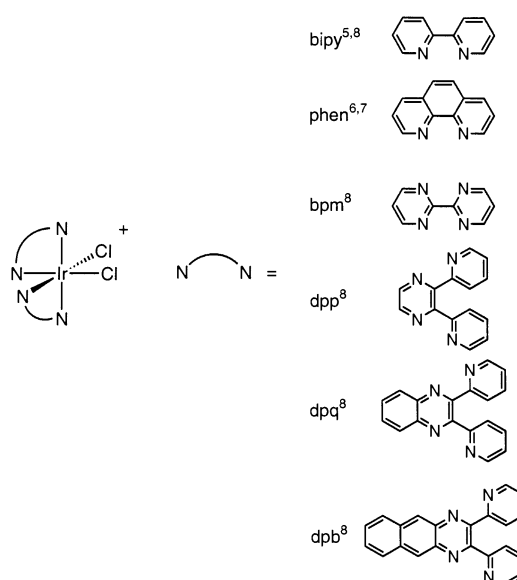


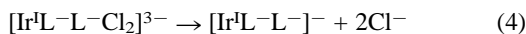
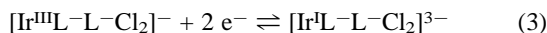
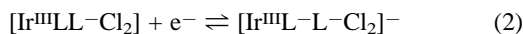
Fig. 1 Representation of [IrL₂Cl₂]⁺ complexes (L = bidentate chelate).

was refluxed with two equivalents of L in EtOH–H₂O for 2 h, and the complexes were obtained in 20–70% yield, depending on the nature of L.

In contrast to related Rh^{III} complexes,⁸ in which the first reduction is metal centred, in these [IrL₂Cl₂]⁺ complexes the first two reduction steps are ligand based. The ligands bpm, dpb, dpq, and dpb (Fig. 1) are all easier to reduce than bpy, and the first reduction potential for these [IrL₂Cl₂]⁺ complexes is clearly related to the extent of electronic delocalisation over the

† Abbreviations: acac = acetylacetonate; bpy = 2,2'-bipyridine; bpm = 2,2'-bipyrimidine; dpb = 2,3-di(2-pyridyl)benzoquinoxaline; dpp = 2,3-di(2-pyridyl)pyrazine; dpq = 2,3-di(2-pyridyl)quinoxaline; HAT = 1,4,5,8,9,12-hexaazatriphenylene; Hbpt = 3,5-di(pyridin-2-yl)-1,2,4-triazole; Hppy = 2-phenylpyridine; Hthpy = 2-(2-thienyl)pyridine; phen = 1,10-phenanthroline; terpy = 2,2':6',2''-terpyridine; terpy-py = 4'(4-pyridyl)terpy; tpp = 2,3,5,6-tetra(2-pyridyl)pyrazine; tterpy = 4'-tolylterpy.

ligand (−1.18, −0.76, −0.83, −0.47, and −0.33 V (*vs* Ag/AgCl) along the series L = bpy, bpm, dpp, dpq, and dpb). After uptake of two electrons by the ligand system (*e.g.*, −0.47 and −0.66 V for [Ir(dpq)₂Cl₂]⁺), a subsequent two-electron metal-centred reduction takes place which leads to expulsion of the chloride ligands, generating a four-coordinate Ir^I complex [eqns. (1)–(4)].



A noteworthy feature of the above reduction pattern is that the reduced two-electron [IrL–L–Cl₂][−] species are stable. This is one reason why multielectron reduction schemes are feasible based either on the monometallic complexes of the series in Fig. 1 or on multimetallic complexes (*vide infra*).

Luminescence data have been obtained at room temperature for the [IrL₂Cl₂]⁺ compounds.⁸ The band maxima can be arranged according to the decrease in energy of the emissive state, giving the series: bpy (510 nm), bpm (525), dpp (562) and dpq (634) (no data are available for dpb). The increase in the reduction potentials follows the same series, as is expected of an emissive state with MLCT character.

The mononuclear complexes described above⁸ have been extended to polynuclear mixed-metal systems with the ability to undergo intercomponent electron-transfer processes on irradiation. [IrL₂Cl₂]⁺ was reacted with two equivalents of Ru(bpy)₂Cl₂ to give a diastereomeric mixture of the corresponding trinuclear complexes in 85–90% yield after heating at reflux in EtOH–H₂O for 3 days.⁹

The trinuclear complexes prepared by Brewer and co-workers (Fig. 2a) demonstrate a rich electrochemistry. The two

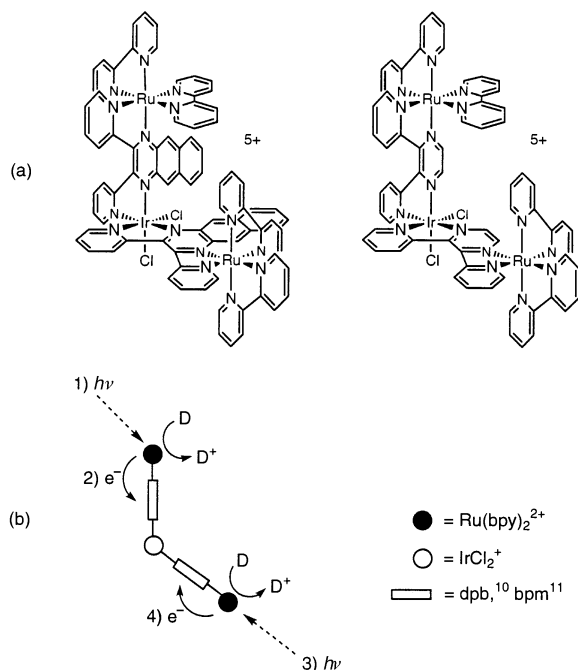


Fig. 2(a) [Ru(bpy)₂(dpb)IrCl₂(dpb)Ru(bpy)₂]⁵⁺ and [Ru(bpy)₂(dpp)IrCl₂(dpp)Ru(bpy)₂]⁵⁺. (b) Photoinduced two-electron uptake by the bridging ligands.

ruthenium(II) centres are oxidized simultaneously and there is also a series of one-electron reductions leading to the storage of four electrons in the bridging ligands before the peripheral bpy ligands are reduced.

For instance, for [(bpy)₂Ru^{II}(dpq)Ir^{III}Cl₂(dpq)Ru^{II}(bpy)₂]⁵⁺, sequential reductions of the bridging ligands (BLs) occur at

−0.12, −0.26, −0.90 and −1.22 V (*vs* Ag/AgCl). The first two reduction processes in this trinuclear complex are easier than the analogous processes in the mononuclear precursor [Ir(dpq)₂Cl₂]⁺. This can be ascribed to the stabilising effect of the Ru^{II} centres towards reduced states involving iridium-containing fragments.

As a consequence of this remarkable electrochemical behaviour, an extension to systems driven by light was proposed.¹⁰ Fig. 2b provides an illustration of a trinuclear complex containing the dpb ligand which can store multiple electrons. Irradiation of the peripheral Ru^{II} centres leads to the transfer of two electrons to the BLs, following which the Ru^{III} donors are re-reduced by the sacrificial electron donor (dimethylaniline, D). This basic photochemical device has potential future applications in one-step two-electron delivery to a substrate.

Two years later, a similar trinuclear system was prepared in the same laboratory, using a different bridging ligand, bpm, which now can take up two electrons (four electrons are collected before the first bpy-localized reduction),¹¹ according to a reduction pattern of the type seen above (Fig. 2b). This reaction proceeded with a 60% isolated yield by heating the starting materials (Ru(bpy)₂Cl₂ and Ir(bpm)₂Cl₂⁺) to reflux in EtOH–H₂O for 5 days.

3.1 (N,C) species

In 1984, Watts *et al.* prepared dichloro-bridged Ir^{III} dimers in 72% yield using Hppy or benzo[*h*]quinoline as *N,C* cyclometallating ligands, by refluxing iridium trichloride hydrate with the ligand in 2-ethoxyethanol–water for one day (Fig. 3a).¹² Six

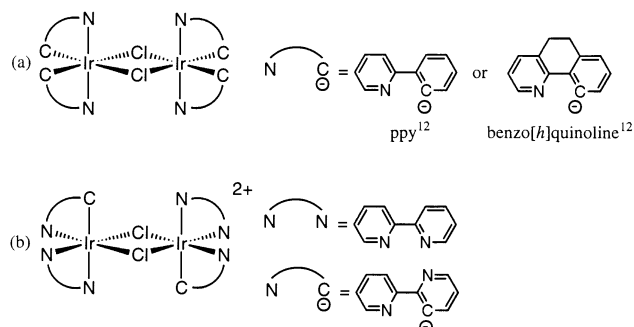


Fig. 3 Representation of cyclometallated dichloro-bridged dimers.

years later, by reacting potassium hexachloroiridium(IV) and potassium hexachloroiridium(III) with bpy in EtOH–H₂O, the same group obtained a dichloro-bridged dimer in which each iridium centre is surrounded by one *N,N*-coordinated bpy and one *N,C*-coordinated bpy (Fig. 3b).¹³

4 [IrL₃]ⁿ⁺ complexes (L = bidentate ligand)

4.1 (N,N) species

In 1958 Ir(bpy)₃³⁺ was first described by Martin *et al.*, as an orange solid, obtained by fusing K₃IrCl₆ and bpy for 20 min.¹⁴ The lack of precise characterization available at that time led Chiswell *et al.* to attempt the preparation of Ir(phen)₃³⁺ in 1964 under similar conditions.⁶ Pale yellow complexes were obtained, although some uncertainty remains regarding their purity.

In 1974, the procedure described by Demas *et al.* was much more precise.¹⁵ K₃IrCl₆·3H₂O was first converted into a halide-free sulfate upon treatment with K₂S₂O₈ and KHSO₄ in boiling water, evaporation to dryness, and fusion in air above 250 °C for 30 min. After cooling, it was mixed with bpy and fused under

CO₂ at 230 °C for 6 h. A laborious work-up led to Ir(bpy)₃³⁺ in a good 50% yield (Fig. 4).

The metal-centred oxidation of Ir(bpy)₃³⁺ occurs at a rather high potential, +2.17 V, while reduction (ligand centred) occurs at -0.76 V (*vs* NHE).^{4,16} Its low temperature luminescence (77 K), which has a lifetime of *ca.* 80 μs, has LC characteristics. At room temperature it exhibits a reasonably long lifetime, $\tau = 2.4$ μs, suggesting emission has some MLCT character (less than 20–30%).^{4,17} From the onset of the emission spectrum, the energy level of the lowest-lying excited state, ³Ir(bpy)₃³⁺, is estimated to be 2.81 eV. According to these electrochemical and spectroscopic data, ³Ir(bpy)₃³⁺ is a good oxidizing agent ($E[{}^3\text{Ir}(\text{bpy})_3^{3+}/\text{Ir}(\text{bpy})_3^{2+}] = +2.05$ V), but a weak reducing agent ($E[\text{Ir}(\text{bpy})_3^{4+}/{}^3\text{Ir}(\text{bpy})_3^{3+}] = -0.64$ V). Scheme 1 shows the relationship between the reduction potentials of Ir(bpy)₃³⁺ and of its tris-cyclometallated analogue, Ir(ppy)₃ (*vide infra*).

Treatment of *cis*-[Ir(bpy)₂Cl₂]⁺ with trifluoromethanesulfonic acid in *o*-dichlorobenzene led to *cis*-[Ir(bpy)₂(OSO₂CF₃)₂]⁺ in 95% yield, as reported by Meyer *et al.* in 1984.¹⁸ This trifluoromethanesulfonato complex proved to be an excellent precursor to Ir(bpy)₃³⁺, the substitution proceeding in 80% yield by heating with bpy in ethylene glycol for 5 h.

4.2 (N,C), (N,Si) and (N,S) species

From the reaction between IrCl₃ and bpy in glycerol at 180 °C for 2 h, performed in 1977 by Watts *et al.*, a complex was isolated, which was identified at that time as Ir(bpy-N,N')₂(bpy-N)(H₂O)³⁺, a complex with one monodentate bpy in which the sixth coordination site is occupied by a water molecule.¹⁹ Four years later using X-ray crystallography, Serpone *et al.* demonstrated that it was in fact Ir(N,N-bpy)₂(NH,C³-bpy)³⁺, the monocyclometallated and N-protonated analogue of Ir(bpy)₃³⁺.²⁰ Further published work confirmed this conclusion in subsequent years.

Reaction of [Ir(ppy)₂Cl]₂¹² with HAT in refluxing CH₂Cl₂-MeOH gave the orange complex Ir(ppy)₂(HAT)⁺ in 80% yield (Fig. 5a).²¹ Irradiation of this complex with visible light leads to luminescent states. At room temperature, Ir(ppy)₂(HAT)⁺ emits at $\lambda > 770$ nm ($\tau < 10$ ns) while at 77 K it has dual-emission properties. The two states responsible for the low-temperature behaviour, which are not thermally equilibrated at 77 K, are identified as MLCT and sigma-bond-to-ligand CT (SBLCT) states (Fig. 5b), with lifetimes of *ca.* 1.5 and 3 μs.

The synthesis of a dinuclear complex incorporating Ru^{II} and Ir^{III} centres linked *via* the bridging ligand HAT was reported by Kirsch-De Mesmaecker *et al.* [(bpy)₂Ru(HAT)Ir(ppy)₂]³⁺ (Fig. 5c) was obtained by reacting [Ru(bpy)₂(HAT)]⁺ with [Ir(ppy)₂-Cl]₂ in refluxing CH₂Cl₂-MeOH for 6 h.²² In this dinuclear complex, the emission is identified as Ir-centred, SBLCT in nature ($\lambda_{\text{max}} = 760$ nm, $\tau < 10$ ns), consistent with Ru → Ir energy transfer.²³

A different dinuclear complex, [(bpy)₂Ru(bpt)Ir(ppy)₂]²⁺, was synthesized by Reedijk *et al.* by reacting [Ru(bpy)₂(bpt)]⁺ and [Ir(ppy)₂Cl]₂ in refluxing 2-methoxyethanol for 2 days.²⁴ In this complex (Fig. 6), the two metal centres are linked *via* a bridging ligand containing a monoanionic triazole unit. Because

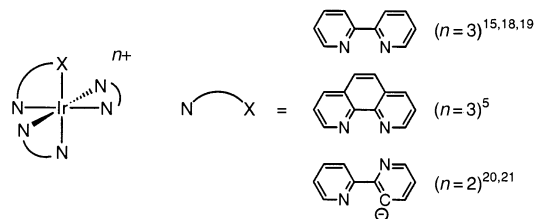


Fig. 4 Representation of Ir(bpy)₃³⁺, Ir(phen)₃³⁺, and Ir(N,N-bpy)₂(N,C-bpy)²⁺.

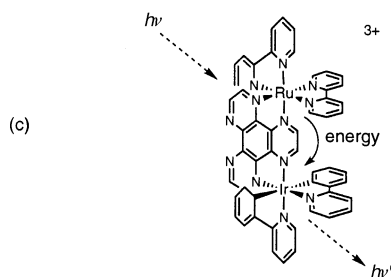
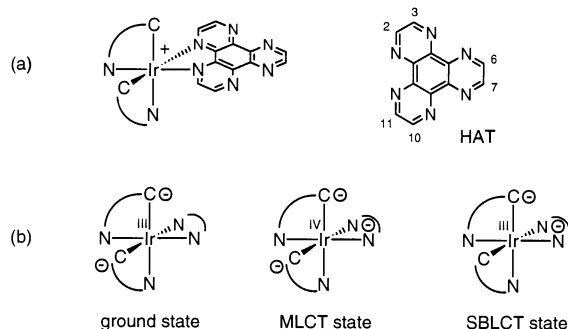


Fig. 5 (a) Representation of Ir(ppy)₂(HAT)⁺ and HAT. (b) Ground and excited states. (c) Energy transfer in [Ru(bpy)₂(HAT)Ir(ppy)₂]³⁺.

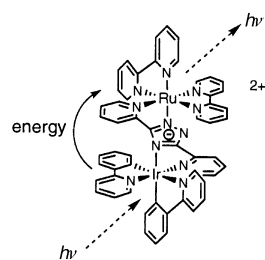
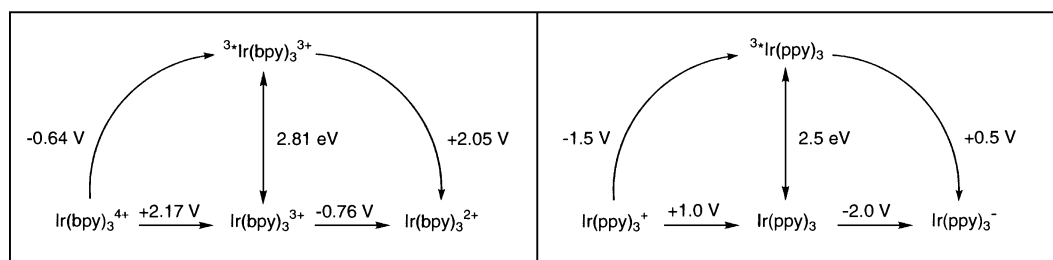


Fig. 6 Energy transfer in [Ru(bpy)₂(bpt)Ir(ppy)₂]²⁺.

of this electronic feature, the MLCT states localised on the two moieties involve the peripheral ligands and not the bridging ligand (as is usual for most dinuclear complexes). In [(bpy)₂Ru(bpt)Ir(ppy)₂]²⁺, emission is only observed from the Ru-based unit and the direction of intercomponent energy transfer is Ir →



Scheme 1 Reduction potentials (*vs.* SHE) of ground and excited states of Ir(bpy)₃³⁺ and Ir(ppy)₃.

Ru, *i.e.* in the opposite direction from that observed for $[(bpy)_2Ru(HAT)Ir(ppy)_2]^{3+}$.

Continuing the series from mono- and dinuclear complexes to multinuclear compounds led Serroni, Campagna *et al.* to investigate tetranuclear heterometallic complexes.²⁵ These were obtained as a mixture of diastereoisomers by reaction of $[Ir(ppy)_2Cl]_2$ with $M(dpp)_3^{2+}$ ($M = Ru^{II}, Os^{II}$) in refluxing CH_2Cl_2 for 2.5 h, in 73 and 70% yields respectively (Fig. 7a). In

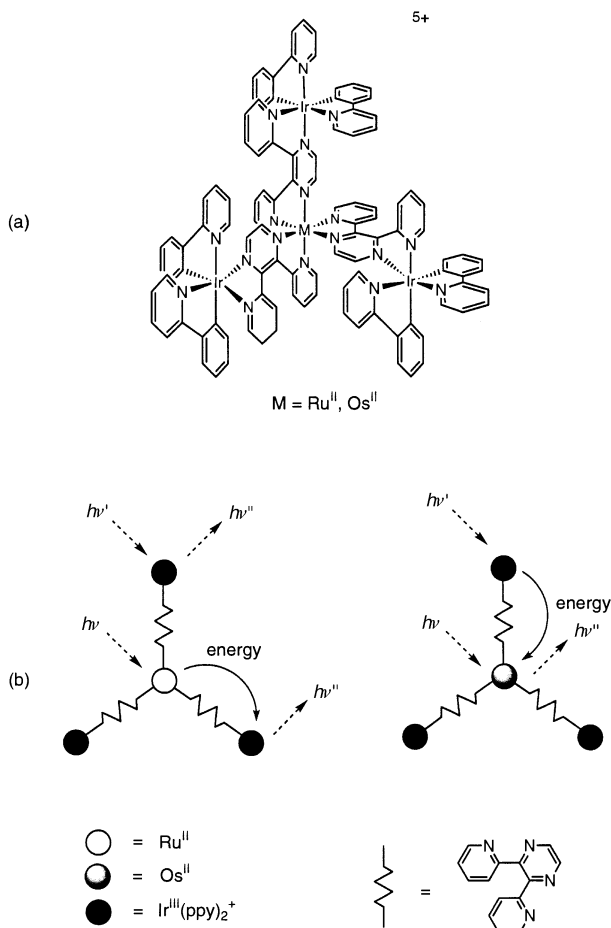


Fig. 7 (a) $\{M[(dpp)Ir(ppy)_2]_3\}^{5+}$ ($M = Ru^{II}, Os^{II}$). (b) Photoinduced energy transfer processes occurring in the Ru^{II} - and Os^{II} -based complexes.

the tetranuclear (bimetallic) compounds, $\{M[(\mu-2,3-dpp)Ir(ppy)_2]_3\}^{5+}$, local excitation is disposed according to predetermined energetic patterns, ultimately governed by the type of metal centre employed. For $\{Ru[(dpp)Ir(ppy)_2]_3\}^{5+}$, the central position is occupied by a $Ru(dpp)_3^{2+}$ unit. The absorption of a single photon by this chromophore results in the excitation being conveyed with unit efficiency to any one of the peripheral $(dpp)Ir(ppy)_2^+$ fragments, which then luminesces (Fig. 7b).

Conversely, for $\{Os[(dpp)Ir(ppy)_2]_3\}^{5+}$, localised absorption by one of the iridium(III) chromophores is followed by a periphery-to-centre excitation energy drain, and the emission is always $Os(dpp)_3^{2+}$ -based. These results agree with the known ordering of the emissive triplet state energy levels: $Ru(dpp)_3^{2+} > (dpp)Ir(ppy)_2^+ > Os(dpp)_3^{2+}$.

Using similar reaction conditions (CH_2Cl_2 -MeOH, 2 h reflux) Neve, in collaboration with the same group, recently prepared some $[Ir(ppy)_2L]^+$ complexes where L is a substituted 6'-phenylbipyridine.²⁶ The emission is ascribed to MLCT states with partial SBLCT character.

fac- $Ir(ppy)_3$, a side-product of the preparation of $[Ir(ppy)_2Cl]_2$ reported by Watts *et al.* in 1985, was isolated soon afterwards in low yield from washing filtrates (Fig. 8).²⁷ Subsequently, other complexes containing substituted ppy were

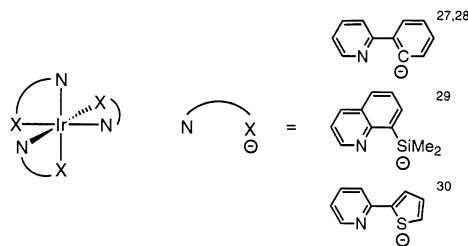


Fig. 8 Representation of tris-cyclometallated complexes with C^- , Si^- and S^- ligands.

prepared in good yields (40–75%) by reaction of $Ir(acac)_3$ with Hppy in refluxing glycerol for 10 h.²⁸ The facial arrangement of the ligands can be explained by the strong *trans*-effect of Ir–C bonds: after coordination of a first ppy, the oxygen atom (from acac) located *trans* to the Ir–C bond is labilized and this vacant coordination site is filled by the nitrogen atom of another ppy. In this way a series of tris-cyclometallated complexes was obtained by Watts *et al.*, which proved to be strong photo-reductants.²⁸ Emission and cyclic voltammetry data for this series of complexes are listed in Table 1. The room temperature

Table 1 Emission and electrochemical data for *fac*-tris-cyclometallated Ir^{III} complexes^a

	$\tau^b/\mu s$	$\lambda^c/(nm)$	$E_{1/2} (Ir^{IV/III})^d/V$
$Ir(5-MeO-ppy)_3$	2.86	539	+0.79
$Ir(4-t-Bu-ppy)_3$	1.97	497	+0.90
$Ir(4-Pr-ppy)_3$	1.93	496	+0.91
$Ir(4-Me-ppy)_3$	1.94	493	+0.94
$Ir(4-MeO-ppy)_3$	2.24	481	+0.99
$Ir(ppy)_3$	1.90	494	+1.01
$Ir(4-F-ppy)_3$	2.04	468	+1.21
$Ir(4-F_3C-ppy)_3$	2.16	494	+1.32

^a From ref. 28. ^b Degassed MeCN, 293 K. ^c Shortest wavelength feature at 77 K, EtOH–MeOH (1:1 by vol.). ^d MeCN, V vs SHE (corresponding to +0.24 V vs SCE; adapted from ref. 28).

luminescence properties are consistent with an MLCT excited state, and high luminescence quantum yields are observed (*ca.* 0.4 in degassed solvent).^{4,27} The wide variation in the $Ir^{IV/III}$ potentials is clearly related to the electron-withdrawing/releasing properties of the ligand substituents.

The excited state energy of $^*Ir(ppy)_3$ is 2.5 eV. This, in combination with the ground state oxidation potential of $Ir(ppy)_3$ (Table 1), places the excited state oxidation potential at -1.5 V (Scheme 1). Thus, these highly luminescent tris-cyclometallated complexes appear to be some of the most powerful reducing agents of the photoactive polyimine complexes.^{1–4}

The first tris-(N,Si)-ligated metal complex was reported the following year, again by Watts *et al.*²⁹ It was obtained in 60% yield by reaction of $Ir(PPh_3)_3(CO)(H)$ with (8-quinolyl)dimeethylsilane in refluxing toluene for 24 h (Fig. 8).

A different procedure was later used by Güdel *et al.* for the preparation of *fac*- $Ir(thpy)_3$.³⁰ In this case, $[Ir(thpy)_2Cl]_2$, excess Hthpy and silver triflate were heated at 110 °C for one day to give the desired orange complex in 58% isolated yield (Fig 8).

5 $[IrL_2]^+$ complexes (L = terdentate ligand)

5.1 $IrLCl_3$ species

In 1937, working on the coordination chemistry of terpy and various metals, Morgan and Burstall reported in a historic paper the preparation of $Ir(terpy)Cl_3$ by reaction of Na_3IrCl_6 and terpy in water.³¹ Fifty five years later, Brewer *et al.* prepared $Ir(tpp)Cl_3$ in 45% yield by reacting $IrCl_3 \cdot 13H_2O$ and tpp in

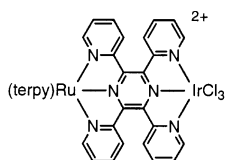


Fig. 9 Formula of (terpy)Ru(tpp)IrCl₃.

refluxing ethylene glycol for 25 min.³² A dinuclear complex was also synthesized, using tpp as bridging ligand: [(terpy)Ru(tpp)IrCl₃]²⁺ was obtained in 62% yield from Ir(tpp)Cl₃ and Ru(terpy)Cl₃ after heating at reflux in DMF–EtOH for 4 h (Fig. 9). For this complex, the emission is of Ru → tpp CT nature, irrespective of the excitation wavelength.³²

5.2 [IrL₂]³⁺ complexes ((N,N,N) species)

In 1990 Demas and co-workers reported the first synthesis of Ir(terpy)₂³⁺ following the initial stage of the procedure they had used in 1974 for the synthesis of Ir(bpy)₃³⁺.³³ The iridium sulfate (prepared *in situ* from K₃IrCl₆) was reacted with terpy in refluxing ethylene glycol for a few minutes, and at 150 °C for 6 h. Tedious workup and purification were necessary to isolate the desired complex (Fig. 10).

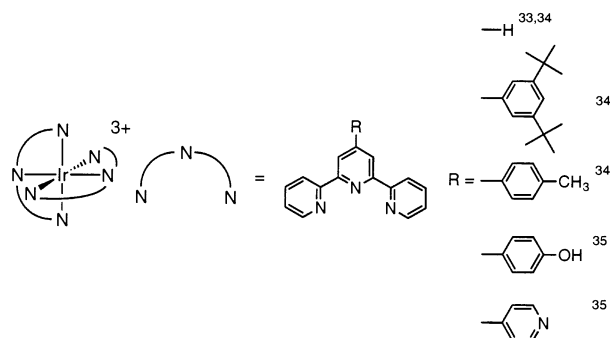


Fig. 10 Representation of bis-terpyridine complexes.

In 1999 a different method was reported,³⁴ based on the stepwise coordination of two terpy ligands under milder

conditions (Fig. 10). Depending on the solubility of the ligand, the first coordination required refluxing EtOH or heating at 160 °C in ethylene glycol. After isolation of the Ir(terpy)Cl₃ intermediate, the second chelation was achieved in ethylene glycol, at temperatures between 140 °C and reflux (196 °C). Purification proceeded either by crystallization or by column chromatography on silica gel. Isolated yields were 10–25% with respect to IrCl₃.

Iridium bis-terpyridine complexes are luminescent at room temperature, with λ_{em} = 458 nm for unsubstituted terpy and 506 nm for 4'-arylterpys.³⁴ The emission is a ligand phosphorescence,³³ possibly with some MLCT character for 4'-arylterpys.³⁴ This gives highly energetic excited states with a lifetime on the microsecond timescale, in striking contrast to the ruthenium(II) analogues (Table 2). With a reduction potential of *ca.* +1.6 V/SCE, the excited state is also a powerful oxidant.

More recently, Williams *et al.* used the same synthetic pathway to prepare bis-terpy complexes bearing pH-sensitive groups (phenol and pyridine, Fig. 10).³⁵ [(terpy)Ir(terpy-py)]³⁺ is luminescent at pH > 6, but its luminescence intensity drops by about one order of magnitude for pH < 4. This complex constitutes a potentially useful pH sensor. The authors ascribe the pH-dependence of the luminescence to a change from predominantly LC emission at higher pH to predominantly MLCT emission at lower pH values, as a consequence of protonation of the appended pyridine site (Fig. 11).

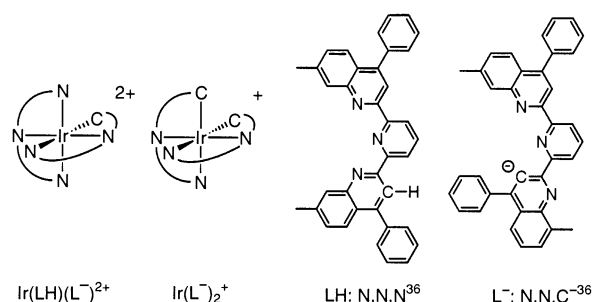


Fig. 12 Representation of mono- and bis-cyclometallated terdentate complexes.

Table 2 Photophysical parameters of Ir^{III} and Ru^{II} bpy, terpy and tterpy complexes at room temperature (PF₆ anions)

	λ _{abs} /(nm) ^a (ε/M ⁻¹ .cm ⁻¹)	λ _{em} /nm ^b	E _{0,0} /eV	τ ^c	Φ _{em}	Ref.
Ir(bpy) ₃ ^{3+d}	344 (3300)	441	2.81	2.4 μs	—	15,17
Ir(terpy) ₂ ^{3+e}	352 (5800)	458	2.71	1.2 μs	2.5 × 10 ⁻²	34
Ir(terpy) ₂ ^{3+e}	373 (29000)	506	2.45	9.5 μs	2.9 × 10 ⁻²	34
Ru(bpy) ₃ ^{2+e}	451 (13000)	610	2.03	860 ns	8.6 × 10 ⁻²	2
Ru(terpy) ₂ ^{2+e}	474 (14600)	—	—	250 ps	—	2
Ru(terpy) ₂ ^{2+d}	490 (28000)	640	1.94	0.95 ns	3.5 × 10 ⁻⁵	38

^a Lowest energy maximum with ε > 1000. ^b Highest energy maximum. ^c Degassed solvent. ^d Alcohol. ^e Acetonitrile.

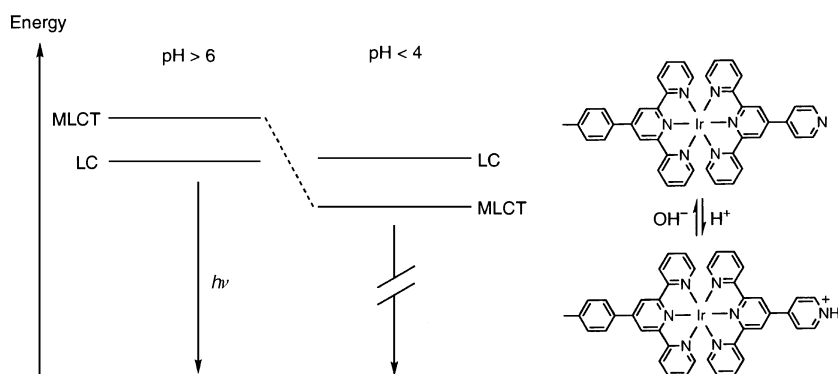


Fig. 11 pH-dependence of the luminescence of a pyridine-containing bis-terpyridine complex.

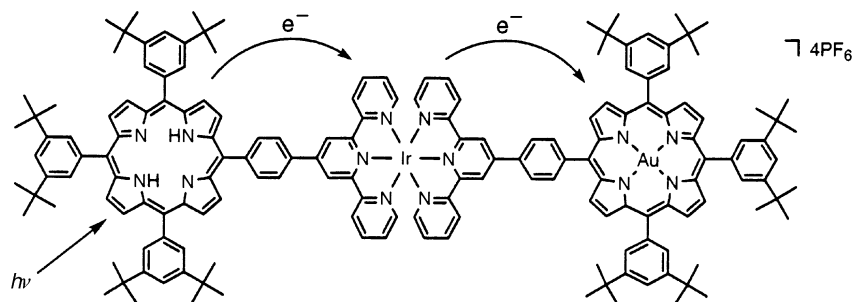


Fig. 13 A porphyrinic molecular triad which undergoes photoinduced charge separation.

5.3 [IrL₂]ⁿ⁺ complexes (n = 1,2) ((N,N,C) species)

The combination of Ir^{III} and cyclometallating terdentate ligands was achieved by Mamo, Campagna *et al.* in 1997, when they reported the preparation of [Ir(LH)(L⁻)]²⁺ and [Ir(L⁻)₂]⁺ [LH = 2,6-bis(7'-methyl-4'-phenyl-2'-quinoly)pyridine] by heating IrCl₃ and LH in refluxing glycerol for 24 h (Fig. 12).³⁶ Both complexes were obtained in the same reaction, with 40 and 10% yields respectively. In all cases the emission is assigned to MLCT levels.

6 Conclusions and perspectives

The coordination chemistry of iridium(III) was originally carried out under harsh reaction conditions. The more recent use of milder conditions has opened the way to the use of ligands bearing chemically sensitive groups. This synthetic approach has led to the preparation of porphyrinic arrays built around an Ir(terpy)₂³⁺ core, with appended electron donor and acceptor units (Fig. 13). In this triad, excitation of the free-base porphyrin with visible light yields, with 50% efficiency, a charge-separated state which has a lifetime of 3.5 ns at room temperature.³⁷

This review has described a wide range of luminescence and redox properties of iridium(III) polyimine complexes. These suggest the complexes have potential for application as devices for light harvesting, for sequential electron storage and delivery, and as models for intercomponent electron and energy transfer processes occurring in natural photosynthesis.

7 Acknowledgements

We thank the French CNRS and the Italian CNR for financial support. ID thanks the French Ministry of Education, Research and Technology, and SE thanks the European Community TMR contract no. CT98-0226. The support by COST program D11/0004/98 is acknowledged.

8 References

- D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum Press, New York, 1994.
- A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85-277, and references therein.
- K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992.
- M. Maestri, V. Balzani, C. Deuschel-Cornioley and A. von Zelewsky, *Adv. Photochem.*, 1992, **17**, 1-68, and references therein.
- R. J. Watts, *Comments Inorg. Chem.*, 1991, **11**, 303-337, and references therein.
- R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, 1969, **8**, 2517-2519.
- B. Chiswell and S. E. Livingstone, *J. Inorg. Nucl. Chem.*, 1964, **26**, 47-51.
- J. A. Broomhead and W. Grumley, *Inorg. Chem.*, 1971, **10**, 2002-2009.
- S. C. Rasmussen, M. M. Richter, E. Yi, H. Place and K. J. Brewer, *Inorg. Chem.*, 1990, **29**, 3926-3932.
- J. S. Bridgewater, L. M. Vogler, S. M. Molnar and K. J. Brewer, *Inorg. Chim. Acta*, 1993, **208**, 179-183.
- S. M. Molnar, G. Nallas, J. S. Bridgewater and K. J. Brewer, *J. Am. Chem. Soc.*, 1994, **116**, 5206-5210.
- G. N. A. Nallas, S. W. Jones and K. J. Brewer, *Inorg. Chem.*, 1996, **35**, 69747-6980.
- S. Sprouse, K. A. King, P. J. Spellane and R. J. Watts, *J. Am. Chem. Soc.*, 1984, **106**, 6647-6653.
- F. O. Garces and R. J. Watts, *Inorg. Chem.*, 1990, **29**, 582-584.
- B. Martin and G. M. Waind, *J. Chem. Soc.*, 1958, 4282-4288.
- C. M. Flynn, Jr and J. N. Demas, *J. Am. Chem. Soc.*, 1974, **96**, 1959-1960.
- J. L. Kahl, K. W. Hanck and M. K. De Armond, *J. Phys. Chem.*, 1978, **82**, 540-545.
- J. N. Demas, E. W. Harris, C. M. Flynn, Jr and D. Diemante, *J. Am. Chem. Soc.*, 1975, **97**, 3838-3839.
- B. P. Sullivan and T. J. Meyer, *J. Chem. Soc. Chem. Commun.*, 1984, 403-405.
- R. J. Watts, J. S. Harrington and J. van Houten, *J. Am. Chem. Soc.*, 1977, **99**, 2179-2187.
- W. A. Wickramasinghe, P. H. Bird and N. Serpone, *J. Chem. Soc., Chem. Commun.*, 1981, 1284-1286.
- P. Didier, I. Ortman, A. Kirsch-De Mesmaecker and R. J. Watts, *Inorg. Chem.*, 1993, **32**, 5239-5245.
- P. Didier, L. Jacquet, A. Kirsch-De Mesmaecker, R. Hueber and A. van Dorsselaer, *Inorg. Chem.*, 1992, **31**, 4803-4809.
- I. Ortman, P. Didier and A. Kirsch-De Mesmaecker, *Inorg. Chem.*, 1995, **35**, 3695-3704.
- J. H. van Diemen, R. Hage, J. G. Haasnoot, H. E. B. Lempers, J. Reedijk, J. G. Vos, L. De Cola, F. Barigelli and V. Balzani, *Inorg. Chem.*, 1992, **31**, 3518-3522.
- S. Serroni, A. Juris, S. Campagna, M. Venturi, G. Denti and V. Balzani, *J. Am. Chem. Soc.*, 1994, **116**, 9086-9091.
- F. Neve, A. Crispini, S. Campagna and S. Serroni, *Inorg. Chem.*, 1999, **38**, 2250-2258.
- K. A. King, P. J. Spellane and R. J. Watts, *J. Am. Chem. Soc.*, 1985, **107**, 1431-1432.
- K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson and R. J. Watts, *Inorg. Chem.*, 1991, **30**, 1685-1687.
- P. I. Djurovich, A. L. Safir, N. L. Keder and R. J. Watts, *Inorg. Chem.*, 1992, **31**, 3195-3196.
- M. G. Colombo, T. C. Brunold, T. Riedener, H. U. Güdel, M. Förtsch and H.-B. Bürgi, *Inorg. Chem.*, 1994, **33**, 545-550.
- G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1937, 1649-1655.
- L. M. Vogler, B. Scott and K. J. Brewer, *Inorg. Chem.*, 1993, **32**, 898-903.
- N. P. Ayala, C. M. Flynn, Jr., L. A. Stacksteder, J. N. Demas and B. A. De Graff, *J. Am. Chem. Soc.*, 1990, **112**, 3837-3844.
- J.-P. Collin, I. M. Dixon, J.-P. Sauvage, J. A. G. Williams, F. Barigelli and L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009-5016.
- M. Licini and J. A. G. Williams, *Chem. Commun.*, 1999, 1943-1944.
- A. Mamo, I. Stefio, M.F. Parisi, A. Credi, M. Venturi, C. Di Pietro and S. Campagna, *Inorg. Chem.*, 1997, **36**, 5947-5950.
- I. M. Dixon, J.-P. Collin, J.-P. Sauvage, F. Barigelli and L. Flamigni, *Angew. Chem., Int. Ed.*, 2000, **39**, 1292-1295.
- J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelli, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993-1019.