

Mono- and di-nuclear iridium(III) complexes. Synthesis and photophysics†

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This paper reports the synthesis and photophysical characterization of heteroleptic mono- and di-nuclear iridium(III) complexes. The complexes contain two ortho-metalating ligands, 2-phenylpyridine, with a bipyridine derivative as the third chelating unit. In the case of the dinuclear complexes the two iridium moieties are connected by a conjugated bridging ligand containing three or four phenyl units. All the complexes emit at room temperature and steady state and time resolved spectroscopy demonstrates that the lowest excited state is a metal-to-ligand charge transfer involving the bipyridine ligand.

Introduction

Iridium(III) complexes have recently attracted a lot of interest as potential triplet emitters in electronic devices¹ and in biological applications as luminescent and electrochemiluminescent labels.² Despite their difficult synthesis many homo- and hetero-leptic ortho-metalated compounds have been reported together with their photophysical properties.^{3–6} In fact iridium complexes as the more well-known ruthenium polypyridine analogues show room temperature emission (from an excited triplet state) with long excited state lifetime and rather high emission quantum yields.^{7,8} Also terpyridine compounds have been described by several authors, since contrary to the isoelectronic ruthenium complexes they show strong low energy (in the visible region) emission with long excited state lifetimes.^{9,10} The main attractive features of the iridium complexes are related to the possibility to tune the colors of their emission and their excited state lifetime by simply changing the chelating ligands.^{3,11} Such diversification in their behavior is related to their excited state properties since often the ligand centered state and the metal-to-ligand excited state are so close in energy that the lowest excited state can be of different nature depending on the nature of the coordinated ligands employed.^{4,6,12}

Polypyridine compounds are often characterized by long lived excited states due to a mixing of metal-to-ligand charge transfer, MLCT and ligand centered, LC states.^{4,6,13} Replacing one or two of the diimine ligands with the structurally similar ortho-metalating chelates such as 2-phenylpyridine, leads to higher metal centered, MC, excited state due to the strong ligand field of the CN *versus* the NN coordinating ligands. Furthermore their strong σ -donation causes a decrease of the energy of the MLCT state increasing the energy gap between the MLCT and LC states. This results in a better absorption of visible light, a lower energy emission and shorter excited state lifetimes.

More recently the rich redox chemistry of iridium complexes and the possibility to create the excited state by charge recombination reactions has led to the development of several types of simple devices based on iridium complexes.¹⁴

In this paper we discuss the synthesis, characterization, and photophysical behavior of mixed-ligand mono- and di-nuclear iridium(III) complexes. A mononuclear species, **[Ir(bpy-ph-Br)]**, containing two ortho-metalating ligands (2-phenylpyridine, ppy), and a bipyridine derivative [4-(*p*-bromo)phenyl-2,2'-bi-

pyridine, **bpy-ph-Br**], and the dinuclear iridium compounds containing a conjugated bridging ligand comprising three or four phenyl units, **[Ir-ph₃-Ir]** and **[Ir-ph₄-Ir]** respectively, are reported (see Fig. 1).

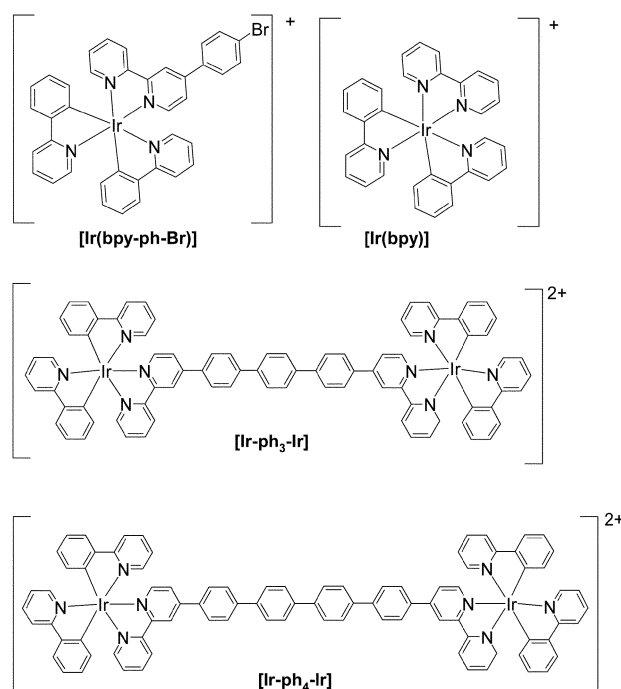


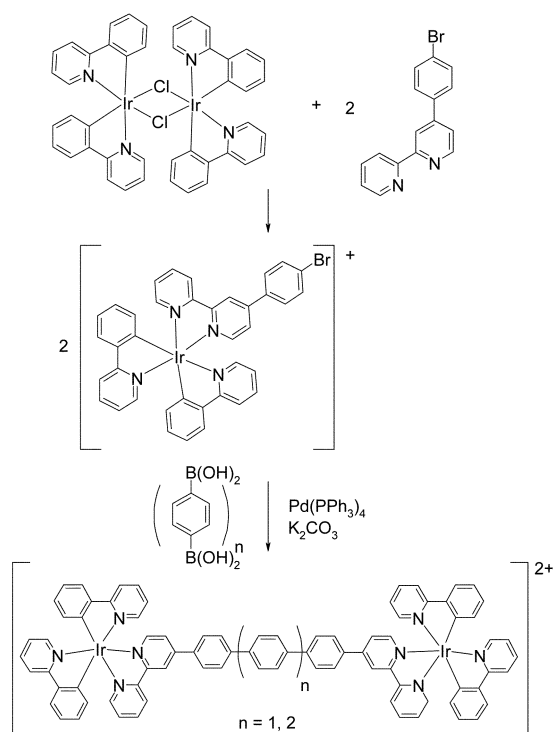
Fig. 1 Schematic formulae of the complexes investigated in this paper.

Results and discussion

Synthesis and characterisation

The synthesis of iridium complexes has received a lot of attention in the last few years^{3,6,15} and many new synthetic methods including microwave preparation have been reported.¹⁶ In our case the complexes have been prepared using the 'complex as precursor' strategy¹⁷ as shown in Scheme 1. The key point is the completion of the desired iridium coordination sphere before the entire complex is assembled *via* coupling through covalent bonding. The dinuclear complexes have been prepared from the mononuclear building block and coupled together through a phenyl bridge. The phenyl bridge is constructed by

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Scheme 1 Synthetic route employed to prepare the iridium compounds.

the reaction of the aryl bromide containing complex and the appropriate aromatic bisboronic acid in a standard Suzuki protocol.¹⁸

All the complexes have been obtained as PF_6^- salts. The complexes have been purified by column chromatography and characterized by ^1H NMR and mass spectrometry. The ligand 4-(*p*-bromophenyl)-2,2'-bipyridine¹⁹ and the iridium dichloride-bridged dimer²⁰ were synthesised as already reported. Reaction between the iridium dichloride precursor and the bipyridine ligand in a methanol–dichloromethane mixture produced the complex in the well documented bridge splitting reaction,²¹ in which the bridging chlorides are replaced with the bipyridine ligand.

To produce the dimeric species two equivalents of the complex **[Ir(bpy-ph-Br)]** as the hexafluorophosphate salt were reacted with one equivalent of the appropriate bisboronic acid in the presence of a catalytic amount of tetrakis(triphenyl)phosphine and an excess of potassium carbonate. Initially the reaction was carried out in dimethylformamide producing reasonable yields, but latterly dimethoxyethane–water mixtures were used due to the high solubility of the complexes in less polar solvents; in this solvent mixture not only was a slightly higher yield possible, but the purification procedure was greatly simplified due to the reduced number of side reactions. The dimeric complexes were purified over silica gel and eluted with dichloromethane, in both cases the complex eluted as the middle of three bands, the first monomer starting material and the third mostly comprising of catalyst and catalyst by-products. The ^1H NMR of the complexes is consistent with those found for similar complexes.²² For the complex **[Ir(bpy-ph-Br)]** the pyridyl resonances can be distinguished from the ppy resonances due to their half equivalent integration and their familiar coupling constants and splitting patterns. The assignment of the resonances for the phenyl bridged dimers becomes more difficult due to the superimposed peaks, however, the resonances assigned to the pyridyls and the phenyl are shifted with respect to the complex **[Ir(bpy-ph-Br)]**. The mass spectrometric data for the complex **[Ir(bpy-ph-Br)]** show only the cationic species, lacking the hexafluorophosphate anions, whereas the two dimeric complexes show cationic and dicationic species

Table 1 Absorption data^a

| Complex | Absorption feature/nm | $10^3 \epsilon/\text{M}^{-1} \text{cm}^{-1}$ |
|-------------------------------|-----------------------|--|
| [Ir(bpy)] | 465 | 0.6 |
| | 455 | 3 |
| | 410 | 5 |
| | 375 | — |
| | 335 | 16 |
| | 310 | 36 |
| | 265 | — |
| | | |
| [Ir(bpy-ph-Br)] | 450 | 2 |
| | 405 | 5 |
| | 375 | 10 |
| | 310 | 30 |
| | 290 | 50 |
| | | |
| [Ir-ph₃-Ir] | 450 | 4 |
| | 355 | 60 |
| | 330 | 65 |
| | 295 | 69 |
| | 270 | 83 |
| | 250 | 90 |
| | | |
| [Ir-ph₄-Ir] | 450 | 4 |
| | 355 | 60 |
| | 340 | 61 |
| | 295 | 59 |
| | 265 | 70 |
| | 255 | 75 |
| | | |

^a Air equilibrated acetonitrile.

separated by 145 mass units which can be attributed to the loss of one then two hexafluorophosphate anions.

Photophysical properties

The absorption spectra in acetonitrile of the complexes are displayed in Fig. 2. The complexes exhibit certain features found also for the complex **[Ir(bpy)]**.^{22,23}

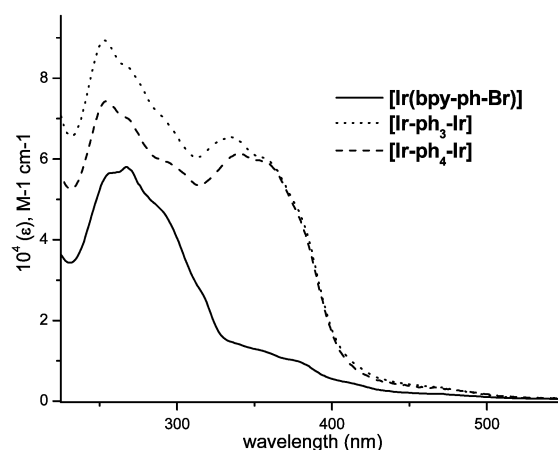


Fig. 2 Absorption spectra in acetonitrile solutions.

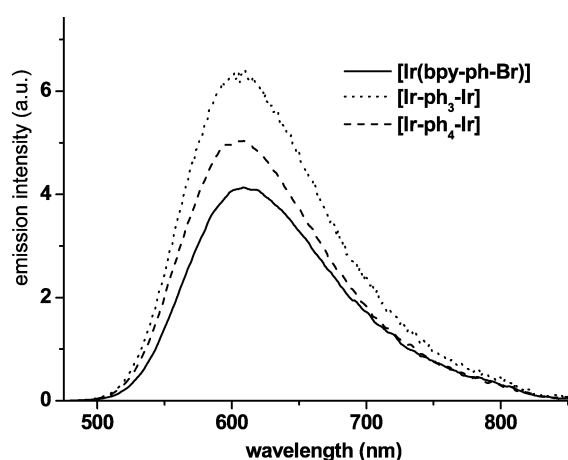
The spectra show moderately intense absorption in the visible region between 380–500 nm (See Table 1 for absorption maxima and molar absorbance) that in the dinuclear species are twice as intense compared with the **[Ir(bpy-ph-Br)]** mononuclear compound. Such a transition can be assigned to metal-to-ligand charge transfer, MLCT, bands ($\text{Ir} \rightarrow \text{bpy}$) both spin allowed and therefore more intense and at higher energy, than the spin forbidden that appear as shoulder in the 420–500 nm region. In fact for iridium complexes it is expected that a strong spin–orbit coupling is induced by the presence of the heavy metal and therefore the singlet \rightarrow triplet transitions become partially allowed. The intense peaks between 265 and 300 nm can be assigned to spin allowed ligand centered, LC, transition involving ppy and bpy, respectively.

Table 2 Emission data

| Complex | Luminescence, 298 K | | | | | Luminescence, 77 K | |
|---|--------------------------------|--------------|--------------|----------|----------|------------------------------|--------------|
| | λ_{max}^a /(nm) | τ^a /ns | τ^b /ns | Φ^b | Φ^a | λ_{max}^c /nm | τ^c /μs |
| [Ir(bpy)] ^d | 606 | — | 337 | — | — | 532 | 5.2 |
| [Ir(bpy-ph-Br)][PF ₆] | 611 | 76 | 334 | 0.127 | 0.024 | 522 | 4.5 |
| [Ir-ph ₃ -Ir][PF ₆] ₂ | 608 | 72 | 390 | 0.094 | 0.022 | 535 | 6.0 |
| [Ir-ph ₄ -Ir][PF ₆] ₂ | 606 | 75 | 411 | 0.175 | 0.023 | 537 | 6.2 |

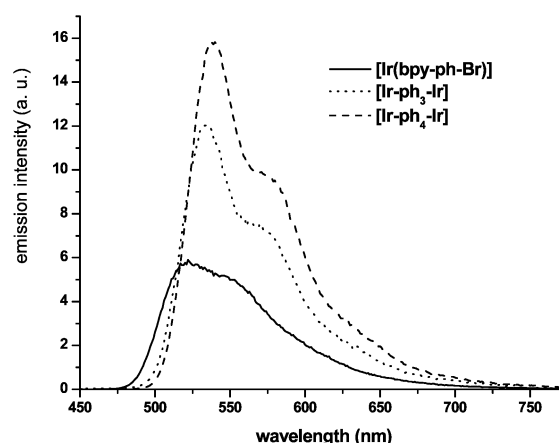
^a In air equilibrated acetonitrile. ^b In deoxygenated acetonitrile. ^c In butyronitrile glass. ^d Data taken from ref. 22.

For the dinuclear [Ir-ph₄-Ir] and [Ir-ph₃-Ir] complexes the peak with a maximum at 340 and 330 nm, respectively, can be assigned to the phenyls of the bridging ligand. The maximum of this band changes according to the number of phenyls present in the bridge since the energy decreases with increasing number of units until the effective conjugation length is reached. The room temperature emission spectra recorded in acetonitrile solution are shown in Fig. 3 and the data summarised in Table 2.

**Fig. 3** Emission spectra at 295 K in acetonitrile, $\lambda_{\text{ex}} = 405$ nm.

The luminescence of all the investigated complexes show broad, structureless, rather intense bands at about 610 nm attributed to ³MLCT transition involving the coordinated bipyridine ligand. The emission properties are very similar for all the investigated compounds and the maxima are almost identical, independent both from the number of iridium units as well as the number of phenyls present in the bridging ligand.

The lowest excited state localized on the substituted bipyridine is therefore very little perturbed by the substitution and further more the metal moieties show very weak electronic interaction. Also the excited state lifetime and emission quantum yield are in agreement with such an assignment (see Table 2). The complex [Ir(bpy-ph-Br)] is slightly red-shifted with respect to the two dimeric complexes, and this can be attributed to the electron withdrawing nature of the bromine lowering the LUMO level.²⁴ The quantum yields of the emissions are highly sensitive to oxygen which also confirms that the emission arises from a triplet state, which seems, in these cases, to be a pure MLCT state and not a mixing of the LC and MLCT states as often reported for polypyridine complexes possessing very long excited state lifetimes even at room temperature. MLCT states are known to be strongly solvent and temperature dependent. In butyronitrile glass at 77 K the charge transfer transitions move to higher energy and the ³LC state could become the lowest excited state. Our experimental data at 77 K show blue-shifted emission with additional structure when compared to the room temperature spectra (Fig. 4 and Table 2). The structured emission could indicate the presence of different emissive excited states. However, the excited state lifetimes observed for

**Fig. 4** Emission spectra at 77 K in butyronitrile glass, $\lambda_{\text{ex}} = 405$ nm.

all the complexes are mono exponentials at any wavelength and quite similar to the MLCT transitions reported for other Ir(III) ortho-metalated complexes containing bpy or phen as the third coordinating ligand.^{9,12,25}

A further proof of our assignment comes from time resolved transient spectroscopy. The transient absorption spectra of the reference complex and of the mono- and di-nuclear complexes synthesised, have been measured in acetonitrile at room temperature. The spectra are strikingly different.

The monomeric complexes, [Ir(bpy-ph-Br)] and [Ir(bpy)] have similar features, but differ from the dimeric complexes. For the monomeric complexes an absorption band appears in the region 400–550 nm, and a weaker band forms within the laser pulse (2 ns) in the region 650–800 nm. Both bands decay mono-exponentially with a lifetime of around 60 ns. Such bands are due to the population of the MLCT state, with the lowest energy band due to the formation of the radical anion $\text{bpy}^{\cdot-}$.²⁶ However, the dinuclear complexes do not appear to show the band between 400–550 nm although this could be hidden under the very intense and broad absorption at lower energy. They exhibit a band that stretches the entire region (400–850 nm), see Fig. 5. This absorption band can be assigned to the ph₃ and ph₄ substituted $\text{bpy}^{\cdot-}$. The conjugated units connected with the chelating ligand favor the delocalisation of the charge promoted on the bpy by light excitation. By comparison, the unsubstituted [Ir(bpy)] or monophenyl [Ir(bpy-ph-Br)] substituted bpy complexes have different transient absorption spectra (see Fig. 5). The lifetimes of the decays are directly related to the emission decays suggesting that the emission is derived from the absorbing species seen in the transient spectra.

Conclusions

Mixed mono- and di-nuclear Ir(III) complexes have been prepared and their photophysical properties investigated. All the complexes exhibit a single emission at room and at low temperature. The lowest excited state is a ³MLCT state and involves the substituted bipyridine. The dinuclear complexes are characterized by a weak electronic coupling between the metal units and

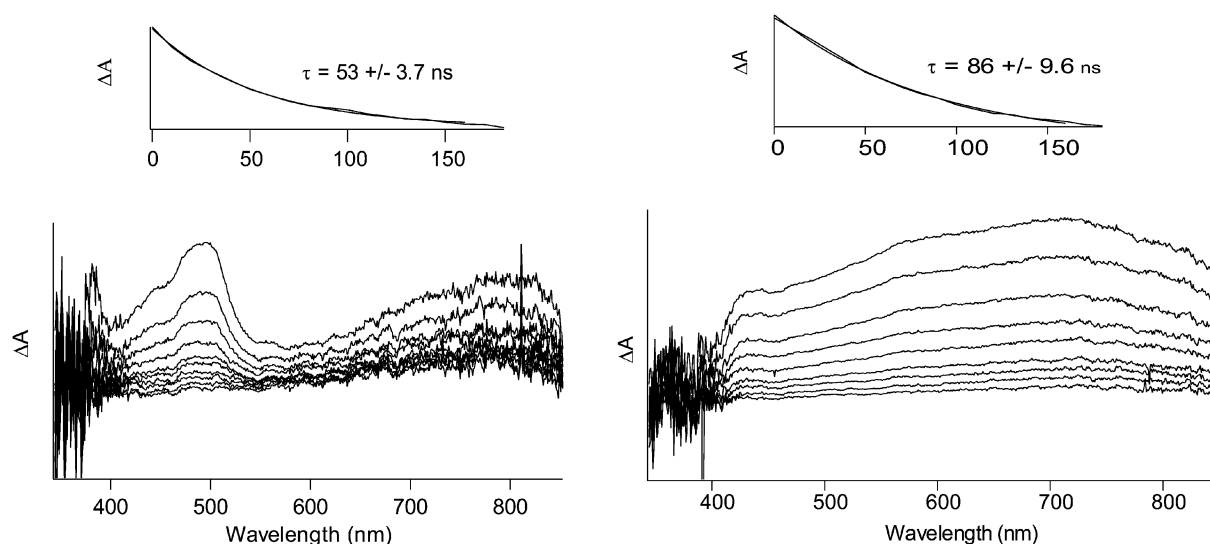


Fig. 5 Transient absorption spectra and decay kinetics in acetonitrile for **[Ir(bpy)]** (left) and **[Ir-Ph₄-Ir]** (right).

time resolved transient spectroscopy clearly shows that the lowest excited state is a significantly delocalized state involving the phenyl units of the bridging ligand. The complexes are interesting materials for electroluminescent devices and studies are in progress to evaluate their performance as light emitting diodes.²⁷

Experimental

Solvents and starting materials

All reagents used were obtained from available commercial sources and used without additional purification unless otherwise indicated. Commercial deuterated solvents were used as received for the characterization of the compounds. Solvents used for spectroscopy (acetonitrile, butyronitrile), were freshly distilled from CaH₂ before use.

Instrumentation

¹H NMR spectra were recorded on a Varian Mercury 300 (300.13 MHz for ¹H). Mass spectra were recorded on a Bruker FTMS 4.7T BioAPEX II in acetonitrile.

Spectroscopy

The emission quantum yields were measured by the method of Demas and Crosby²⁸ with [Ru(bpy)₃](PF₆)₂ in air equilibrated acetonitrile solution as the standard ($\Phi = 0.016$). Deaerated samples were prepared by use of the freeze–pump–thaw method. At least three cycles were used. The UV–Vis absorption spectra were recorded on a Hewlett-Packard diode array 8453 spectrophotometer. Recording of the emission spectra was done with a SPEX Fluorolog spectrofluorometer. Low-temperature (77 K) emission spectra for glasses and solid-state samples were recorded in 5 mm diameter quartz tubes which were placed in a liquid nitrogen Dewar equipped with quartz walls. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability. Sample and standard solutions were degassed with at least three freeze–pump–thaw cycles. Lifetimes were determined using a Coherent Infinity Nd:YAG-XPO laser (1 ns pulses FWHM) and a Hamamatsu C5680–21 streak camera equipped with a Hamamatsu M5677 low-speed single-sweep unit. Transient absorption spectroscopy was performed by irradiation of the sample with a Coherent Infinity Nd:YAG-XPO laser (1 ns pulses FWHM). The sample was probed by a low-pressure, high-power EG&G FX-504 Xe lamp. The passed light was dispersed by an Acton SpectraPro-150s imaging spectrograph

equipped with 150 or 600 g mm^{−1} grating and tunable slit (1–500 μm) resulting in a 6 or 1.2 nm maximum resolution, respectively. The data were collected with a system containing a gated intensified CCD detector (Princeton Instruments ICCD-576G/RB-EM) and an EG&G Princeton Applied Research Model 9650 digital delay generator. *I* and *I*₀ were measured simultaneously using a double 8 kernel 200 μm optical fiber with OMA-4 setup. WINSPEC (version 1.6.1, Princeton Instruments) used under Windows, programmed and accessed the setup.

Synthesis

[Ir(bpy-ph-Br)](PF₆). Ir₂Cl₂ppy₂ (0.13 g, 0.123 mmol) and 4-(*p*-bromo)phenyl-2,2′-bipyridine (0.06 g, 0.194 mmol) were heated to reflux in a dichloromethane–methanol (3 : 1, 20 cm³) mixture under a nitrogen atmosphere for 3 hours. The volume of the solution was reduced to 5 cm³ and methanol added (10 cm³). An excess of saturated methanolic ammonium hexafluorophosphate was added. The resulting precipitate was filtered off and washed with ether (20 cm³) to yield **[Ir(bpy-ph-Br)](PF₆)** as a bright yellow solid (0.141 g, 60%). ¹H NMR (300 MHz, MeCN) δ : 8.76 (1H, s, H3′), 8.73 (1H, d, *J* = 8.1 Hz, H), 8.19 (1H, dt, *J* = 7.8, 1.5 Hz), 8.11 (2H, d, *J* = 8.1 Hz), 8.06 (1H, d, *J* = 5.1 Hz), 8.01 (1H, d, *J* = 5.7 Hz), 7.92–7.76 (9H, m), 7.68 (2H, t, *J* = 6 Hz), 7.56 (1H, t, *J* = 5.4 Hz), 7.08 (4H, m), 6.97 (2H, t, *J* = 7.2 Hz), 6.34 (2H, d, *J* = 7.5 Hz). ESI-MS (MeCN) *m/z*: 811.1 (100%) **[Ir(bpy-Ph-Br)]**⁺.

[Ir-ph₃-Ir](PF₆)₂. **[Ir(bpy-ph-Br)](PF₆)** (0.025 g, 0.026 mmol), K₂CO₃ (20 mg, excess) in H₂O (5 cm³) and phenyl bisboronic acid (0.0021 g, 0.013 mmol) in anhydrous DME (30 cm³) were degassed three times using the freeze–pump–thaw technique. Palladium tetrakis(triphenylphosphine) (0.3 mg, 0.00026 mmol) was then added. The mixture was heated to reflux under a nitrogen atmosphere for 18 hours. The DME was removed under vacuum. The resulting solid was washed with water (3 × 20 cm³), methanol (20 cm³) and diethyl ether (20 cm³) before being dissolved in dichloromethane and applied to a silica column eluted with dichloromethane to yield **[Ir-ph₃-Ir](PF₆)₂** as a yellow–orange solid (0.011 g, 42%). ¹H NMR (300 MHz, MeCN) δ : 8.85 (2H, s), 8.79 (2H, d, *J* = 7.8 Hz), 8.22–7.86 (32H, m), 7.70 (4H, t, *J* = 5.4 Hz), 7.56 (2H, t, *J* = 6.6 Hz), 7.09 (8H, m), 6.97 (4H, t, *J* = 6.3 Hz) 6.34 (4H, d, *J* = 7.2 Hz).

[Ir-ph₄-Ir](PF₆)₂. **[Ir(bpy-ph-Br)](PF₆)** (0.035 g, 0.036 mmol), K₂CO₃ (0.04 g, excess) in H₂O (5 cm³) and biphenyl bisboronic acid (0.004 g, 0.018 mmol) in anhydrous DMF (35 cm³) was

degassed three times using the freeze–pump–thaw technique. Palladium[tetrakis(triphenylphosphine)] (0.4 mg, 0.00036 mmol) was then added. The mixture was heated to reflux under a nitrogen atmosphere for 18 hours. The DME was removed under vacuum. The resulting solid was washed with water ($3 \times 30 \text{ cm}^3$), methanol (30 cm^3) and diethyl ether (30 cm^3) and then dissolved in dichloromethane and applied to a silica column eluted with dichloromethane to yield $[\text{Ir-ph}_4\text{-Ir}][\text{PF}_6]_2$ as a yellow–orange solid (0.017 g, 52%). ^1H NMR (300 MHz, MeCN) δ : 8.84 (2H, s), 8.77 (2H, d, $J = 7.8 \text{ Hz}$), 8.22 (2H, t, $J = 7.8 \text{ Hz}$), 8.17–7.82 (38H, m), 7.71 (4H, t, $J = 5.1 \text{ Hz}$), 7.56 (2H, t, $J = 6.6 \text{ Hz}$), 7.09 (8H, m), 6.97 (4H, t, $J = 6.6 \text{ Hz}$), 6.34 (4H, d, $J = 7.8 \text{ Hz}$). MS-ESI (MeCN) m/z : 732 (95%) $[\text{Ir-ph}_4\text{-Ir}]^{2+}$, 1609 (1%) $[\text{Ir-ph}_4\text{-Ir}][\text{PF}_6]^+$.

Acknowledgements

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