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Polypyridyl Complexes

Synthesis and Isotope Effects on the Excited State Properties of N[^]N Bound [Ir(polypyridyl)₂Cl₂]PF₆ Complexes

Suraj Soman,^{[a][‡]} Hamid M. Younis,^{[a][‡‡]} Wesley R. Browne,^[b] Johannes G. Vos,^[a] and Mary T. Pryce^{*[a]}

Abstract: A versatile approach to the preparation of [Ir(LL)₂Cl₂](PF₆) type complexes is reported, in which LL is an N[^]N bound polypyridyl ligand [X₂bpy, X₂phen, where X = H-, CH₃-, (CH₃)₃C-, or phenyl-, and bpy = 2,2'-bipyridyl, phen = 1,10-phenanthroline] as well as their deuterated analogues. In the synthesis of [Ir(bpy)₂Cl₂]PF₆ (I) and its deuterated analogue (III), the cyclometallated complexes [Ir(bpy)₂(bpy-C-N)](PF₆)₂ (II) and

[Ir([D₈]-bpy)₂([D₈]-bpy-C-N)](PF₆)₂ (IV) were also obtained. The complexes are characterised by ¹H NMR, UV/Vis absorption and emission spectroscopy. The effect of deuteration on emission quantum yields and emission lifetimes is discussed. The ready availability of these complexes through efficient scalable synthetic routes opens new opportunities for their use, especially in energy related applications.

Introduction

Iridium(III) compounds have attracted widespread interest in recent years, predominantly due to their application as blue emitters in OLED devices,^[1–6] photoredox catalysis^[7] and in particular, cyclometallated Ir^{III} complexes have shown promise as photosensitizers in multicomponent systems for photocatalytic H₂ generation from water. For example Bernhard and co-workers reported that [Ir(ppy)₂(bpy)]⁺ and related compounds, combined with a Pt^{II} catalyst, are effective photosensitizers.^[8–10] Cyclometallating ligands (namely C[^]N coordination), such as phenylpyridines (ppy) and phenyltriazoles, are widely used in comparison to N[^]N coordinating ligands with pyridine^[11] and pyrazinetriazoles, which were only introduced in heteroleptic ppy-based complexes recently.^[12] Indeed, Ir^{III} complexes of the type [Ir(LL)₂Cl₂]⁺ and heteroleptic complexes [Ir(LL)₂(L[^]L')]⁺ based on N[^]N coordinated ligands such as 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen) derivatives have not been studied extensively since the 1980s,^[13–17] principally due to the absence of efficient methods for their preparation.^[18] Methods reported for the preparation of N[^]N coordinated [Ir(LL)₂Cl₂]⁺

type compounds were cumbersome multistep procedures, and yielded significant amounts of side products.^[13,14,19–26] In part, this was due to the slow ligand exchange rates, but also due to competition between N[^]N and C[^]N binding in bipyridyl-based

Figure 1. Structures of all compounds and numbering system used.

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ligands.^[27–31] Recently, a microwave synthesis has been reported for $[\text{Ir}(\text{LL})_2\text{Cl}_2]\text{Cl}$ and $[\text{Ir}(\text{LL})_3]\text{Cl}_3$ -type complexes, but little information about the synthetic process was provided.^[32,33] In an earlier publication, we established the potential of $[\text{Ir}(\text{LL})_2\text{Cl}_2](\text{PF}_6)$ complexes as precursors for heteroleptic complexes of the type $[\text{Ir}(\text{LL})_2(\text{L}^{\wedge}\text{L}')]\text{X}_n$, such as $[\text{Ir}(\text{dmbpy})_2(\text{phpytr})](\text{CF}_3\text{SO}_3)_2$, for which dmbpy is 4,4'-dimethyl-2,2'-bipyridyl and Hphpytr is (3-phenyl)-5-(pyridine-2-yl)-1,2,4-triazole.^[34]

Here we further develop this approach towards the synthesis of heteroleptic $\text{N}^{\wedge}\text{N}$ coordinated complexes by introducing substituted polypyridyl ligands, thereby expanding the range of properties accessible (Figure 1). We show that the yield and side product formation are critically dependent on both the temperature and the reaction duration, as determined by reaction progress monitoring with HPLC and ^1H NMR spectroscopy.

Results and Discussion

The general synthetic procedure is as follows: IrCl_3 was treated with a two equivalents of the polypyridyl ligand (LL) in ethylene glycol, in ethanol, methoxyethanol, or ethanol/ H_2O (1:1). Reaction times were varied systematically from 10 minutes to 3 days, and their progress was monitored by HPLC and ^1H NMR spectroscopy. The highest yields of the desired products, $[\text{Ir}(\text{LL})_2\text{Cl}_2]^+$, were obtained in glycerol under vigorous reflux, consistent with the need to displace the kinetically inert chlorido ligands. HPLC chromatograms (Figure 2) and ^1H NMR spectra, recorded at 5 minute intervals during the synthesis of complex **I**, show that a new species with a retention time (R_t) of 2.33 minutes, Figure 2a) forms within the first 5 minutes. After 10 minutes the concentration of the species (R_t 2.33 min) increases, and the peak at 1.69 minutes, assigned to the bpy ligand, appears more structured as it co-elutes with another species, which is tentatively assigned to an intermediate chloride-bridged iridium dimer.^[35] This is supported by ^1H NMR spectroscopy with signals at $\delta = 6.50$, 6.85 and 9.75 ppm (Figure 3b).

The concentration of bpy decreases over 25 minutes, as expected, concomitant with the increase in peaks at 2.33 and 10.44 minutes. The HPLC feature at 2.33 minutes is assigned to the target compound $[\text{Ir}(\text{bpy})_2\text{Cl}_2]^+$ (**I**), whereas the peak at 10.44 minutes is ascribed to $[\text{Ir}(\text{bpy})_2(\text{bpy}-\text{C}^{\wedge}\text{N})]^{2+}$ (**II**) as confirmed by ^1H NMR spectra of these two samples. The doublet at $\delta = 6.58$ ppm and a multiplet at $\delta = 7.08$ ppm are characteristic of the H4 and H5 protons, respectively, of ring **A** in a cyclometallated bpy ligand (Figure 4).^[36]

Complexes **I** and **II** were isolated following repeated washing and re-precipitation steps (see Experimental section) and notably other side products were not observed with a reaction time of 25 minutes. An important aspect of the synthetic procedure developed is that attempts to directly precipitate $[\text{Ir}(\text{bpy})_2\text{Cl}_2]^+$ in the original reaction mixture by adding PF_6^- leads to the precipitation of a mixture of products **I** and **II**, which are difficult to separate chromatographically. However, initial isolation of $[\text{Ir}(\text{bpy})_2\text{Cl}_2](\text{PF}_6)$ was successful (for further details see Experimental section and Figures S1–S3). The com-

Figure 2. HPLC chromatograms of samples taken during the reaction of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with two equivalents of bpy in glycerol at a) 5, b) 10, c) 15, d) 20, and e) 25 min.

Figure 3. ^1H NMR spectra (400 MHz, $[\text{D}_6]\text{DMSO}$) of samples withdrawn during the reaction of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with two equivalents of bpy in glycerol at a) 5, b) 10, c) 15, d) 20, and e) 25 min.

Figure 4. Structures and ring numbering of compounds **I** and **II** used in ^1H NMR spectral assignments.

pounds **V–XII** were prepared in high yield with an analogous one step procedure without the formation of the cyclometallated side products as expected.

Deuteration of ligands can have a considerable effect on the photophysics of metal complexes, therefore deuterated ligands were also prepared.^[37] It is notable that the ratio of $[\text{Ir}(\text{D}_8\text{-bpy})_2\text{Cl}_2]^+$ (**III**) to $[\text{Ir}(\text{D}_8\text{-bpy})_2(\text{D}_7\text{-bpy-C}^{\wedge}\text{N})]^{2+}$ (**IV**) was 3:1 instead of 2:1, consistent with C–H activation as a rate-limiting step in the formation of **IV**.

Assignment of the ^1H NMR spectra of the complexes (see Figure 4 and Figure S4) was made by comparison with related Ir^{III} ,^[35,38,39,40] and Pt^{II} ^[41] compounds reported in the literature and ^1H – ^1H COSY, DEPT-135, ^{13}C NMR and HMBC spectra (Figures S5–S14, and Experimental section).

Electronic Properties

The high yield preparation of $\text{N}^{\wedge}\text{N}$ coordinated $[\text{Ir}(\text{LL})_2\text{Cl}_2]^+$ compounds and their heteroleptic analogues^[34] is of interest for a wide range of applications. Therefore, this synthetic method allows for the opportunity to revisit earlier investigations of these compounds, and in particular to explore how their photophysical properties compare with those of their cyclometallated analogues. For many phenylpyridine (ppy)-based cyclometallated Ir^{III} complexes, the HOMO is located on the phenyl moiety of the ppy ligand with a substantial contribution from the d-orbitals. The LUMO is localised on the pyridine unit of the ppy

ligand.^[1,11] The UV/Vis absorption spectra of the $[\text{Ir}(\text{LL})_2\text{Cl}_2]^+$ complexes are dominated by Ir^{III} to LL charge-transfer bands ($\text{d}-\pi^*$) in the visible region and ligand-based bands ($\pi-\pi^*$) in the UV.^[14–16] The excited state properties of compounds **I** to **XII** compare well with literature data, where available (Table 1).^[14,42]

The influence of phenyl moieties in the UV/Vis absorption spectra on the phenanthroline-based complexes is apparent in Figure 5. The spectra of bpy-based complexes **VII**, **VIII** and **XI** (Figures S15 and S16) indicate that the absorption features for bpy complexes are less affected by the nature of substituents.

Figure 5. UV/Vis absorption spectra of complexes (**V**) (black) and (**XII**) (red) in acetonitrile (0.1 mM).

All complexes examined are emissive in acetonitrile at room temperature in the range 500–550 nm (Table 1). The spectra at 77 K are blueshifted as expected due to rigidochromic effects (Figures S17–S20). In contrast to ruthenium(II) polypyridyl complexes, for which the electronic properties are mainly related to metal to ligand charge transfer transitions (MLCT), for $[\text{Ir}(\text{LL})_2\text{Cl}_2]^+$ complexes, the energy gap between $\pi-\pi^*$ and $\text{d}-\pi^*$ states is generally small resulting in mixing of states. Previous results suggested that at 298 K emission may take place from an equilibrated $(\pi-\pi^*)-(\text{d}-\pi^*)$ excited state.^[14,30,31] Accordingly, the luminescence spectra of $[\text{Ir}(\text{phen})_2\text{Cl}_2]^+$ and $[\text{Ir}(\text{bpy})_2\text{Cl}_2]^+$ ^[14,31b] recorded at 77 K were assigned by Crosby

Table 1. Photophysical properties of $[\text{Ir}(\text{LL})_2\text{Cl}_2]\text{PF}_6$ compounds.

	λ_{abs} [nm] ^[a] (ϵ [$\text{L M}^{-1} \text{cm}^{-1} \times 10^3$])	λ_{em} ^[b] [nm] (298 K)	λ_{em} ^[c] [nm] (298 K)	λ_{em} ^[d] [nm] (77 K)	λ_{em} ^[e] [nm] (77 K)	Φ ^[e] [%]	τ ^[f] [ns] (298 K)	τ ^[c] [ns] (298 K)	τ ^[g] [μs] (77 K)
I	239 (14.9), 280 (15.0), 302 (12.6), 380 (1.4)	500	497, 535	470, 498	473, 425	5.7	401	390	6.2
III	239 (14.7), 280 (15.2), 302 (12.3), 380 (1.3)	500	497	470, 498	–	5.2	763	720	7.0
V	265 (22.5), 275 (19.5), 338 (3.4), 390 (1.8)	530	529	473, 504	473, 451	4.7	400	270	8.6
VI	265 (22.1), 275 (19.3), 338 (3.2), 390 (1.7)	530	–	473, 504	–	3.9	613	–	8.4
VII	275 (15.8), 311 (9.9), 341 (2.7), 385 (1.8)	502	532	470, 502	473, 429	1.9	296	280	7.6
VIII	275 (15.3), 311 (9.6), 341 (2.8), 385 (1.7)	502	–	470, 502	–	1.1	625	–	8.2
IX	274 (15.9), 308 (11.1), 340 (3.1), 383 (1.9)	508	–	468, 490	–	3.0	339	–	4.5
X	274 (15.6), 308 (11.2), 340 (3.0), 383 (1.7)	508	–	468, 490	–	2.1	518	–	6.5
XI	290 (14.9), 330 (6.7), 405 (1.7)	520	505	–	490, 431	19.5	813	660	–
XII	290 (20.5), 330 (9.1), 405 (2.3)	520	543	–	513, 476	19.4	660	470	–

[a] At 298 K in CH_3CN . [b] In CH_3CN . [c] From ref.^[14,16,17,18,22,32] [d] In ethanol/methanol (4:1), λ_{ex} = 380 nm. [e] At 298 K in CH_3CN . [f] In CH_3CN , λ_{ex} = 355 nm. [g] In ethanol/methanol (4:1), λ_{ex} = 355 nm.

to a mixture of charge-transfer ($d-\pi^*$) and ligand centred ($\pi-\pi^*$) transitions.^[15,17] DeArmond and Hillis^[16b] suggested that this emission could be considered as ligand delocalised due to significant mixing of d and π orbitals. Overall the excited state data reported here are in agreement with earlier studies.

For the last number of years we have been actively involved in the development of novel synthetic pathways towards deuterated polypyridyl ligands. The aim of these studies is to probe the excited state properties of mixed-ligand polypyridyl complexes by full or partial deuteration of some of the ligands.^[43] As a result, when using resonance Raman techniques on partly deuterated compounds, the nature of the excited state can be established, since resonance Raman spectra of deuterated ligands are different from those observed for protonated analogues.^[44] Such studies can be further extended to emission and emission-lifetime investigations so that the effect of deuteration on the excited state lifetimes at both room temperature and 77 K can be studied. In Table 1, a number of the complexes exhibit the influence of deuteration on the emission lifetime. An added advantage to selective deuteration is that the deuterated ligands are silent in ^1H NMR, thereby simplifying the characterisation of the compounds obtained.^[45] The deuterated analogues of the polypyridyl complexes obtained in this study show, apart from compounds **V**/**VI**, lifetimes at 77 K that are longer than their non-deuterated analogues. The values obtained suggest that the emission is not from a purely $\pi-\pi^*$ excited state, since the triplet emission lifetimes for the deuterated ligands are in the range of 80–100 μs .^[27,31,41] The lifetimes obtained for the deuterated complexes are in the range of 4.5–8.4 μs , thus indicating that emission occurs from mixed ($d-\pi^*$)-($\pi-\pi^*$) excited states, and that lower-energy vibrational modes (such as Ir–N) are involved in the relaxation. However, further detailed measurements, including solvent and temperature dependent photophysical measurements along with resonance Raman, are required to further confirm the assignments, including the effect of deuteration on emission properties.

Conclusions

A synthetic approach is outlined for the preparation of iridium polypyridyl complexes based on N^N coordinated polypyridyl ligands. The compounds were obtained in high yields and purity and on at least a several-hundred milligram scale, which considerably increases their accessibility in comparison with earlier reported methods. With the present method, no significant side products are obtained, and the reaction times are short. Furthermore, the isolation of the products as PF_6^- salts increases their solubility in organic solvents, facilitating their use as precursors for the synthesis of a wide range of novel heteroleptic Ir^{III} compounds. The availability of deuterated analogues allows for more detailed studies into the photophysical properties of these compounds.

In conclusion, with the synthetic methods reported here, and the data obtained with the heteroleptic Ir^{III} compounds reported in our earlier paper^[34] there are now new opportunities to reopen investigations onto the use of a range of Ir^{III} compounds with N^N coordinated ligands. This may lead to the

preparation of compounds with novel excited state properties for application in OLED design, photocatalytic hydrogen generation and other related technologies such as DSSCs.

Experimental Section

Experimental Details: Deuteration of 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridyl (dmbipy) and 4,4'-di-*t*-butyl-2,2'-bipyridyl (dtbpy) was carried out as described earlier,^[43] using a general purpose Teflon-lined dissolution Bomb P/N 4744 from Scientific Medical Products. Hydrogen–deuterium exchange was carried out by dissolution of the ligand for 2×3 days in basic D_2O (20 cm^3 of 1 M NaOD/ D_2O) at 200 °C. The extent of hydrogen/deuterium exchange was determined by ^1H NMR spectroscopy.^[43] % H/D exchange; [D_8]-2,2'-bipyridine (95 %); [D_8]-1,10-phenanthroline (90 %); [D_{12}]-4,4'-dimethyl-2,2'-bipyridyl (90 %); [D_{24}]-4,4'-di-*t*-butyl-2,2'-bipyridyl (95 %). Elemental analysis was carried out by the Microanalysis department of University College Dublin. The analysis of deuterium content was as described earlier.^[43] High-Performance Liquid Chromatography (HPLC) was carried out using a Varian ProStar (model 335.71) photodiode array detector, a Varian (model 210) pump, a 20 μL injector loop and a strong cation exchange Luna SCX 100A column (25 $\text{cm} \times 4.6$ mm, Phenomenex), controlled by Varian Star software. The mobile phase [80:20 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ with KNO_3 (0.1 M)] was filtered and degassed prior to use, with flow rates of between 1.5 and 2 $\text{cm}^3 \text{min}^{-1}$. The ^1H NMR and COSY spectra were recorded on a Bruker AC400 (400 MHz) spectrometer or a Bruker Avance 3 (600 MHz) spectrometer in [D_6]DMSO. UV/Vis absorption spectra were obtained on Agilent HP8453 UV/Vis absorption spectrometer and were recorded in the range 200 to 800 nm. Emission spectra were recorded using a Perkin–Elmer LS50B luminescence spectrometer with λ_{exc} 360. Emission quantum yields were determined in CH_3CN at room temperature with $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ ($\phi_{\text{em}} = 0.062$) as reference.^[46] Emission spectra at 77 K were recorded in a pyrex tube mounted in an Oxford Instruments liquid N_2 cooled PE1704 cryostat controlled with an Oxford Instruments ITC 601 unit. Emission lifetimes were determined by excitation with a Q-switched Nd-YAG laser (355 nm) with transients recorded using an Applied photophysics transient absorption/emission system. Spectrometric grade acetonitrile was used at room temperature with deoxygenation by nitrogen gas purge. Spectra were recorded at 77 K in EtOH/MeOH (4:1).

Synthesis of Complexes

[Ir(bpy) $_2$ Cl $_2$](PF $_6$) (I) and [Ir(bpy) $_2$ (bpy-C-N)](PF $_6$) $_2$ (II): $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.10 g, 0.28 mmol) in glycerol (1 cm^3) was heated at vigorous reflux for 25 min after the addition of bpy (2 equiv., 0.09 g, 0.56 mmol). The solution changed from red to straw yellow. The solution was cooled to room temperature, 5 cm^3 of water was added and subsequently filtered. The filtrate was washed with 5 cm^3 of diethyl ether. 10 cm^3 of saturated NaCl(aq) was added to the filtrate to precipitate $[\text{Ir}(\text{bpy})_2\text{Cl}_2]\text{Cl}$, which was filtered and dried. The complex was metathesized with saturated aqueous KPF_6 and the precipitated yellow solid isolated by filtration and washed with 20 cm^3 of deionised water and air dried. The solid was then dissolved in a minimal amount of acetone and precipitated with diethyl ether and hexane and recovered by vacuum filtration, and washed with diethyl ether and hexane. The latter procedure was repeated 3–4 times to remove residual glycerol. (Yield: 0.12 g, 60 %). ^1H NMR (400 MHz, [D_6]DMSO), δ (ppm): 7.51 (t, 2 H, H $5'$), 7.83 (d, 2 H, H $6'$), 8.12 (t, 2 H, H 5), 8.20 (t, 2 H, H $4'$), 8.52 (t, 2 H, H 4), 8.82 (d, 2 H, H $3'$), 8.93 (d, 2 H, H 3), 9.65 (d, 2 H, H 6). ESI-MS: m/z calcd. 575.49; found 575.03.

Elemental analysis for **1**, $C_{20}H_{16}Cl_2F_6IrN_4P$ (720.05): calcd. C 33.34, H 2.24, N 7.78; found C 33.3, H 2.1, N 7.4.

After isolation of compound **I**, the remaining solution was concentrated in vacuo, dichloromethane (20 cm³) was added, and the solid formed was filtered. This purification process was repeated until all remaining traces of bpy and compound **I** were removed. The yellow residue was dried and dry methanol (20 cm³) was added. The solution was then stirred, filtered, concentrated and chromatographed on Sephadex (LH 20) using ethanol to yield $[Ir(bpy)_2(bpy-C^{\wedge}N)](Cl)_2$. The complex was then dissolved in water, to which saturated aqueous KPF_6 was added (10 mL), resulting in the precipitation of **2**, which was vacuum-filtered, washed with deionised water and dried. (Yield: 0.015 g, 5 %). ¹H NMR (400 MHz, [D₆]DMSO) For location of rings A–F Figure 1, δ (ppm): 9.04 (d, 1 H, D3), 9.01 (d, 1 H, C3'), 8.96 (m, 2 H, E3', F3'), 8.45 (m, 3 H, C4', E4', F4), 8.42 (d, 1 H, A6), 8.38 (m, 2 H, B3', B4'), 8.21 (t, 1 H, D4), 8.01 (d, 1 H, D6), 7.91 (d, 1 H, D5), 7.90 (d, 1 H, C6'), 7.81 (m, 2 H, E6', F6), 7.72 (d, 1 H, B6'), 7.67 (m, 3 H, C5', E5', F5), 7.48 (t, 1 H, B5'), 7.08 (m, 1 H, A5), 6.58 (d, 1 H, A4).

[Ir(d₈-bpy)₂Cl₂]PF₆ (III) and [Ir([D₈]-bpy)₂([D₈]-bpy-C[^]N)](PF₆)₂ (IV): These compounds were obtained using the method outlined above. $IrCl_3 \cdot 3H_2O$ (0.10 g, 0.28 mmol) [D₈]-bpy (0.1153 g, 0.56 mmol) were dissolved in 1 cm³ of glycerol. $[Ir([D_8]-bpy)_2Cl_2]PF_6$ (Yield: 0.15 g, 70 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 7.51 (residue s, H5'), 7.83 (residue s, H6'), 8.12 (residue s, H5), 8.20 (residue s, H4'), 8.52 (residue s, H4), 8.82 (residue s, H3'), 8.93 (residue s, H3), 9.65 (residue s, H6). Elemental analysis for complex **III**, $C_{20}D_{16}Cl_2F_6IrN_4P$ (736.06): calcd. C 32.58, H 2.17, N 7.60; found C 32.8, H 2.1, N 7.8.

[Ir([D₈]-bpy)₂([D₈]-bpy-C[^]N)](PF₆)₂ (IV): (Yield: 0.010 g, 3 %). ¹H NMR (400 MHz, [D₆]DMSO), For location of rings A–F see Figure 1 δ (ppm): 9.04 (residue s, D3), 9.01 (residue s, C3'), 8.96 (residue s, E3', F3'), 8.45 (residue s, C4', E4', F4), 8.42 (residue s, A6), 8.38 (residue s, B3', B4'), 8.21 (residue s, D4), 8.01 (residue s, D6), 7.91 (residue s, D5), 7.90 (residue s, C6'), 7.81 (residue s, E6', F6), 7.72 (residue s, B6'), 7.67 (residue s, C5', E5', F5), 7.48 (residue s, B5'), 7.08 (residue s, A5), 6.58 (residue s, A4).

[Ir(phen)₂Cl₂]PF₆ (V): $IrCl_3 \cdot 3H_2O$ (0.10 g, 0.28 mmol) was combined with two equivalents of phen (0.102 g, 0.56 mmol) and dissolved in glycerol (1 cm³). The reaction was heated at vigorous reflux for 10 min, at which point the colour of the solution changed from red to straw yellow. The solution was cooled to room temperature and water (5 cm³) was added. The mixture was filtered and washed with diethyl ether (5 cm³). Saturated NaCl(aq) (10 cm³) was added to the filtrate yielding $[Ir(phen)_2Cl_2]Cl$, which was filtered and air-dried. The complex was then dissolved in water, and saturated KPF_6 (aq) was added (10 mL) to yield a yellow precipitate that was recovered by filtration, washed with deionised water (20 cm³) and air-dried. The product was dissolved in a minimal amount of acetone and precipitated by addition of excess diethyl ether and *n*-hexane, and recovered by vacuum filtration, washed with diethyl ether and hexane. This procedure was repeated 3–4 times in order to remove traces of glycerol. (Yield: 0.160 g, 75 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 7.69 (m, 2 H, H8), 8.08 (d, 2 H, H9), 8.38 (d, 2 H, H6), 8.49 (m, 4 H, H4, H5), 8.76 (d, 2 H, H7), 9.16 (d, 2 H, H3), 9.94 (d, 2 H, H2). Elemental analysis for complex **V**, $C_{24}H_{16}Cl_2F_6IrN_4P$ (768.05): calcd C 37.51, H 2.10, N 7.29; found C 37.5, H 2.1, N 7.3.

Synthesis of [Ir([D₈]-phen)₂Cl₂]PF₆ (VI): $IrCl_3 \cdot 3H_2O$ (0.10 g, 0.28 mmol) was combined with two equivalents of [D₈]-phen (0.106 g, 0.56 mmol) and dissolved in glycerol (1 cm³). The synthetic procedure is as reported for compound **V** above. (Yield: 0.19 g,

85 %). For numbering of atoms see Figure S5. ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 7.69 (residue s, H8), 8.08 (residue s, H9), 8.38 (residue s, H6), 8.49 (residue s, H4, H5), 8.76 (residue s, H7), 9.16 (residue s, H3), 9.94 (residue s, H2). Elemental analysis for complex **VI**, $C_{24}D_{16}Cl_2F_6IrN_4P$: calcd. C 36.74, H 2.05, N 7.14; found C 36.9, H 1.8, N 7.5.

[Ir(dmbpy)₂Cl₂]PF₆ (VII): $IrCl_3 \cdot 3H_2O$ (0.10 g, 0.28 mmol) and dmbpy (0.105 g, 0.56 mmol) were reacted in glycerol (1 cm³) as described **V**. Yield 0.20 g (90 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 2.56 [s, 6 H (CH₃)], 2.76 (s, 6H CH₃), 7.32 (dd, 2 H, H5'), 7.59 (d, 2 H, H6'), 7.93 (dd, 2 H, H5), 8.66 (s, 2 H, H3'), 8.76 (s, 2 H, H3), 9.42 (d, 2 H, H6). Elemental analysis for complex **VII**, $C_{24}H_{24}Cl_2F_6IrN_4P$ (776.06): calcd. C 37.12, H 3.12, N 7.21; found C 36.8, H 2.9, N 7.0.

[Ir([D₁₂]-dmbpy)₂Cl₂]PF₆ (VIII): $IrCl_3 \cdot 3H_2O$ (0.10 g, 0.28 mmol) was combined with two equivalents of [D₁₂]-dmbpy (0.111 g, 0.56 mmol) and dissolved in glycerol (1 cm³). The synthetic procedure is as reported for compound **V** above. (Yield: 0.20 g, 90 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 2.56 (residue s, 3 H), 2.76 (residue s, 3 H), 7.32 (residue s, H5'), 7.59 (residue s, H6'), 7.93 (residue s, H5), 8.66 (residue s, H3'), 8.76 (residue s, H3), 9.42 (residue s, H6). Elemental analysis for complex **VIII**, $C_{24}D_{24}Cl_2F_6IrN_4P$ (800.07): calcd. C 36.00, H 3.02, N 7.00; found C 36.4, H 2.8, N 7.3.

[Ir(dtbpy)₂Cl₂]PF₆ (IX): $IrCl_3 \cdot 3H_2O$ (0.10 g, 0.28 mmol) was combined with two equivalents of dtbpy (0.152 g, 0.56 mmol) and dissolved in glycerol (1 cm³). The synthetic procedure is as reported for compound **V** above. (Yield: 0.16 g, 60 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 1.36 (s, 18 H), 1.543 (s, 18 H), 7.48 (dd, 2 H, H5'), 7.62 (d, 2 H, H6'), 8.09 (dd, 2 H, H5), 8.83 (s, 2 H, H3'), 8.93 (s, 2 H, H3), 9.48 (d, 2 H, H6). Elemental analysis for complex **IX**, $C_{36}H_{48}Cl_2F_6IrN_4P$ (944.09): calcd. C 45.76, H 5.12, N 5.93; found: C 45.3, H 5.1, N 5.7.

[Ir(d₂₄-dtbpy)₂Cl₂]PF₆ (X): $IrCl_3 \cdot 3H_2O$ (0.10 g, 0.28 mmol) was combined with two equivalents of d₂₄dtbpy (0.165 g, 0.56 mmol) and dissolved in glycerol (1 cm³). The synthetic procedure is as reported for compound **V** above. (Yield: 0.18 g, 60 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 1.36 (residue s), 1.54 (residue s), 7.48 (residue s, H5'), 7.62 (residue s, H6'), 8.09 (residue s, H5), 8.83 (residue s, H3'), 8.93 (residue s, H3), 9.48 (residue s, H6). Elemental analysis for complex **X**, $C_{36}D_{48}Cl_2F_6IrN_4P \cdot 2H_2O$ (1029.02): calcd. C 42.05, H 5.05, N 5.44; found C 42.3, H 5.2, N 5.7.

[Ir(dpbpy)₂Cl₂]PF₆ (XI): $IrCl_3 \cdot 3H_2O$ (0.20 g, 0.56 mmol) was combined with two equivalents of dpbpy ligand (0.35 g, 1.13 mmol) and dissolved in glycerol (1 cm³). The synthetic procedure is as reported for compound **V** above. (Yield: 0.45 g, 77 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 7.65 (m, 10 H, Ph), 7.75 (d, 4 H, Ph), 7.80 (t, 4 H, Ph), 7.92 (d, 4 H, H3', Ph), 8.25 (d, 2 H, H3), 8.37 (m, 4 H, H5, H5'), 8.55 (d, 2 H, H6'), 10.11 (d, 2 H, H6). Elemental analysis for complex **XI**, $C_{44}H_{32}Cl_2F_6IrN_4P$ (1024.09): calcd. C 51.57, H 3.15, N 5.47; found C 51.5, H 3.2, N 5.4.

[Ir(dpphen)₂Cl₂]PF₆ (XII): $IrCl_3 \cdot 3H_2O$ (0.20 g, 0.56 mmol) was combined with two equivalents of 4,4'-diphenyl-1,10 phenanthroline (dpphen) (0.37 g, 1.13 mmol) and dissolved in glycerol (1 cm³). The synthetic procedure is as reported for compound **V** above. (Yield: 0.48 g, 78 %). ¹H NMR (400 MHz, [D₆]DMSO), δ (ppm): 7.63 (m, 10 H, Ph), 7.74 (d, 4 H, Ph), 7.79 (t, 4 H, Ph), 7.90 (d, 4 H, H8, Ph), 8.24 (d, 2 H, H9), 8.36–8.40 (m, 4 H, H5, H6), 8.54 (d, 2 H, H3), 10.10 (d, 2 H, H2). Elemental analysis for complex **XII**, $C_{48}H_{32}Cl_2F_6IrN_4P$ (1072.09): calcd. C 53.74, H 3.01, N 5.22; found C 53.45, H 3.0, N 5.0.

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- [1] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, 123, 4304.
- [2] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* **2001**, 40, 1704.
- [3] A. B. Tamayo, S. Garon, T. Sajoto, P. I. Djurovich, I. M. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, 44, 8723.
- [4] S. Culham, P.-H. Lanoë, V. L. Whittle, M. C. Durrant, J. A. G. Williams, V. N. Kozhevnikov, *Inorg. Chem.* **2013**, 52, 10992.
- [5] I. M. Dixon, J. P. Collin, J. P. Sauvage, L. Flamigni, S. Encinas, F. Barigelletti, *Chem. Soc. Rev.* **2000**, 29, 385.
- [6] H. Nakanotani, K. Masui, J. Nishide, T. Shibata, C. Adachi, *Sci. Rep.* **2013**, 2127, 3.
- [7] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, 81, 6898–6926.
- [8] L. L. Tinker, N. D. McDaniel, P. N. Curtin, C. K. Smith, M. J. Ireland, S. Bernhard, *Chem. Eur. J.* **2007**, 13, 8726.
- [9] P. N. Curtin, L. L. Tinker, C. M. Burgess, E. D. Cline, S. Bernhard, *Inorg. Chem.* **2009**, 48, 10498.
- [10] a) S. Metz, S. Bernhard, *Chem. Commun.* **2010**, 46, 7551; b) E. D. Cline, S. E. Adamson, S. Bernhard, *Inorg. Chem.* **2008**, 47, 10378.
- [11] P. Coppo, E. A. Plummer, L. De Cola, *Chem. Commun.* **2004**, 1774.
- [12] C. S. K. Mak, A. Hayer, S. I. Pascu, S. E. Watkins, A. B. Holmes, A. Köhler, R. H. Friend, *Chem. Commun.* **2005**, 4708.
- [13] B. Chiswell, S. E. Livingstone, *J. Inorg. Nucl. Chem.* **1964**, 26, 47.
- [14] a) R. J. Watts, G. A. Crosby, *J. Am. Chem. Soc.* **1971**, 93, 3184; b) R. J. Watts, J. V. Houten, *J. Am. Chem. Soc.* **1974**, 96, 4334; c) R. J. Watts, M. J. Brown, B. G. Griffith, J. S. Harrington, *J. Am. Chem. Soc.* **1975**, 97, 6029.
- [15] G. A. Crosby, R. J. Watts, D. H. W. Carstens, *Science* **1970**, 170, 1195.
- [16] a) R. J. Watts, S. Efrima, H. Metiu, *J. Am. Chem. Soc.* **1979**, 101, 2742; b) M. K. DeArmond, J. E. Hillis, *J. Chem. Phys.* **1971**, 54, 2247; c) Y. Ohashi, T. Kobayashi, *Bull. Chem. Soc. Jpn.* **1979**, 52, 2214; d) T. L. Cremers, G. A. Crosby, *Chem. Phys. Lett.* **1980**, 73, 541.
- [17] R. J. Watts, G. A. Crosby, J. L. Sansregret, *Inorg. Chem.* **1972**, 11, 1474.
- [18] R. Ballardini, G. Varani, L. Moggi, V. Balzani, *J. Am. Chem. Soc.* **1977**, 99, 6881.
- [19] R. D. Gillard, B. T. Heaton, *J. Chem. Soc. A* **1969**, 451.
- [20] R. E. De Simone, R. S. Drago, *J. Org. Chem.* **1969**, 8, 2517.
- [21] G. Nord, A. C. Hazell, R. G. Hazell, O. Farver, *Inorg. Chem.* **1983**, 22, 3429.
- [22] B. Martin, G. M. Waind, *J. Chem. Soc.* **1958**, 4284.
- [23] C. M. Flynn, J. N. Demas, *J. Am. Chem. Soc.* **1974**, 96, 1959.
- [24] W. A. Wickramasinghe, P. H. Bird, N. Serpone, *J. Chem. Soc., Chem. Commun.* **1981**, 1284.
- [25] P. Spellane, R. J. Watts, *Inorg. Chem.* **1981**, 20, 3561.
- [26] J. A. Broomhead, W. Grumley, *J. Chem. Soc., Chem. Commun.* **1968**, 1211.
- [27] B. P. Sullivan, T. J. Meyer, *J. Chem. Soc., Chem. Commun.* **1984**, 403.
- [28] J. L. Kahl, K. W. Hanck, K. DeArmond, *J. Phys. Chem.* **1979**, 83, 2606.
- [29] J. L. Kahl, K. W. Hanck, K. DeArmond, *J. Phys. Chem.* **1978**, 82, 540.
- [30] a) M. M. Muir, W. L. Huang, *Inorg. Chem.* **1973**, 12, 1930; b) J. A. Broomhead, W. Grumley, *Inorg. Chem.* **1971**, 10, 2002; c) L. H. Berka, G. E. Philippo, *J. Inorg. Nucl. Chem.* **1970**, 32, 3355; d) B. Divisia, P. C. Ford, R. J. Watts, *J. Am. Chem. Soc.* **1980**, 102, 7264.
- [31] a) P. A. Marnot, R. R. Ruppert, J. P. Sauvage, *Nouv. J. Chim.* **1981**, 5, 543; b) J. Hawecker, J. M. Lehn, R. Ziessel, *J. Chem. Soc., Chem. Commun.* **1983**, 536.
- [32] a) N. Yoshikawa, T. Matsumura-Inoue, *Anal. Sci.* **2003**, 19, 761; b) N. Yoshikawa, J. Sakamoto, T. M. Inoue, H. Takashima, K. Tsukahara, N. Kanehisa, Y. Kai, *Anal. Sci.* **2004**, 20, 711.
- [33] N. Yoshikawa, Y. Masuda, T. Matsumura-Inoue, *Chem. Lett.* **2000**, 29, 1206.
- [34] S. Soman, J. C. Manton, J. L. Inglis, Y. Halpin, B. Twamley, E. Otten, W. R. Browne, L. De Cola, J. G. Vos, M. T. Pryce, *Chem. Commun.* **2014**, 50, 6461.
- [35] F. O. Garces, R. J. Watts, *Inorg. Chem.* **1990**, 29, 582.
- [36] P. J. Spellane, R. J. Watts, C. J. Curtis, *Inorg. Chem.* **1983**, 22, 4060.
- [37] W. R. Browne, J. G. Vos, *Coord. Chem. Rev.* **2001**, 219–221, 761–787.
- [38] E. Orselli, G. S. Kottas, A. E. Konradsson, P. Coppo, R. Fröhlich, L. De Cola, A. van Dijken, M. Büchel, H. Börner, *Inorg. Chem.* **2007**, 46, 11082.
- [39] V. T. Coombe, G. A. Heath, A. J. MacKenzie, *Inorg. Chem.* **1984**, 23, 3423.
- [40] J. L. Kahl, K. Hanck, K. DeArmond, *J. Inorg. Nucl. Chem.* **1979**, 41, 495.
- [41] O. Farver, O. Monsted, G. Nord, *J. Am. Chem. Soc.* **1979**, 101, 6118.
- [42] R. J. Watts, G. A. Crosby, *J. Am. Chem. Soc.* **1972**, 94, 2606.
- [43] W. R. Browne, C. M. O'Connor, J. S. Killeen, A. L. Guckian, M. Burke, P. James, M. Burke, J. G. Vos, *Inorg. Chem.* **2002**, 41, 4245.
- [44] W. R. Browne, N. M. O'Boyle, W. Henry, A. L. Guckian, S. Horn, T. Fett, C. M. O'Connor, M. Duati, L. De Cola, C. G. Coates, K. L. Ronayne, J. J. McGarvey, J. G. Vos, *J. Am. Chem. Soc.* **2005**, 127, 1229.
- [45] N. Das, G. Singh Bindra, A. Paul, J. G. Vos, M. Schulz, M. T. Pryce, *Chem. Eur. J.* **2017**, 23, 1.
- [46] J. V. Caspar, T. J. Meyer, *Inorg. Chem.* **1983**, 22, 2444.

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