Synthesis, Characterisation and Application of Iridium(III) Photosensitisers for Catalytic Water Reduction

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Abstract: The synthesis of novel, monocationic iridium(III) photosensitisers (Ir-PSs) with the general formula $[Ir^{III}(C^N)_2(N^N)]^+$ (C^N: cyclometallating phenylpyridine ligand, N^N: neutral bidentate ligand) is described. The structures obtained were examined by cyclic voltammetry, UV/Vis and photoluminescence spectroscopy and X-ray analysis. All iridium complexes were tested for their ability as photosensitisers to promote homogeneously catalysed hydrogen generation from water. In the presence of [HNEt₃]- $[HFe_3(CO)_{11}]$ as a water-reduction catalyst (WRC) and triethylamine as a sacrificial reductant (SR), seven of the new iridium complexes showed activity. $[Ir(6-iPr-bpy)(ppy)_2]PF_6$ (bpy: 2,2'-bipyridine, ppy: 2-phenylpyridine) turned out to be the most efficient photosensitiser. This complex was also tested in combination with other WRCs based

Keywords: hydrogen • iridium • iron • photochemistry • photosensitizers • water splitting on rhodium, platinum, cobalt and manganese. In all cases, significant hydrogen evolution took place. Maximum turnover numbers of 4550 for this Ir-PS and 2770 for the Fe WRC generated in situ from [HNEt₃][HFe₃(CO)₁₁] and tris[3,5-bis(trifluoromethyl)phenyl]phosphine was obtained. These are the highest overall efficiencies for any Ir/ Fe water-reduction system reported to date. The incident photon to hydrogen yield reaches 16.4% with the best system.

Introduction

The production of hydrogen and oxygen directly from water with the aid of visible light and suitable catalysts is one of the most exciting and challenging tasks for science in general. In this respect, photocatalytic water splitting is an option for sustainable energy generation in the mid-term future.^[1] To simplify the study of water splitting,^[2] the reaction is typically separated into its two half reactions: water oxidation and water reduction.^[3,4]

For the latter, so-called three-component water-reduction systems are used. They comprise a photosensitiser (PS), a water-reduction catalyst (WRC) and a sacrificial reductant (SR), typically a tertiary amine (e.g., triethylamine) as the final electron donor in the system.^[4] The principle of water reduction when applying such catalytic systems is shown in Figure 1.

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Figure 1. Reaction principle of a water-reduction cascade with an iridium photosensitiser (Ir-PS), a water-reduction catalyst (WRC) and a sacrificial reductant (SR).

A sufficient reduction potential is generated by light excitation and subsequent quenching of the photosensitiser. The reduction potential of this reduced state has to be high enough to transfer an electron onto the WRC. Then, the anionic WRC reduces aqueous protons to evolve hydrogen. This electron-transfer cascade is inspired by nature (Zscheme), in which reduced states are generated in photosystems II and I.^[5] At the end of this cascade, nature's reduction equivalents are stored as nicotinamide adenine dinucle-

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otide phosphate (NADPH). Instead of hydrogen production, NADPH is used for CO_2 fixation to build up biomass.

As photosensitisers, ruthenium diimine complexes, such as the classical $[Ru(bpy)_3]^{3+[6]}$ (bpy: 2,2'-bipyridine) and derivatives,^[7] but also terpyridyl complexes of platinum,^[8,9] rhenium complexes,^[10] zinc complexes^[11] and organic dyes^[12] can be used. Recently, it has been shown by the Bernhard group that complexes of the general formula $[Ir(bpy)(ppy)_2]^+$ (ppy: 2-phenylpyridine) can act as efficient photosensitisers with long-lived excited states.^[13,14] The reduced state of these complexes possess sufficient reduction potentials to drive hydrogen generation from water in the presence of WRCs based on cobalt,^[12,15] rhodium and platinum.^[13]

Only few effective iron WRCs have been reported to date.^[4d,16] Recently, we developed an active three-component system based on simple iron carbonyls.^[17] More specifically, we showed that the activity of inexpensive [Fe₃(CO)₁₂] was comparable to well-established cobalt oxime catalysts. The iron hydride [HNEt₃][HFe₃(CO)₁₁] was identified as an active species by using in situ FTIR techniques and DFT calculations. With in situ catalysts applying monodentate electron-deficient phosphines, activities of up to 1500 catalyst turnover numbers (TONs) were obtained.^[17b]

Based on this work, we became interested in the synthesis of novel photosensitisers. Herein, we report the synthesis and characterisation of novel iridium(III) complexes (PS1–PS13) and their performances as catalytic photosensitisers in promoting water reduction with $[\text{HNEt}_3][\text{HFe}_3(\text{CO})_{11}]$ as a WRC. $[\text{Ir}(6-i\text{Pr})(\text{ppy})_2]\text{PF}_6$ (PS1) turned out to be the best candidate and was tested with various other WRCs.

Results and Discussion

Ligand synthesis: Inspired by the basic structure of the iridium complex $[Ir(bpy)(ppy)_2]^+$ (PS13), we became interested in the variation of the ligand sphere. We synthesised a number of neutral bidentate N^N ligands analogous to bipyridine by following the concept shown in Scheme 1. The first class of ligands has 6-, or 6,6'-substituents in the bipyridine unit. In the second class, one pyridine subunit was changed into five-membered heterocycles. In each case the 1,4-bisimine basic structure for coordination to Ir^{III} was retained.

The isopropyl- (L1) and sec-butyl (L2)-substituted ligands

were obtained in two steps from 2-acetylpyridine. In the first step, condensation of 2acetylpyridine with *N*,*N*-dimethylformamide dimethyl acetal yielded 3-(dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one. Reaction with the enolate of 3methylbutan-2-one or of 4methylpentan-2-one, respectively, and cyclisation with ammonium acetate gave L1 and L2, re-



Scheme 1. General ligand concepts for variation of the neutral N,N ligand.

spectively, in good overall yields. Ligands L3 and L4 were synthesised by cyanation or chlorination of bipyridine Noxide with trimethylsilyl cyanide (TMS-CN) or POCl₃, respectively.^[18] Nucleophilic attack of phenyl lithium towards bipyridine (one or two equivalents) afforded L5 and L6.^[19] Ligand L7 was prepared by the reaction of 2-methoxypyridine with lithiated pyridine.^[19b] Ligands L8 and L9 were synthesised by condensation of aniline or pyridine amidine with either 2-pyridinecarboxaldehyde (for L9^[20]) or 1,3,5-triazole (for L8).^[21] A copper/proline-catalysed coupling of 2-bromopyridine and pyrazole was used to obtain L10.^[22] Following the general protocol for the condensation of 2-cyanopyridine with 1,2-diamines, established in our group, we prepared L11 and L12.^[23]



Complex synthesis: The synthesis of iridium complexes with the general formula $[Ir^{III}(C^{N})_2(N^{N})]PF_6$ has been established and several protocols are available.^[24] We applied the synthetic sequence shown in Scheme 2, which offers a



Scheme 2. General synthetic approach towards iridium complexes with the structure $[Ir^{III}(C^N)_2(N^N)]PF_6$ (PS1–PS13).

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straightforward approach with no time-consuming purification steps. Starting from IrCl₃·H₂O the chloro-bridged dimer is formed by cyclometallation with phenylpyridine. In the second step the dimer is reacted with neutral N^N ligands to give the corresponding monocationic iridium(III) complexes. The PF₆ complexes PS1–PS12 were obtained by anion exchange from the chloro complexes by using NH₄PF₆.^[25] Single crystals of PS7 were grown from a mixture of DMSO/water and were suitable for X-ray diffraction (Figure 2).



Figure 2. ORTEP representation of the cation $[PS7]^+$. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.^[27]



In this complex, the iridium(III) centre is surrounded by the $(C^N)_2(N^N)$ ligand regime in a distorted octahedral geometry. The bpy ligand and the two coordinated carbon atoms of ppy are located almost in one plane (mean deviation from the best plane defined by N3, C23–C32, N4, C1 and C2: 0.051 Å), both nitrogen atoms of the ppy ligand are coordinated *trans* to each other. The distances between the metal centre and the nitrogen atoms of the bpy ligand (2.151(4) Å for Ir1–N3 and 2.186(4) Å for Ir1–N4) as well as the iridium–carbon (Ir1–C2: 2.008(4) Å and Ir1–C1 2.019(5) Å) and iridium–nitrogen (ppy) bonds (2.046(4) Å for Ir1–N1 and Ir1–N2) are in the same range as similar examples.^[26]

Due to the asymmetric substitution of the bipyridines in ligands L1–L5 and L7, the corresponding photosensitisers are obtained as racemic mixtures of two enantiomers derived by the helicoidal chirality of the complexes. The chirality of the complexes can be seen in the ¹H NMR spectrum of PS1. The methyl groups of the *i*Pr moiety are diastereotopic and give two independent signals with significantly different shifts (Figure 3).



1.4 1.2 1.0 0.8 0.6 0.4 0.2 -0.0δ [ppm]

Figure 3. Alkyl part of the ¹H NMR spectrum of PS1. The chirality of the octahedron leads to two diastereotopic CH_3 groups in the *i*Pr moiety with distinguishable shifts in the ¹H NMR spectrum.

Cyclic voltammetry, UV/Vis spectroscopy and photoluminescence studies: For successful application of PS1-PS12 as photosensitisers in light-driven hydrogen generation from water, three prerequisites have to be fulfilled: 1) absorption in the visible part of the spectrum, 2) photoluminescence that can be quenched by the sacrificial reductant, and 3) a sufficient reduction potential of the reduced state to transfer an electron onto the WRC. UV/Vis absorption measurements were carried out to characterise the absorption properties of PS1-PS13 (Figure 4; for additional spectra see the Supporting Information). All complexes show a strong absorption in the UV region that can be attributed to $\pi - \pi^*$ transitions. In the visible range of the spectrum ($\lambda > 390$ nm) all complexes show absorptions that level off at longer wavelengths. No absorption was observed at $\lambda > 500$ nm. The cyano-substituted complex PS3 had a significantly stronger absorption in the visible region. This redshift was in agreement with other literature examples.^[28]

As shown in Table 1, the luminescence behaviour of PS1– PS13 can be divided into three groups: 1) all complexes with 6- or 6,6'-substituted bpy ligands (PS1–PS7) show strong photoluminescence in the range of 570–640 nm (Table 1, entries 1–8) that can be quenched with triethylamine (Figure 5



Figure 4. UV/Vis spectra of all catalytically active iridium photosensitisers (PS1–PS7, PS13). Conditions: $0.1 \text{ mmol } L^{-1}$ degassed solutions in acetonitrile.^[29]

Table 1. Electrochemical characterisations by cyclic voltammetry and photoluminescence wavelengths of all synthesised photosensitisers.^[a] Results from catalytic tests of the iridium photosensitisers PS1–PS13 in photocatalytic hydrogen production from water are also given.

Entry	Structure	1st (2nd) $E^{\text{red}} [V]^{[a]}$	λ_{em} [nm]	H ₂ [mL] 15 h ^[b]	TON Ir-PS ^[c]	TON WRC ^[d]
1	PS1	-1.30	570	32	1840	210
2	PS2	-1.30	571	32	1830	210
3	PS4	-1.25	571	29	1680	190
4	PS13	-1.23	590	27	1590	180
5	PS6	-1.26	605	27	1550	180
6	PS5	-1.25	605	26	1530	170
7	PS3	-1.00	633	24	1370	160
8	PS7	-1.27	595	23	1360	150
9 ^[e]	PS8	-0.68 (-1.44)	440 (weak)	<2	<25	<15
10 ^[e]	PS9	-0.85 (-1.48)	no emission	<2	<25	<15
11 ^[e]	PS12	-1.09	640 (very weak)	<2	<25	<15
12 ^[e]	PS10	-1.66 ^[f]	479 and 505 (no quench- ing)	<2	<25	<15
13 ^[e]	PS11	$-1.43^{[f]}$	no emission	<2	<25	<15

[a] Reaction conditions: solutions in acetonitrile, $0.1 \le NBu_4BF_4$, working electrode: glassy carbon, reference electrode: Ag/AgCl, counter electrode: Pt. [b] Conditions: Ir-PS (1.40 µmol), [HNEt₃][HFe₃(CO)₁₁] (6.2 µmol), THF/NEt₃/H₂O (4/1/1; 10 mL), 25 °C, Xe light irradiation (output 1.5 W), no light filter, gas evolution quantitatively measured with an automatic gas burette, gas analysis by GC. [c] TON Ir-PS = n(H)/n(Ir-PS). [d] TON Fe = $n(H_2)/n$ (Fe trimer). [e] Ir-PS (7.5 µmol) for the hydrogen evolution experiment. [f] Irreversible.

and the Supporting Information), 2) PS8, PS9, PS12 and PS11 give weak or no emission (Table 1, entries 9–11, 13) and 3) complex PS10 exhibits emission at 479 and 505 nm, but only negligible quenching is observed in the presence of NEt₃ (Table 1, entry 12).

Furthermore, electrochemical measurements were carried out to determine the reduction and oxidation potentials of the respective complexes (Table 1). For PS1–PS13, the oxi-



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Figure 5. Photoluminescence spectrum (blue) of PS1, excitation spectrum (red) and quenching experiments with triethylamine (olive, 50 μ L NEt₃/ 2 mL CH₃CN). Conditions: 0.1 mmol L⁻¹ degassed solutions in acetoni-trile.^[30]

dation potentials are in the same range, showing that the first oxidation (Ir^{III}/Ir^{IV}) is only slightly influenced by the substitution of the N^N ligand (Table S1 in the Supporting Information, entries 1–13). Among the reduction potentials within the 6,6'-substituted bpy complexes, only PS3 has a relatively positively shifted reduction potential than PS13, PS1, PS2 and PS4–PS7 (Table 1, entries 1–8). This may be due to the electron-withdrawing and mesomeric effect of the nitrile moiety in PS3. Other iridium(III) complexes with 6- and 6,6'-substituted bpy ligands show comparable or more negative reduction potentials than the basic structure PS13, ranging from -1.25 to -1.30 V (Table 1). Notably, the triazine ligand in PS8 can be reduced in two independent steps (-0.68 and -1.44 V, Table 1, entry 9). Complexes PS9 and PS12 also possess more positive reduction potentials than PS13 (Table 1, entries 1, 10 and 11). In the case of PS10 and PS11, an irreversible reduction at a much more negative potential is observed (-1.66 V for PS10 and -1.43 for PS11; Table 1, entries 12 and 13).

Hydrogen evolution experiments: All synthesised iridium complexes were tested as photosensitisers for hydrogen generation. Thus, we used complexes PS1-PS13 in combination with our previously developed WRC, [HNEt₃][HFe₃(CO)₁₁], in a mixture of THF/NEt₃/H₂O. Under light irradiation, hydrogen evolution takes place and the evolved gas volumes were measured by automatic gas burettes.^[17b,31] The collected gas was analysed by GC. Apart from argon, traces of solvent vapour and CO dissociating from the WRC, only hydrogen was found in the gas mixture. The results are summarised in Table 1. Compared with the known complex PS13, PS1 and PS2 were more stable and resulted in improved TONs of more than 1800 after 15 h (Table 1, entries 1, 2 and 4). No significant change in activity was observed in the presence of PS5 and PS6, derived from the 6phenyl- or 6,6'-diphenyl-substituted bpy ligands (Table 1, entries 5 and 6). Lower activities were found with 6-methoxy and cyano substituents (PS7 and PS3, Table 1, entries 7 and 8). Unfortunately, the other iridium complexes with pyridyltriazyl (PS8), pyridylpyrazyl (PS11) or other 1,4-bisiminetype structures (PS10, PS12 and PS9; Table 1, entries 8-12) showed no significant activity. In summary, the results of photocatalytic hydrogen-evolution experiments are consistent with the spectroscopic and CV data presented above. Reduction potentials, luminescence and quenching proper-

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ties for PS8–12 are not sufficient enough or irreversible to allow light-driven hydrogen generation.

Next, the best photosensitiser (PS1) was also tested with other potential WRCs. In order to demonstrate that visible light is sufficient to drive photocatalysis, we introduced a 395 nm cut-off filter to exclude UV irradiation (Table 2). In

Table 2. Hydrogen evolution using PS1 with different WRCs.

Entry ^[a]	WRC	$V H_2 [mL]$ 3 h (max ^[b])	TON Ir- PS ^[c] 3 h $(max^{[b]})$	TON WRC ^[f] 3 h (max ^[b])
1	[HNEt ₃][HFe ₃ (CO) ₁₁]	9 (41)	200 (950)	70 (330)
2	[HNEt ₃][HFe ₃ (CO) ₁₁]/	11 (89)	260 (2060)	90 (720)
	$P[C_6H_3-3-5-(CF_3)_2]_3$			
3	$[Mn_2(CO)_{10}]$	3	70	25
4	Co(BF ₄) ₂ /dmg ^[e]	10 (28)	235 (650)	80 (230)
5	K ₂ [PtCl ₆]	23 (31)	530 (725)	190 (250)
6 ^[d]	K ₂ [PtCl ₆]	31 (43)	730 (1000)	2560 (3500)
7	RhCl ₃	15 (23)	355 (530)	120 (185)
8 ^[g]	RhCl ₃	16 (26)	370 (600)	1285 (2110)

[a] Reaction conditions: PS1 (3.50 µmol), WRC (5.00 µmol), THF/NEt₃/H₂O (3/2/1; 10 mL), 25 °C, Xe light irradiation (output 1.5 W), 395 nm light filter, gas volumes measured with an automatic gas burette, gas analysis by GC. [b] Gas volume measured until gas evolution ceased. [c] TON Ir-PS = n(H)/n(Ir-PS). [d] K₂PtCl₆ (0.5 µmol). [e] dmg: dimethyl-glyoxime. [f] TON WRC = $n(H_2)/n(WRC)$.^[32] [g] RhCl₃ (0.5 µmol).

reactions with either $[HNEt_3][HFe_3(CO)_{11}]$ or the improved catalyst system using $[HNEt_3][HFe_3(CO)_{11}]$ in combination with tris[3,5-bis(trifluoromethyl)phenyl]phosphine,^[17b] TONs of 330 and 720, respectively, were achieved (Table 2, entries 1 and 2). Interestingly, with $[Mn_2(CO)_{10}]$ some activity was also observed (Table 2, entry 3). However, only little hydrogen evolution was obtained with a standard cobalt WRC (Table 3, entry 4). WRCs based on rhodium or platinum (Table 2, entries 5–7) showed even higher activity than the optimised iron WRC system (Table 2, entry 2).

Table 3. Performance of the catalytic system comprising PS1 and the Fe-WRC/PR $_3$ catalytic system.

Entry ^[a]	PS1 [µmol]	H ₂ [mL] 20 h	TON Ir-PS ^[b] 20 h	TON WRC ^[c] 20 h
1	15.0	225	1220	2770
2	0.5	28	4550	345

[a] Reaction conditions: [HNEt₃][HFe₃(CO)₁₁] (3.3 µmol), P[C₆H₃-3-5-(CF₃)₂]₃ (5.0 µmol), 440 nm irradiation 1.5 W, THF/NEt₃/H₂O (3/2/1; 20 mL), 25 °C, gas volumes measured with an automatic gas burette, gas analysis by GC. [b] TON Ir-PS=n(H)/n(Ir-PS) [c] TON Fe= $n(H_2)/n(Fe trimer)$.

For the determination of the incident photon to hydrogen yield, we used blue light (440 nm) introduced by a glass fibre into the reaction vessel.^[17b] For a typical hydrogen evolution curve (Figure 6), the initial (first 2 h) incident photon to hydrogen yield is 16.4%. The scope of the catalytic system was investigated by use of excess or only small amounts of PS1 (Table 3). The maximum TONs obtained in these experiments were 2770 (Table 3, entry 1) for the iron



Figure 6. Hydrogen evolution curve obtained in the experiment for the determination of the incident photon to hydrogen yield. Reaction conditions: $[HNEt_3][HFe_3(CO)_{11}]$ (3.3 µmol), PS1 (15.0 µmol), P[C₆H₃-3,5-(CF₃)₂]₃ (5.0 µmol), 440 nm irradiation 1.5 W, THF/NEt₃/H₂O (3/2/1; 20 mL), 25 °C, gas volumes quantitatively measured with automatic gas burettes, gas analysis by GC.

WRC and 4550 for the iridium photosensitiser (Table 3, entry 2). To the best of our knowledge, these values are the highest reported to date for a water-reduction system containing an iridium PS and iron WRCs.

Conclusion

The syntheses of new iridium(III) complexes of the general formula [Ir(N^N)(ppy)₂]PF₆ were described. These complexes were fully characterised and studied by cyclic voltammetry and UV/Vis and photoluminescence spectroscopy. Additionally, the crystal structure of [Ir(6-OMe-bpy)- $(ppy)_2$]PF₆ was reported. All complexes were tested as photosensitisers in light-driven hydrogen generation from water. Together with [HNEt₃][HFe₃(CO)₁₁] as WRC, seven new Ir-PS complexes showed significant activity and the complex PS1 was identified as the most robust photosensitiser. Complex PS1 was also tested with other WRCs, such as the in situ generated system [HNEt₃][HFe₃(CO)₁₁]/tris[3,5-bis(trifluoromethyl)phenyl]phosphine, cobalt oximes, $[Mn_2(CO)_{10}]$, as well as rhodium and platinum catalysts. The highest TONs were 2770 for the best iron-based WRC and up to 4550 TONs were obtained for the Ir-PS. These values are the highest ever reported for a water-reduction system containing an iron WRC.

Experimental Section

General: All experiments were carried out in an argon atmosphere with the exclusion of air. Solvents were purified and degassed with standard procedures prior to use. Precursors were purchased from commercial suppliers (Aldrich, Alfa Aesar, Acros) and were used as received. Ligands L3,^[18] L4,^[18] L5,^[19] L6,^[19] L7,^[18] L9^[20] and L10^[22] were synthesised according to literature procedures. The amounts of evolved gases were measured with an automatic gas burette, in a setup that has already been described elsewhere.^[17b] GC was used for analysis of gases (gas chromato-

graph HP6890N, carboxen 1000, TCD or TCD + methanizer/FID, external calibration). The light source was a 300 W Xe lamp. $^{[33]}$

General procedure for hydrogen evolution experiments: A doublewalled, thermostatically controlled reaction vessel was evacuated and filled with argon six times to remove any other gas. The iridium photosensitiser and the respective WRC were added through Teflon crucibles or freshly prepared stock solutions were used. The solvent mixture of THF/NEt₃/H₂O was added and the temperature was maintained at 25 °C by a thermostat. The reaction was started after stirring for 8 min at that temperature by switching on the light source. The variability of gas evolution was typically 1–10%.

Synthesis of L1: A solution of 2-acetylpyridine (1.0 g; 8.3 mmol) and N,N-dimethylformamide dimethyl acetal (2.3 g; 17.4 mmol) in toluene (5 mL) was heated at reflux while methanol was gradually removed by distillation. The reaction was heated until no more methanol was formed (ca. 12 h). Toluene was removed under reduced pressure to give 3-(dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one as a dark green oil (1.4 g; 98%). The purity of the obtained product was >95% (as determined by NMR spectroscopy) and was used for the next step without any purifica-3-(Dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one tion. (1.4 g: 8.1 mmol, 95% purity) was added to a solution of the enolate of 3-methylbutan-2-one (1.0 equiv), previously prepared by the reaction of the substrate with lithium diisopropylamide (LDA; 1 equiv) in anhydrous THF (25 mL). The solution was stirred for 20 h at room temperature. Then solid ammonium acetate (6.2 g; 81 mmol) and acetic acid (12 mL) were added. The resulting mixture was heated at reflux while THF and acetic acid were slowly removed by distillation over 3 h. The residue was dissolved in CH₂Cl₂, washed with a 10% aqueous solution of K₂CO₃ and dried with Na2SO4. The solvent was removed under reduced pressure and the product was distilled under reduced pressure to give a pale yellow oil (yield 57%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 8.56 (d, J = 4.7 Hz, 1H), 8.41 (d, J=8.1 Hz, 1H), 8.12 (d, J=7.8 Hz, 1H), 7.70 (td, J=7.8, 1.8 Hz, 1 H), 7.62 (t, J = 7.8 Hz, 1 H), 7.19–7.16 (m, 1 H), 7.08 (d, J =7.8 Hz, 1 H), 3.04 (heptet, J=6.8 Hz, 1 H), 1.26 ppm (d, J=6.8 Hz, 6 H); ¹³C NMR (75.5 MHz, CDCl₃, 298 K): $\delta = 166.8$, 156.7, 154.9, 148.9, 137.3, 137.1, 123.6, 121.5, 120.9, 118.4, 36.4, 22.8 ppm; HRMS (ESI): m/z calcd for C₁₃H₁₅N₂: 199.12297 [*M*+H]⁺; found: 199.12244.

Synthesis of L2: Ligand L2 was prepared with the same procedure as that used for **L1** from the enolate of 4-methylpentan-2-one.

Synthesis of L8: Pyridine amidine hydrochloride (700 mg, 4.4 mmol, 1.0 equiv) was dissolved in MeOH (0.5 mL) and *s*-triazine (360 mg, 4.4 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 24 h at ambient temperature. After evaporation of the solvent, the product was purified by column chromatography (eluent: ethyl acetate/triethylamine = 50/1) and isolated as a slightly yellow solid (282 mg, 40%). ¹H NMR (CD₃OD, 300 MHz, 298 K): δ = 9.40 (s, 1 H), 9.39 (s, 1 H), 8.81–8.79 (m, 1 H), 8.70–8.66 (m, 1 H), 8.11–8.05 (m, 1 H), 7.70–7.64 ppm (m, 1 H); ¹³C NMR (75.5 MHz, CD₃OD, 298 K): δ = 168.1 (2C), 151.1, 139.3, 128.6, 125.9 ppm; HRMS (ESI): *m*/*z* calcd for C₈H₇N₄: 159.0665 [*M*+H]⁺; found: 159.0667.

Synthesis of L12: Methyl picolinimidate (3.2 g, 23.5 mmol, 1.0 equiv) and 2-aminoethanethiol (1.8 g, 23.5 mmol, 1.0 equiv) were dissolved in CH₂Cl₂ (140 mL) and the mixture was heated at reflux for 48 h. The resulting mixture was dropped into water (200 mL) and the mixture was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated. The product was purified by column chromatography (eluent: ethyl acetate/cyclohexane 1/2, 2% triethylamine) and isolated as a pale yellow solid (3.13 g, 81%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 8.62–8.60 (m, 11H), 8.03–8.00 (m, 1H), 7.74–7.68 (m, 1H), 7.33–7.28 (m, 1H), 4.48 (t, *J* = 9.0 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃, 298 K): δ = 170.9, 151.2, 149.3, 136.5, 125.3, 121.5, 65.8, 32.5 ppm; HRMS (ESI): *m/z* calcd for C₈H₉N₂S: 165.0481 [*M*+H]⁺; found: 165.04812.

Synthesis of L11: Ligand L11 was synthesised by using the procedure as that described for L11. The product was purified by recrystallisation from ethyl acetate and isolated as white crystals (50% yield). ¹H NMR (300 MHz, CDCl₃): δ =8.49–8.47 (m, 1H), 8.07–8.04 (m, 1H), 7.70–7.67 (m, 1H), 7.28–7.24 (m, 1H), 5.68 (brs, 1H; NH), 3.75 ppm (brs, 4H;

-CH₂CH₂-); ¹³C NMR (75.5 MHz, CDCl₃): δ = 164.3, 148.63, 148.60, 136.5, 125.0, 122.2, 50.8 ppm (brs, CH₂CH₂); HRMS (ESI) *m*/*z*: calcd for C₈H₁₀N₃: 148.08692 [*M*+H]⁺; found: 148.08683.

Synthesis of tetrakis(2-phenylpyridine)- μ -(dichloro)diiridium(III): 2-Phenylpyridine (1.0 mmol) was added to iridium chloride (0.5 mmol) in a mixture of methoxyethanol/water (3:1, 22 mL). The reaction mixture was heated at reflux (120 °C) with constant stirring for 24 h. The resulting precipitate was collected by suction filtration, washed with diethyl ether and dried to yield the product as a yellow powder (60–70%), which was used without further purification.

General protocol for the preparation of $[Ir(N^N)(ppy)_2]PF_6$ complexes Method A: In CH₂Cl₂/EtOH: The appropriate N^N ligand (0.35 mmol) and [[IrCl(ppy)₂]₂] (0.14 mmol) were stirred in a mixture of dichloromethane (3.5 mL) and ethanol (1.5 mL) for 4–24 h. A clear yellow–orange solution was obtained and the solvent was removed under reduced pressure. The residue was dissolved in H₂O (30 mL) and the water layer was extracted with Et₂O (3× 20 mL). The product was precipitated by counterion metathesis with NH₄PF₆ (0.5 g in H₂O). The solid was isolated by suction filtration, washed with water and dried under high vacuum to yield the pure iridium complexes as yellow to orange solids.

Method B: In ethylene glycol: The appropriate ligand (0.20 mmol) and [[IrCl(ppy)₂]₂] (0.09 mmol) were suspended in ethylene glycol (6 mL) and the resulting mixture was heated to 150 °C for 12 h. After cooling to ambient temperature, the solution was dropped into water (60 mL) and the aqueous solution was extracted with diethyl ether (3×20 mL). Remaining traces of diethyl ether were removed by heating the aqueous layer to 85 °C for 5 min. A solution of ammonium hexafluorophosphate (1g in H₂O) was added to the cooled solution. The resulting precipitate was collected by suction filtration and washed with water and diethyl ether. After drying under vacuum the photosensitiser was obtained as a yellow to orange solid.

Synthesis of PS1: Prepared by using method A (CH₂Cl₂, EtOH procedure) to give PS1 as a yellow solid (90%). ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.83 (d, *J* = 8.2 Hz, 1 H), 8.72 (d, *J* = 7.7 Hz, 1 H), 8.30–8.20 (m, 4H), 7.99–7.92 (m, 3H), 7.89–7.85 (m, 2H), 7.73–7.69 (m, 2H), 7.60–7.55 (m, 2H), 7.26–7.23 (m, 1H), 7.15–7.12 (m, 1H), 7.02–6.98 (m, 1H), 6.91–6.81 (m, 3H), 6.10 (d, *J* = 7.34, 1H), 5.94 (d, *J* = 7.48, 1H), 3.56 (m, 1H; -CH-), 0.96 (d, *J* = 6.8 Hz, 3H), 0.28 ppm (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, [D₆]DMSO): δ = 172.4, 167.4, 166.2, 157.3, 154.9, 150.8, 150.0, 149.2, 148.4, 146.9, 143.4, 143.0, 140.3, 139.5, 138.8, 138.7, 130.9, 130.5, 129.9, 129.7, 127.8, 125.3, 125.1, 125.0, 124.8, 124.1, 123.4, 123.1, 122.6, 121.5, 120.3, 119.9, 37.5, 22.7, 22.5 ppm; ATR-IR: $\bar{\nu}$ = 3049 (w), 2965 (w), 2928 (w), 2871 (w), 1606 (w), 1583 (w), 1478 (w), 1166 (w), 835 (s), 762 (m), 734 (m), 556 cm⁻¹ (m); HRMS (ESI): *m/z* calcd for [C₃₅H₃₀IrN₄]⁺: 697.2071; found: 697.2077 [*M*]⁺.

Synthesis of PS2: Prepared by using method A (CH2Cl2, EtOH procedure) to give PS2 as a yellow solid (60%). ¹H NMR (400 MHz, $[D_6]DMSO$): $\delta = 8.82$ (d, J = 8.5 Hz, 1H), 8.76 (t, J = 7.2 Hz, 1H), 8.34– 8.18 (m, 4H), 8.01-7.54 (m, 9H), 7.24-7.12 (m, 2H), 7.01-6.96 (m, 1H), 6.92-6.76 (m, 3H), 6.08 (dd, J=7.6, 3.3 Hz, 1H), 5.96 (m, 1H), 3.06-3.01 (m, 0.5H; CH), 1.56-1.50 (m, 0.5H; CH), 1.28-1.21 (m, 1H; CH₂), 0.98-0.86 (m, 1H; CH₂), 0.81 (d, J=7.0 Hz, 1.5H; CH₃), 0.52 (t, J=7.3 Hz, 1.5H; CH₃), 0.17 (d, J = 6.6 Hz, 1.5H; CH₃), -0.12 ppm (t, J = 7.3 Hz, 1.5H; CH₃); ¹³C NMR (100 MHz, [D₆]DMSO): $\delta = 171.9$, 171.7, 167.4, 167.4, 166.2, 166.2, 157.3, 157.2, 155.1, 155.0, 151.1, 151.0, 149.9, 149.2, 149.2, 149.1, 148.7, 147.0, 146.9, 143.6, 143.3, 143.0, 142.9, 140.4, 140.4, 139.5, 138.9, 138.9, 138.7, 138.7, 131.2, 130.9, 130.6, 130.6, 129.9, 129.7, 129.6, 129.4, 127.8, 127.7, 125.5, 125.3, 125.2, 125.2, 125.1, 125.0, 124.9, 124.1, 123.9, 123.4, 123.4, 123.2, 123.2, 122.6, 121.5, 121.4, 120.3, 120.1, 119.9, 43.8, 42.7, 29.4, 29.1, 20.6, 20.4, 11.6, 10.3 ppm (several signals in the aromatic region overlapped); ATR-IR: $\tilde{v} = 3045$ (w), 2627 (w), 1983 (w), 1607 (m), 1585 (m), 1564 (m), 1477 (m), 1452 (m), 1421 (m), 1307 (w), 1271 (w), 1229 (w), 1163 (w), 1128 (w), 1063 (w), 1030 (w), 1003 (w), 827 (s), 752 (s), 729 (s), 694 cm⁻¹ (s); HRMS (ESI): m/z: calcd for [C₃₆H₃₂IrN₄]⁺: 711.2227; found: 711.2224 [*M*]⁺.

Synthesis of PS3: Prepared by using method A (CH₂Cl₂, EtOH procedure) to give PS3 as an orange solid (99%). ¹H NMR (400 MHz, $[D_6]DMSO$): $\delta = 9.16$ (d, J = 7.5 Hz, 1H), 8.96 (d, J = 8.3 Hz, 1H), 8.50 (t,

 $J=8.0 \text{ Hz}, 1 \text{ H}), 8.30-8.24 \text{ (m, 4H)}, 8.06 \text{ (d, } J=5.3 \text{ Hz}, 1 \text{ H}), 7.97-7.81 \text{ (m, 4H)}, 7.74-7.71 \text{ (m, 2H)}, 7.50 \text{ (d, } J=6.2 \text{ Hz}, 1 \text{ H}), 7.21-7.16 \text{ (m, 1H)}, 7.12-7.08 \text{ (m, 1H)}, 7.05-6.99 \text{ (m, 1H)}, 6.91-6.86 \text{ (m, 2H)}, 6.73 \text{ (t, } J=7.5 \text{ Hz}, 1 \text{ H}), 6.07 \text{ (d, } J=7.3 \text{ Hz}, 1 \text{ H}), 5.98 \text{ ppm} \text{ (d, } J=7.7 \text{ Hz}, 1 \text{ H}); ^{13}\text{C NMR} (100 \text{ MHz}, [D_6]\text{DMSO}): \delta=167.6, 165.9, 158.1, 154.7, 150.6, 150.4, 149.6, 148.7, 147.0, 143.7, 143.2, 141.0, 139.9, 139.0, 135.8, 134.8, 131.9, 130.5, 130.1, 130.1, 129.2, 128.4, 126.3, 125.1, 125.0, 124.2, 124.1, 123.4, 122.8, 122.2, 210.2, 119.9, 113.7 \text{ ppm} (-\text{CN}); \text{ATR-IR: } \tilde{\nu}=3043 \text{ (w)}, 1607 \text{ (w)}, 1583 \text{ (w)}, 1479 \text{ (w)}, 1446 \text{ (w)}, 1165(\text{w)}, 836 \text{ (s)}, 759 \text{ (m)}, 736 \text{ (m)}, 556 \text{ cm}^{-1} \text{ (m)}; \text{HRMS} (\text{ESI}): m/z \text{ calcd for } [\text{C}_{33}\text{H}_{23}\text{IrN}_5]^+: 682.1579; \text{ found: } 682.1588 [M]^+.$

Synthesis of PS4: Prepared by using method A (CH₂Cl₂, EtOH procedure) to give PS4 as a yellow solid (90%). ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 8.86$ (d, J = 8.0 Hz, 2H), 8.31-8.23 (m, 4H), 8.12 (d, J = 5.5 Hz, 1H), 8.00-7.88 (m, 3H), 7.82-7.78 (m, 2H), 7.73-7.65 (m, 2H), 7.54 (d, J = 5.5 Hz, 1H), 7.23 (t, J = 6.4 Hz, 1H), 7.13 (t, J = 6.4 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.89-6.84 (m, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.07 (d, J = 7.5 Hz, 1H), 5.96 ppm (d, J = 7.6 Hz, 1H); 13 C NMR (100 MHz, [D₆]DMSO): $\delta = 167.6$, 165.9, 157.0, 155.9, 154.6, 152.2, 150.8, 149.4, 148.5, 146.1, 143.3, 143.1, 142.4, 139.7, 138.8, 131.5, 130.4, 129.8, 129.2, 129.2, 128.5, 126.0, 125.1, 124.6, 124.1, 123.7, 123.4, 122.6, 121.3, 120.2, 119.8 ppm (several signals in the aromatic region overlapped); ATR-IR: $\tilde{\nu} = 3042$ (w), 1007 (w), 1595 (w), 1478 (w), 757 (m), 731 (m), 702 (w), 556 cm⁻¹ (m); HRMS (ESI): m/z: calcd for $[C_{32}H_{23}IrN_4]^+$: 689.1212; found: $689.1214 [M]^+$.

Synthesis of PS5: Prepared by using method A (CH₂Cl₂, EtOH procedure) to give PS5 as a yellow solid (99%). ¹H NMR (400 MHz, $[D_6]DMSO$: $\delta = 8.88-8.85$ (m, 2H), 8.34 (t, J = 7.9 Hz, 1H), 8.26-8.22 (m, 1H), 8.14-8.09 (m, 2H), 8.00-7.96 (m, 1H), 7.92-7.88 (m, 1H), 7.78 (d, J=5.6 Hz, 1 H), 7.74–7.70 (m, 3 H), 7.61–7.54 (m, 2 H), 7.36 (d, J= 7.4 Hz, 1H), 7.25-7.22 (m, 1H), 7.18-7.15 (m, 1H), 6.93-6.87 (m, 2H), 6.70–6.71 (m, 3H), 6.59–6.49 (m, 3H), 6.30–6.26 (m, 1H), 5.82 (d, J =7.5 Hz, 1 H), 5.43 ppm (d, J = 7.6, 1 H); ¹³C NMR (100 MHz, [D₆]DMSO): $\delta = 168.0, 166.2, 164.6, 156.7, 156.4, 151.1, 149.7, 149.2, 149.0, 147.0, 143.0,$ 142.8, 139.8, 139.5, 138.7, 138.4, 138.0, 130.9, 130.3, 129.8, 129.6, 128.8, 128.4, 127.9, 127.4, 127.2, 125.4, 124.7, 124.3, 123.9, 122.8, 122.4, 120.0, 112.0, 119.9 ppm (several signals in the aromatic region overlapped); ATR-IR: v=3047 (w), 1607 (w), 1582 (w), 1477 (m), 1450 (w), 1423 (w), 1269 (w), 1226 (w), 1169 (w), 1064 (w), 836 (s), 781 (w), 758 (m), 738 (m), 696 (w), 557 cm⁻¹ (m); HRMS (ESI): m/z: calcd for $[C_{38}H_{28}IrN_4]^+$: 733.1940; found: 733.1939 [M]+.

Synthesis of PS6:^[25] Prepared by using method A (CH₂Cl₂, EtOH procedure) to give PS6 as a yellow solid (99%). ¹H NMR (300 MHz, CD₂Cl₂): δ =8.42 (d, *J*=8.0 Hz, 2H), 8.26 (d, *J*=5.7 Hz, 2H), 8.15 (t, *J*=7.9 Hz, 2H), 7.83 (t, *J*=7.8 Hz, 2H), 7.65 (d, *J*=8.2 Hz, 2H), 7.34 (d, *J*=7.7 Hz, 2H), 7.16 (t, *J*=6.6 Hz, 2H), 7.11 (d, *J*=7.8 Hz, 2H), 7.01 (t, *J*=6.3 Hz, 2H), 6.76 (t, *J*=7.8, 5.9 Hz, 4H), 6.60 (d, *J*=6.2 Hz, 4H), 6.55 (t, *J*=6.1 Hz, 2H), 6.21 (t, *J*=6.2 Hz, 2H), 5.24 (d, *J*=7.8 Hz, 2H); ATR-IR: $\tilde{\nu}$ =3043 (w), 1607 (w), 1583 (w), 1478 (w), 1450 (w), 1269 (w), 1227 (w), 1165 (w), 1064 (w), 1031 (w), 836 (s), 757 (m), 733 (m), 696 (w), 556 (m), 491 cm⁻¹ (w).

Synthesis of PS7: Prepared by using method A to give PS7 as a yellow powder (99%). ¹H NMR (400 MHz, $[D_6]DMSO$): δ =8.79 (d, J=8.2 Hz, 1H), 8.41 (d, J=7.5 Hz, 1H), 8.30–8.14 (m, 4H), 7.96–7.84 (m, 4H), 7.81 (d, J=6.7 Hz, 1H), 7.73 (d, J=4.6 Hz, 1H), 7.60 (t, J=6.0 Hz, 1H), 7.48 (d, J=5.1 Hz, 1H), 7.20–7.13 (m, 2H), 7.09 (t, J=6.6 Hz, 1H), 6.98 (t, J=7.5 Hz, 1H), 6.85 (t, J=7.5 Hz, 2H), 6.78 (t, J=7.3 Hz, 1H), 6.08–6.00 (m, 2H), 3.16 ppm (s, 3H); ¹³C NMR (100 MHz, $[D_6]DMSO$): δ =167.9, 166.4, 165.9, 156.2, 153.7, 152.2, 150.0, 149.4, 149.3, 148.3, 143.4, 143.0, 142.7, 139.3, 138.5, 138.4, 130.6, 130.3, 130.1, 128.9, 128.1, 125.2, 125.0, 124.1, 123.9, 123.1, 122.1, 120.4, 119.9, 119.5, 117.3, 110.0, 56.2 ppm; ATR-IR: \tilde{r} =3042 (w), 1606 (w), 1581 (w), 1473 (w), 1435 (w), 1288 (w), 1138 (w), 836 (s), 773 (w), 758 (m), 731 (m), 642 (w), 557 cm⁻¹ (m); HRMS (ESI): *m*/z calcd for $[C_{33}H_{26}IrN_4O]^+$: 685.1707; found: 685.1715

Synthesis of PS8: Prepared by using method A (CH₂Cl₂, EtOH procedure) to give PS8 as a brown solid (60%). ¹H NMR (300 MHz,

$$\begin{split} & [\mathrm{D}_6]\mathrm{DMSO}): \delta = 9.72 \ (\mathrm{d}, J = 0.7 \ \mathrm{Hz}, 1 \ \mathrm{H}), 8.95 \ (\mathrm{d}, J = 8.0 \ \mathrm{Hz}, 1 \ \mathrm{H}), 8.46 \ (\mathrm{d}, J = 0.7 \ \mathrm{Hz}, 1 \ \mathrm{H}), 8.40 - 8.36 \ (\mathrm{m}, 1 \ \mathrm{H}), 8.28 - 8.26 \ (\mathrm{m}, 2 \ \mathrm{H}), 8.20 - 8.19 \ (\mathrm{m}, 1 \ \mathrm{H}), 7.99 - 7.91 \ (\mathrm{m}, 6 \ \mathrm{H}), 7.64 - 7.62 \ (\mathrm{m}, 1 \ \mathrm{H}), 7.20 - 7.13 \ (\mathrm{m}, 2 \ \mathrm{H}), 7.06 - 7.01 \ (\mathrm{m}, 2 \ \mathrm{H}), 6.91 \ (\mathrm{dt}, J = 1.0, 7.4 \ \mathrm{Hz}, 2 \ \mathrm{H}), 6.21 \ (\mathrm{d}, J = 7.6 \ \mathrm{Hz}, 1 \ \mathrm{H}), 6.14 \ \mathrm{ppm} \ (\mathrm{d}, J = 7.5 \ \mathrm{Hz}, 1 \ \mathrm{H}); 1^{3} \ \mathrm{C} \ \mathrm{NMR} \ (75 \ \mathrm{MHz}, \ [\mathrm{D}_6] \ \mathrm{DMSO}): \delta = 171. \ 6, 167.3, 166.5, 166.3, 165.2, 151.0, 150.3, 150.8, 149.8, 148.8, 146.8, 144.0, 143.8, 140.4, 139.0, 132.6, 131.3, 130.8, 130.3, 130.2, 128.6, 125.1, 124.1, 123.8, 122.7, 122.6, 120.2, 112.0 \ \mathrm{ppm} \ (several signals in the aromatic region overlapped); \ \mathrm{ATR-IR}: \ \tilde{\nu} = 3045 \ (\mathrm{w}), 1608 \ (\mathrm{w}), 1558 \ (\mathrm{w}), 1527 \ (\mathrm{w}), 1479 \ (\mathrm{w}), 1426 \ (\mathrm{m}), 1387 \ (\mathrm{w}), 1269 \ (\mathrm{w}), 1031 \ (\mathrm{w}), 836 \ (\mathrm{s}), 756 \ (\mathrm{m}), 738 \ (\mathrm{w}), 661 \ (\mathrm{w}), 556 \ (\mathrm{m}), 418 \ \mathrm{cm}^{-1} \ (\mathrm{w}); \ \mathrm{HRMS} \ (\mathrm{ESI}): \ m/z \ \mathrm{calcd} \ \mathrm{for} \ [\mathrm{C}_{30}\mathrm{H}_{22}\mathrm{IrN_6}]^+: 657.1506; \ \mathrm{found}: 657.1505 \ [M]^+. \end{split}$$

Synthesis of PS9: Prepared by using method B (ethylene glycol procedure) to give PS9 as a red solid (76%).¹H NMR (300 MHz, [D₆]DMSO): δ =9.58 (s, 1H), 8.51 (d, *J*=7.6 Hz, 1H), 8.46 (d, *J*=5.0 Hz, 1H), 8.32–8.27 (m, 2H), 8.09 (d, *J*=7.9 Hz, 1H), 8.00–7.90 (m, 3H), 7.83–7.75 (m, 2H), 7.62–7.59 (m, 2H), 7.35–7.22 (m, 2H), 7.19–6.98 (m, 4H), 6.94–6.85 (m, 3H), 6.84–6.70 (m, 2H), 6.11 (dd, *J*=7.6, 0.9 Hz, 1H), 6.02 ppm (dd. *J*=7.4, Hz, 1.1 Hz, 1H); ¹³C NMR (75 MHz, [D₆]DMSO): δ =169.8, 166.9, 166.5, 155.4, 150.7, 150.1, 149.9, 149.3, 148.7, 147.6, 143.7, 143.4, 139.7, 138.8, 131.2, 130.9, 130.8, 130.4, 130.3, 129.6, 128.5, 128.3, 125.1, 124.5, 124.1, 123.8, 122.5, 122.4, 121.7, 120.1, 119.6 ppm (several signals in the aromatic region overlapped); ATR-IR: $\tilde{\nu}$ =3043 (w), 1608 (w), 1584 (w), 1479 (m), 1421 (w), 1269 (w), 1164 (w), 1064 (w), 1031 (w), 836 (s), 757 (m), 738 (m), 693 (w), 556 cm⁻¹ (m); HRMS (ESI): *m/z*: calcd for [C₃₄H₂₆IrN₄]⁺: 683.1781; found: 683.1783 [*M*]⁺.

Synthesis of PS10: Prepared by using method B to give PS10 as a yellow solid (90%).¹H NMR (300 MHz, [D₆]DMSO): δ =9.31 (d, *J*=3.0 Hz, 1H), 8.54 (d, *J*=8.5 Hz, 1H), 8.36-8.33 (m, 1H), 8.28 (d, *J*=8.3 Hz, 2H), 7.99-7.87 (m, 4H), 7.78 (d, *J*=5.8 Hz, 1H), 7.73 (d, *J*=5.8 Hz, 1H), 7.66 (dd, *J*=5.6, 1.2 Hz, 1H), 7.56 (dt, *J*=7.3, 1.0 Hz, 1H), 7.29 (d, *J*=2.0 Hz, 1H), 7.23-7.19 (m, 2H), 7.02-6.99 (m, 2H), 6.98-6.85 (m, 3H), 6.21-6.19 ppm (m, 2H); ¹³C NMR (75 MHz, [D₆]DMSO): δ =166.8, 166.7, 149.2, 149.2, 149.1, 148.7, 148.2, 146.1, 144.1, 144.0, 143.3, 141.7, 138.9, 138.8, 132.7, 131.3, 131.1, 130.1, 129.7, 125.3, 125.1, 124.7, 123.9, 123.8, 122.3, 122.1, 112.0, 119.9, 113.5, 111.5 ppm; ATR-IR: $\tilde{\nu}$ =3041 (w), 1610 (w), 1583 (w), 1479 (w), 1409 (w), 1354 (w), 1269 (w), 1067 (w), 881 (w), 834 (s), 776 (w), 755 (s), 729 (w), 670 (w), 556 (s), 416 cm⁻¹ (w); HRMS (ESI): *m/z* calcd for [C₃₀H₂₃IrN₅]⁺: 646.1577; found: 646.1592 [*M*]⁺.

Synthesis of PS11: Prepared by using method B to give PS11 as a yellow solid (81%).¹H NMR (300 MHz, $[D_6]DMSO$): δ =8.94 (s, 1H), 8.38 (d, J=6. 5 Hz, 1H), 8.28–8.20 (m, 4H), 7.99–7.78 (m, 5H), 7.73–7.68 (m, 1H), 7.58 (d, J=5.7 Hz, 1H), 7.32 (t, J=6.3 Hz, 1H), 7.22 (t, J=6.3 Hz, 1H), 6.99–6.83 (m, 3H), 6.77 (t, J=7.4 Hz, 1H), 6.22 (d, J=7.5 Hz, 1H), 6.16 (d, J=7.5 Hz, 1H), 3.96–3.89 (m, 1H), 3.78–3.62 (m, 2H), 3.09–3.01 ppm (m, 1H); ¹³C NMR (75 MHz, $[D_6]DMSO$): δ =168.4, 167.3, 167.1, 152.9, 150.4, 150.1, 149.0, 147.7, 146.6, 144.5, 143.8, 139.4, 138.4, 138.2, 131.4, 131.1, 130.0, 129.9, 129.3, 125.7, 124.9, 124.5, 123.7, 121.8, 121.4, 119.6, 119.4, 51.6, 44.9 ppm (several signals in the aromatic region overlapped); ATR-IR: \tilde{r} =3409 (w), 1606 (w), 1583 (w), 1451 (w), 1418 (w), 1286 (w), 1267 (w), 1164 (w), 1033 (w), 832 (s), 756 (s), 736 (s), 668 (w), 630 (w), 555 (s), 416 cm⁻¹ (w); HRMS (ESI): *m/z* calcd for $[C_{30}H_{25}IrN_5]^+$: 646.1710; found: 646.1716 [*M*]+.

Synthesis of PS12: Prepared by using method B to give PS12 as a solid (99%). ¹H NMR (300 MHz, [D₆]DMSO): δ =8.29–8.23 (m, 5H), 8.04–7.94 (m, 2H), 7.90–7.75 (m, 4H), 7.60 (d, 1H, $J_{\rm HH}$ =7.3 Hz), 7.31 (t, 1H, $J_{\rm HH}$ =6.9 Hz), 7.25 (t, 1H, $J_{\rm HH}$ =6.2 Hz), 7.02–6.80 (m, 4H), 6.18 (d, 1H, $J_{\rm HH}$ =7.5 Hz), 6.13 (d, 1H, $J_{\rm HH}$ =7.5 Hz), 4.27–4.16 (m, 1H), 3.97–3.87 (m, 1H), 3.74–3.65 (m, 1H), 3.55–3.43 ppm (m, 1H); ¹³C NMR (75 MHz, [D₆]DMSO) δ =176.5, 166.9, 166.7, 150.3, 150.2, 150.0, 149.3, 147.1, 143.9, 143.9, 140.2, 138.8, 131.2, 130.9, 130.7, 130.0, 129.6, 128.8, 125.0, 124.7, 124.0, 122.3, 122.0, 119.8, 119.7, 61.8, 33.8 ppm (several signals in the aromatic region overlapped); ATR-IR: $\tilde{\nu}$ =3044 (w), 1607 (w), 1582 (w), 1478 (w), 1420 (w), 1269 (w), 1247 (w), 1164 (w), 1054 (w), 1032 (w), 836 (s), 758 (m), 738 (m), 670 (w), 556 cm⁻¹ (m); HRMS (ESI): *m*/*z*: calcd for [C₃₀H₂₄IrN₄S]+: 663.1222; found: 663.1324 [*M*]+.

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numbers (especially for Rh and Pt), our reported TONs have to be multiplied by a factor of two.

[33] Specification of the Xe light source (Lot-Oriel-300-W-Xe-lamp, LSB530) and UV cut-off filter (ITOS, GG385): please see: http:// www.lot-oriel.com.

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