Enhanced photooxidation sensitizers: the first examples of cyclometalated pyrenyl complexes of Iridium(III)

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Supplementary Information

Experimental

All reactions were performed with the use of vacuum line and Schlenk techniques. Reagents were commercial grade and were used without further purification except for 1,5-dihydroxynaphthalene (**DHN**), which was purchased from Sun Chemical Technology (Shanghai, P. R. China) Co,. Ltd. and was used after recrystallization in ethanol.. ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded on an NMR-FT Bruker 400 MHz or Joel Eclipse 300 MHz spectrometer and recorded in $CDCl_3$. ^{1}H and ^{13}C-{^{1}H} NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Low-resolution mass spectra were obtained by the staff at Cardiff University. High-resolution mass spectra were carried out at the EPSRC National Mass Spectrometry Service at Swansea University, UK. Photophysical data were obtained on a JobinYvon–Horiba Fluorolog spectrometer fitted with a JY TBX picoseconds photodetection module as MeCN solutions. Emission spectra were uncorrected and excitation spectra were instrument corrected. The pulsed source was a Nano-LED configured for 372 nm output operating at 500 kHz. Luminescence lifetime profiles were obtained using the JobinYvon–Horiba FluoroHub single photon counting module and the data fits yielded the lifetime values using the provided DAS6 deconvolution software. UV-vis absorption spectra were measured with a HP8453 UV-visible spectrophotometer. Triplet excited state lifetimes were measured on a LP-920 pump-probe spectrometer (Edinburgh Instruments). Quantum yield measurements were obtained on aerated acetonitrile solutions of the complexes, using $[Ru(bpy)_3](PF_6)_2$ in aerated acetonitrile as a standard ($\Phi_{em} = 0.016$).[18]

Data collection and processing

Diffraction data for **$[Ir(L^3)_2(bpy)]PF_6$** were collected on a Rigaku AFC12 diffractometer equipped with an enhanced sensitivity (HG) *Saturn724+* CCD detector mounted at the window of an *FR-E+ SuperBright* rotating anode generator (Mo-Kα radiation (λ = 0.71075 Å)) with VHF *Varimax* optics (70 μm focus) at 100 K (ω scans to fill asymmetric unit sphere). Software package CrystalClear-SM Expert 2.0 r13 [1] was used for the cell determination, data collection, integration, scaling and absorption correction.

Structure analysis and refinement

The structure was solved by direct methods using SHELXS-97[2] and was completed by iterative cycles of ΔF-syntheses and full-matrix least squares refinement. All non-H atoms were refined anisotropically and difference Fourier syntheses were employed in positioning idealized hydrogen atoms and were allowed to ride on their parent C-atoms. Where the structures are disordered, various geometrical (SAME) and displacement (SIMU) parameters were employed. All refinements were against F^2 and used SHELXL-97. Figures were created using the ORTEP3 software package.[3]

Density Functional Theory

Scalar relativistic calculations were performed on the Gaussian 03 program[4] Geometry optimisations were carried out without constraints using the B3PW91 functional. The LANL2DZ basis set was used for the Ir centres, and was invoked with pseudo-potentials for the core electrons, a 6-31G(d,p) basis set for all coordinating atoms with a 6-31G basis set for all remaining atoms. All optimisations were followed by frequency calculations to ascertain the nature of the stationary point (minimum or saddle point).

Photooxidation Measurements

10 mL CH_2Cl_2/MeOH (9/1) solution containing DHN (2.0×10^{-4} M) and a sensitizer (2.0×10^{-5} M) was placed into a round-bottom flask and was irradiated by a 35 W xenon lamp through a 0.72 M $NaNO_2$ solution to cut off the light shorter than 385 nm. At intervals of 2–5 min, 2 mL of the mixture was sampling and was put back immediately after recording the absorption spectra, and UV-vis absorption spectra were recorded on the Agilent 8453 UV-visible spectrophotometer. The power density was tuned to 20 mW cm^{-2} and was measured with a solar power meter. The DHN consumption was monitored by a decrease in the absorption at 301 nm, the concentration of DHN was calculated by using its molar extinction coefficient ($\varepsilon = 7664\ M^{-1}\ cm^{-1}$) at 301 nm. The Juglone production was monitored by an increase in the absorption at 427 nm, the concentration of Juglone was calculated by using its molar extinction coefficient ($\varepsilon = 3811\ M^{-1}\ cm^{-1}$), and the yield of Juglone was obtained by dividing the concentration of Juglone with the initial concentration of DHN.

Singlet oxygen ($^1O_2$) quantum yields (Φ_Δ)

Values of the triplet photosensitizers were calculated according to a modified literature method.[1] The light source of a spectrofluorometer was used for irradiation light source to get the constant monochromatic light. The irradiation wavelength for the samples and the reference was the same. Quantum yields for singlet oxygen generation in CH_2Cl_2 were determined by monitoring the photooxidation of 1,3- diphenylisobenzofuran (DPBF) sensitized by the Ir complexes. The absorbance of DPBF was adjusted around 1.0 at 414 nm in air saturated CH_2Cl_2, and absorbance of the sensitizers were adjusted to 0.2-0.3 at the irradiation wavelength. The photooxidation of DPBF was monitored at the interval of 10 s. The quantum yields of singlet oxygen generation (Φ_Δ) were calculated by a relative method using TPP ($\Phi_\Delta = 0.62$)[2] as the reference. The following equation was used,

$$\Phi_\Delta^{unk} = \Phi_\Delta^{std} \frac{m^{unk} F^{std}}{m^{std} F^{unk}} \quad (1)$$

where superscripts ‘unk’ and ‘std’ designate Ir complexes and TPP, respectively, Φ_Δ is the quantum yield of singlet oxygen, m is the slope of a plot of difference in change in absorbance of DPBF (at 420 nm) with the irradiation time and F is the absorption correction factor, which is given by $F = 1 - 10^{-A}$ (Absorbance at the irradiation wavelength).

[1] Adarsh, N.; Avirah, R. R.; Ramaiah, D.; *Org. Lett.* 2010, *12*, 5720–5723.

[2] Gao, R.; Ho, D. G.; Hernandez, B.; Selke, M.; Murphy, D.; Djurovich, P. I.; Thompson, M. E. *J. Am. Chem. Soc.* 2002 , *124* , 14828–14829.

Nanosecond time-resolved transient absorption

The nanosecond time-resolved transient difference absorption spectra were measured by Edinburgh analytical instruments (LP 920, Edinburgh Instruments, Livingston, U.K.) and recorded on a Tektronix TDS 3012B oscilloscope. The lifetime values (by monitoring the decay trace of the transients) were obtained with the LP900 software. The samples in flash photolysis experiments were deaerated with Ar for ca. 15 min before measurement and the gas flow is kept during the measurement.

Procedures for the syntheses of the ligands and complexes

Ligand LH^1

1,2-Phenylenediamine (0.452 g, 4.17 mmol) and 1-pyrenecarboxaldehyde (0.962 g, 4.17mmol) were heated at 120 °C in nitrobenzene (15 ml) for 18 h. After cooling, Et_2O (60 ml) was added and the mixture stirred for 10 min to give a yellow precipitate. The product was filtered, washed with Et_2O (2 × 40 ml) and dried *in vacuo* to give 2-(pyren-1-yl)-1H-benzo[*d*]imidazole (yield = 1.221 g, 92 %).^{5} 2-(pyren-1-yl)-1H-benzo[*d*]imidazole (0.248 g, 0.80 mmol), 1-bromobutane (0.1 ml, 0.92 mmol) and NPr_4I (0.102 g, 0.33 mmol) were heated at 100 °C in a mixture of 3-pentanone (10 ml) and sodium hydroxide solution (50 % , 10 ml) for 12 h. The solvent was then removed *in vacuo*, the crude product dissolved in CH_2Cl_2 (15 ml) and washed with water (2 × 20 ml) and brine (20 ml). The organic fraction was dried over $MgSO_4$ and filtered. The solvent was then removed *in vacuo* to give **LH^1** as a yellow powder (yield = 0.232 g, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.22-8.00 (6H, m), 7.95 (2H, m), 7.88 (2H, m), 7.42 (1H, m), 7.30 (2H, m), 3.95 (2H, t, $^3J_{HH}$ = 7.4 Hz), 2.30 (2H, q, $^3J_{HH}$ = 7.3 Hz), 1.50 (2H, m), 0.49 (3H, t, $^3J_{HH}$ = 7.3Hz) ppm. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 153.2, 143.7, 135.3, 132.4, 131.3, 130.9, 130.6, 129.8, 129.8, 128.7, 128.0, 127.4, 126.5, 126.0, 125.9, 125.1, 124.8, 124.6, 124.6, 122.9, 122.5, 120.3, 110.3, 44.5, 31.7, 19.8, 13.5 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 247(251oo), 280(22000), 347(17900) nm. EI MS found *m/z* 374.2, calculated *m/z* 374.4 for $[M]^+$. HR MS found m/z 375.1856, calculated m/z 375.1856 for $[C_{27}H_{23}N_2]^+$. Other spectroscopic characterisations were as previously reported.^{6}

Ligand LH^2

Prepared similarly from 2-(pyren-1-yl)-1H-benzo[*d*]imidazole (0.253 g, 0.80 mmol) and 1-bromooctane (0.15 ml, 0.87 mmol), (yield = 0.260 g, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.22-8.05 (6H, m), 7.98 (2H, m), 7.88 (2H, m), 7.42 (1H, m), 7.31 (2H, m), 4.00 (2H, t, $^3J_{HH}$ = 7.2 Hz), 2.35 (2H, q, $^3J_{HH}$ = 7.4 Hz), 1.75 (2H, m), 1.52 (6H, m), 0.95 (2H, t, $^3J_{HH}$ = 7.3 Hz), 0.60 (3H, t, $^3J_{HH}$ = 7.2 Hz) ppm. ^{13}C-{^{1}H} (75 MHz, $CDCl_3$) δ_C 153.2, 143.6, 135.2, 132.4, 132.4, 131.7, 131.3, 131.2, 128.9, 128.7, 128.0, 127.4, 126.5, 126.0, 125.8, 125.1, 124.8, 124.7, 124.5, 122.8, 122.4, 120.3, 110.3, 44.6, 31.6, 30.6, 28.9, 28.8, 26.5, 22.5, 14.0 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 247(30200), 280(28100), 348(19900) nm. ES MS found *m/z* 431.2, calculated *m/z* 430.7 for $[M+H]^+$. HR MS found *m/z* 431.2481, calculated *m/z* 431.2482 for $[C_{31}H_{31}N_2]^+$.

Ligand LH^3

Prepared similarly from 2-(pyren-1-yl)-1H-benzo[*d*]imidazole (0.251 g, 0.79 mmol) and benzyl bromide (0.10 ml, 0.84 mmol), (yield = 0.203 g, 63 %).^{1}H NMR (250 MHz, $CDCl_3$) δ_H 8.22-7.89 (8H, m), 7.35-7.04 (10H, m), 5.20 (2H, s) ppm. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 153.5, 143.6, 140.4, 139.3, 136.9, 136.1, 135.4, 132.5, 130.8, 129.0, 128.8, 128.5, 128.4, 127.9, 127.7, 127.3, 127.2, 127.0, 126.5, 126.4, 126.3, 126.3, 125.9, 124.6, 124.4, 123.2, 122.7, 120.2, 110.8, 77.3 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 248(36000), 280(31700), 347(25500) nm. ES MS found *m/z* 409.2, calculated *m/z* 408.6 for $[M+H]^+$. HR MS found *m/z* 409.1695, calculated *m/z* 409.1699 for $[C_{30}H_{21}N_2]^+$.

Ligand LH^4

Prepared similarly from 2-(pyren-1-yl)-1H-benzo[*d*]imidazole (0.252 g, 0.79 mmol) and *tert*-butylbromoacetate (0.14 ml, 0.95 mmol), (yield = 0.294 g, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.21-8.05 (6H, m), 8.02-7.90 (5H, m), 7.32 (2H, m), 4.55 (2H, s), 1.25 (9H, s) ppm. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 166.6, 153.4, 143.4, 136.8, 135.7, 132.6, 131.2, 130.8, 130.6, 129.1, 128.9, 128.2, 127.8, 127.4, 127.3, 126.5, 126.0, 125.9, 124.5, 123.9, 123.4, 122.9, 120.3, 109.7, 73.7, 61.8, 29.8 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 251(31900), 280(41000), 350(27500). ES MS found *m/z* 433.2, calculated *m/z* 432.4 for $[M+H]^+$. HR MS found *m/z* 433.1908, calculated *m/z* 433.1911 for $[C_{29}H_{25}N_2O_2]^+$.

Complex [Ir(L^1)$_3$]

Ligand **LH^1** (0.248 g, 0.78 mmol) and $IrCl_3.xH_2O$ (0.042 g, 0.14 mmol) in 2-methoxyethanol/water (3:1, 8 ml) were heated at 120 °C for 12 h. The mixture was filtered and washed with water (2 × 10 ml). The product was dried *in vacuo* and isolated as a bright red precipitate (yield = 0.140 g, 74 %). [The filtrate was evaporated to dryness *in vacuo* to give a red powder which was identified as a mixrture which contained the bridged chloride dimer [$(L^1)_2Ir(\mu\text{-}Cl)_2Ir(L^1)_2$] and used in subsequent reactions without further purification or characterisation]. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.90-7.55 (15H, m), 7.65 (3H, d, $^3J_{HH}$ = 7.5 Hz), 7.27 (3H, app. t {coincident dd}, $^3J_{HH}$ = 7.5 Hz), 6.95-6.70 (6H, m), 6.69 (6H, app. t, $^3J_{HH}$ = 8.7 Hz), 6.45 (3H, s), 6.42 (3H, app. t, $^3J_{HH}$ = 7.2 Hz), 4.10 (3H, m), 3.75 (3H, m), 1.15 (6H, m), 0.75 (6H, tq, $^3J_{HH}$ = 6.8 and 7.3 Hz), 0.60 (9H, t, $^3J_{HH}$ = 7.4 Hz) ppm. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 149.5, 141.1, 139.3, 137.0, 136.0, 135.8, 133.4, 132.8, 131.7, 130.6, 128.2, 127.2, 126.3, 125.1, 124.2, 123.6, 122.5, 122.3, 121.9, 121.4, 120.9, 120.4, 109.1, 47.2, 31.2, 19.5, 13.5 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 276(65000), 348(11500) nm. ES MS found *m/z* 1351.4, calculated *m/z* 1351.5 for $[M+K]^+$. HR MS found *m/z* 1349.4355, calculated *m/z* 1349.4352 for $[C_{81}H_{63}N_6{}^{191}IrK]^+$.

Complex [Ir(L^2)$_3$]

Prepared similarly from ligand **LH^2** (0.152 g, 0.35 mmol) and $IrCl_3.xH_2O$ (0.042 g, 0.14 mmol), (yield = 0.170 g, 82 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ_H 7.91 (12H, m), 7.67 (3H, d, $^3J_{HH}$ = 7.8 Hz), 6.88-6.79 (9H, m), 6.70 (6H, d, $^3J_{HH}$ = 7.8 Hz), 6.48 (3H, s), 6.40 (3H, dd, $^3J_{HH}$ = 7.5 and 8.0 Hz), 4.09 (6H, t, $^3J_{HH}$ = 7.6 Hz), 1.25-1.15 (12H, m), 0.95-0.78 (24H, m), 0.58 (9H, t, $^3J_{HH}$ = 7.3 Hz) ppm. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 149.6, 141.0, 139.4, 136.3, 135.8, 133.2, 132.8, 131.7, 130.6, 128.9, 128.4, 126.4, 125.1, 124.3, 123.5, 123.2, 122.8, 122.2, 121.9, 121.5, 120.6, 118.7, 109.0, 47.0, 31.6, 31.0, 29.1, 28.7, 26.1, 22.5, 14.0 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 276(65900), 348(26200), 428(12100) nm. ES MS found *m/z* 1519.6, calculated *m/z* 1520.0 for $[M+K]^+$. HR MS found *m/z* 1517.6231, calculated *m/z* 1517.6235 for $[C_{93}H_{87}N_6{}^{191}IrK]^+$.

Complex [Ir(L^3)$_3$]

Ligand **LH^3** (0.198 g, 0.49 mmol) and $IrCl_3.xH_2O$ (0.054 g, 0.18 mmol) in 2-methoxyethanol/water (3:1, 8 ml) were heated at 120 °C for 12 h. The mixture was filtered and washed with water (2 × 10 ml). This product was assumed to be the bridged chloride dimer [$(L^3)_2Ir(\mu\text{-}Cl)_2Ir(L^3)_2$] and was used without further purification or characterisation. Thus, [$(L^3)_2Ir(\mu\text{-}Cl)_2Ir(L^3)_2$] (0.049 g, 0.023 mmol), **LH^3** (0.028 g, 0.068 mmol), $AgNO_3$ (0.011 g, 0.065 mmol), and Na_2CO_3 (0.037 g, 0.35 mmol) were heated in 2-methoxyethanol (10 ml) at 120 °C for 12 h. The solvent was removed *in vacuo*, the crude product dissolved in CH_2Cl_2 (20 ml), washed with water (2 × 20 ml) and brine (20 ml) and dried over $MgSO_4$. After filtering, the solvent was removed *in vacuo* to yield **[Ir(L^3)$_3$]** as a bright red crystalline solid (yield = 0.048 g, 73 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.28-7.95 (20H, m), 7.45-7.38 (14H, m), 7.38 (1H, dd, $^3J_{HH}$ = 7.0 Hz), 7.35 (3H, s), 7.22-7.13 (8H, m), 6.90 (6H, m), 5.25 (6H, s) ppm. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 153.5, 143.6, 136.1, 135.4, 132.5, 131.3, 130.9, 130.7, 129.3, 128.6, 128.5, 128.0, 127.8, 126.6, 126.5, 126.3, 126.0, 125.6, 125.9, 124.8, 124.6, 124.5, 123.2, 122.7, 120.3, 110.8, 48.4 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 284(46100), 348(37400), 406(4200) nm. ES MS found *m/z* 1415.4, calculated *m/z*

1415.6 [M+H]$^+$. HR MS found *m/z* 1413.4326, calculated *m/z* 1413.4328 for [$C_{90}H_{58}N_6{}^{191}Ir$]$^+$.

Complex [Ir(L^4)$_3$]

Prepared similarly to **[Ir(L^1)$_3$]**, but using ligand **LH^4** (0.197 g, 0.46 mmol) and $IrCl_3.xH_2O$ (0.054 g, 0.18 mmol), (yield = 0.122 g, 45 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.09-7.73 (14H, m), 7.38 (1H, dd, $^3J_{HH}$ = 7.3 and 7.4 Hz), 7.25 (14H, m), 7.07 (1H, dd, $^3J_{HH}$ = 7.1 and 7.3 Hz), 7.86 (4H, m), 6.62 (2H, dd, $^3J_{HH}$ = 7.4 and 7.5 Hz), 4.70 (6H, dd, $^3J_{HH}$ =7 .6 and 7.3 Hz), 1.22 (27H, s) ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 278(57400), 347(39900), 415(21300) nm. ES MS found *m/z* 1487.5, calculated *m/z* 1487.7 [M+H]$^+$. HR MS found *m/z* 1485.4956, calculated *m/z* 1485.4963 for [$C_{90}H_{58}N_6{}^{191}Ir$]$^+$.

Complex [Ir(L^1)$_2$(bpy)]PF_6

[(L^1)$_2$Ir(μ-Cl)$_2$Ir(L^1)$_2$] (0.046 g, 0.022 mmol) and 2,2′-bipyridine (0.010 g, 0.064 mmol) in 2-methoxyethanol (9 ml) were heated at 100 °C for 12 h. The solvent was removed *in vacuo* and the crude product dissolved in acetonitrile (5 ml). KPF_6 (0.980 g, 6.76 mmol) in water (1 ml) was added and the solution stirred for 20 minutes. Water (20 ml) was added and the product extracted with dichloromethane (2 × 20 ml). The combined organic phases were washed with water (30 ml) and brine (30 ml) before being dried over $MgSO_4$. The solution was filtered and the solvent removed *in vacuo*. The product was purified by column chromatography (silica, CH_2Cl_2) and was eluted as the first red fraction with CH_2Cl_2/MeOH (9:1). The solvent was lowered in volume (to *ca*. 3 ml) and the product precipitated by the slow addition of Et_2O (5 ml) and dried *in vacuo* (yield = 0.036 g, 68 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ_H 8.45-7.81 (21H, m), 7.85-7.65 (4H, m), 7.60-7.38 (5H, m), 7.20 (2H, s), 4.31-4.05 (2H, m), 4.0 (2H, t, $^3J_{HH}$ = 7.2 Hz), 1.15 (4H, t, $^3J_{HH}$ = 7.0 Hz), 1.05-0.89 (4H, m), 0.5 (6H, t, $^3J_{HH}$ = 7.5 Hz) ppm. ^{13}C-{^{1}H} (75 MHz, $CDCl_3$) δ_C 152.4, 149.0, 137.2, 135.4, 134.7, 131.9, 130.2, 129.4, 129.0, 127.9, 126.1, 125.8, 125.4, 125.0, 124.2, 123.8, 123.0, 121.0, 120.8, 119.2, 116.0, 111.4, 45.6, 29.2, 18.6, 11.9 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 281(101500), 348(56500), 423(10400) nm. ES MS found *m/z* 1095.3, calculated *m/z* 1095.4 for [M-PF_6]$^+$. HR MS found *m/z* 1093.3693, calculated *m/z* 1093.3697 for [$C_{64}H_{50}N_6{}^{191}Ir$]$^+$.

Complex [Ir(L^3)$_2$(bpy)]PF_6

Prepared similarly from [(L^3)$_2$Ir(μ-Cl)$_2$Ir(L^3)$_2$] (0.042 g, 0.020 mmol) and 2,2′-bipyridine (0.010 g, 0.064 mmol), (yield = 0.043 g, 83 %) ^{1}H NMR (250 MHz, $CDCl_3$) δ_H 8.35-7.5 (11H, m), 7.50-6.15 (31H, m), 5.20 (4H, s) ppm. ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ_C 152.4, 149.0, 137.1, 135.4, 134.7, 132.0, 130.2, 129.4, 129.0, 127.9, 126.1, 125.8, 125.3, 125.0, 124.3, 123.8, 123.0, 121.0, 120.8, 119.1, 116.0, 111.4, 53.6 ppm. UV-vis ($CHCl_3$): λ_{max} (ε mol^{-1}dm^{3}cm^{-1}) 280(63900), 345(26200), 425(21100) nm. ES MS found *m/z* 1163.7, calculated *m/z* 1163.4 for $[M\text{-}PF_6]^+$. HR MS found *m/z* 1161.3378, calculated *m/z* 1161.3384 for $[C_{70}H_{46}N_6{}^{191}Ir]^+$.

Table S1. Crystal data and structure refinement.

Empirical formula	$C_{78}H_{66}F_6IrN_6O_2P$	
Formula weight	1456.54	
Temperature	100(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.07(2) Å	α = 90°
	b = 14.37(2) Å	β = 96.315(19)°
	c = 33.86(5) Å	γ = 90°
Volume	6804(17) Å^3	
Z	4	
Density (calculated)	1.422 Mg / m^3	
Absorption coefficient	2.054 mm^{-1}	
F(000)	2952	
Crystal	Sheet; Dark Orange	
Crystal size	0.10 × 0.06 × 0.01 mm^3	
θ range for data collection	2.91 – 25.03°	
Index ranges	$-15 \leq h \leq 16$, $-8 \leq k \leq 17$, $-28 \leq l \leq 40$	
Reflections collected	28188	
Independent reflections	11878 [R_{int} = 0.1815]	
Completeness to θ = 25.03°	98.9 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	0.9798 and 0.8210	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11878 / 777 / 880	
Goodness-of-fit on F^2	1.166	
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.1538, $wR2$ = 0.2622	
R indices (all data)	$R1$ = 0.2465, $wR2$ = 0.3154	
Largest diff. peak and hole	2.291 and −1.403 e Å^{-3}	

Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with HF *Varimax* optics (100µm focus). **Cell determination and data collection**: *CrystalClear-SM Expert 2.0 r11* (Rigaku, 2011). **Data reduction, cell refinement and absorption correction**: *CrystalClear-SM Expert 2.0 r13* (Rigaku, 2011). **Structure solution**: *SHELXS97* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Structure refinement**: *SHELXL97* (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122). **Graphics:** *ORTEP3 for Windows* (L. J. Farrugia, J. Appl. Crystallogr. 1997, 30, 565

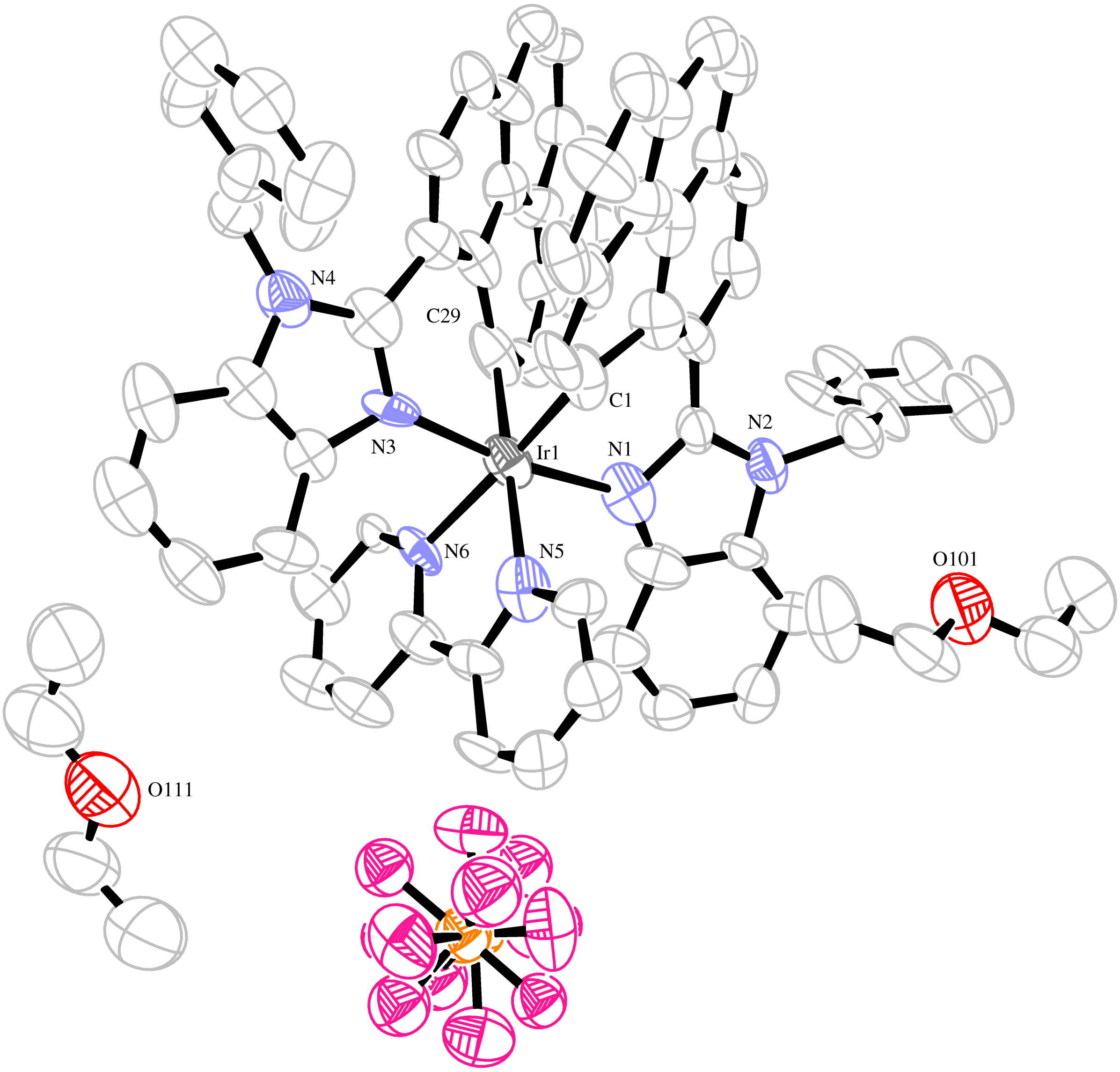


Figure S1. All hydrogen atoms were fixed using a standard riding model. Data quality was not optimum due to streaky and double reflections, thus crystal not completely single. As such a loose global displacement restraint (SIMU) has been employed. Disorder of the PF_6 anion has resulted in the atoms of the lesser component left as isotropic.

Table S2. Bond lengths [Å] and angles [°].

Ir1–C1	2.07(2)
Ir1–C29	2.08(2)
Ir1–N3	2.103(16)
Ir1–N1	2.135(18)
Ir1–N5	2.177(17)
Ir1–N6	2.214(13)

C1–Ir1–C29	87.6(7)
C1–Ir1–N3	86.2(7)
C29–Ir1–N3	84.6(8)
C1–Ir1–N1	88.7(7)
C29–Ir1–N1	88.3(8)
N3–Ir1–N1	171.4(6)
C1–Ir1–N5	97.5(7)
C29–Ir1–N5	173.6(8)
N3–Ir1–N5	99.5(6)

Table S3 Absorption and emission properties of the ligands in aerated chloroform.

Ligand	Abs. λ_{max} nm, (ε/mol^{-1}dm^{3}cm^{-1})	Em. λ_{max} (nm)	τ(ns)
LH^{1}	247 (25100), 280 (22000), 347 (17900)	400	3.6
LH^{2}	247 (30200), 280 (28100), 348 (19900)	401	3.6
LH^{3}	248 (36000), 280 (31700), 347 (25500)	401, 416	<5
LH^{4}	251 (31900), 280 (41000), 350 (27500)	400	2.8

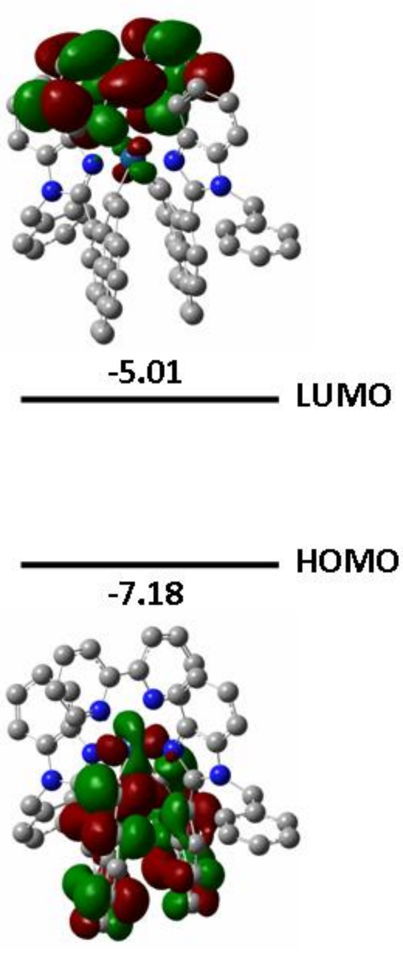


Figure S2. Frontier orbital representations from a single-point energy DFT calculation on [Ir(L3)2(bpy)]$^+$.

Table S4. Emission properties of the iridium complexes in aerated chloroform (10^{-5} M).

Complex	Em. λ_{max} nm	τ (ns)
[Ir(L^1)$_3$]	425	2.7
[Ir(L^2)$_3$]	429	2.8
[Ir(L^3)$_3$]	425	2.5
[Ir(L^4)$_3$]	446	3.0
[Ir(L^1)$_2$(bpy)]PF$_6$	435	2.7
[Ir(L^3)$_2$(bpy)]PF$_6$	407	2.6

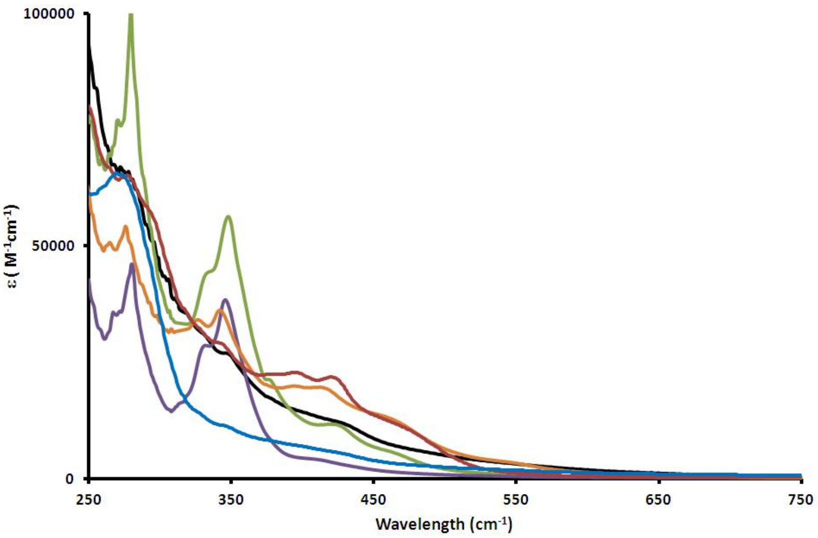


Figure S3. Absorption spectra of the complexes {blue, [Ir(L^1)$_3$]; black, [Ir(L^2)$_3$]; purple, [Ir(L^3)$_3$]; orange, [Ir(L^4)$_3$]; green, [Ir(L^3)$_2$(bpy)](PF_6); red, [Ir(L^3)$_2$(bpy)](PF_6)} in aerated dichloromethane.

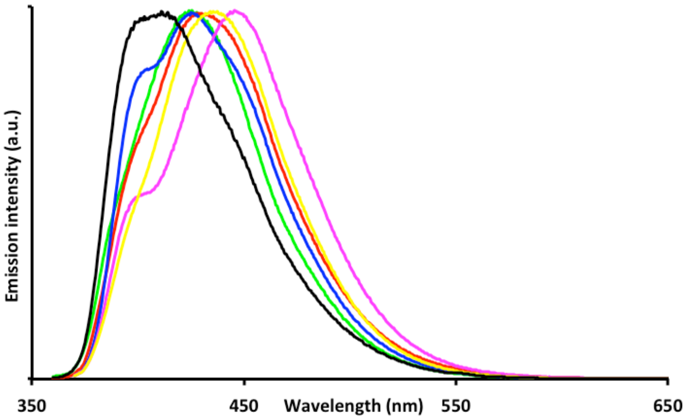


Figure S4. Normalized emission spectra of each Ir(III) complexes in aerated chloroform (λ_{ex} = 345 nm), {black, [Ir(L^3)$_2$(bpy)](PF_6); blue, [Ir(L^3)$_3$]; red, Ir(L^2)$_3$]; pink, [Ir(L^4)$_3$]; green, [Ir(L^1)$_3$]; yellow, [Ir(L^1)$_2$(bpy)](PF_6)}.

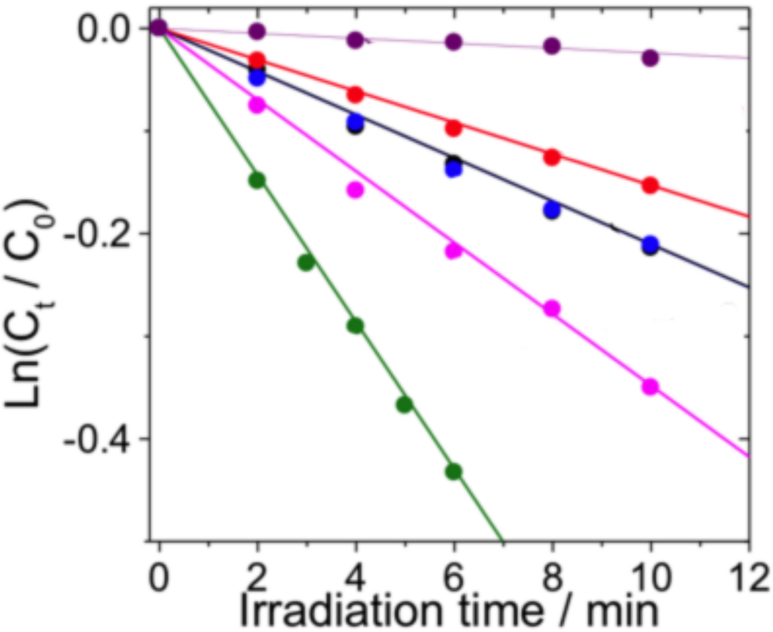
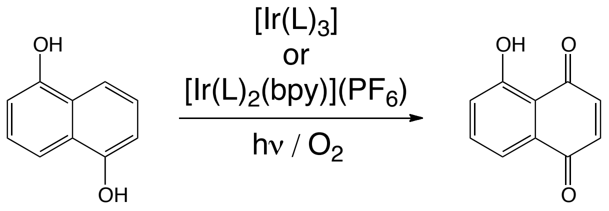


Figure S5. Plots of ln(C_t/C_0) vs. irradiation time (t) for the photooxidation of DHN using Ir complexes and **TPP** as sensitizers {top-to-bottom: [Ir(ppy)$_2$(bpy)](PF_6), [Ir(L^4)$_3$], [Ir(L^1)$_3$], [Ir(L^1)$_2$(bpy)](PF_6), [Ir(L^3)$_2$(bpy)](PF_6), TPP}. Irradiation power: 23 mW/ cm^2. $c_{[DHN]}$ = 2×10^{-4} M, $c_{[sensitizers]}$ = 2×10^{-5} M. 20 °C.



Scheme S1. Reaction for the oxidation of 1,5-DHN to Juglone.

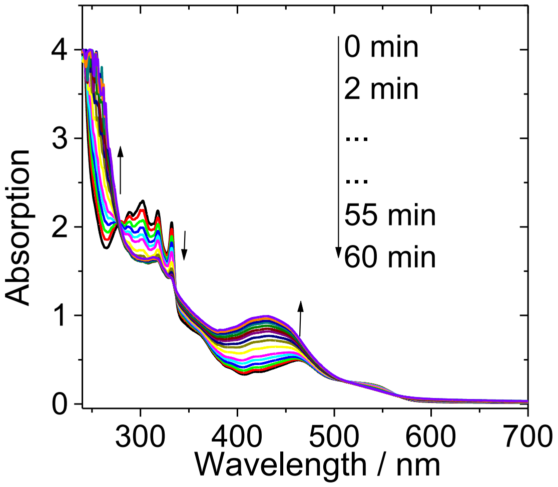


Figure S6a. Absorption spectral change for the photooxidation of DHN using **[Ir(L^1)$_3$]** as a sensitizer in dichloromethane. $c_{\text{[DHN]}} = 2\times10^{-4}$ M, $c_{\text{[sensitizers]}} = 2\times10^{-5}$ M. 20 °C.

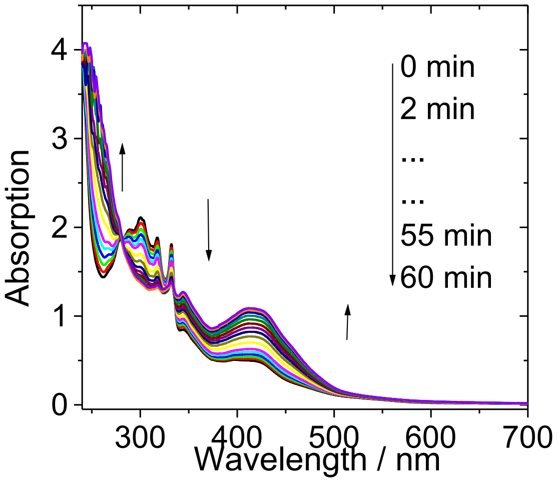


Figure S6b. Absorption spectral change for the photooxidation of DHN using **[Ir(L^4)$_3$]** as a sensitizer in dichloromethane. $c_{\text{[DHN]}} = 2\times10^{-4}$ M, $c_{\text{[sensitizers]}} = 2\times10^{-5}$ M. 20 °C.

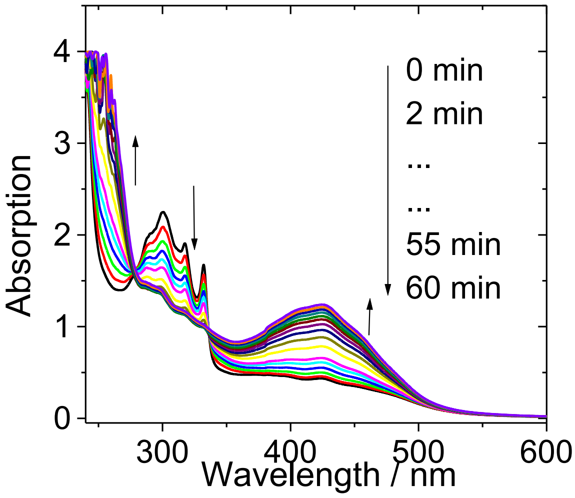


Figure S6c. Absorption spectral change for the photooxidation of DHN using **[Ir(L^3)$_2$(bpy)](PF$_6$)** as a sensitizer in dichloromethane. $c_{\text{[DHN]}} = 2\times10^{-4}$ M, $c_{\text{[sensitizers]}} = 2\times10^{-5}$ M. 20 °C.

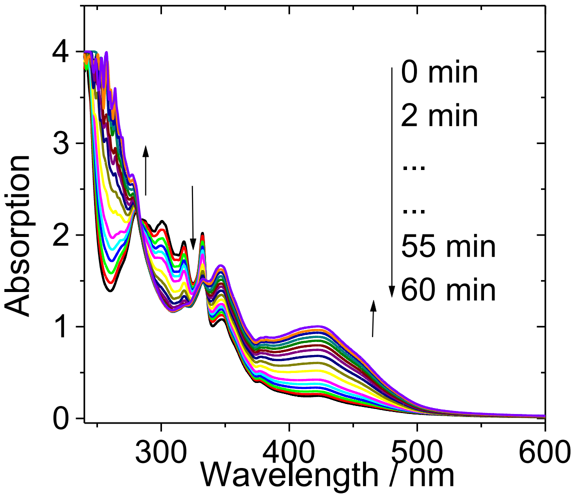


Figure S6d. Absorption spectral change for the photooxidation of DHN using **[Ir(L^1)$_2$(bpy)](PF$_6$)** as a sensitizer in dichloromethane. $c_{\text{[DHN]}} = 2\times10^{-4}$ M, $c_{\text{[sensitizers]}} = 2\times10^{-5}$ M. 20 °C.

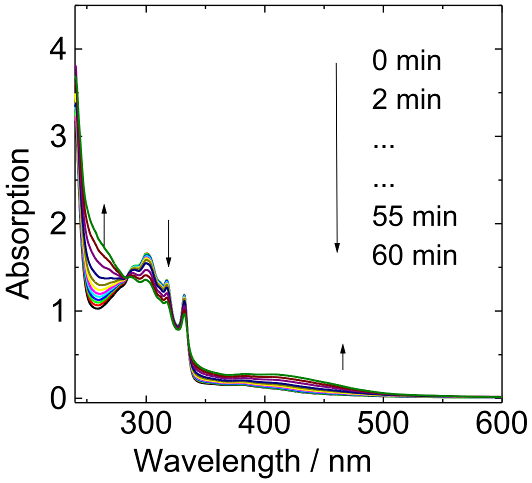


Figure S6e. Absorption spectral change for the photooxidation of DHN using **[Ir(ppy)$_2$(bpy)](PF$_6$)** as a sensitizer in dichloromethane. $c_{\text{[DHN]}} = 2\times10^{-4}$ M, $c_{\text{[sensitizers]}} = 2\times10^{-5}$ M. 20 °C.

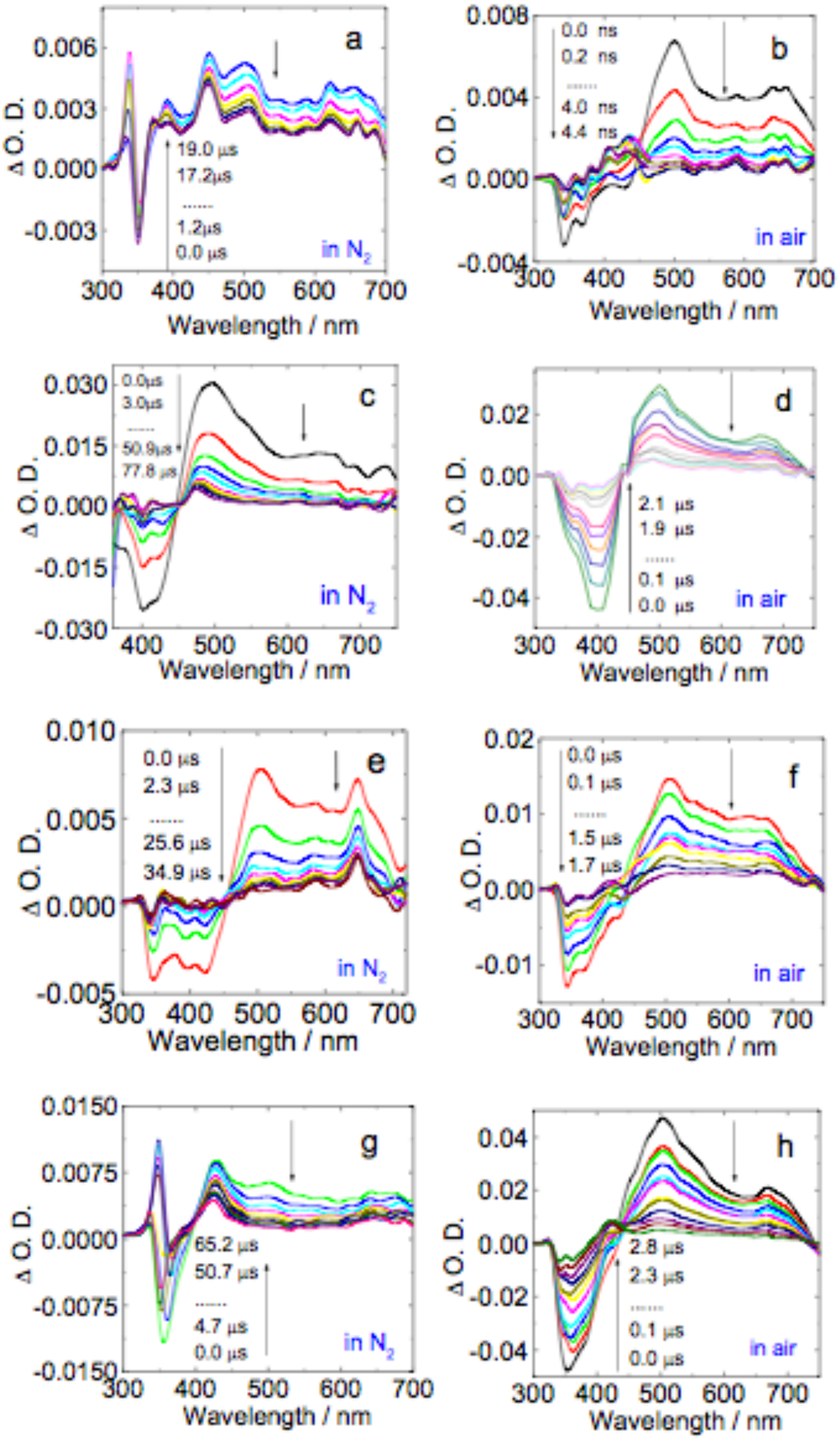


Figure S7. Nanosecond time-resolved transient difference absorption spectra of (a) [
[Ir(L^3)$_2$(bpy)](PF$_6$), (g) **[Ir(L^1)$_2$(bpy)](PF$_6$)** in deoxygenated dichloromethane (2.0 × 10^{-5}
[Ir(L^4)$_3$], (f) **[Ir(L^3)$_2$(bpy)](PF$_6$)**, (h) **[Ir(L^1)$_2$(bpy)](PF$_6$)** are the nanosecond time-res
absorption spectra of the complexes in aerated dichloromethane (2.0 × 10^{-5} M, 25 °C). A
time after 355 nm laser flash.

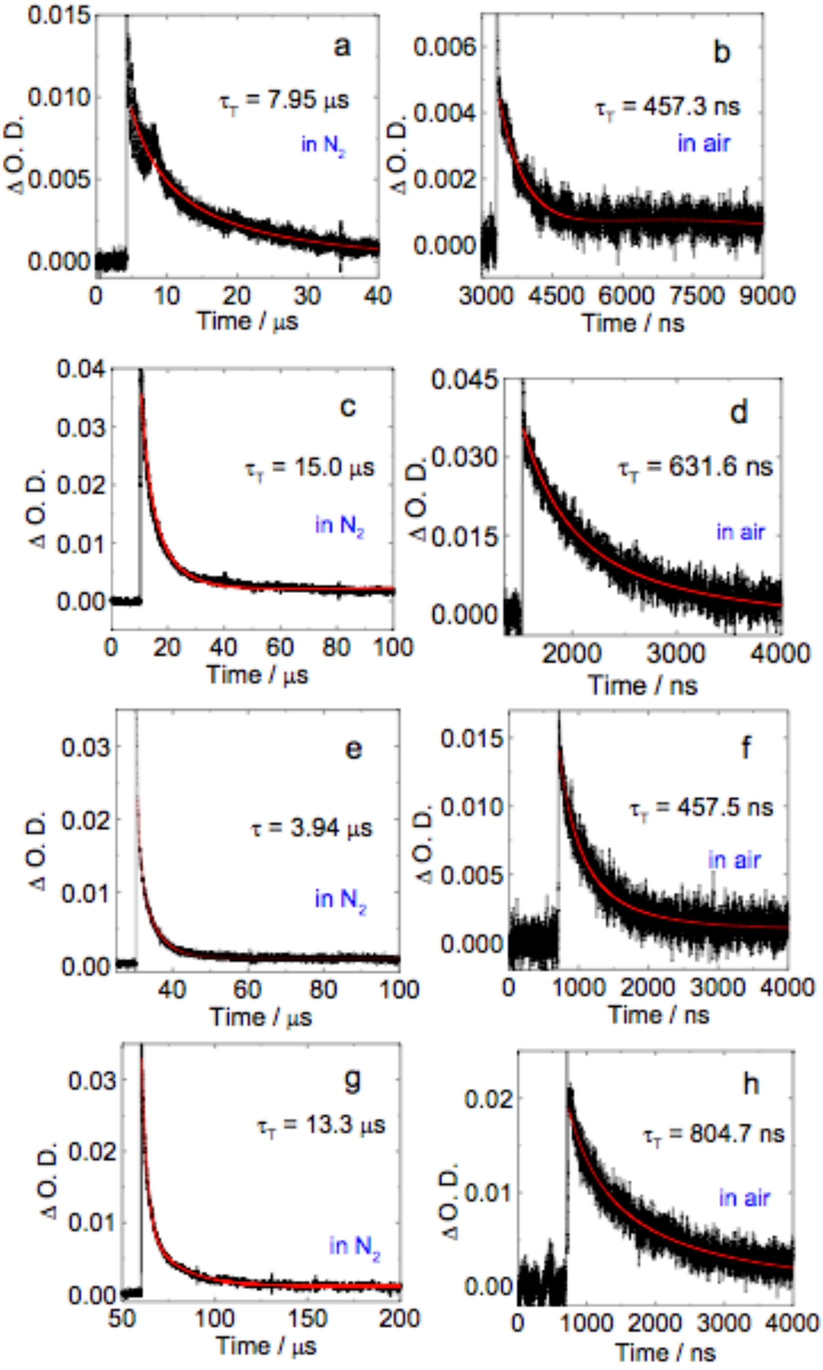


Figure S8. The triplet state lifetimes of (a) **$[Ir(L^1)_3]$** (the decay was monitored at $\lambda = 520$ nm), (c)**$[Ir(L^4)_3]$** ($\lambda = 390$ nm), (e) **$[Ir(L^3)_2(bpy)](PF_6)$** ($\lambda = 510$ nm), (g) **$[Ir(L^1)_2(bpy)](PF_6)$** ($\lambda = 510$ nm) by following the decay of transients in *deoxygenated* dichloromethane. The triplet state lifetimes of (b)**$[Ir(L^1)_3]$** ($\lambda = 580$ nm), (d) **$[Ir(L^4)_3]$** ($\lambda = 650$ nm), (f)**$[Ir(L^3)_2(bpy)](PF_6)$** ($\lambda = 670$ nm), (h) **$[Ir(L^1)_2(bpy)](PF_6)$** ($\lambda = 690$ nm) by following the decay of the transients in *aerated* dichloromethane (2.0×10^{-5} M, 25 °C).

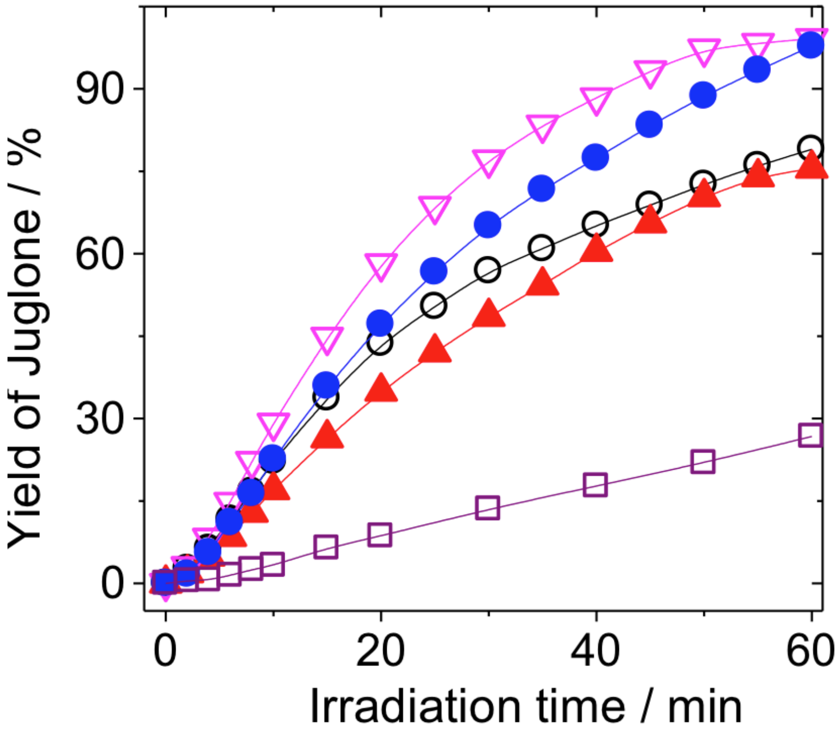


Figure S9. Plots of chemical yield of Juglone as a function of irradiation time for the photooxidation of DHN using **Ir** complexes {top-to-bottom: $[Ir(L^3)_2(bpy)](PF_6)$, $[Ir(L^1)_2(bpy)](PF_6)$, $[Ir(L^1)_3]$, $[Ir(L^4)_3]$, $[Ir(ppy)_2(bpy)](PF_6)$} as sensitizers. $c_{[DHN]} = 2\times10^{-4}$ M, $c_{[sensitizers]} = 2\times10^{-5}$ M. 20 °C.

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