Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Exploiting coumarin-6 as ancillary ligands in 1,10-phenanthroline Ir(III) complexes: generating triplet photosensitisers with high upconversion capabilities

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Experimental Section

General experiment

The di-μ-chlorido-bridged Ir(III) dimer of Coumarin 6 (**Ir-0**) was prepared following a modified literature procedure.[1] 3-Bromo-phen and 3,8-dibromo-phen, and $Pd(PPh_3)Cl_2$ were synthesised according to the methods reported by Y. Saitoh *et al* and S. Grim *et al* respectively.[2-3] Starting materials 1,10-phenanthroline, bromine, ethyltrimethylsiliane, pyrene, triphenylamine, CuI, PPh_3 and solvents CH_2Cl_2, MeOH, THF, toluene, CD_3CN, CD_2Cl_2, ethyl acetate and diethyl ether were purchased from Sigma-Aldrich or Alfa Aesar without further purification. Flash chromatography was performed using silica gel as the stationary phase. Triethylamine and acetonitrile were distilled before use.

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker Advance DPX-400 MHz, Bruker AV-400 MHz, or a Bruker AV-600 MHz spectrometer in CD_2Cl_2 or CD_3CN with tetramethylsilane as internal standard. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer using an α-cyano-4-hydroxy cinnamic acid matrix. UV/Vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence lifetimes and low temperature emissions were measured on an OB920 spectrometer (TCSPC, Edinburgh instruments, U.K.). Nanosecond time-resolved transient absorption spectra were measured on a LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK). All samples in laser flash photolysis experiments were de-aerated with Ar or N_2 for ~15 mins before measurement, and the gas flow was kept constant during the measurement.

Geometry optimization were calculated by using B3LYP functional with the 6-31G(d)/LanL2DZ basis set with density functional theory (DFT). The spin-density of the triplet excited state was calculated with their energy-minimized triplet geometries. The solvents were used in the calculations (CPCM model). All calculations were performed with the Gaussian 09W software (Gaussian Inc.).

$^1O_2$ Sensitization: The singlet oxygen quantum yield (Φ_Δ) was determined and calculated using tris(bipyridine)ruthenium(II) dichloride $[Ru(bpy)_3]Cl_2$ (Φ_Δ = 0.57 in CH_3CN) as a reference standard and 1,3-diphenylisobenzofuran (DPBF) as an $^1O_2$ scavenger. The reaction between DPBF and $^1O_2$ to give *o*-dibenzoylbenzene as an end product was monitored by the decrease of the absorbance intensity at 410 nm. The absorbance of the $^1O_2$ scavenger DPBF was adjusted around 1.0 in air-saturated CH_2Cl_2. The photosensitiser was then added to the cuvette, and the photosensitiser absorbance was adjusted to around 0.2–0.3. The solution in the cuvette was irradiated with monochromatic light at the peak absorption wavelength. The absorbance was measured after each irradiation at 5, 10 or 20 second intervals for 45, 90 or 160 seconds respectively. The slope of the absorbance maxima of DPBF at λ = 410 nm versus the accumulated photoirradiation time was calculated. The singlet-oxygen quantum yield was then calculated using the following equation:[4]

$$\Phi_{\Delta unk} = \Phi_{\Delta ref} \times \frac{k_{unk}}{k_{ref}} \times \frac{F_{ref}}{F_{unk}} \times \left(\frac{\eta_{unk}}{\eta_{ref}}\right)^2$$

The subscripts "unk" and "ref" refer to the photosensitiser and the reference, respectively; *k* is the slope of the difference in change in absorbance of DPBF (λ = 410 nm) with irradiation time, and *F* refers to the absorption correction factor, which is given by $F = 1 - 10^{-OD}$ (OD (optical density)) at the irradiation wavelength. η_{unk} and η_{ref} are the refractive indices of the corresponding solutions.

TTA Upconversion: A diode-pumped solid-state laser (473 nm, continuous wave, CW) was used for the upconversion measurements. The diameter of the laser spot was ~ 3 mm. For the upconversion experiments, the mixed solution of the photosensitisers and DPA (triplet acceptor) was degassed in CH_2Cl_2 for at least 15 min with N_2, and the gas flow was kept constant during the measurement. The solution was excited with a laser. The upconverted fluorescence of DPA was recorded with a spectrofluorometer. In order to reduce the scattered laser, a small black box was put behind the cuvette to trap the laser beam after it passed through the cuvette. The upconversion quantum yields (Φ_{UC}) were determined with the prompt fluorescence of bodipy as the standard (Φ_{F} = 71.2 % in CH_3CN) using the following equation:[5]

$$\Phi_{UC} = 2\Phi_{std} \times \left(\frac{1-10^{-A_{std}}}{1-10^{-A_{sam}}}\right) \times \left(\frac{I_{sam}}{I_{std}}\right) \times \left(\frac{\eta_{sam}}{\eta_{std}}\right)^2$$

The subscripts "sam" and "std" refer to the photosensitiser and the standard, respectively. Φ, A, I, and η represent the quantum yield, absorbance, integrated photoluminescence intensity, and the refractive index of the solvents used for the standard and the samples, respectively. The equation is multiplied by a factor of 2 in order for the maximum quantum yield to be unity.

Experiments

[Ir(III)(coumarin)$_2$(3-bromo-1,10-phenanthroline)](PF$_6$) (Ir-1): Di-μ-chlorido-bridged Ir(III) dimer of coumarin 6 (**Ir-0**) (150.0 mg, 0.081 mmol) and 3-bromo-1,10-phenanthroline (44.0 mg, 0.17 mmol) were dissolved in CH_2Cl_2 (10 mL) and MeOH (1 mL). The reaction mixture was refluxed at 40 °C for 4 h. The product was precipitated out by adding saturated NH_4PF_6 solution (in MeOH). The red solid was filtered and washed with diethyl ether. The product was dried under vacuum. Yield: 195.1 mg, 93%. ^{1}H-NMR (400 MHz, 20 °C, CD_3CN, δ in ppm): 9.12 (d, 1H, J = 5.2 Hz), 9.08 (d, 1H, J = 1.8 Hz), 8.92 (d, 1H, J = 1.8 Hz), 8.71 (d, 1H, J = 8.3 Hz), 8.08-8.03 (m, 2H), 7.96 (d, 1H, J = 8.9 Hz), 7.83 (d, 1H, J = 8.0 Hz), 7.13-7.07 (m, 2H), 6.80 (td, 1H, J = 7.9 Hz), 6.69 (t, 1H, J = 7.9 Hz), 6.44 (m, 2H), 6.14-6.03 (m, 4H), 5.83 (d, 1H, J = 8.5 Hz), 5.61 (d, 1H, J = 8.5 Hz), 3.32-3.26 (m, 8H), 1.03-0.99 (m, 12H). ^{13}C-NMR (101 MHz, 20 °C, CD_3CN, δ in ppm): 181.2, 180.1, 178.7, 178.7, 158.6, 158.5, 156.2, 156.1, 153.7, 153.7, 152.8, 152.4, 148.8, 148.8, 147.4, 146.1, 143.6, 141.4, 133.1, 133.1, 132.4, 132.3, 132.1, 132.0, 130.4, 128.7, 128.2, 128.1, 128.0, 125.6, 125.5, 124.5, 124.4, 123.1, 122.8, 122.7, 120.0, 119.3, 116.4, 116.0, 110.8, 110.7, 97.3, 97.2, 45.3, 12.6. MALDI-HRMS: calcd ($[C_{52}H_{41}N_6O_4S_2BrIr]^+$) m/z = 1149.1444, found m/z = 1149.1423.

[Ir(III)(coumarin)$_2$(3,8-dibromo-1,10-phenanthroline)](PF$_6$) (Ir-2): Ir-0 (250.0 mg, 0.135 mmol) and 3,8-dibromo-1,10-phenanthroline (91.3 mg, 0.27 mmol) were dissolved in a mixture of CH_2Cl_2 (20 mL) and MeOH (a few drops). The mixture was refluxed at 40 °C for 4 h. The product was precipitated out by adding saturated NH_4PF_6 solution (in MeOH). The red solid was filtered and washed with diethyl ether. The product was dried under *vacuo*. Yield: 287.3 mg, 78%. ^{1}H-NMR (400 MHz, 20 °C, CD_2Cl_2, δ in ppm): 8.93 (d, 2H, J = 1.8 Hz), 8.86 (d, 2H, J = 1.8 Hz), 8.04 (s, 2H), 7.79 (d, 2H, J = 8.0 Hz), 7.15 (t, 2H, J = 7.5 Hz), 6.79 (t, 2H, J = 7.5 Hz), 6.43 (d, 2H, J = 2.5 Hz), 6.03 (d, 2H, J = 9.5 Hz), 5.94 (dd, 2H, J = 9.5 Hz), 5.62 (d, 2H, J = 8.5 Hz),3.35-3.26 (m, 8H), 1.08 (t, 12H, J = 7.0 Hz). ^{13}C-NMR (101 MHz, 20 °C, CD_2Cl_2, δ in ppm): 178.2, 178.0, 157.9, 155.7, 153.3, 151.8, 148.1, 145.7, 142.9, 132.4, 132.1, 131.7, 129.4, 128.0, 125.3, 124.0, 123.3, 121.8, 118.8, 115.3, 110.4, 97.1, 45.3, 12.6. MALDI-HRMS: calcd ($[C_{52}H_{40}N_6O_4S_2Br_2Ir]^+$) m/z = 1227.0548, found m/z = 1227.0551.

[Ir(III)(coumarin)$_2$(3-(1-ethynylpyrene)-1,10-phenanthroline)](PF$_6$) (Ir-3): Ir-1 (100.0 mg, 0.077 mmol), 1-ethynylpyrene (34.9 mg, 0.154 mmol), Pd(PPh)$_3$Cl$_2$ (2.7 mg, 0.004 mmol), CuI (1.5 mg, 0.008 mmol) and PPh$_3$ (2.0 mg, 0.008 mmol) were combined in a two-necked round bottom flask under an Ar atmosphere. A mixed solvent of 5.0 mL of anhydrous DMF and 2.0 mL Et$_3$N was deaerated and added into the round bottom flask. The reaction mixture was heated at 60 °C for 4 h. The solvent was removed by rotary evaporator and the crude product was subjected to column chromatography (silica gel, eluted with CH$_2$Cl$_2$:ethyl acetate = 20:1, v/v). The product was obtained as a red solid. Yield: 84.8 mg, 77%. ^{1}H-NMR (400 MHz, 20 °C, CD$_2$Cl$_2$, δ in ppm): 9.21 (d, 1H, J = 1.2 Hz), 9.03 (d, 1H, J = 4.8 Hz), 8.88 (d, 1H, J = 1.2 Hz), 8.70 (d, 1H, J = 8.1 Hz), 8.62 (d, 1H, J = 8.0 Hz), 8.47 (d, 1H, J = 9.1 Hz), 8.40 (d, 1H, J = 7.6 Hz), 8.32 (d, 2H, J = 7.9 Hz), 8.23 (d, 2H, J = 7.5 Hz), 8.15-8.04 (m, 5H), 7.78 (d, 2H, J = 8.0 Hz), 7.13 (t, 2H, J = 7.6 Hz), 6.83 (d, 1H, J = 7.9 Hz), 6.75 (t, 1H, J = 7.9 Hz), 6.48 (d, 1H, J = 1.2 Hz), 6.45 (d, 1H, J = 1.2 Hz), 6.14 (d, 2H, J = 9.4 Hz), 5.97 (d, 2H, J = 9.4 Hz), 5.87 (d, 1H, J = 8.5 Hz), 5.67 (d, 1H, J = 8.5 Hz), 3.34-3.26 (m, 8H), 1.11-1.04 (m, 12H). ^{13}C-NMR (101 MHz, 20 °C, CD$_2$Cl$_2$, δ in ppm): 180.2, 179.6, 178.4, 178.3, 158.2, 158.1, 155.8, 155.7, 153.3, 153.3, 152.3, 151.2, 148.4, 148.4, 147.4, 145.7, 141.6, 140.9, 133.2, 133.1, 132.7, 131.8, 131.8, 131.7, 131.6, 131.4, 131.2, 130.5, 130.1, 129.8, 129.8, 128.6, 127.9, 127.8, 127.7, 127.6, 127.1, 126.9, 126.9, 125.2, 125.1, 124.8, 124.8, 124.4, 123.9, 123.8, 122.3, 122.2, 119.3, 119.1, 115.7, 115.6, 115.2, 110.4, 110.4, 98.5, 97.2, 97.1, 89.8, 45.3, 45.2, 12.7. MALDI-HRMS: calcd ([C$_{70}$H$_{50}$N$_6$O$_4$S$_2$Ir]$^+$) m/z = 1295.2694, found m/z = 1295.2990.

[Ir(III)(coumarin)$_2$(3-bromo-8-(1-ethynylpyrene)-1,10-phenanthroline)](PF$_6$) (Ir-4) and [Ir(III)(coumarin)$_2$(3,8-di(1-ethynylpyrene)-1,10-phenanthroline)](PF$_6$) (Ir-5): Under an atmosphere of Ar, **Ir-15** (250.0 mg, 0.182 mmol), ethynylpyrene (41.2 mg, 0.182 mmol), Pd(PPh)$_3$Cl$_2$ (6.4 mg, 0.009 mmol), CuI (3.5 mg, 0.018 mmol) and PPh$_3$ (4.8 mg, 0.018 mmol) were combined in a two-necked round bottom flask. A mixture of 5.0 mL of anhydrous DMF and 2.0 mL Et$_3$N was deaerated and added into the round bottom flask. The reaction mixture was heated at 60 °C for 4 h. The solvent was removed by rotary evaporator and the crude product was subjected to column chromatography (silica gel, eluted with CH$_2$Cl$_2$:ethyl acetate = 20:1, v/v). The first and second red bands were collected separately to give **Ir-4** and **Ir-5** respectively. Yield: **Ir-4**: 95.5 mg, 34.6%. **Ir-5**: 32.6 mg, 10.8%.

Ir-4: ^{1}H-NMR (400 MHz, 20 °C, CD$_2$Cl$_2$, δ in ppm): 9.18 (d, 1H, J = 1.5 Hz), 8.97 (d, 1H, J = 1.8 Hz), 8.90 (d, 1H, J = 1.5 Hz), 8.85 (d, 1H, J = 1.8 Hz), 8.61 (d, 1H, J = 9.0 Hz), 8.47 (d, 1H, J = 9.1 Hz), 8.39 (d, 1H, J = 7.6 Hz), 8.33-8.31 (m, 2H), 8.25-8.22 (m, 2H), 8.15-8.11 (m, 2H), 8.04 (d, 1H, J = 8.9 Hz), 7.80 (d, 2H, J = 7.9 Hz), 7.19-7.13 (m, 2H), 6.86-6.82 (m, 2H), 6.48-6.45 (m, 2H), 6.13-6.09 (m, 2H), 6.00-5.95 (m, 2H), 5.79 (d, 1H, J = 8.5 Hz), 5.74 (d, 1H, J = 8.5 Hz), 3.35-3.26 (m, 8H), 1.12-1.04 (m, 12H). ^{13}C-NMR (101 MHz, 20 °C, (CD$_3$)$_2$SO, δ in ppm): 179.2, 177.2, 157.2, 157.1, 155.0, 154.9, 152.5, 152.4, 151.5, 147.2, 144.2, 144.1, 142.8, 142.1, 132.1, 131.9, 131.9, 131.8, 131.7, 131.2, 130.7, 130.5, 130.5, 130.5, 130.0, 129.6, 129.3, 129.1, 128.2, 127.4, 127.4, 127.3, 127.1, 126.6, 125.1, 124.7, 124.6, 124.1, 124.1, 123.6, 123.2, 122.9, 122.2, 121.5, 121.4, 118.8, 115.5, 115.4, 114.8, 109.6, 96.4, 96.3, 96.1, 90.8, 44.0, 12.4. MALDI-HRMS: calcd ([C$_{70}$H$_{49}$N$_6$O$_4$S$_2$BrIr]$^+$) m/z = 1373.2070, found m/z = 1373.2067.

Ir-5: ^{1}H-NMR (400 MHz, 20 °C, CD$_2$Cl$_2$, δ in ppm): 9.21 (d, 2H, J = 1.5 Hz), 8.89 (d, 2H, J = 1.5 Hz), 8.63 (d, 2H, J = 9.1 Hz), 8.49 (d, 2H, J = 9.1 Hz), 8.40 (d, 2H, J = 7.5 Hz), 8.33 (d, 4H, J = 7.9 Hz), 8.24 (d, 4H, J = 7.9 Hz), 8.15 (d, 4H, J = 8.0 Hz), 8.12 (s, 2H), 7.82 (d, 2H, J = 7.9 Hz), 7.17 (t, 2H, J = 7.6

Hz), 6.88 (t, 2H, *J* = 7.9 Hz), 6.50 (d, 2H, *J* = 2.4 Hz), 6.18 (d, 2H, *J* = 9.4 Hz), 6.02-5.99 (m, 2H), 5.92 (d, 2H, *J* = 8.5 Hz), 3.35-3.26 (m, 8H), 1.07 (t, 12H, *J* = 7.0 Hz). ^{13}C-NMR (101 MHz, 20 °C, CD_2Cl_2, δ in ppm): 179.4, 178.3, 158.1, 155.8, 153.3, 152.4, 148.4, 145.5, 141.5, 133.2, 133.1, 132.7, 131.8, 131.6, 131.4, 131.3, 130.5, 130.1, 129.8, 129.4, 128.0, 127.6, 127.1, 126.9, 126.9, 125.2, 125.1, 125.1, 124.8, 124.7, 124.4, 124.0, 122.2, 119.1, 115.8, 115.1, 110.4, 98.8, 97.2, 90.0, 45.2, 12.6. MALDI-HRMS: calcd ($[C_{88}H_{58}N_6O_4S_2Ir]^+$) *m/z* = 1519.3590, found *m/z* = 1519.3621.

Spectroscopic Characterisation

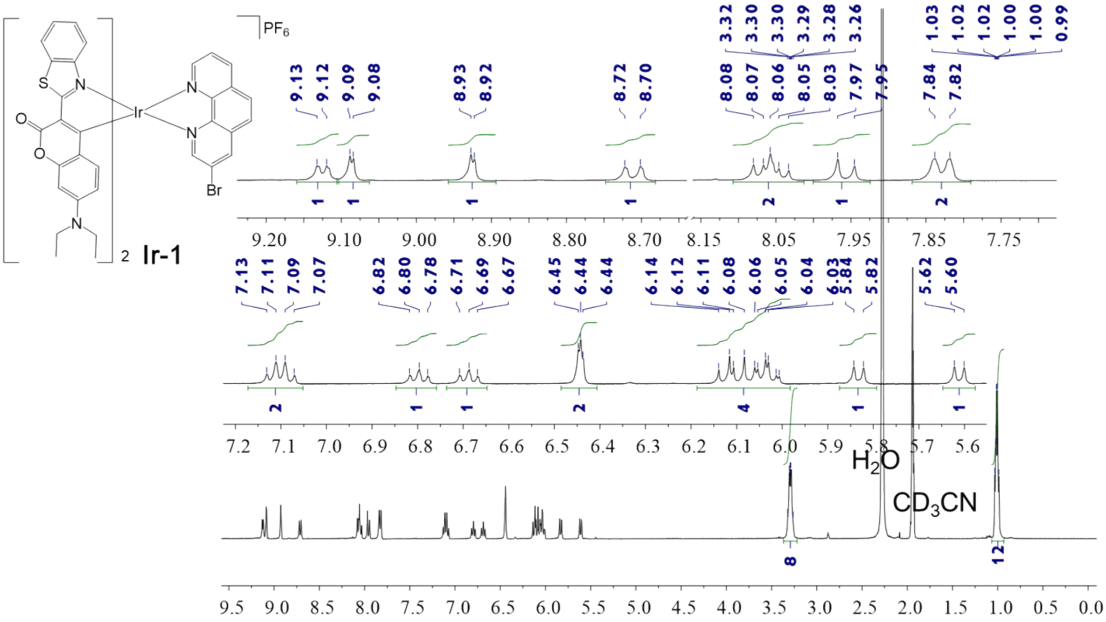

Figure S1. ^{1}H NMR spectrum of **Ir-1** (inset shows the expanded aromatic region).

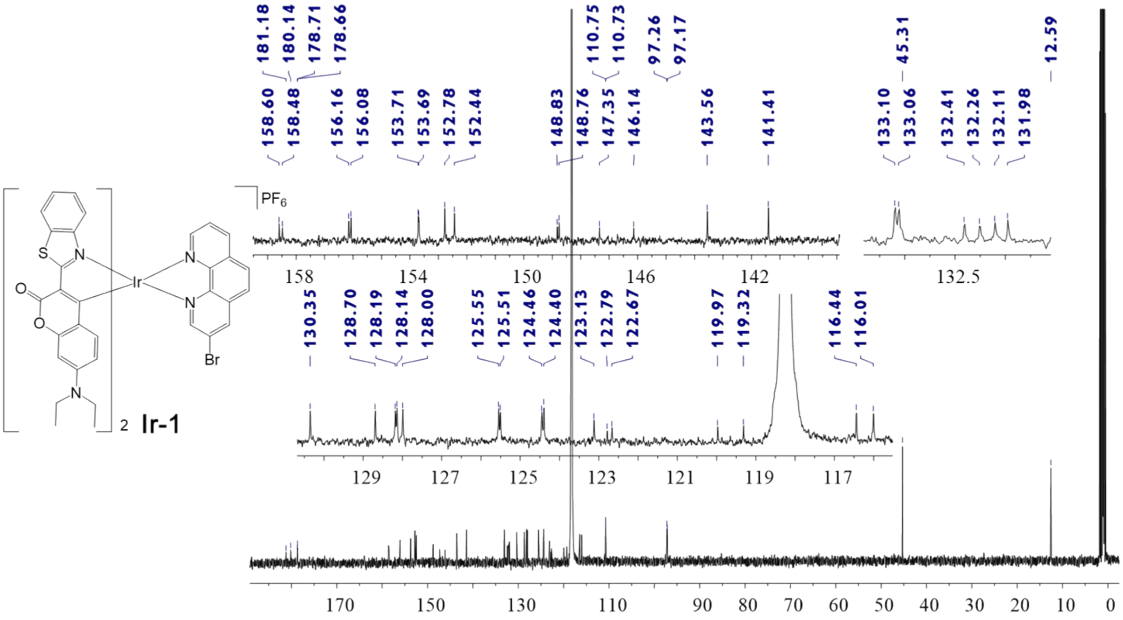

Figure S2. ^{13}C NMR spectrum of **Ir-1** (inset shows the expanded aromatic region).

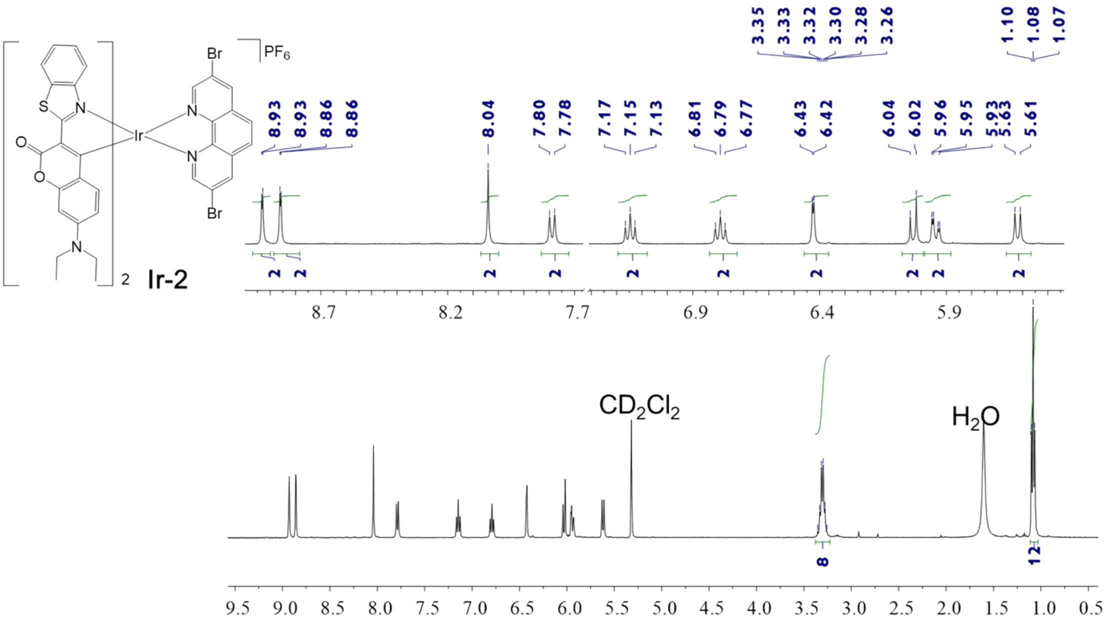

Figure S3. ^{1}H NMR spectrum of **Ir-2** (inset shows the expanded aromatic region).

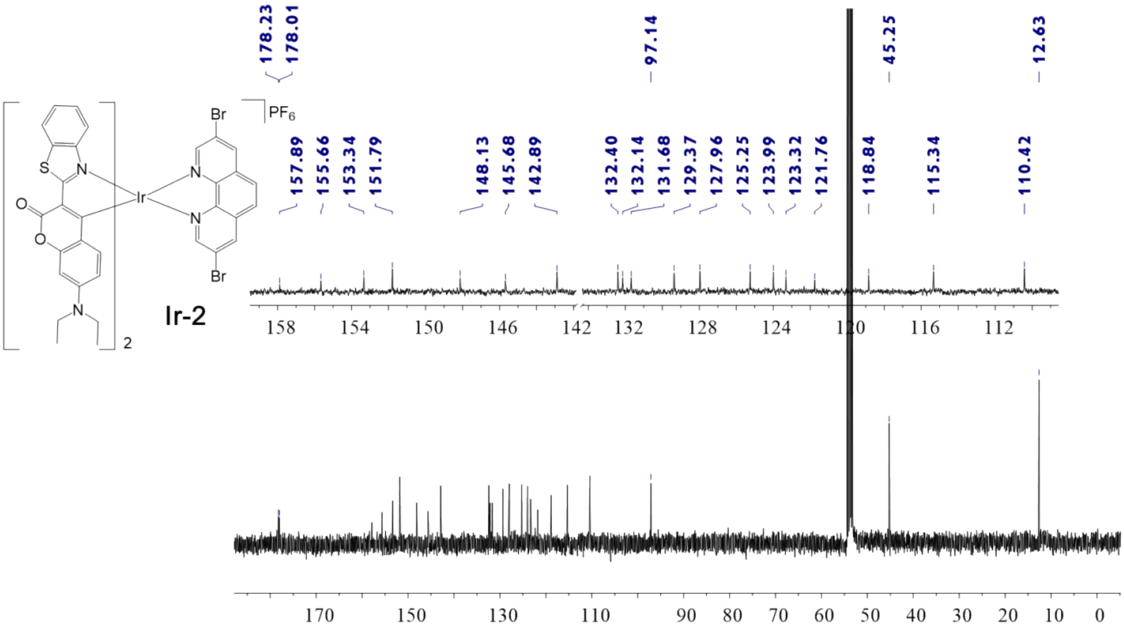

Figure S4. ^{13}C NMR spectrum of **Ir-2** (inset shows the expanded aromatic region).

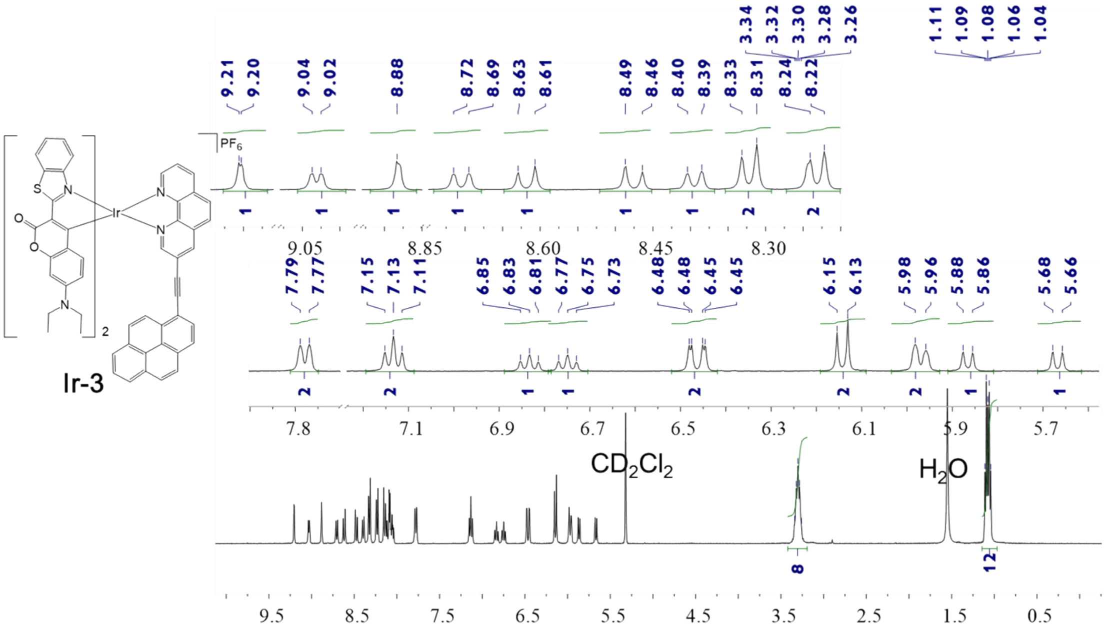

Figure S5. ^{1}H NMR spectrum of **Ir-3** (inset shows the expanded aromatic region).

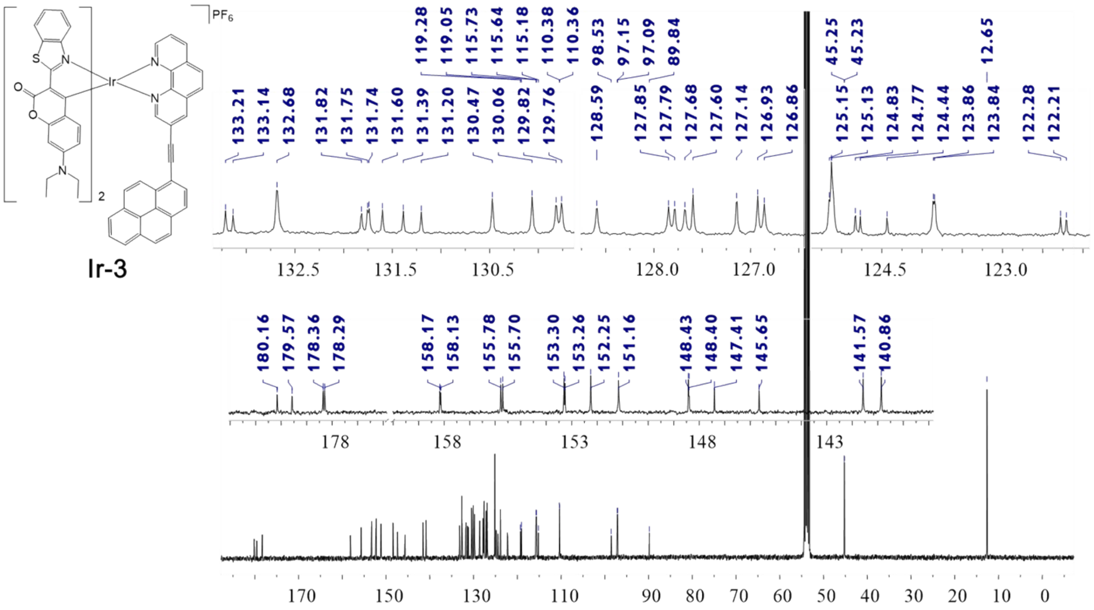

Figure S6. ^{13}C NMR spectrum of **Ir-3** (inset shows the expanded aromatic region).

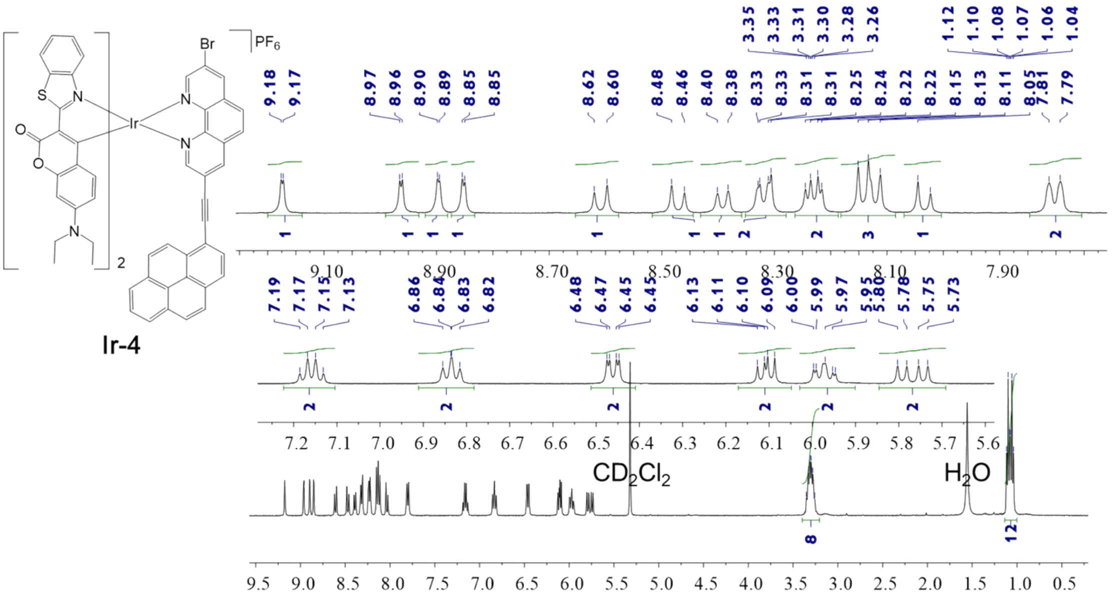

Figure S7. ^{1}H NMR spectrum of **Ir-4** (inset shows the expanded aromatic region).

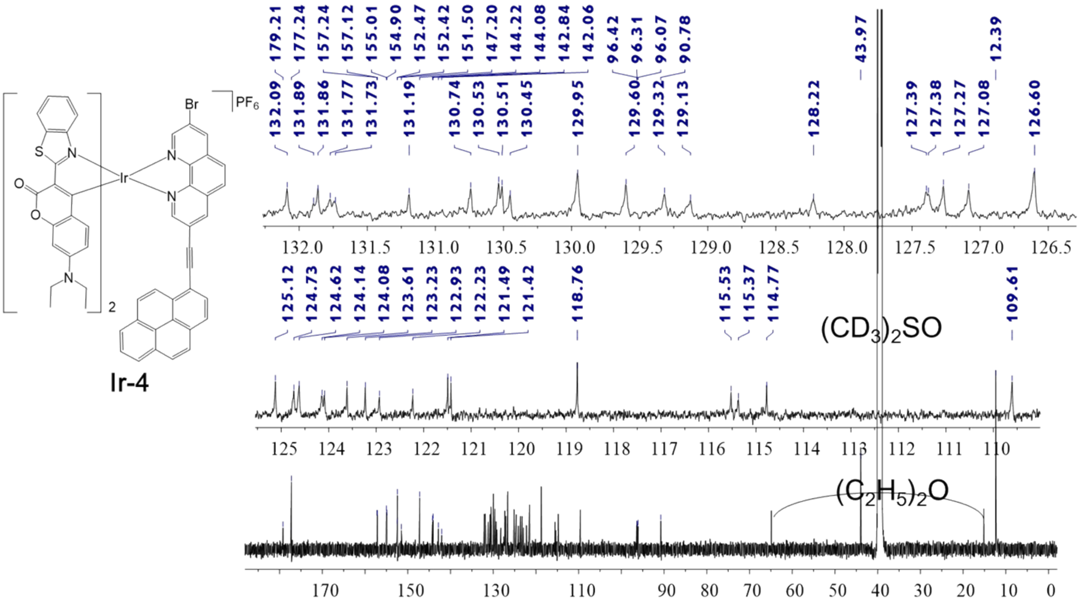

Figure S8. ^{13}C NMR spectrum of **Ir-4** (inset shows the expanded aromatic region).

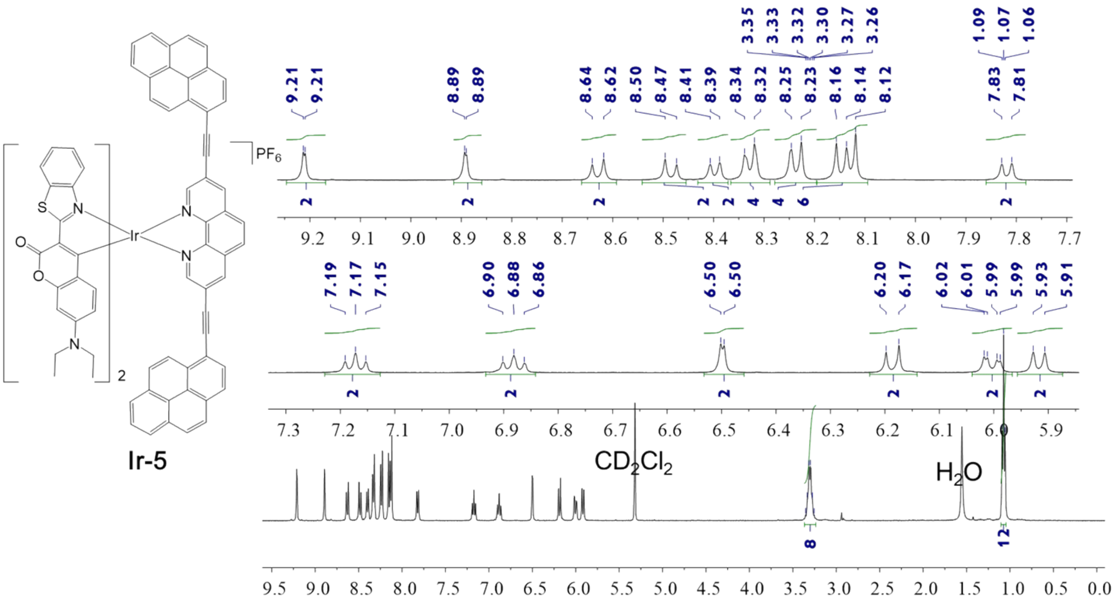

Figure S9. ^{1}H NMR spectrum of **Ir-5** (inset shows the expanded aromatic region).

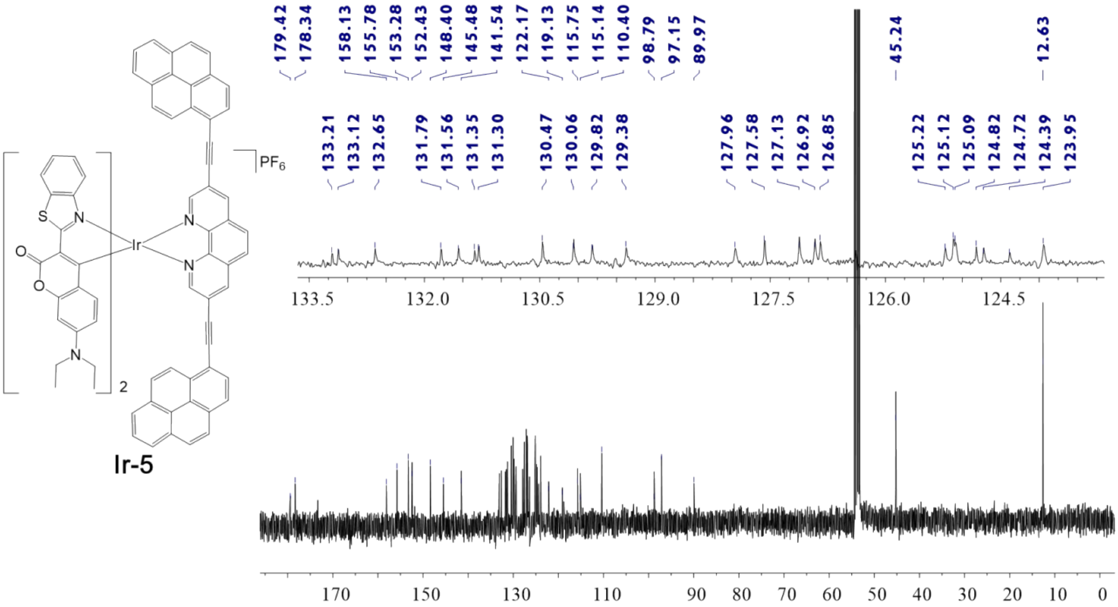

Figure S10. ^{13}C NMR spectrum of **Ir-5** (inset shows the expanded aromatic region).

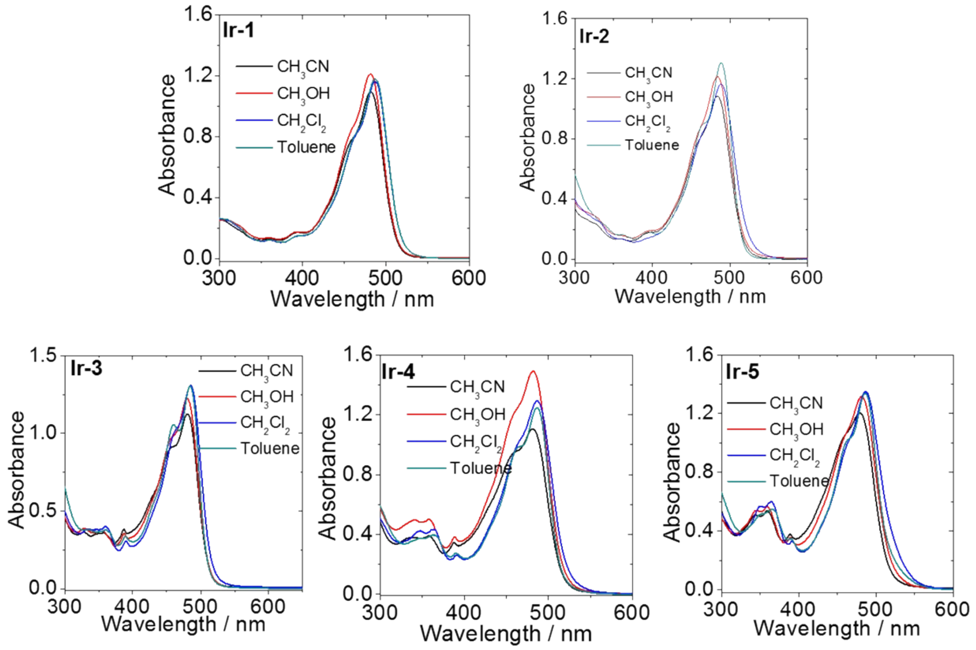

Figure S11. UV-vis absorption spectra of **Ir-1**–**Ir-5** in different solvents, c = 1 × 10^{-5} M, RT.

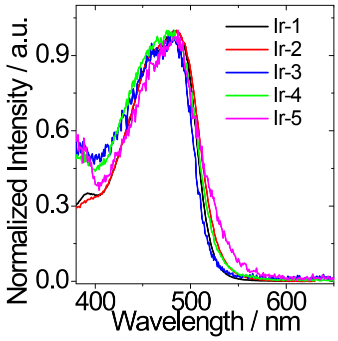

Figure S12. Normalised excitation spectra of **Ir-1**–**Ir-5**, c = 1 × 10^{-5} M, CH_2Cl_2, RT. **Ir-1**: λ_{em} = 640 nm; **Ir-2**: λ_{em} = 650 nm; **Ir-3**: λ_{em} = 680 nm; **Ir-4**: λ_{em} = 680 nm; **Ir-5**: λ_{em} = 690 nm.

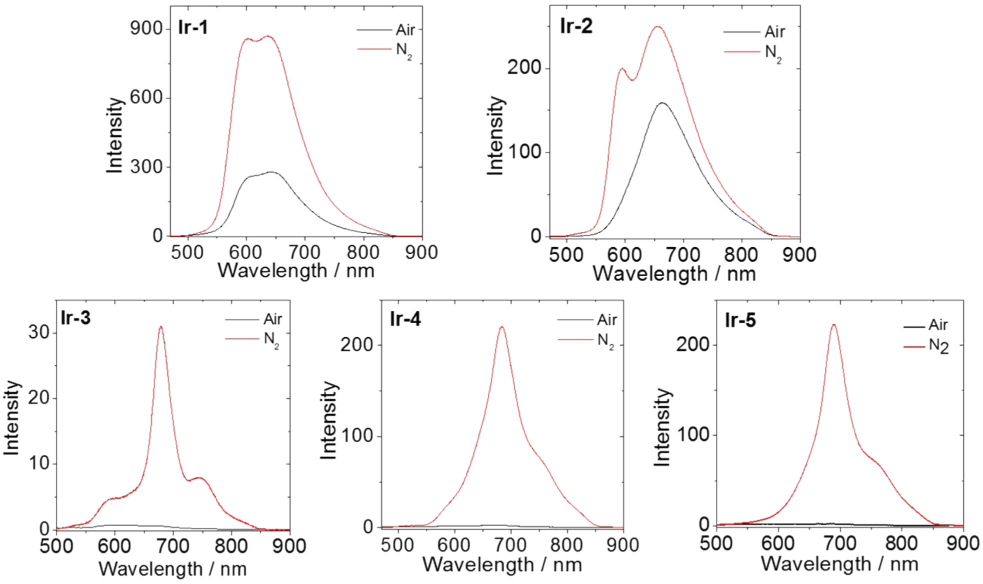

Figure S13. Emission spectra of **Ir-1**–**Ir-5** measured in the air and under N_2, in CH_2Cl_2, c = 1 × 10^{-5} M, RT.

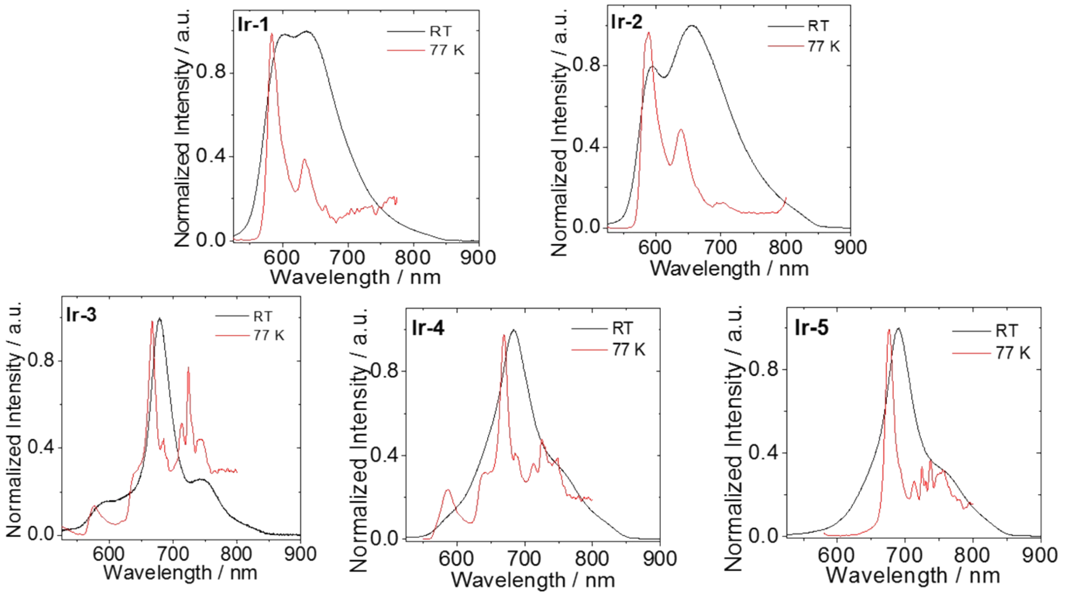

Figure S14. Photoluminescence spectra of **Ir-1**–**Ir-5** at RT and 77 K in CH_2Cl_2, c = 1 × 10^{-5} M.

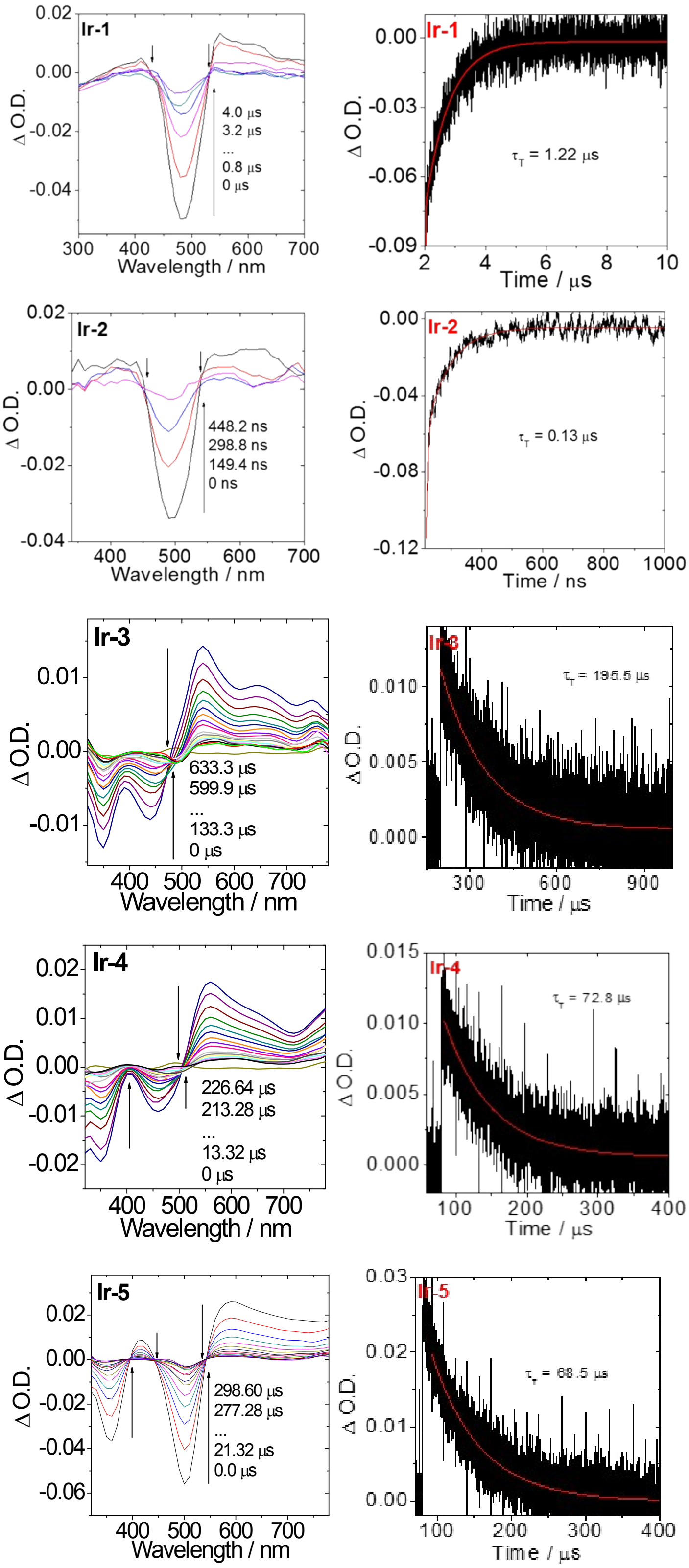

Figure S15. Nanosecond time-resolved transient difference absorption spectra (left) and decay traces of the triplet lifetimes (right) of **Ir-1** to **Ir-5**, **Ir-1** (λ_{ex}= 355 nm, λ_{em}= 486 nm), **Ir-2** (λ_{ex}= 355 nm, λ_{em}= 486 nm), **Ir-3** (λ_{ex} = 486 nm, λ_{em} = 690 nm), **Ir-4** (λ_{ex} = 486 nm, λ_{ex} = 684 nm) and **Ir-5** (λ_{ex} = 486 nm, λ_{ex} = 690 nm) in deaerated CH_2Cl_2, c = 1.0 × 10^{-5} M, RT.

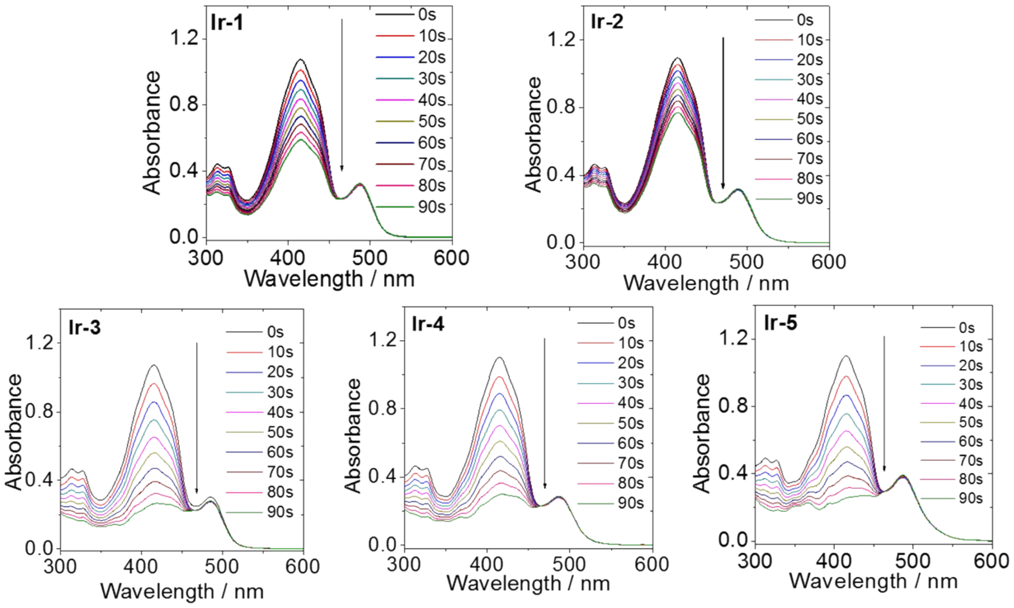

Figure S16. The absorption change of DPBF in the presence of the respective photosensitiser (**Ir-1**–**Ir-5**) after each irradiation. **Ir-1** (λ_{ex} = 461 nm), **Ir-2** (λ_{ex} = 461 nm), **Ir-3** (λ_{ex} = 464 nm), **Ir-4** (λ_{ex} = 461 nm) and **Ir-5** (λ_{ex} = 454 nm) at 10 second intervals for 90 seconds.

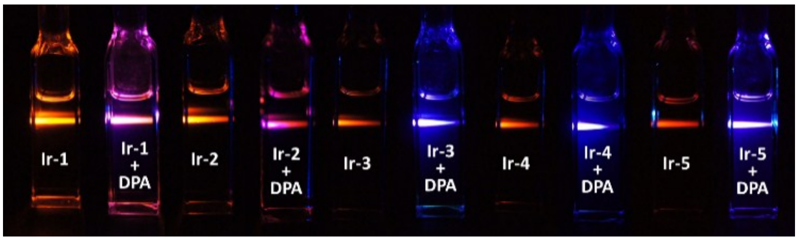

Figure S17. Photographs of the emissions of the triplet photosensitisers (**Ir-1**–**Ir-5**) alone, and with the triplet annihilator (DPA), in deaerated CH_2Cl_2, RT.

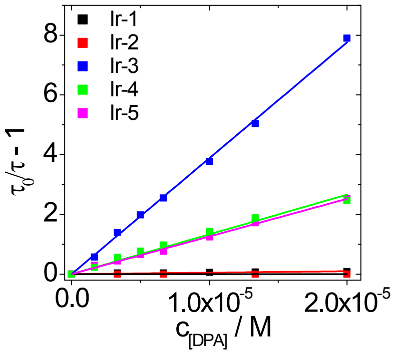

Figure S18. Stern-Volmer plots generated from the quenching of the lifetime of **Ir-1**–**Ir-5** (λ_{ex} = 486 nm) measured as a function of DPA (triplet quencher) concentration. [complex] = 1.0 × 10^{-5} M, in deaerated CH_2Cl_2, RT.

References

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