Electronic Supplementary Information for:

Visible light-harvesting cyclometalated Ir(III) complexes as triplet photosensitizers for triplet-triplet annihilation based upconversion

Lihua Ma, Huimin Guo, Qiuting Li, Song Guo and Jianzhang Zhao**

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology,
E-208 West Campus, 2 Ling-Gong Road, Dalian 116012, P.R. China.
zhaojzh@dlut.edu.cn (J.Z.), guohm@dlut.edu.cn (H.G.);
web: http://finechem.dlut.edu.cn/photochem

Index

1.0 General.

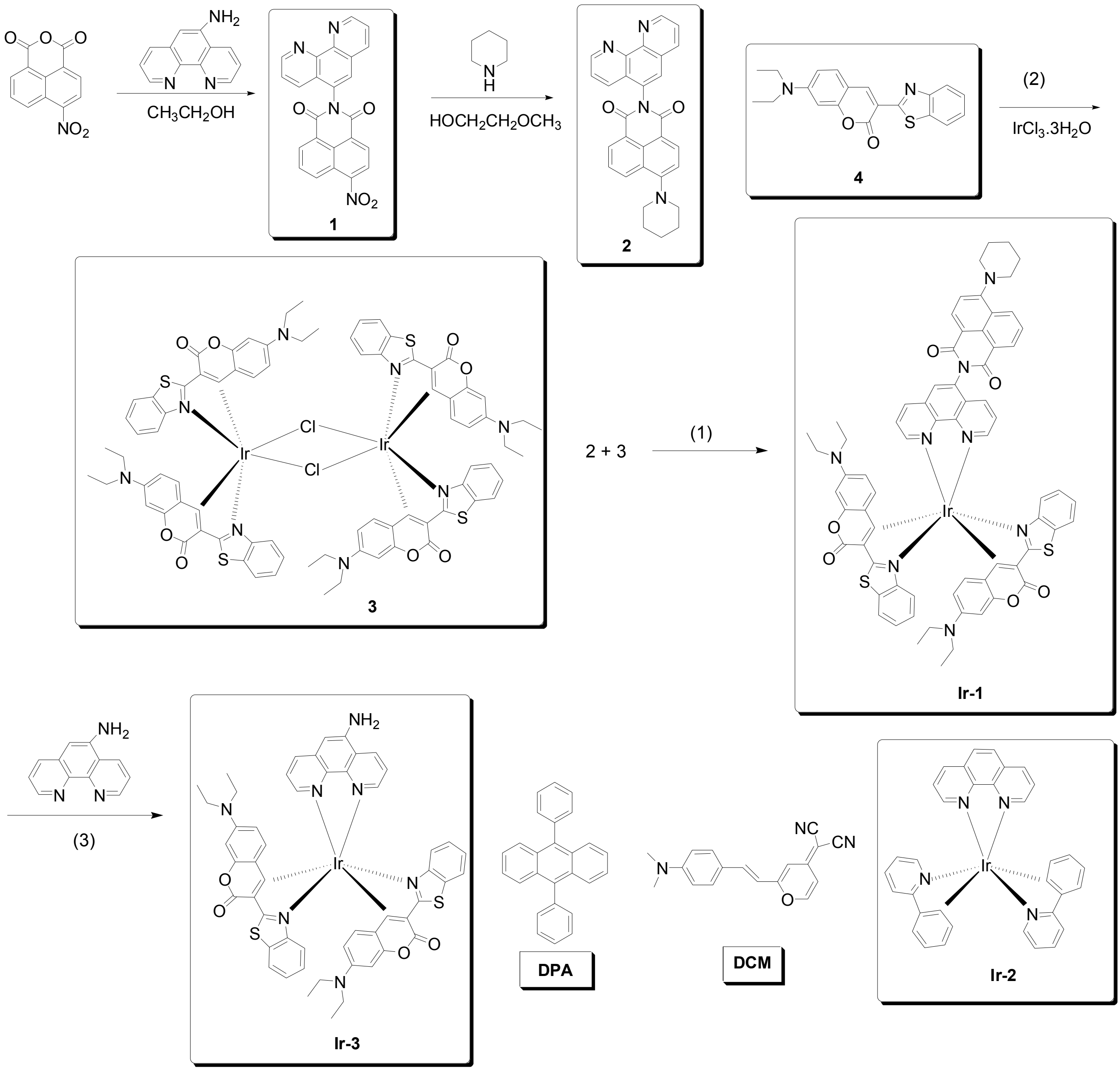
All the chemicals used in synthesis are analytical pure and were used as received. Solvents were dried and distilled before used for synthesis. Phosphorescence quantum yields were measured with DCM as the standard ($\Phi_F = 0.10$ in CH_2Cl_2). All the data were independently measured for three times (with different solutions samples). phosphorescence lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument. The nanosecond time-resolved transient absorption spectra were detected by Edinburgh analytical instruments (LP900, Edinburgh Instruments, 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. All samples in flash photolysis experiments were deaerated with argon for ca. 15 min before measurement and the gas flow is kept during the measurement. The upconversion quantum yields (Φ_{UC}) of **Ir-1**, **Ir-2** and **Ir-3** were determined with the prompt fluorescence of **DCM** as the standard. The upconversion quantum yields were calculated with the following equation, where Φ_{UC}, *A*unk, *I*unk and ηunk represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the samples and the solvents (**Eq. 1**). The equation is multiplied by factor 2 in order to make the maximum quantum yield to be unity. All these data were independently measured for three times (with different solutions samples).

$$\Phi_{\mathrm{UC}} = 2\Phi_{\mathrm{std}}\left(\frac{F_{\mathrm{std}}}{F_{\mathrm{unk}}}\right)\left(\frac{I_{\mathrm{unk}}}{I_{\mathrm{std}}}\right)\left(\frac{\eta_{\mathrm{unk}}}{\eta_{\mathrm{std}}}\right)^2 \qquad \textbf{(Eq. 1)}$$

For the measurement of the TTET efficiency, i.e. the Stern-Volmer quenching constants, the concentration of the sensitizer was fixed at 1.0×10^{-5} M, the lifetime of the sensitizer was measured with increasing the DPA concentration in the solution.

For the upconversion experiments, the mixed solution of the complex (triplet sensitizer) and DPA (triplet acceptor) was degassed for at least 15 min with N_2 or Ar. Then the solution was excited with laser. The upconverted fluorescence of DPA was observed with spectrofluorometer. In order to repress the scattered laser, a black box with a small hole on it was put behind the fluorescent cell to trap the laser beam behind the vial (the small hole as the entrance of the laser into the black box). The CIE coordinates (*x*, y) of the emission of the sensitizers alone and the emission of the upconversion were derived from the emission spectra with the software of CIE color Matching Linear Algebra. The density functional theory (DFT) calculations were used for optimization of the ground state geometries, for both singlet states and triplet states. The energy level of the T_1 state (energy gap between S_0 state and T_1 state) were calculated with the time-dependent DFT (TDDFT), based on the optimized triplet state geometries. These TDDFT calculations were used for the prediction of the UV-vis absorption of the T_1 state of the organic triplet sensitizers, in our case it is the transient absorption of the organic triplet sensitizers after the laser flash (the pulsed excitation of the organic triplet sensitizer solution). Please note that the bleaching bands in the time-resolved transient absorption spectra can not be predicted by the TDDFT calculations. All the calculations were performed with Gaussian 09.

2.0 Synthesis and molecular structural characterization data



Scheme S1. Synthesis of the triplet sensitizers **Ir-1** and **Ir-3**. The known compound **Ir-2** were prepared for comparison. Reagents and conditions: 1) CH_3CH_2OH/CH_2Cl_2 (1:2, v/v), reflux, 6 h; 2) 2-ethoxyethanol and water, reflux, 24 h; 3) CH_3CH_2OH/CH_2Cl_2 (1:2, v/v), reflux, 6 h.

3.0 NMR and HR-MS spectra

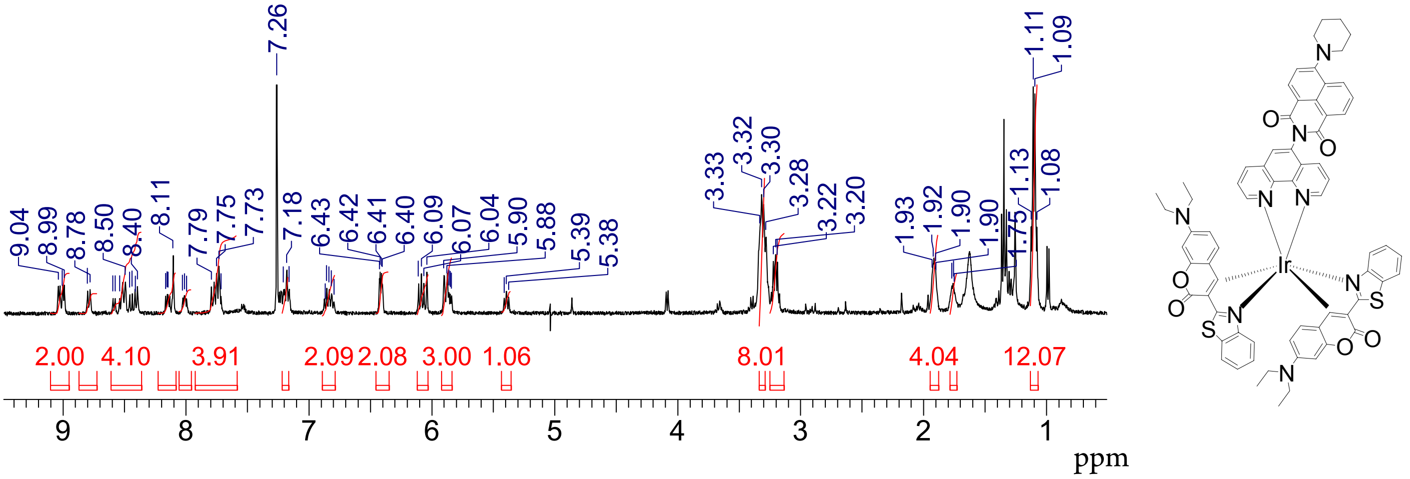


Figure S1. ^{1}H NMR of **Ir-1** (400 MHz, $CDCl_3$).

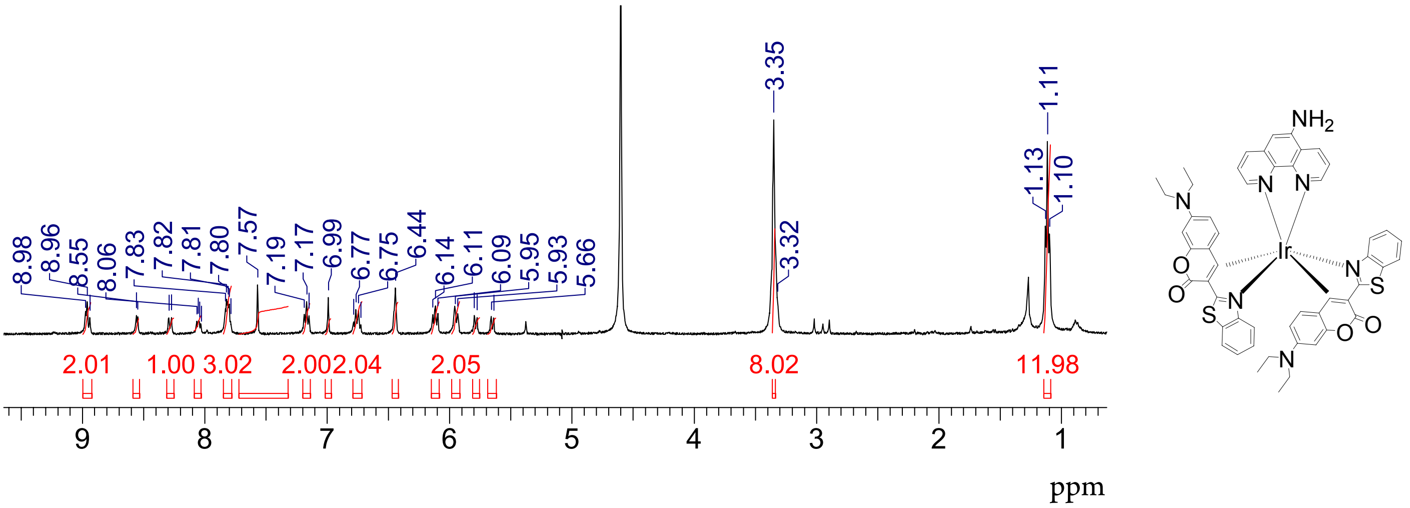


Figure S2. ^{1}H NMR of **Ir-3** (400 MHz, $CDCl_3$).

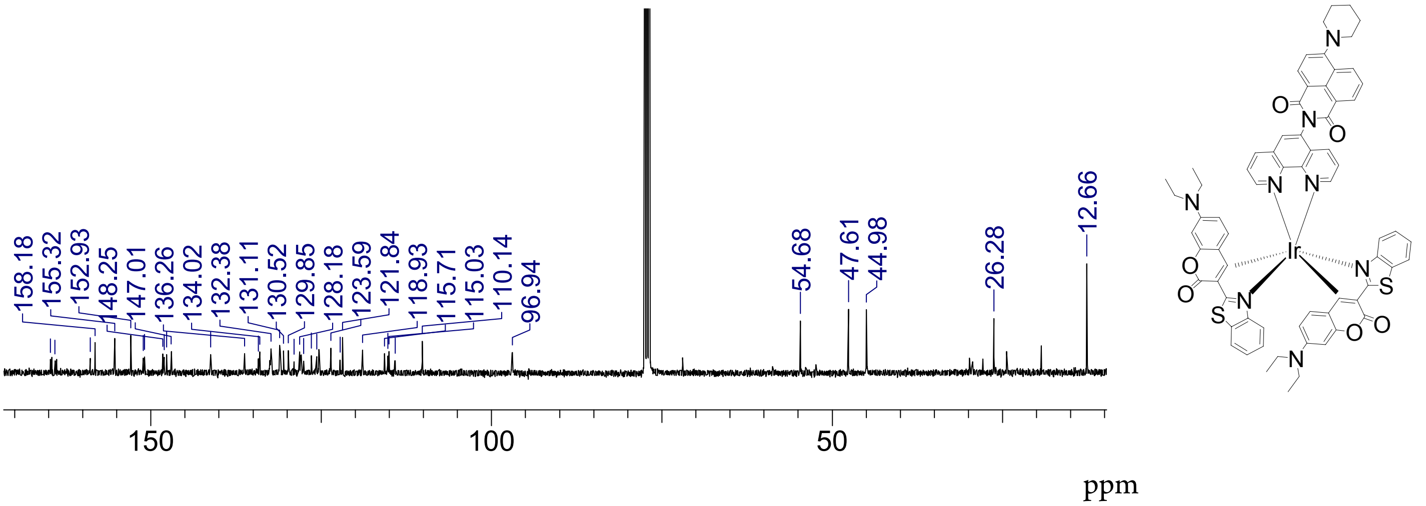


Figure S3. ^{13}C NMR of **Ir-1** (100 MHz, $CDCl_3$)

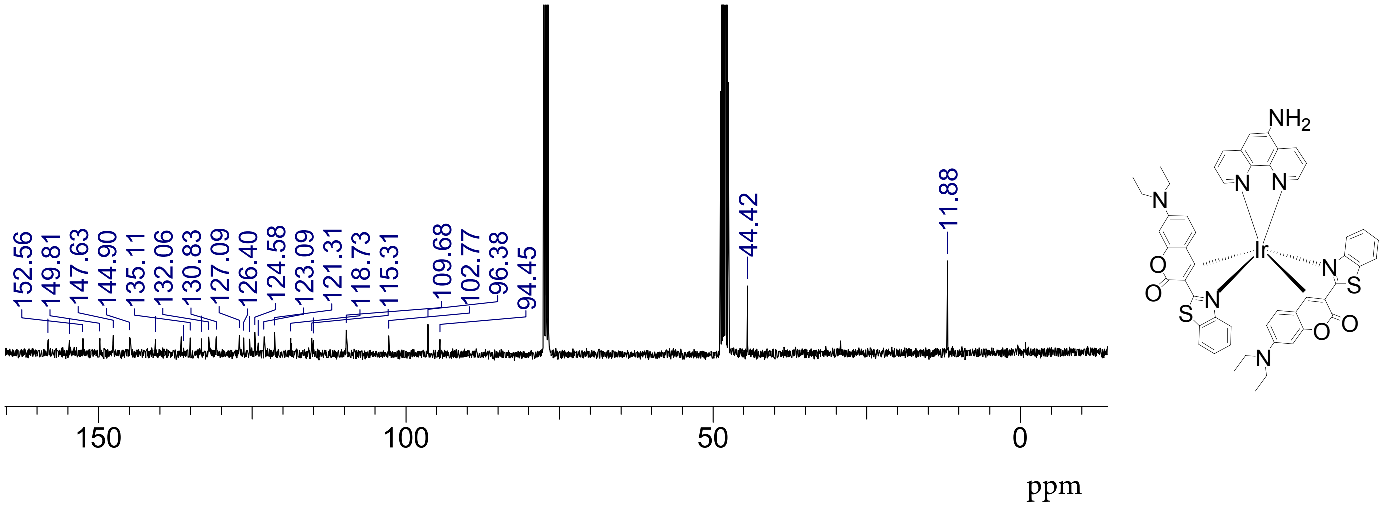


Figure S4. ^{13}C NMR of **Ir-3** (100 MHz, $CDCl_3$)

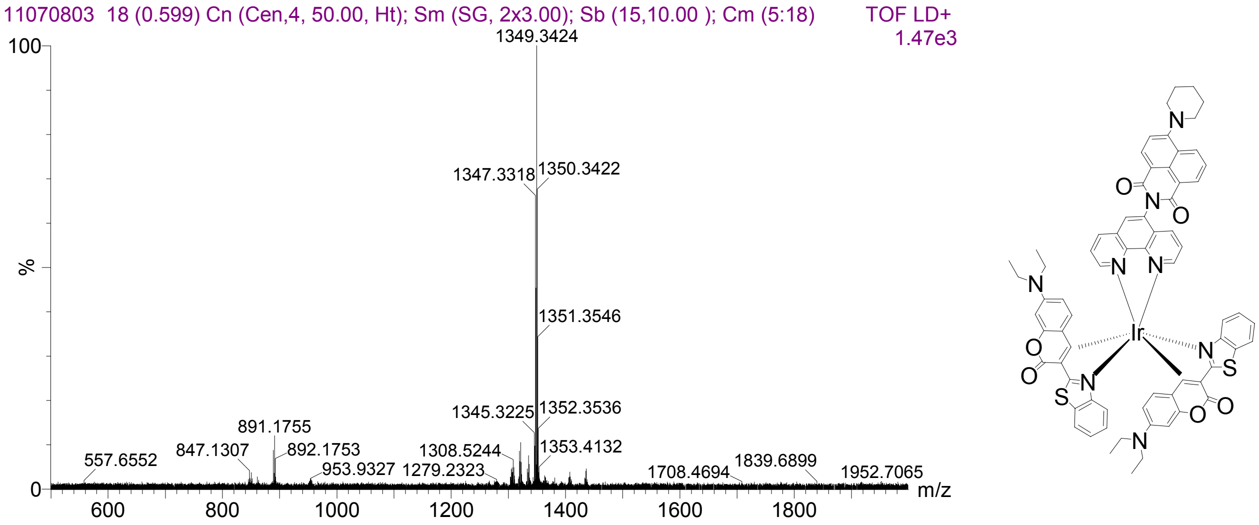


Figure S5. TOF HRMS ESI of **Ir-1**.

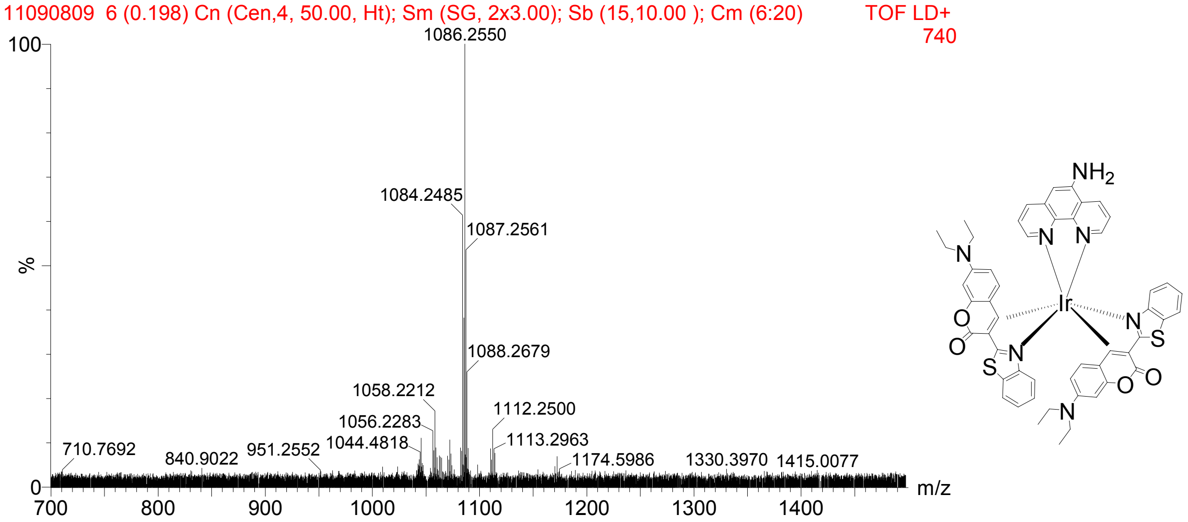


Figure S6. TOF HRMS ESI of **Ir-3**.

4.0 Up-conversion details.

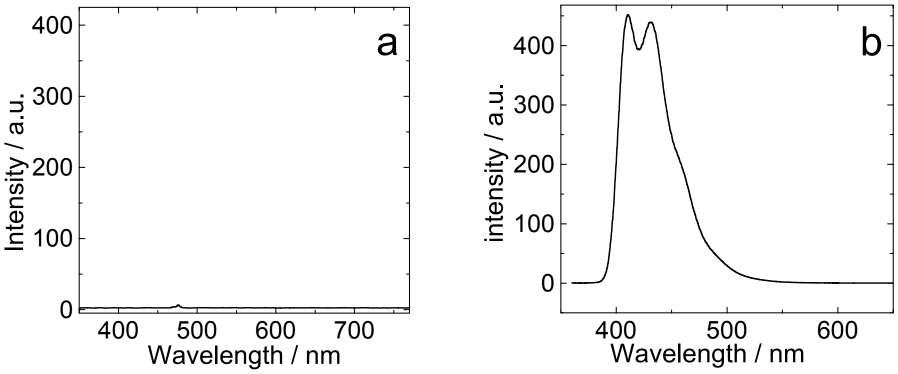


Figure S7. (a) Emission of DPA with irradiation (λ_{ex} = 532 nm 5mW). (b) Fluorescence emission of DPA (λ_{ex} = 350 nm). *c* = 1.0×10^{-5} M in CH_2Cl_2, 20°C.

5.0 Lifetime and Emission in RT and 77 K.

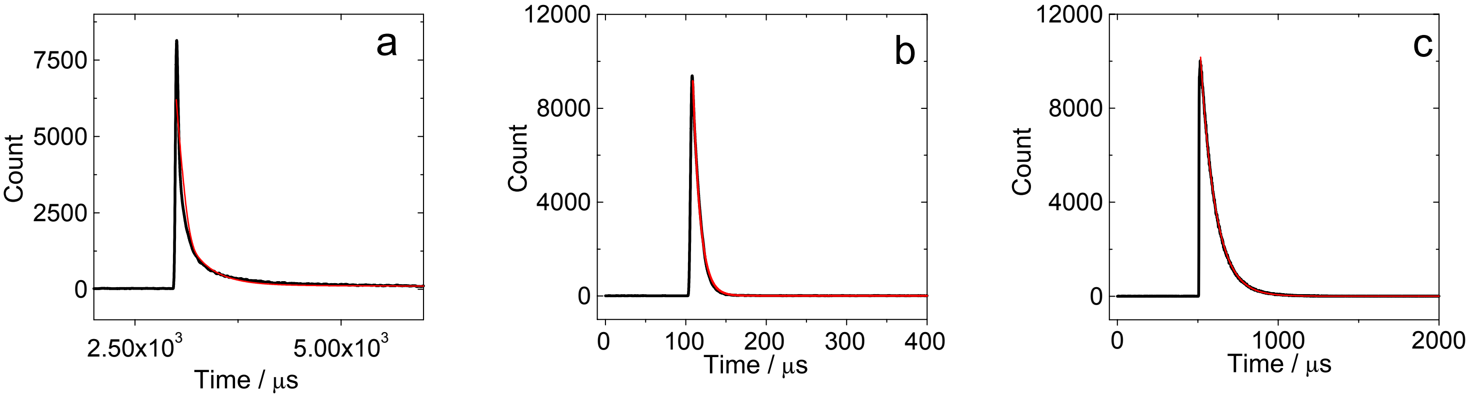


Figure S8. lifetimes of (a) **Ir-1** (λ_{ex} = 483 nm, τ_T = 3690 µs), (b) **Ir-2** (λ_{ex} = 400 nm, τ_T = 15 µs), (c) **Ir-3** (λ_{ex} = 470 nm, τ_T = 96 µs), $c = 1.0\times10^{-5}$ M, 77 K (in EtOH–MeOH, 4 : 1, v/v).

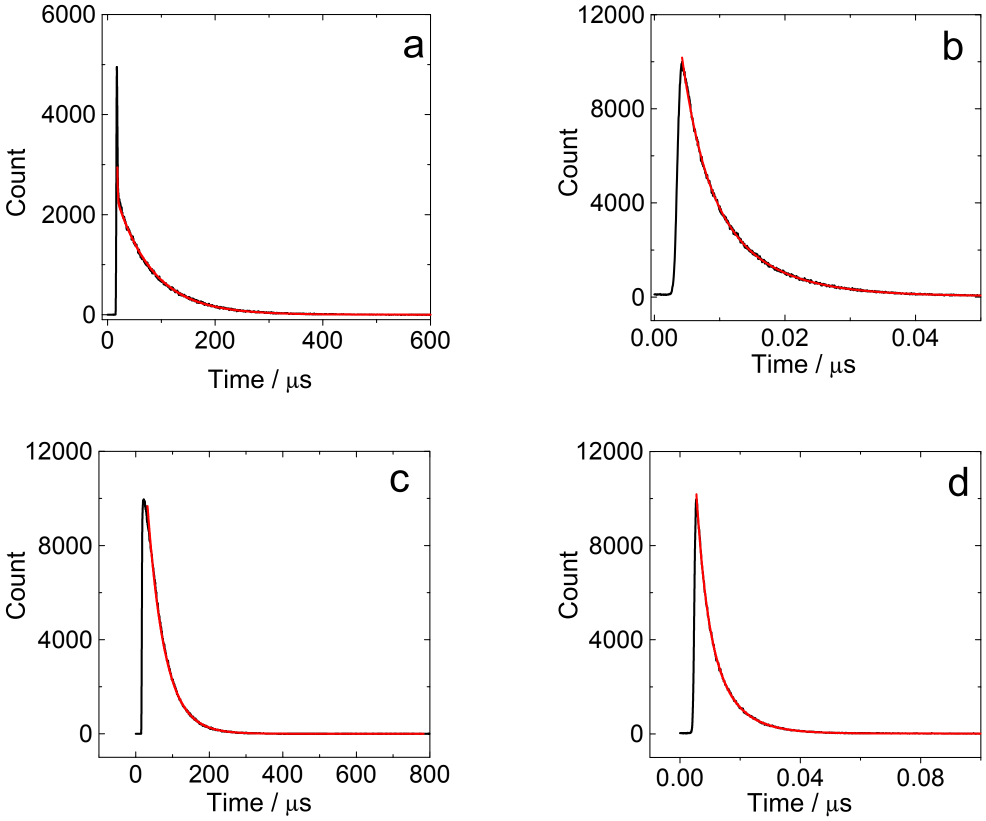


Figure S9. Lifetimes of (a) **Ir-1** (λ_{ex} = 483 nm, τ_T = 68.7, 0.86 µs), (b) **Ir-2** (λ_{ex} = 400 nm, τ_T = 1.0 µs), (c) **Ir-3** (λ_{ex} = 470 nm, τ_T = 46.7 µs) and (d) compound 2 (λ_{ex} = 418 nm, τ = 3.39 ns), $c = 1.0\times10^{-5}$ M in CH_2Cl_2, 20°C.

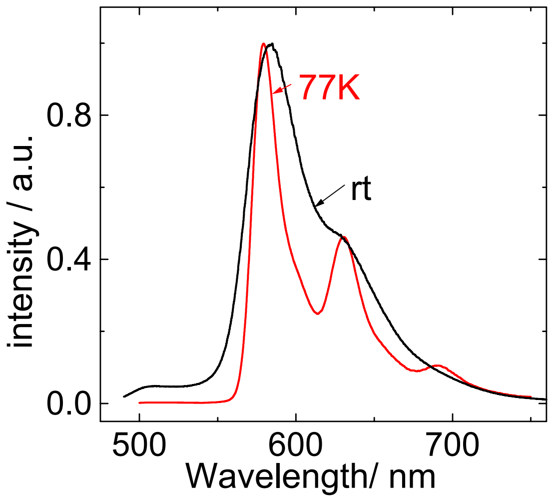


Figure S10. Photoluminescence spectra of **Ir-3** at RT (in CH_2Cl_2) and 77 K (in EtOH–MeOH, 4 : 1, v/v).

6.0 Transient absorption details

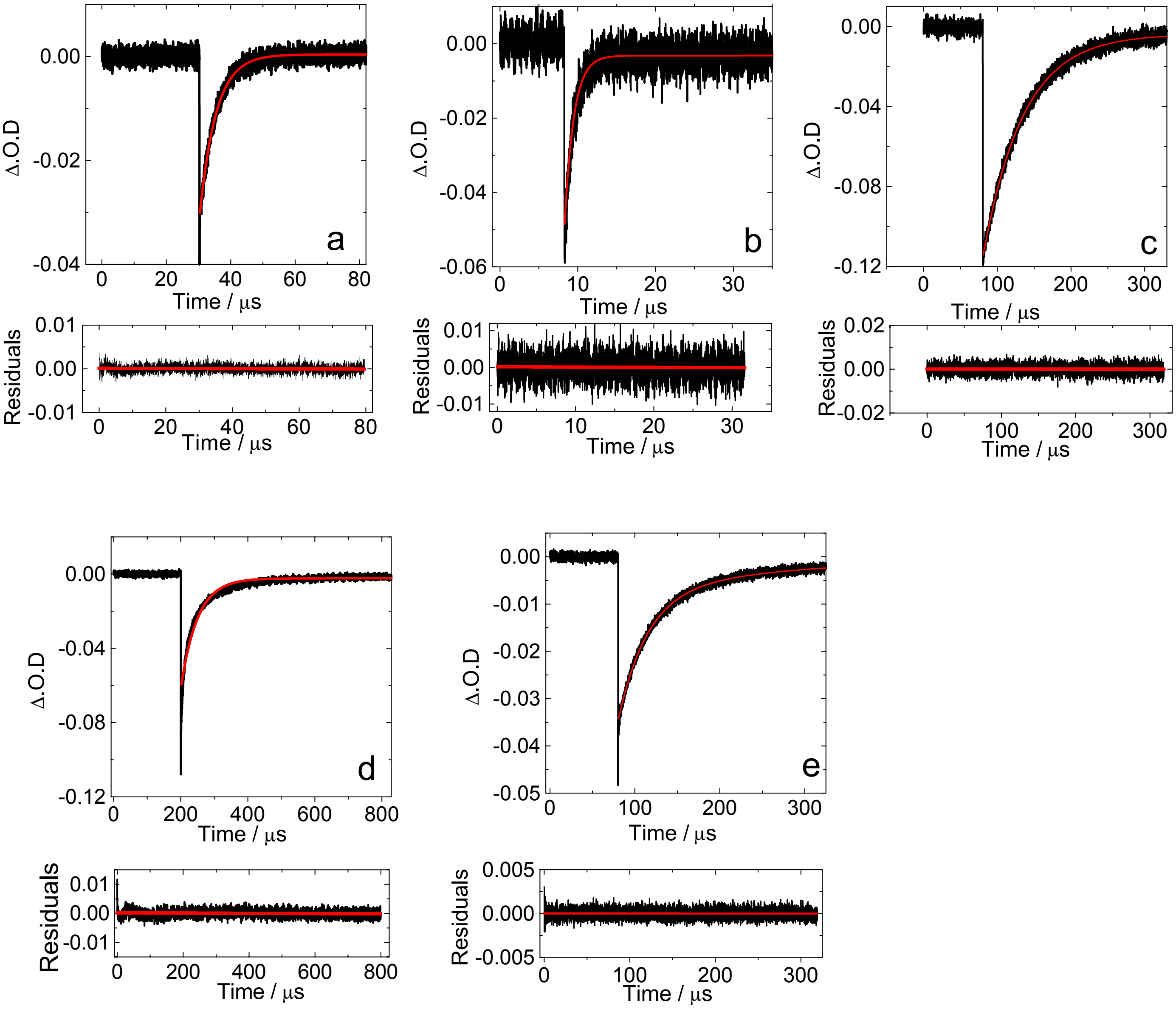


Figure S11. Nanosecond time-resolved transient absorption decay trace (a) Complex **Ir-1** at 490 nm. 20 °C. In deaerated CH_2Cl_2 after pulsed excitation at 532 nm in deaerated CH_2Cl_2. (b) Complex **Ir-2** at 310 nm. 20 °C. In deaerated CH_2Cl_2 after pulsed excitation at 355 nm. (c) Complex **Ir-3** at 490 nm. 20 °C. In deaerated CH_2Cl_2 after pulsed excitation at 532 nm. (d) Compound TPP at 416 nm. 20 °C. In deaerated CH_2Cl_2 after pulsed excitation at 355 nm. (e) Compound MB at 295 nm. 20 °C. In deaerated CH_2Cl_2 after pulsed excitation at 355 nm.

7.0 Stability of the Ir(III) complexes with irradiation by the a 35 W Xenon lamp

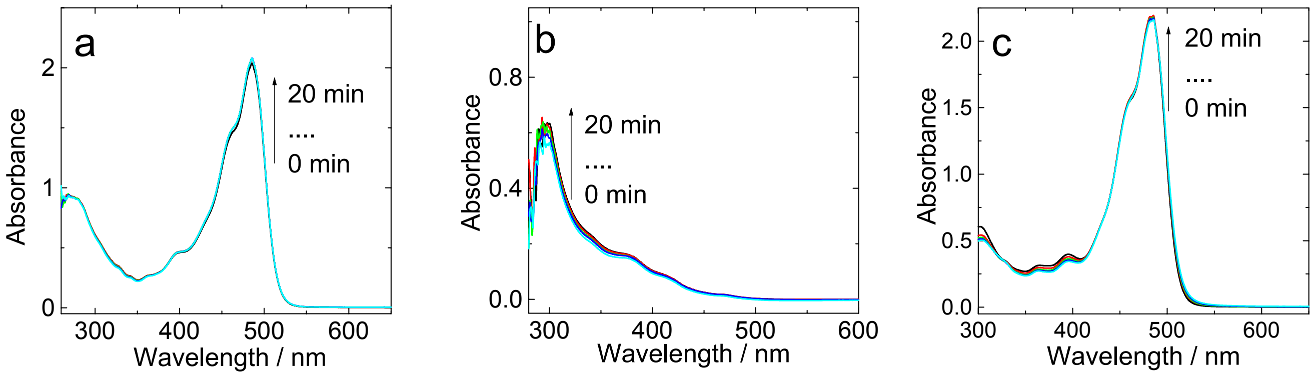


Figure S12. UV-vis absorption spectra of the sensitizers **Ir-1**, **Ir-2** and **Ir-3** (in DMSO) before and after the irradiation (150 mW cm^{-2}) by a 35 W Xenon lamp. 1.0×10^{-5} M. 20 °C.

8.0 Excitation, Absorbance and phosphorescence spectra

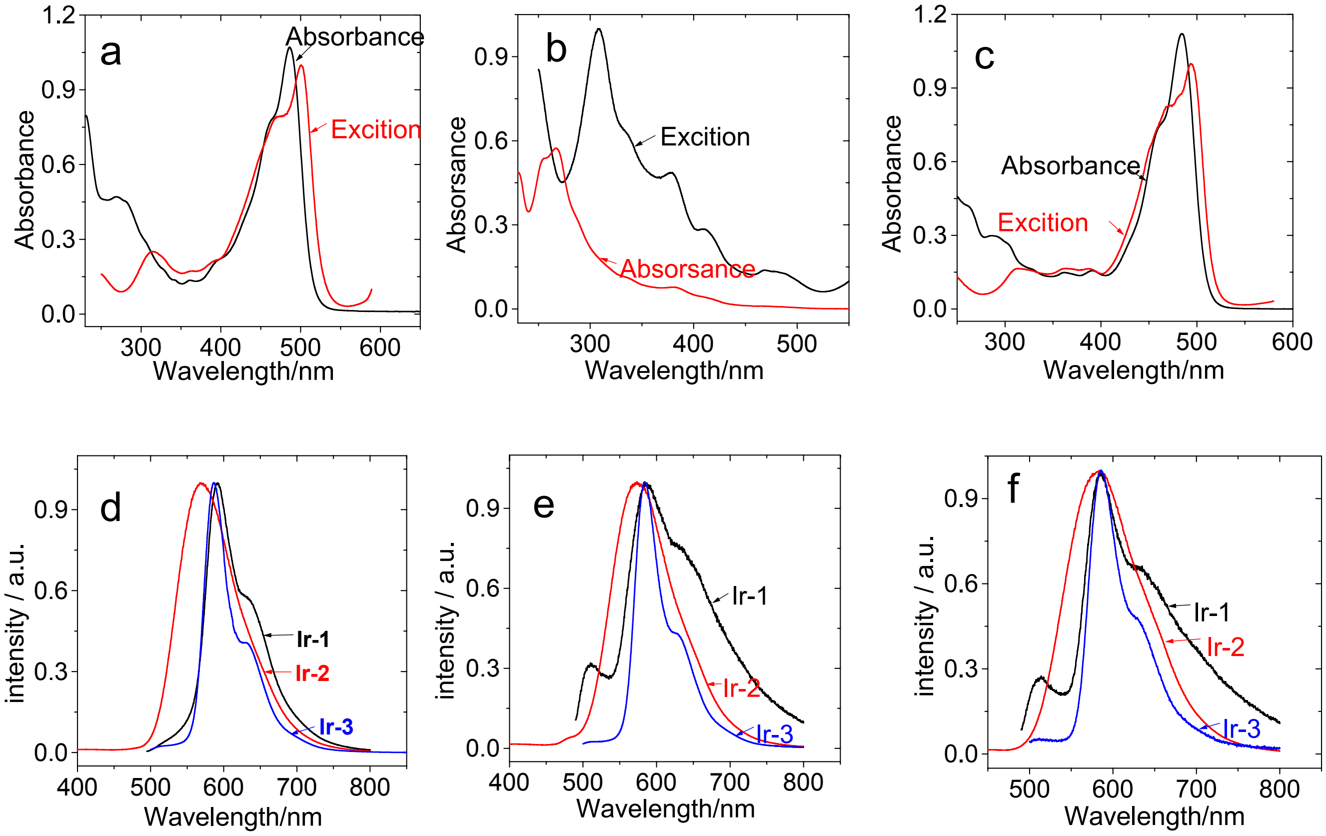


Figure S13. Excitation and Absorbance Spectra of (a) **Ir-1**, (b) **Ir-2** and (c) **Ir-3** in CH_2Cl_2; 1×10^{-5} mol/L, 20°C. Emission spectra of **Ir-1**, **Ir-2**, and **Ir-3** in (d) CH_2Cl_2, (e) CH_3OH and (f) CH_3CN respectively.

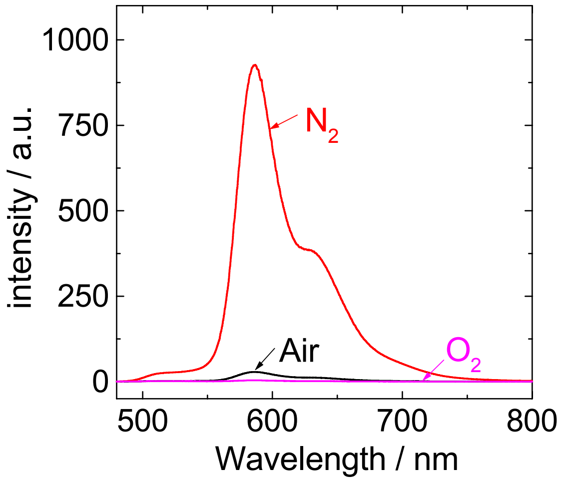


Figure S14. Emission spectra of **Ir-3** (λ_{ex} = 483 nm) in CH_2Cl_2 saturated with air, O_2 and N_2. $c = 1.0\times10^{-5}$ M. 20°C.

9.0 Delayed fluorescence

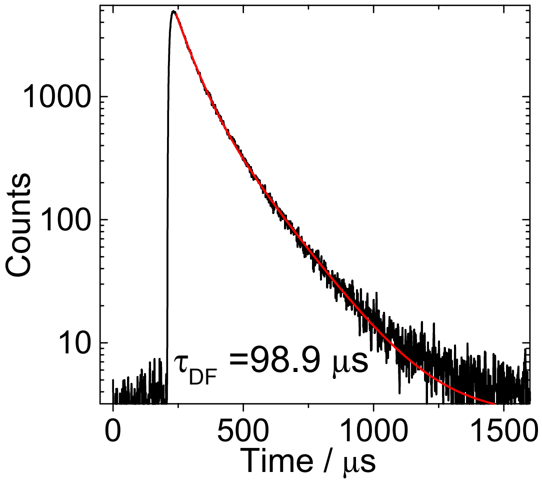


Figure S15. Delayed fluorescence observed in the TTA upconversion with compound **Ir-3**, as triplet photosensitizer and DPA as the triplet acceptor. Excited at 473 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 410 nm respectively. Under this circumstance the compound **Ir-3** is selectively excited and the emission is due to the upconverted emission of DPA. In deaerated CH_2Cl_2. *c*[Sensitizers] = 1.0×10^{-5} M; *c* [DPA] = 4.0×10^{-4} M; 20 °C.