Electronic Supplementary Information for:

Exploit the Benefit of $S_0 \rightarrow T_1$ Excitation in Triplet-Triplet Annihilation Upconversion to Attain Large Anti-Stokes Shifts: Tuning the Triplet State Lifetime of a Tris(2,2'-Bipyridine) Osmium(II) Complex

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1. General

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

Φ_Δ value of the triplet photosensitizers were measured with Rose Bangle (Φ_Δ = 0.8 in MeOH) as standard. Quantum yields for singlet oxygen generation in CH_3CN were determined by monitoring the photooxidation of 1,3-diphenylisobenzofuran (DPBF) sensitized by the Pt(II) complexes. 1,3-Diphenylisobenzofuran (DPBF) was used as the $^1O_2$ scavenger, due to its fast reaction with $^1O_2$. The absorbance of DPBF was adjusted to around 1.0 at 410 nm in air saturated CH_3CN. Then, the photosensitizer was added to cuvette and photosensitizer's absorbance was adjusted to around 0.2−0.3. Then, the cuvette was exposed to monochromatic light at the specific wavelength for 20 seconds depending on the efficiency of the triplet photosensitizers. The photosensitizer and RB were irradiated at the same wavelength. Absorbance was measured six times after each irradiation. Then, the slope of the curves of absorbance maxima of DPBF at 410 nm versus irradiation time for each photosensitizer were calculated. Singlet oxygen quantum yield (Φ_Δ) were calculated according to the equation (eqn (1)):

$$\Phi_{\Delta sam} = \Phi_{\Delta \mathrm{std}} \left(\frac{m_{\mathrm{sam}}}{m_{\mathrm{std}}} \right) \left(\frac{F_{\mathrm{std}}}{F_{\mathrm{sam}}} \right) \qquad \text{(eqn } \mathbf{1}\text{)}$$

where "sam" and "std" designate the "Os(II) photosensitizers" and "RB", respectively. "*m*" is the slope of difference in change in absorbance of DPBF (at 410 nm) with the irradiation time, "*F*" is the absorption correction factor, which is given by $F = 1 - 10^{-OD}$ (OD is the absorbance at the irradiation wavelength).

2. NMR and HR MS spectra

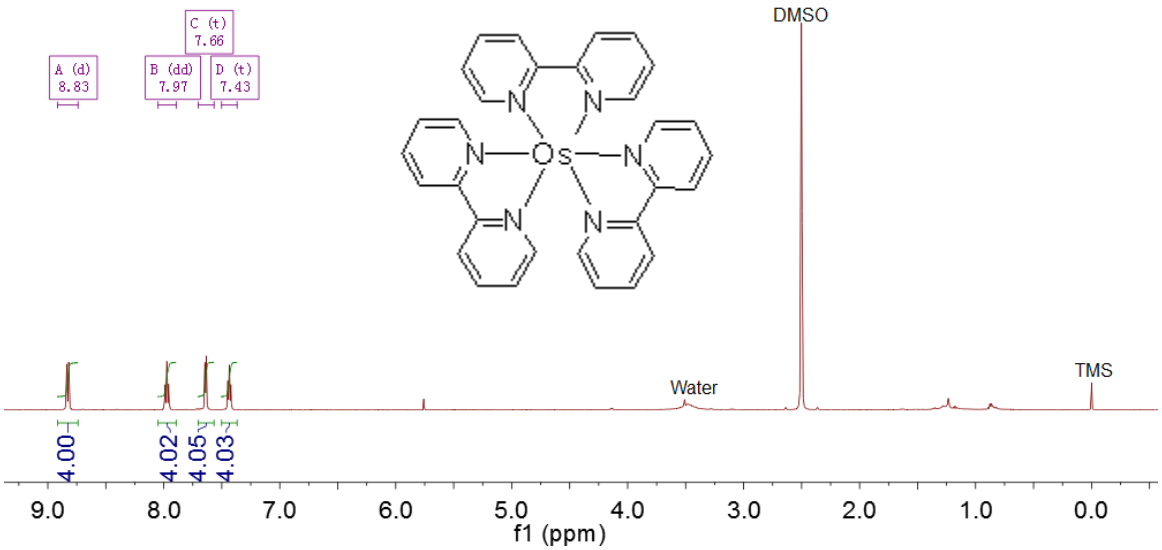

Fig. S1 ^{1}H NMR (400 MHz, d_6-DMSO) of complex **Os(bpy)$_3$**.

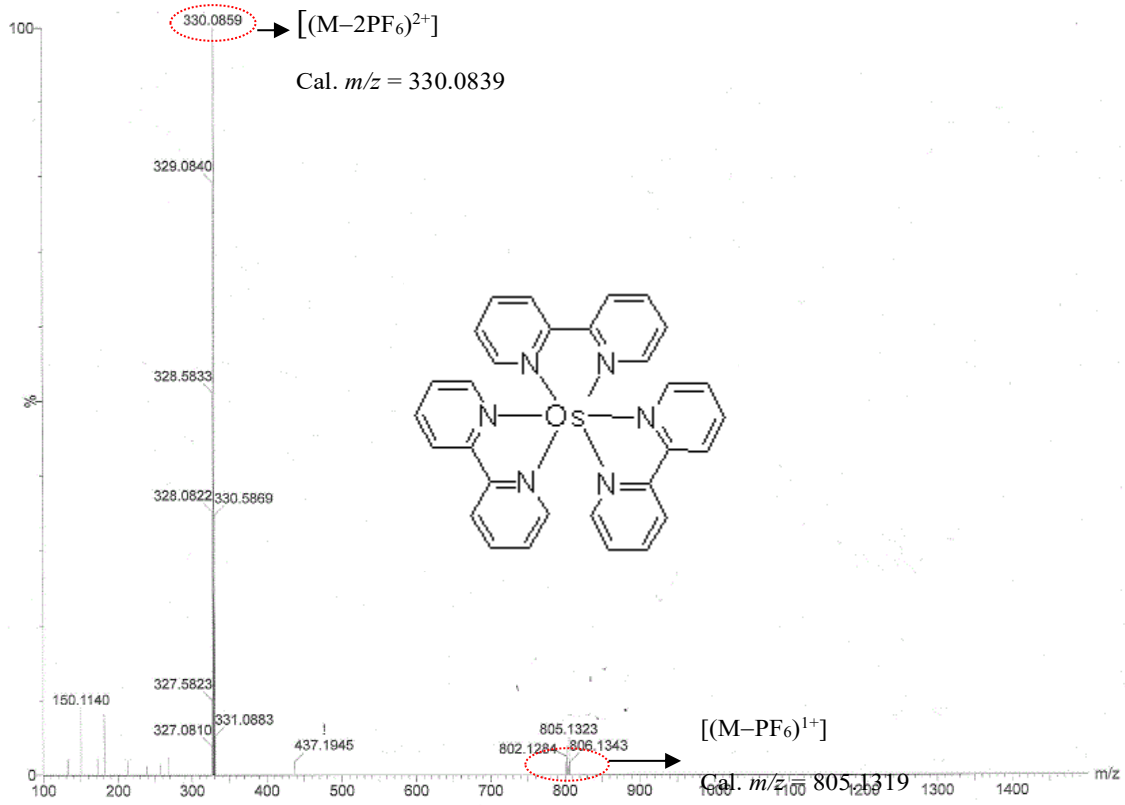

Fig. S2 TOF ES+ HRMS of complex **Os(bpy)$_3$**.

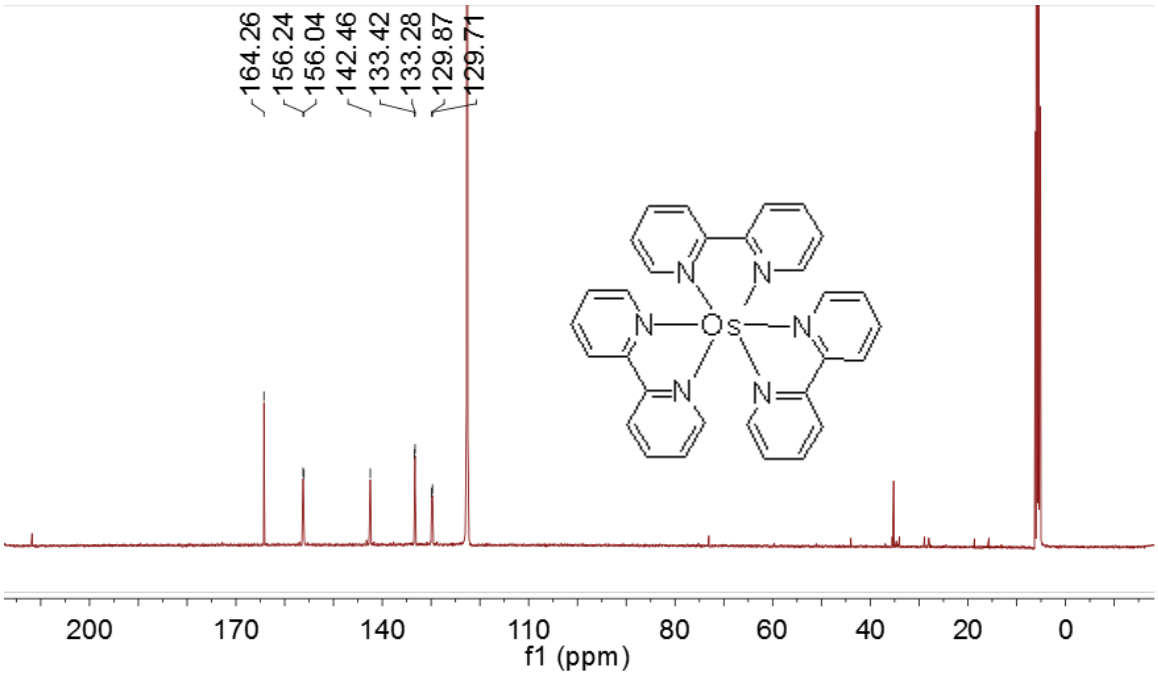

Fig. S3 ^{13}C NMR (100 MHz, CD_3CN) of complex **Os(bpy)$_3$**.

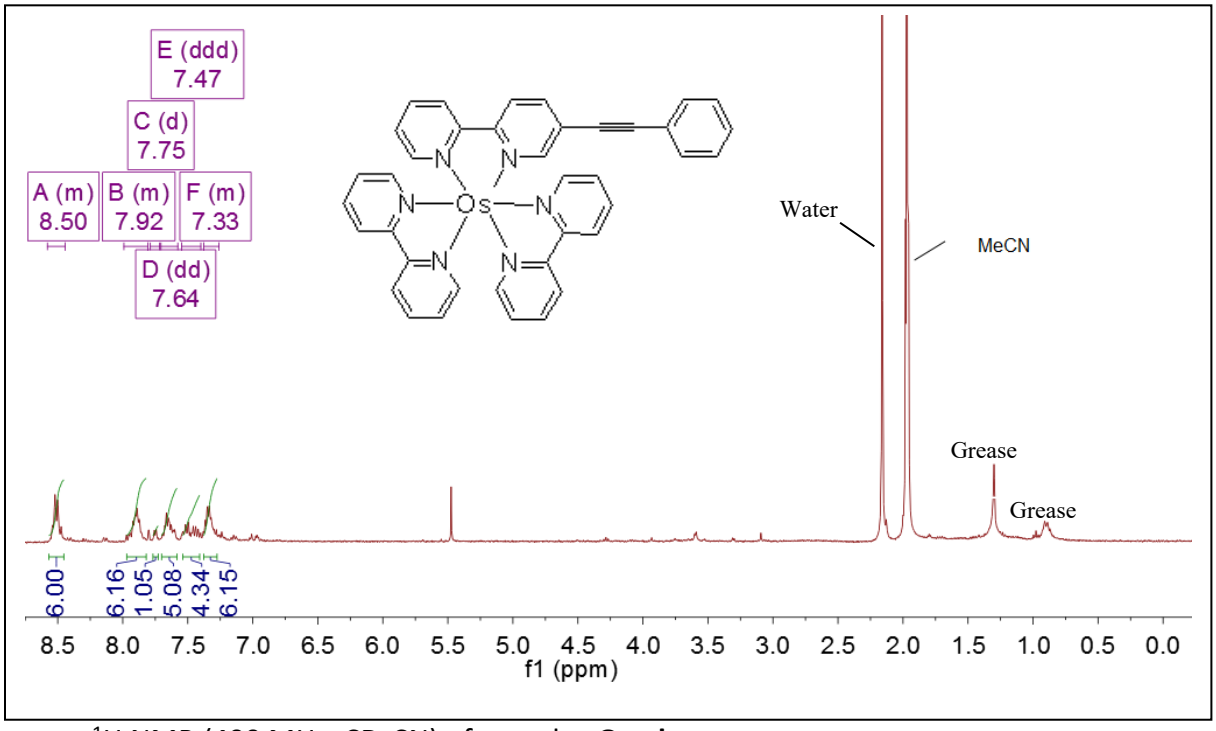

Fig. S4 ^{1}H NMR (400 MHz, CD_3CN) of complex **Os-ph**.

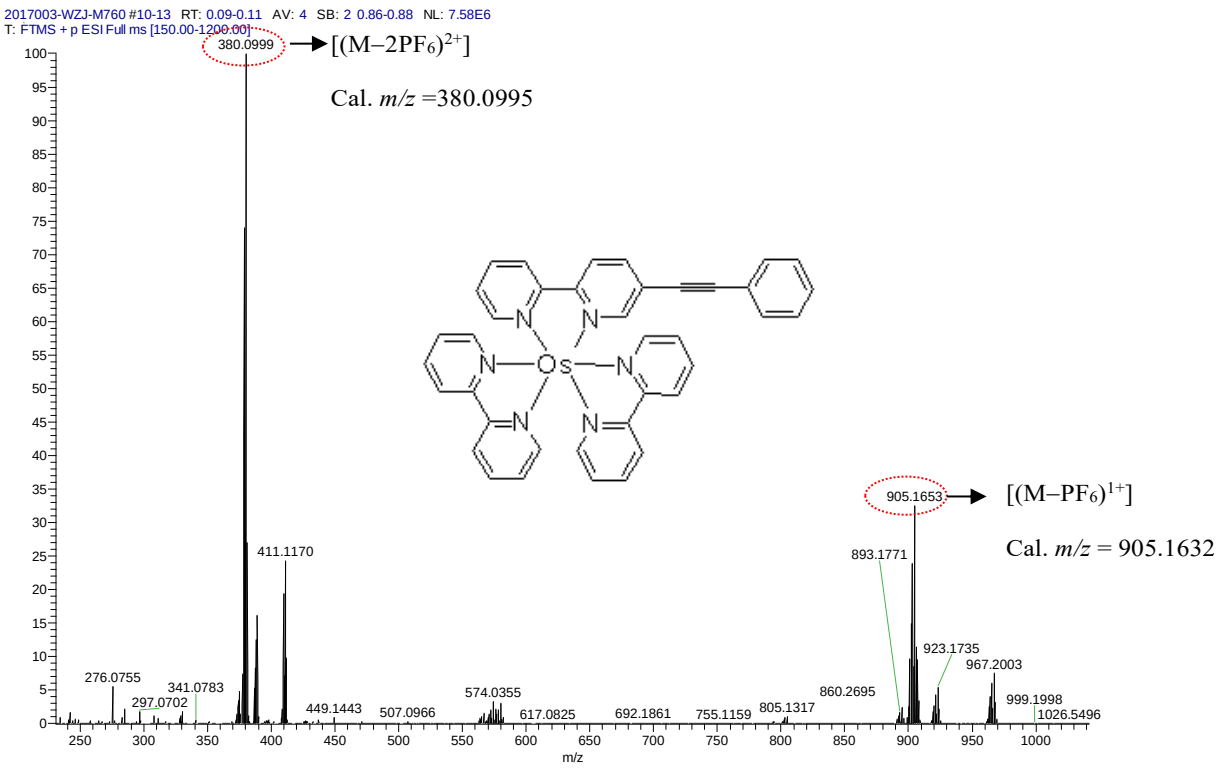

Fig. S5 ESI-HRMS of complex **Os-ph**.

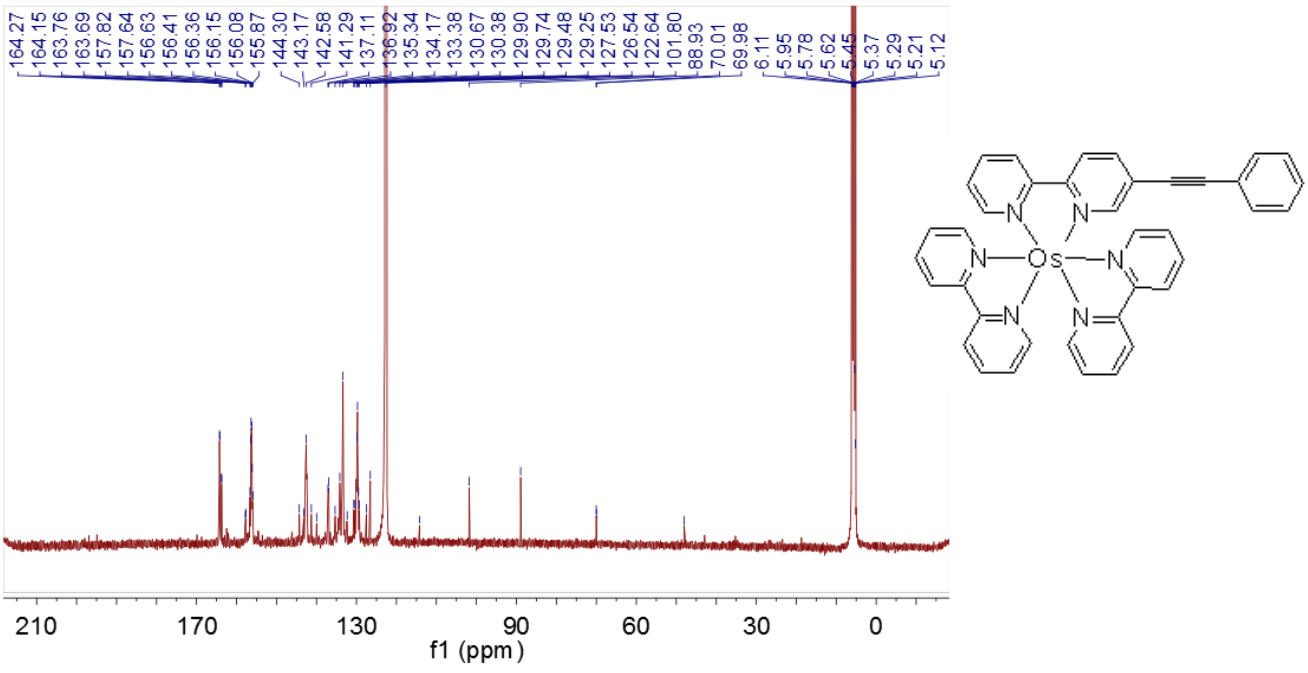

Fig. S6 ^{13}C NMR (100 MHz, CD_3CN) of complex **Os-ph**.

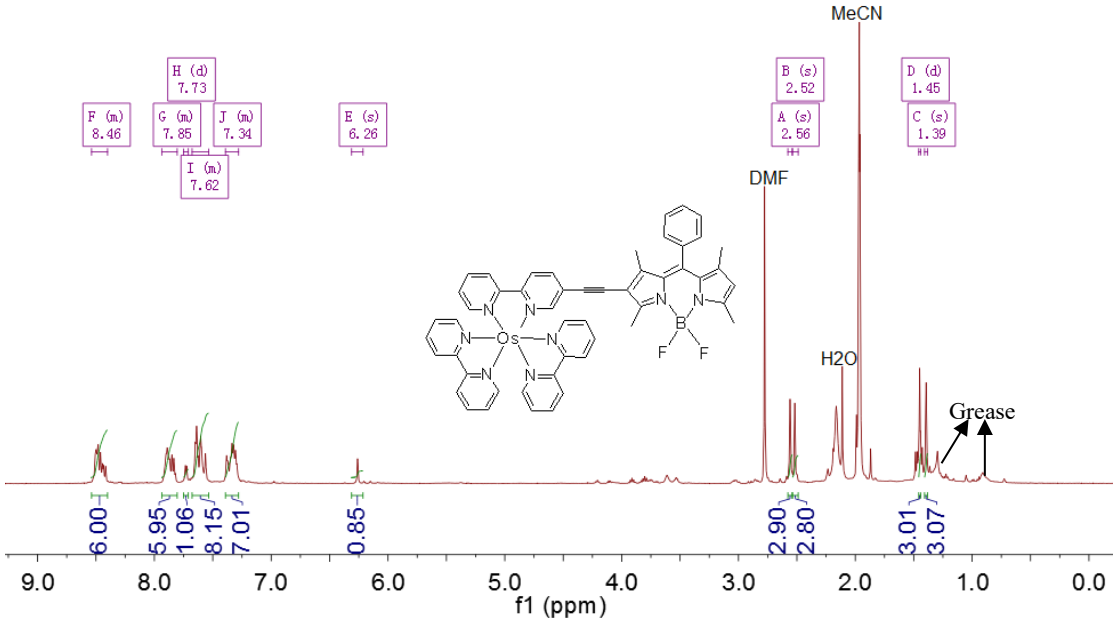

Fig. S7 ^{1}H NMR(400 MHz, CD_3CN) of complex Os-BDP.

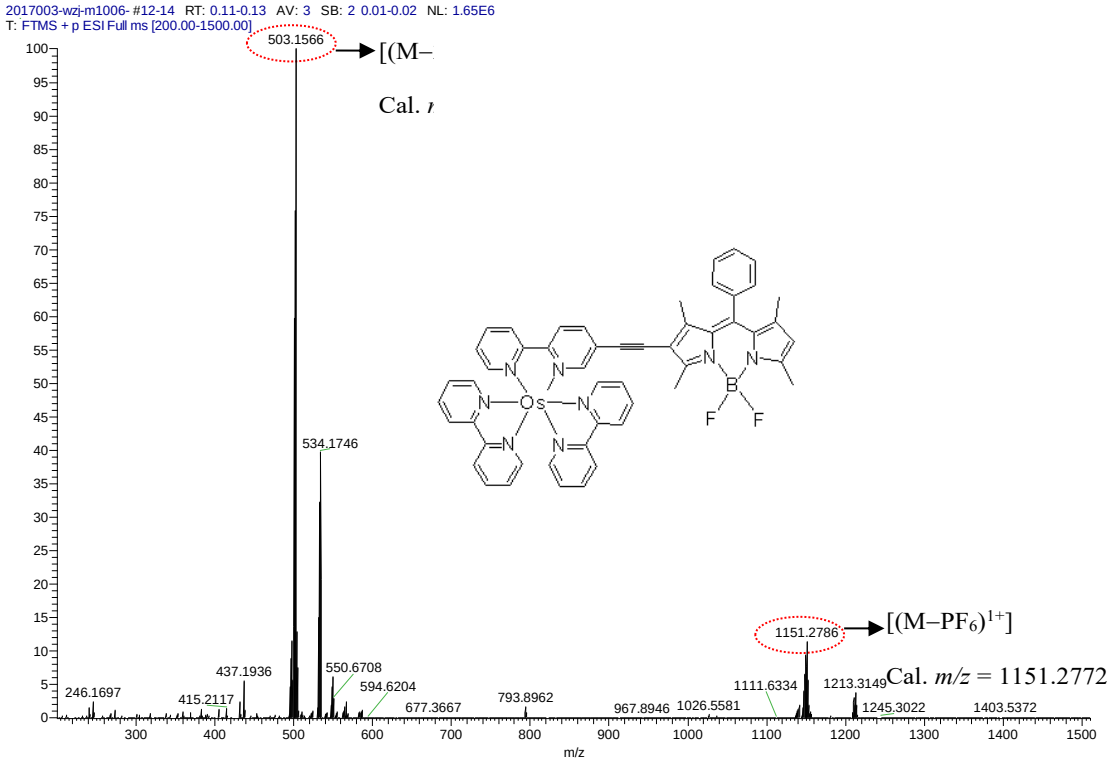

Fig. S8 ESI-HRMS of complex **Os-BDP**.

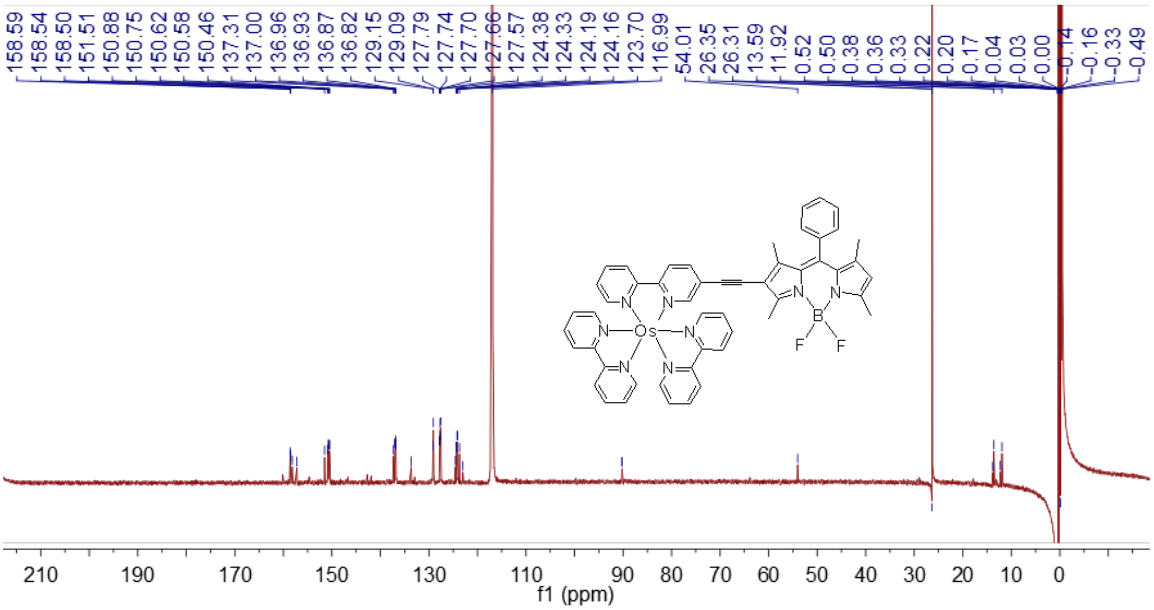

Fig. S9 ^{13}C NMR (100 MHz, CD_3CN) of complex **Os-BDP**.

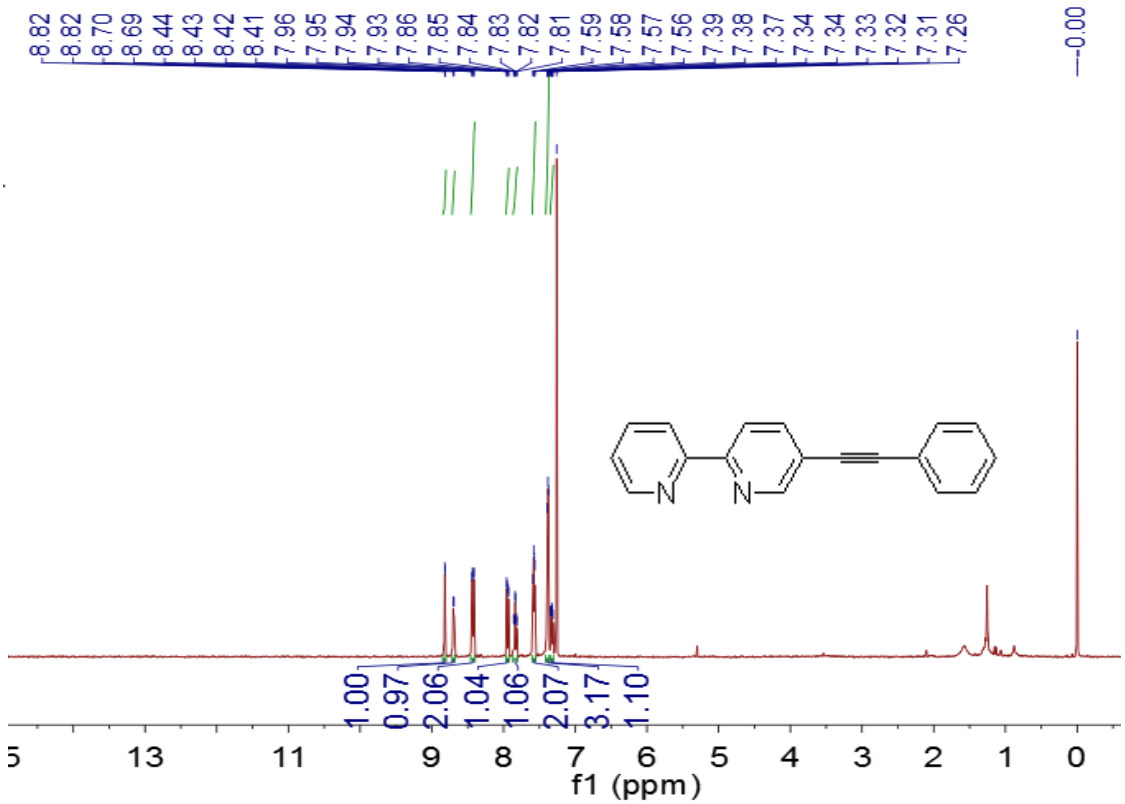

Fig. S10 ^{1}H NMR (400 MHz, D_2O) of **L1**.

3. UV-Vis absorption spectra of the complexes in different solvents

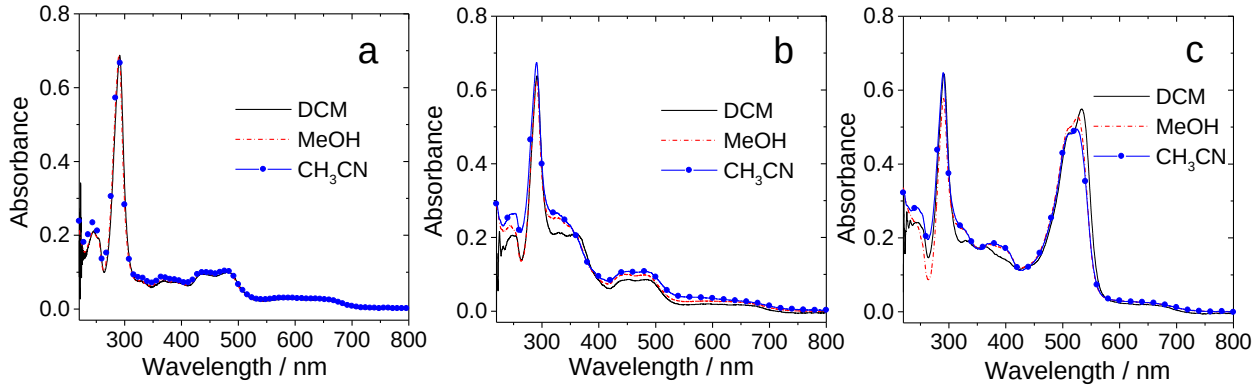

Fig. S11 Solvent-polarity-dependence of the absorption spectra of (a) **Os(bpy)$_3$**, (b) **Os-ph**, (c) **Os-BDP**. *c* = 1.0 ×10^{-5} M. 25 °C.

4. Emission Spectra of the complexes

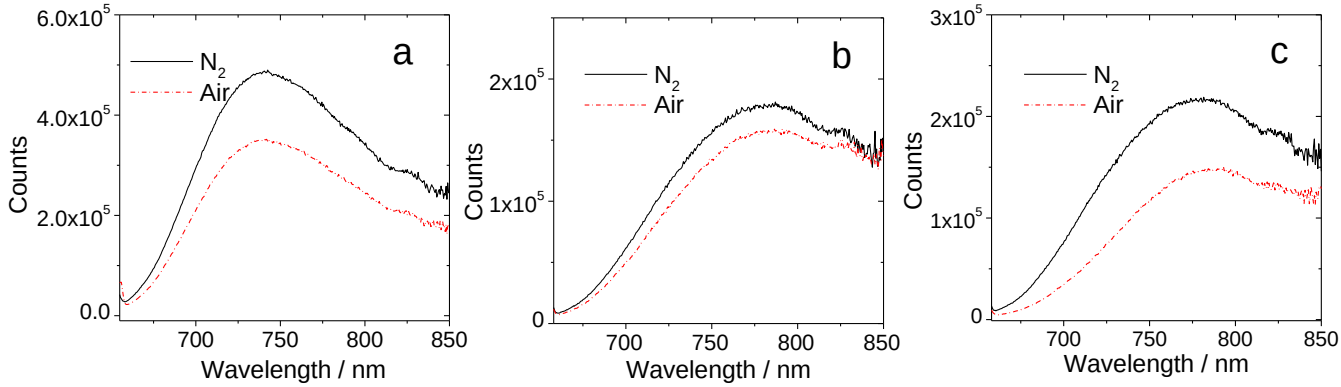

Fig. S12 Emission spectra of (a) **Os(bpy)$_3$**, (b) **Os-ph**, (c) **Os-BDP** in N_2 and air saturated solution, λ_{ex} = 650 nm, *c* = 1.0 ×10^{-5} M , in CH_3CN, 25 °C.

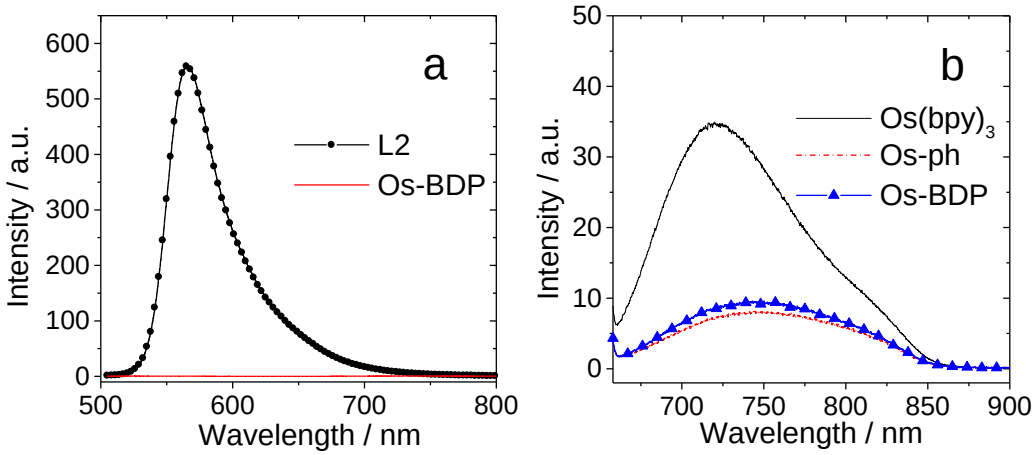

Fig. S13 Emission spectra of (a) **L2** and **Os-BDP** (λ_{ex} = 500 nm, A = 0.5806), (b) **Os(bpy)$_3$**, **Os-ph**, and **Os-BDP** (λ_{ex} = 650 nm, *A* = 0.0366), in aerated CH_3CN, 25 °C.

5. Luminescence and Luminescence Lifetime Spectroscopy

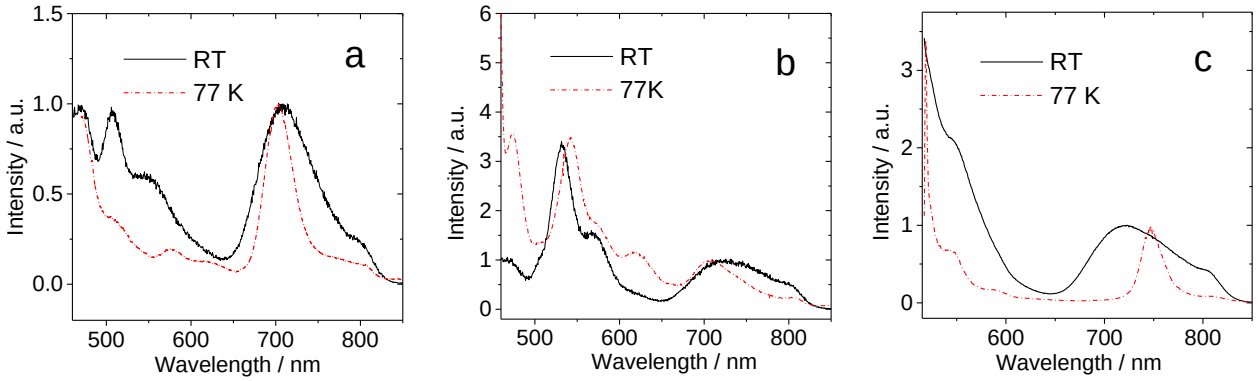

Fig. S14 Comparison of the emission spectra of (a) **Os(bpy)$_3$** (λ_{ex} = 445 nm), (b) **Os-ph** (λ_{ex} = 445 nm), (c) **Os-BDP** (λ_{ex} = 510 nm); *c* = 1.0 ×10^{-5} M, in EtOH/MeOH mixed solvent (4:1, v/v).

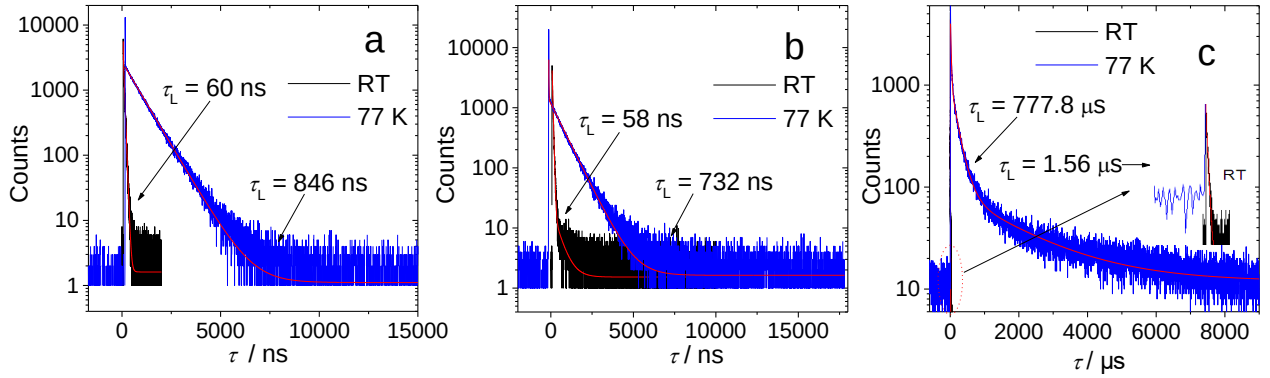

Fig. S15 Luminescence lifetime decay traces of (a) **Os(bpy)$_3$**, (b) **Os-ph**, (c) **Os-BDP**. The decay traces were monitored at 700 - 745 nm, λ_{ex} = 510 nm, c = 1.0 ×10^{-5} M, in aerated EtOH/MeOH (4:1, v/v).

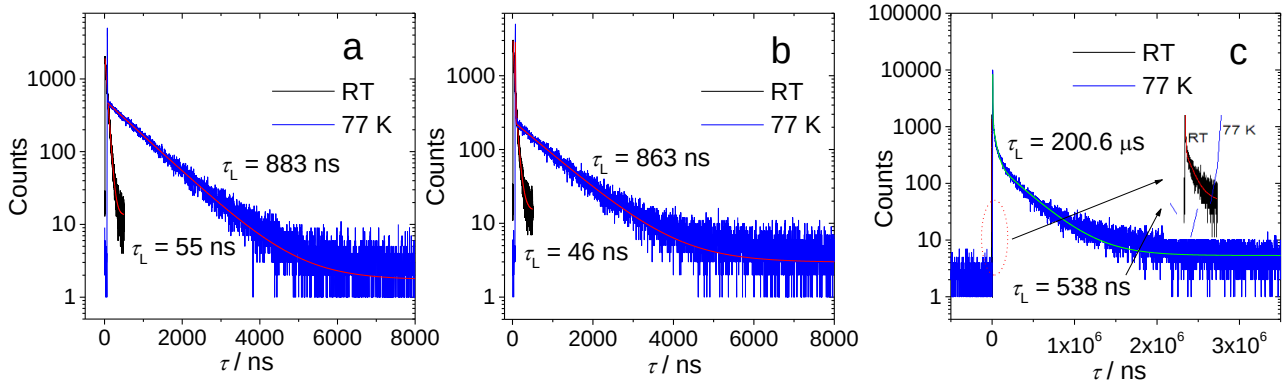

Fig. S16 Luminescence lifetimes decay traces of (a) **Os(bpy)$_3$**, (b) **Os-ph**, (c) **Os-BDP**. The decay traces were monitored at 700 - 745 nm, λ_{ex} = 445 nm, c = 1.0 ×10^{-5} M, in aerated EtOH/MeOH (4:1, v/v).

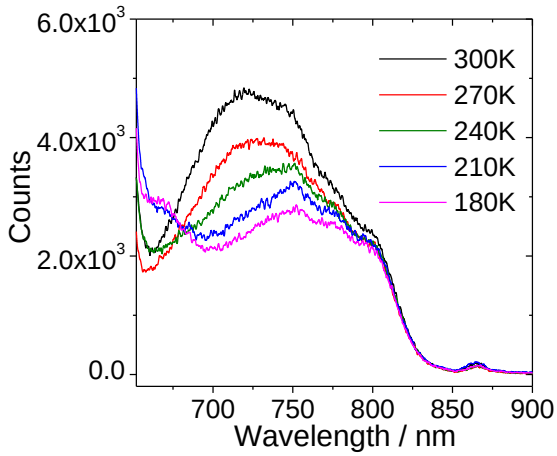

Fig. S17 Comparison of the luminescence spectra of **Os-BDP** at decreasing temperature. λ_{ex} = 635 nm, c = 1.0 × 10^{-5} M in deaerated EtOH/MeOH (4:1, v/v).

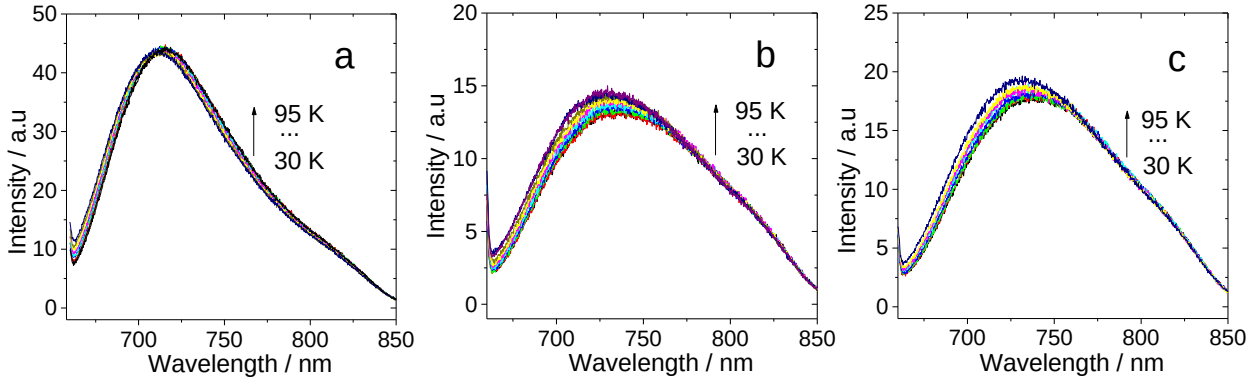

Fig. S18 Comparison of the luminescence spectra of (a) **Os(bpy)$_3$**, (b) **Os-ph** and (c) **Os-BDP** at different temperature. λ_{ex} = 650 nm, c = 1.0 × 10^{-5} M, in deaerated PhCN.

6. Nanosecond Transient Absorption Spectroscopy

The nanosecond transient absorption spectra were measured on LP980 laser flash photolysis spectrometer (Edinburgh Instruments, UK) and recorded on a Tektronix TDS 3012B oscilloscope and with a nanosecond pulsed laser (OpoletteTM 355II+UV nanosecond pulsed laser, typical pulse length: 7 ns. Pulse repetition: 1 Hz. Peak OPO energy: 4 mJ. The wavelength is tunable in the range of 410−2200 nm. OPOTEK, USA). 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 N2 for ca.15 min before measurement and the gas flow is kept during the measurement.

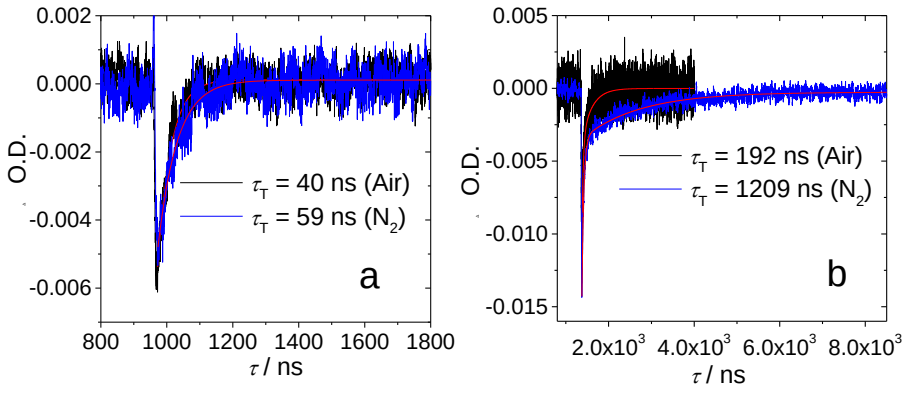

Fig. S19 Triplet state lifetime decay traces of (a) **Os(bpy)$_3$** under N_2 and air, c = 5.0 ×10^{-5} M; (b) **Os-BDP** under N_2 and air, c = 1.0 ×10^{-5} M; λ_{ex} = 650 nm, in CH_3CN, 25 °C.

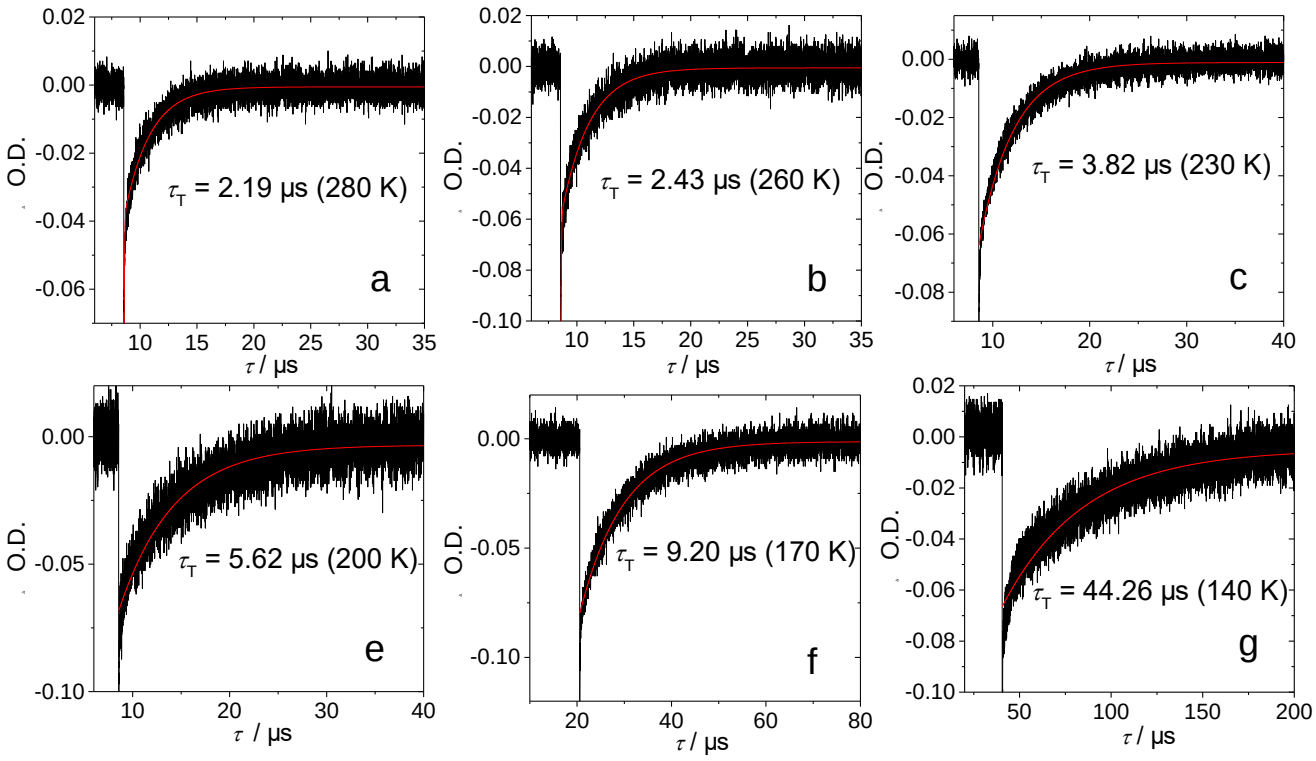

Fig. S20 Triplet state lifetime decay traces of **Os-BDP** at different temperatures, λ_{ex} = 500 nm, c = 1.0 × 10^{-5} M, in deaerated EtOH/MeOH (4:1, v/v).

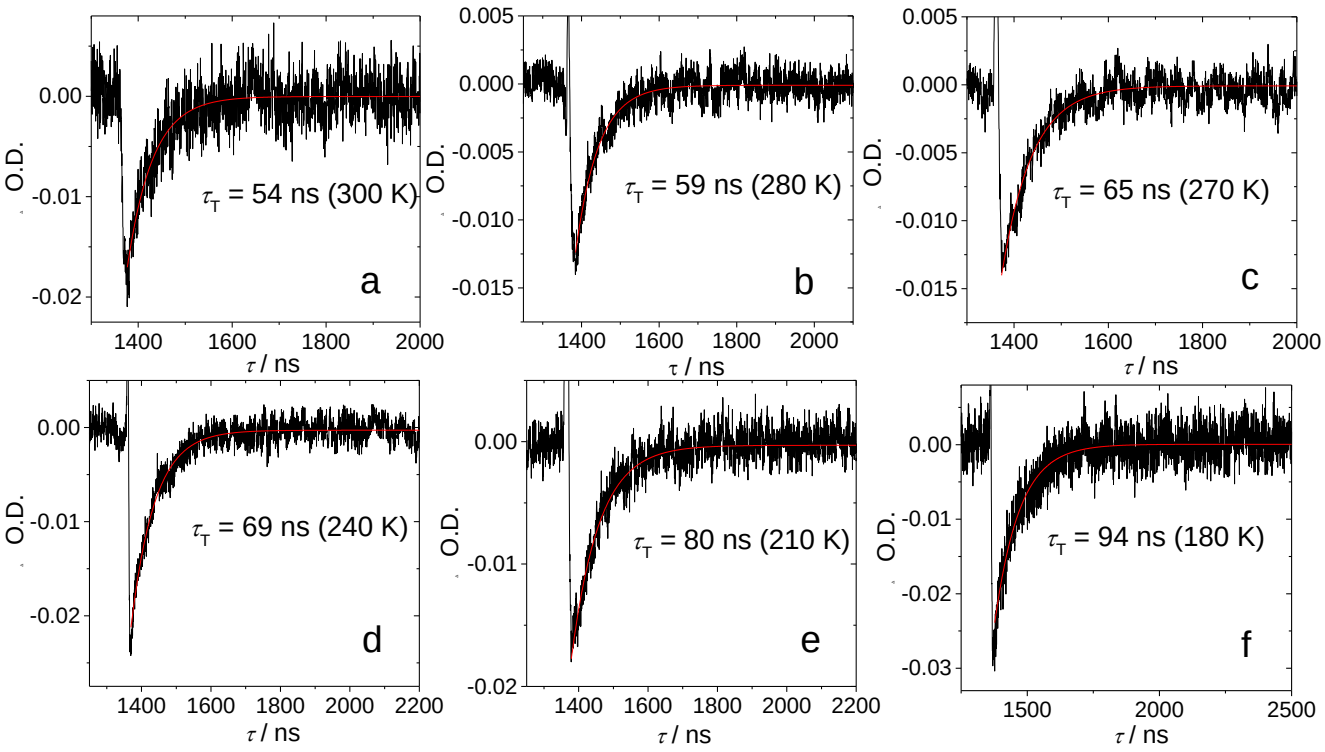

Fig. S21 Triplet lifetime decay trace of Os(II) complexes at different temperatures, λ_{ex} = 480 nm, c = 1.0 × 10^{-5} M, in deaerated EtOH/MeOH (4:1, v/v).

7. TTA Upconversion

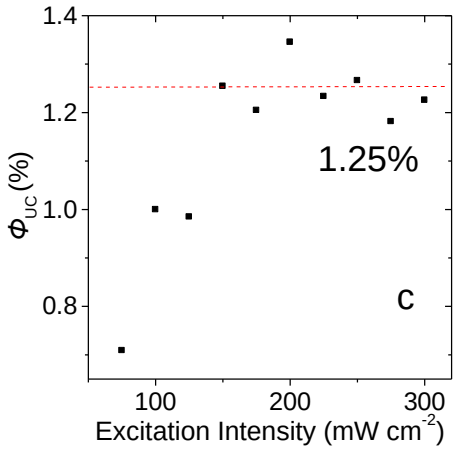

Fig. S22 Upconversion quantum yield (Φ_{UC}) of **Os-BDP** with **PBI** as a function of excitation power intensity of the 635 nm cw laser. [Sensitizer] = 1.0×10^{-4} M and [**PBI**] = 2.5×10^{-3} M in deaerated DCM. 25 °C.