Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Near-infrared phosphorescent terpyridine osmium(II) complexes photosensitizers for photodynamic and photooxidation therapy

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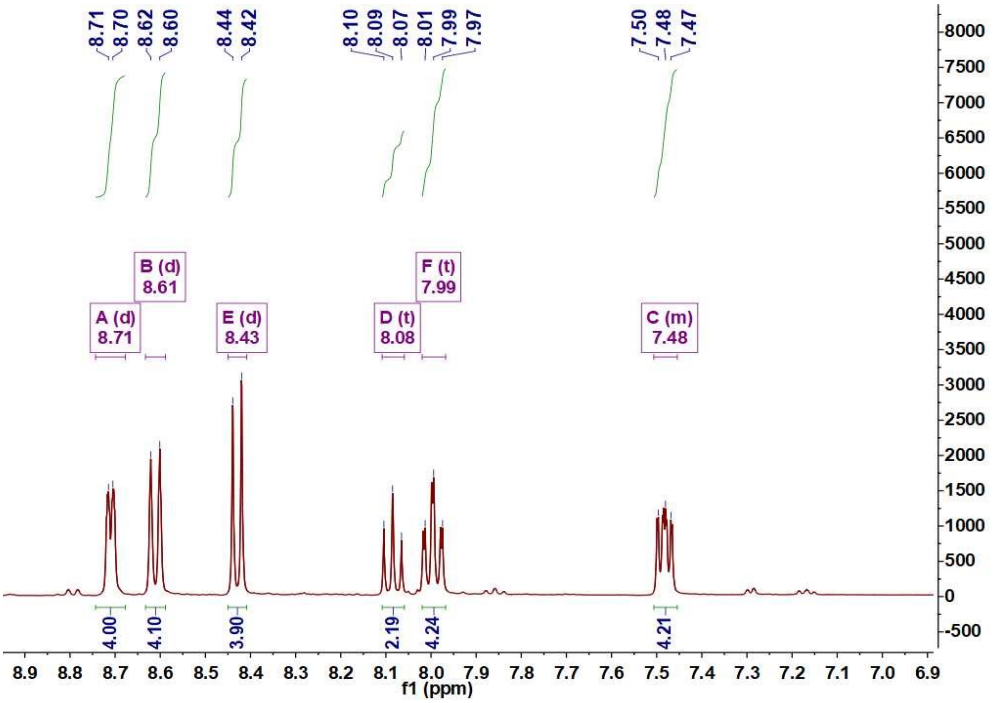

Figure S1. The 500 MHz ^{1}H NMR spectrum of **Os1** in the DMSO-d^{6} solution.

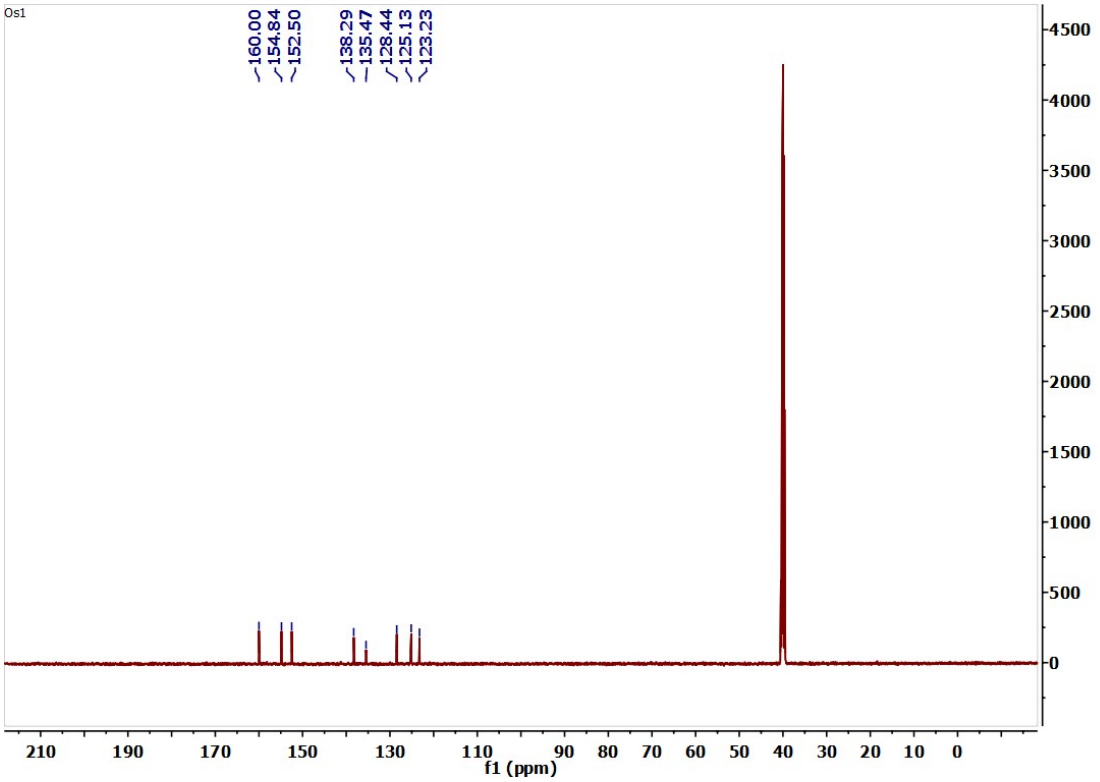

Figure S2. The 126 MHz ^{13}C NMR spectrum of **Os1** in the DMSO-d^{6} solution.

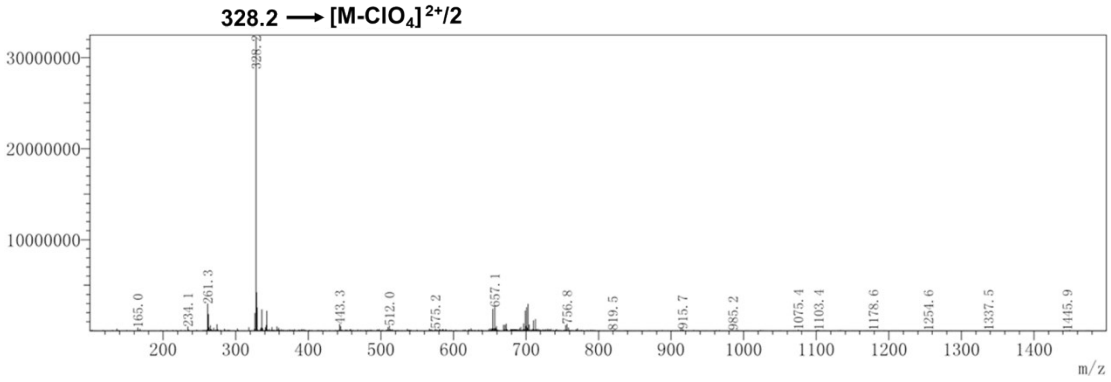

Figure S3. The ESI-MS spectrum of **Os1** (CH_3OH).

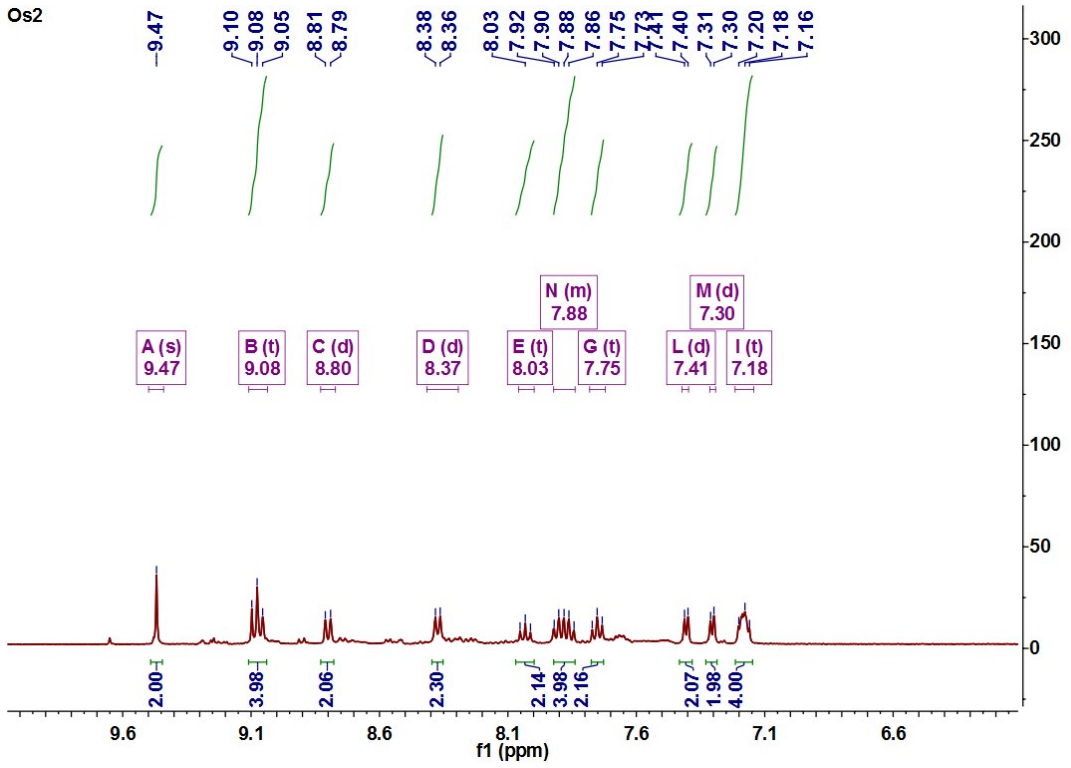

Figure S4. The 500 MHz ^{1}H NMR spectrum of **Os2** in the DMSO-d^6 solution.

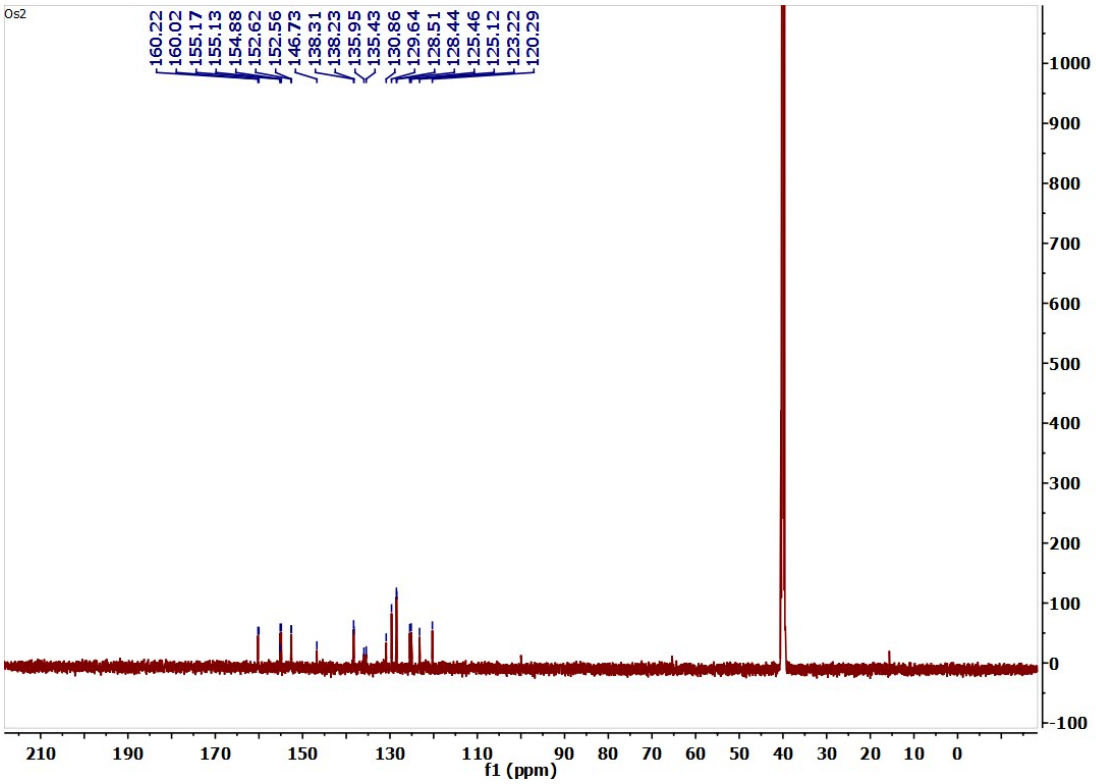

Figure S5. The 126 MHz ^{13}C NMR spectrum of **Os2** in the DMSO-d^6 solution.

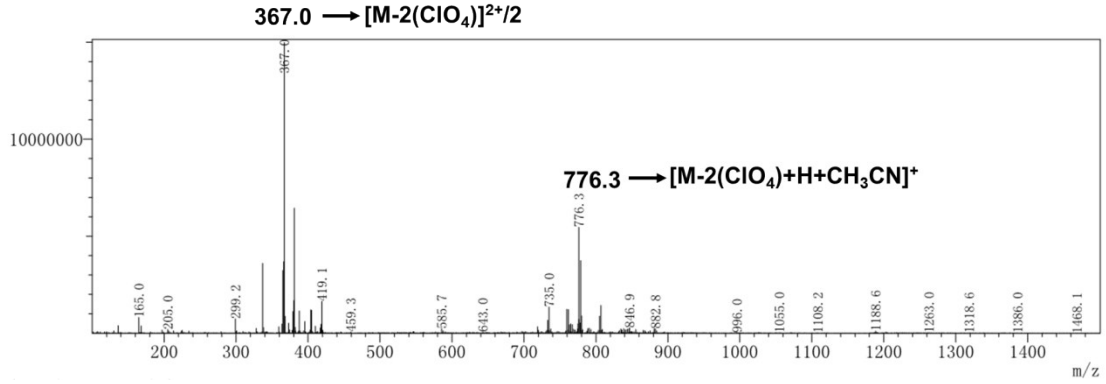

Figure S6. The ESI-MS spectrum of **Os2** (CH_3OH).

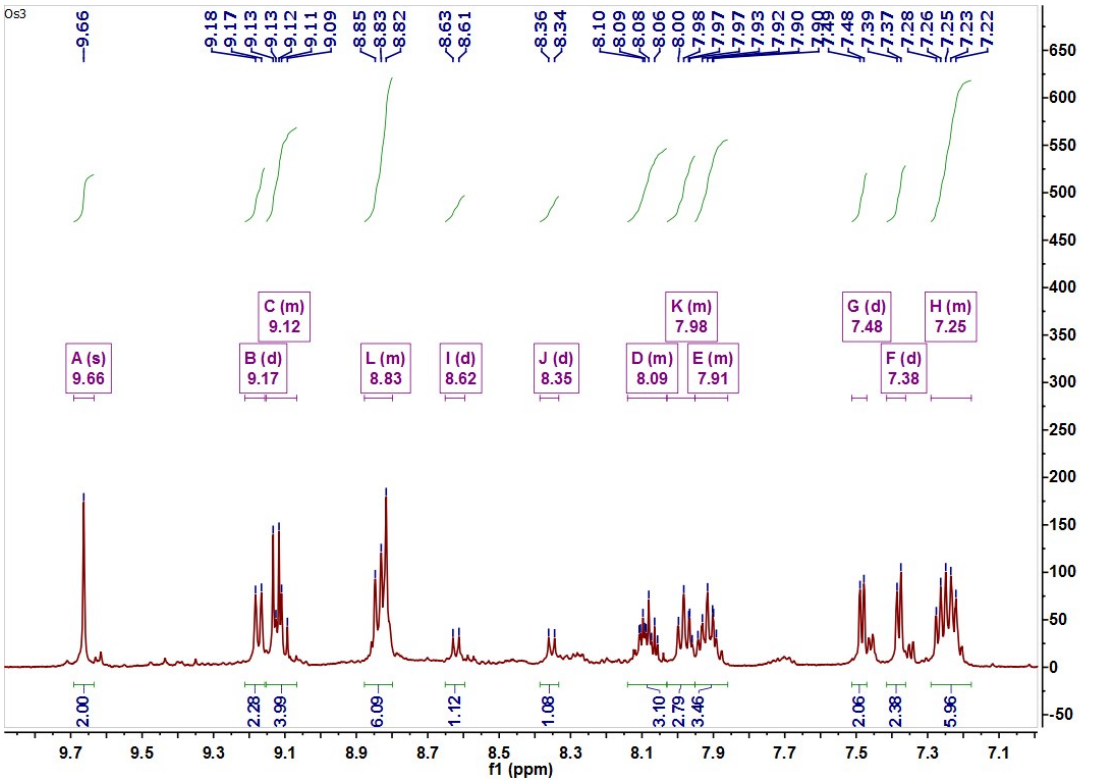

Figure S7. The 500 MHz ^{1}H NMR spectrum of **Os3** in the DMSO-d^{6} solution.

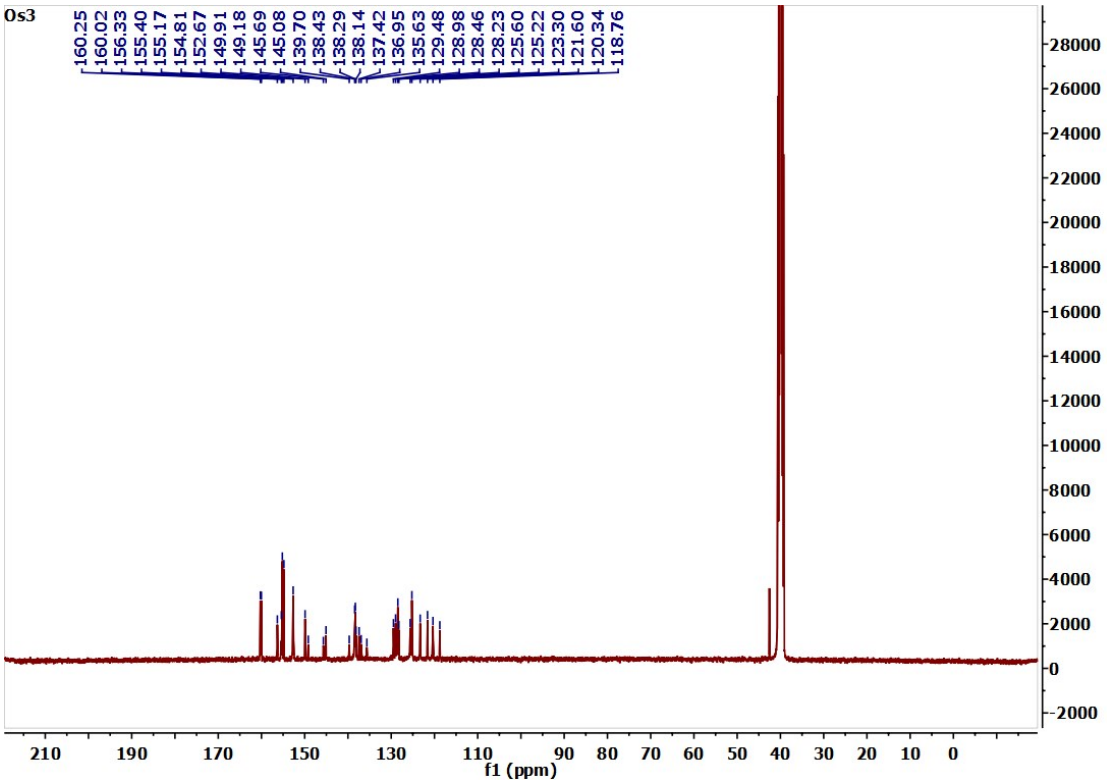

Figure S8. The 126 MHz ^{13}C NMR spectrum of **Os3** in the DMSO-d^{6} solution.

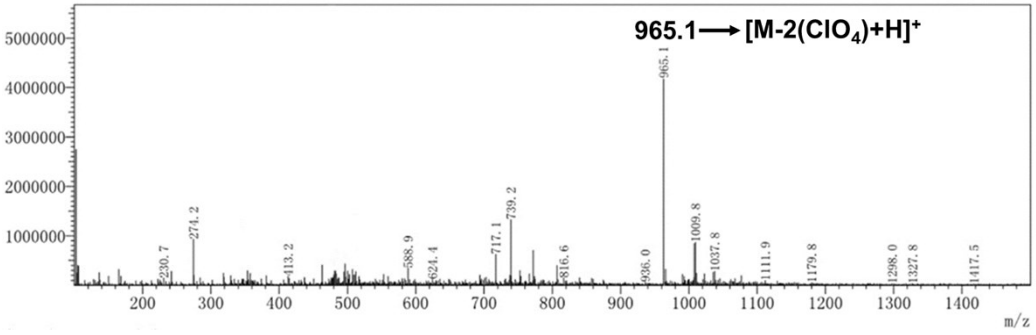

Figure S9. The ESI-MS spectrum of **Os3** (CH_3OH).

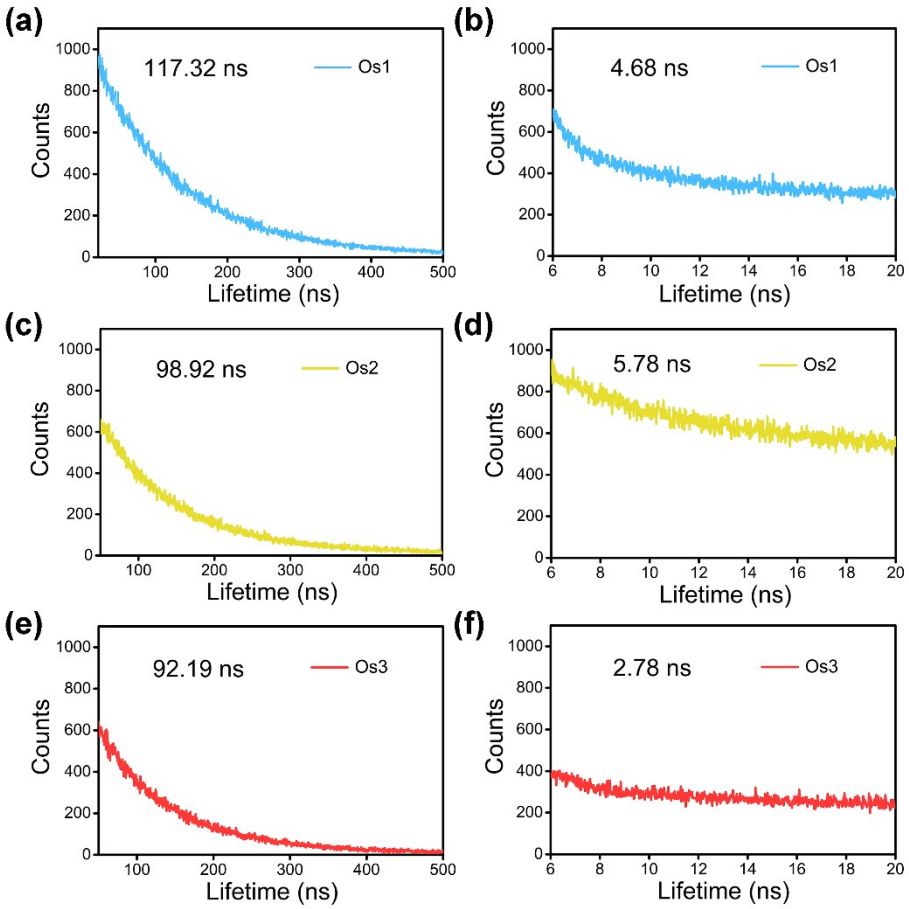

Figure S10. The phosphorescence lifetimes of **Os1-Os3** in water. The excitation wavelength was 488 nm. (a), (c) and (e) were collected NIR emission from 700-750 nm. (b), (d) and (f) were collected Vis emission from 550-600 nm.

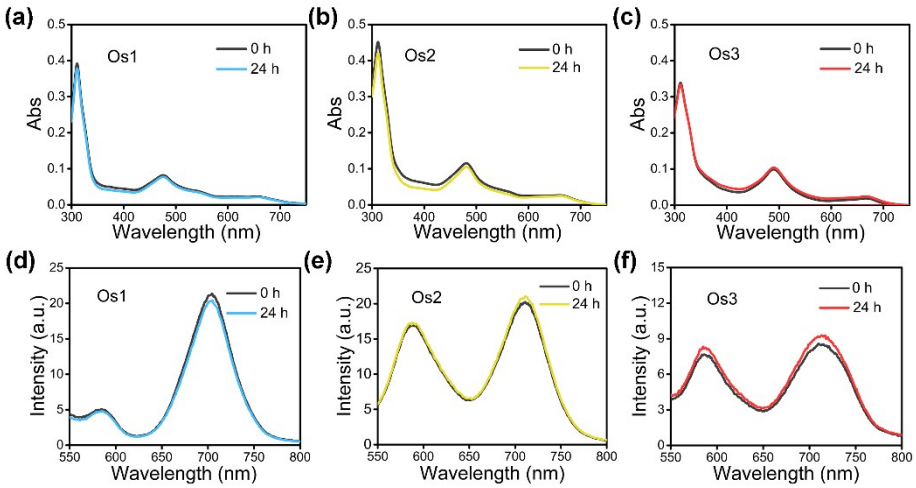

Figure S11. The absorption (a-c) and emission (d-f) spectra of **Os1-Os3** (10 μM) in PBS solution for 24 h at room temperature.

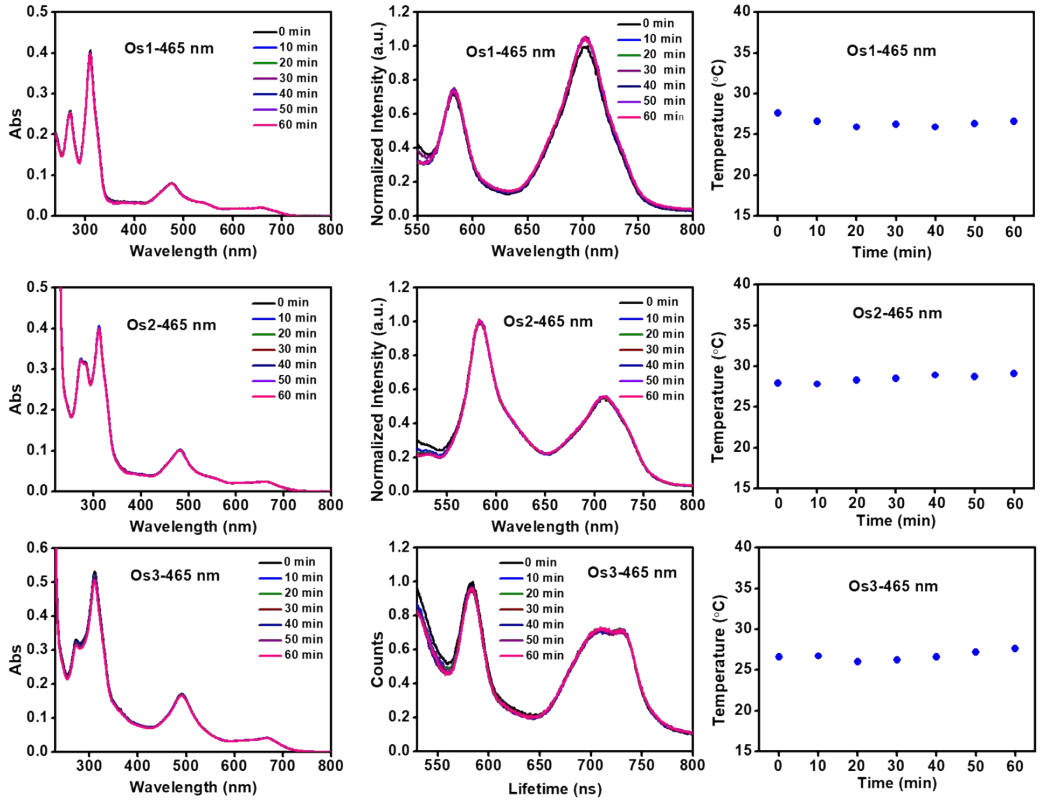

Figure S12. The photostability of **Os1-Os3** in PBS solution, as monitored by UV-vis spectroscopy (left) and fluorescence spectrometer (middle), which recorded every 10 min under blue LED light irradiation (465 nm, 13 mW/cm^2). The changes of temperature of **Os1-Os3** solution after irradiation was recorded as well (right).

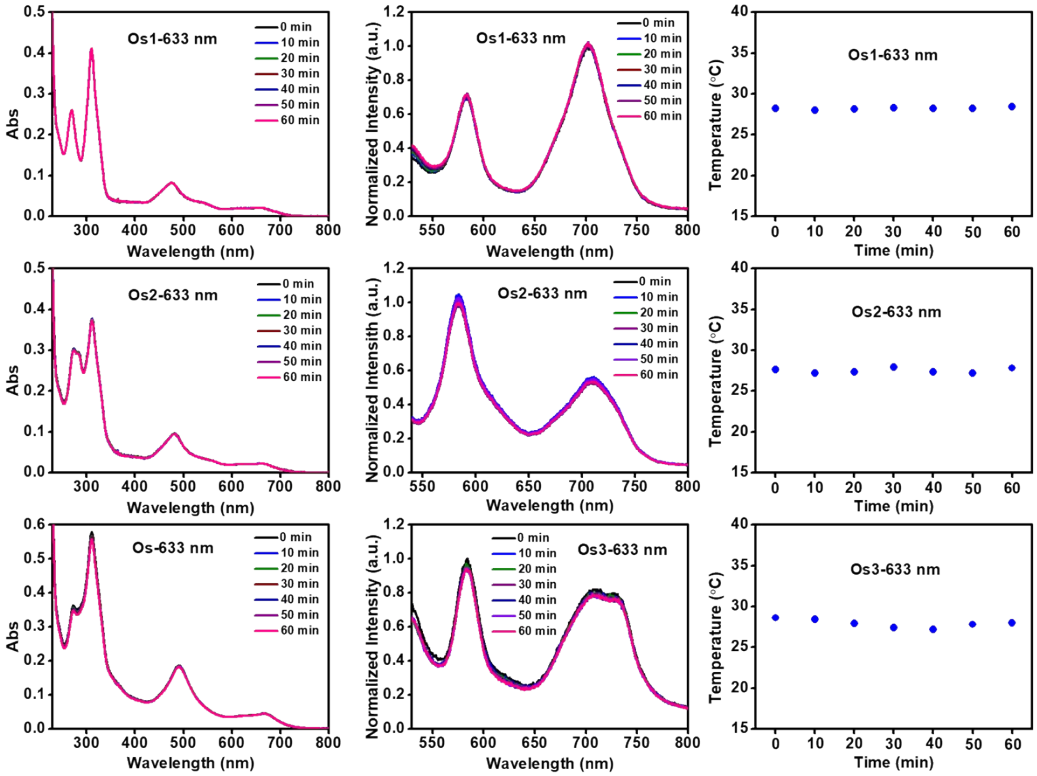

Figure S13. The photostability of **Os1-Os3** in PBS solution, as monitored by UV-vis spectroscopy (left) and fluorescence spectrometer (middle), which recorded every 10 min under blue LED light irradiation (633 nm, 20 mW/cm^2). The changes of temperature of **Os1-Os3** solution after irradiation was recorded as well (right).

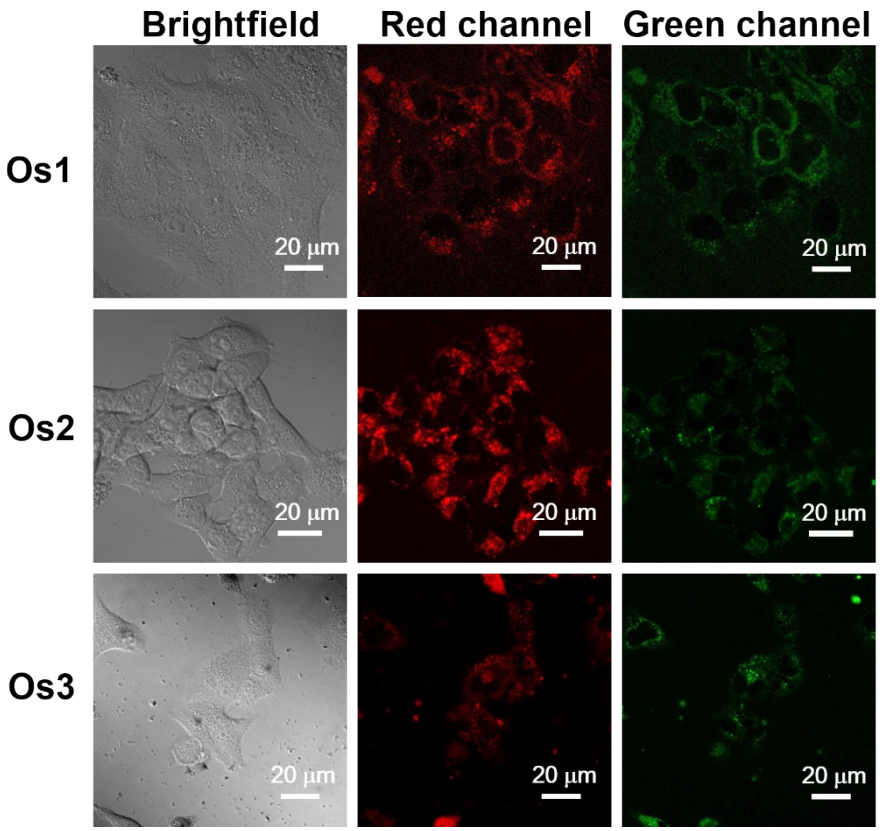

Figure S14. Images of live Hep-G2 cells stained with **Os1-Os3** (10 μM) for 2 h. Red channel: λ_{ex} = 488 nm, λ_{em} = 650-800 nm. Green channel: λ_{ex} = 488 nm, λ_{em} = 550-600 nm. Scale bar: 20 μm.

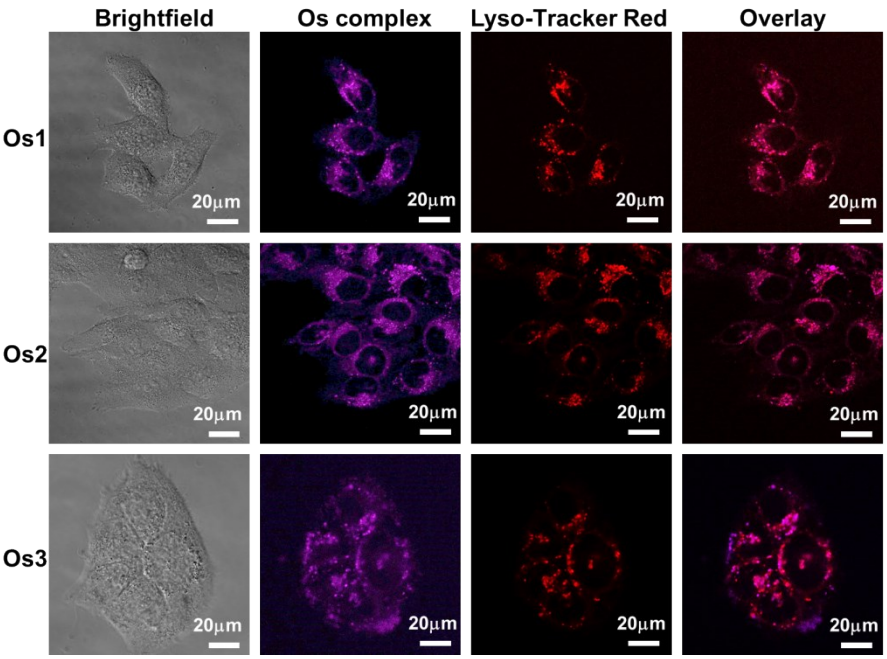

Figure S15. Confocal microscopy images of Hep-G2 cells treated with complexes **Os1-Os3** (10 μM, 2 h) and Lyso-Tracker Red (100 nM) for 30 min. Os complexes Red channel: λ_{ex} = 488 nm, λ_{em} = 650-800 nm. Lyso-Tracker Red channel: λ_{ex} = 543 nm, λ_{em} = 560-620 nm.

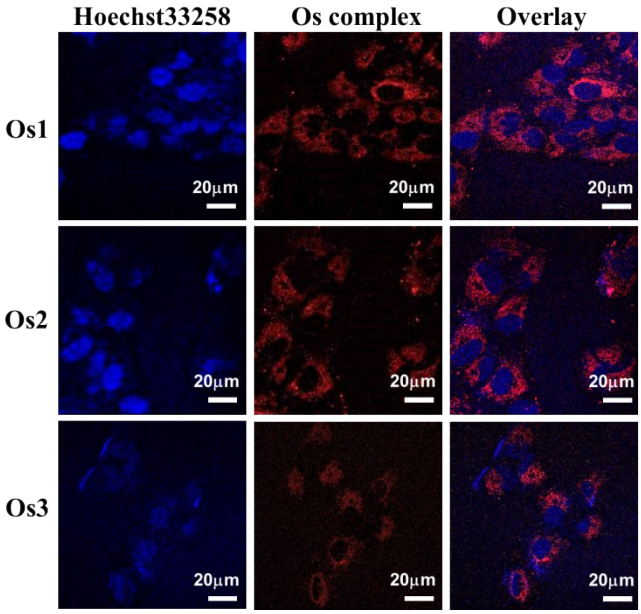

Figure S16. Confocal images of the A549 cells colabeled with **Os1-Os3** (10 μM, 2 h) and Hoechst 33258 (500 nM, 30 min).

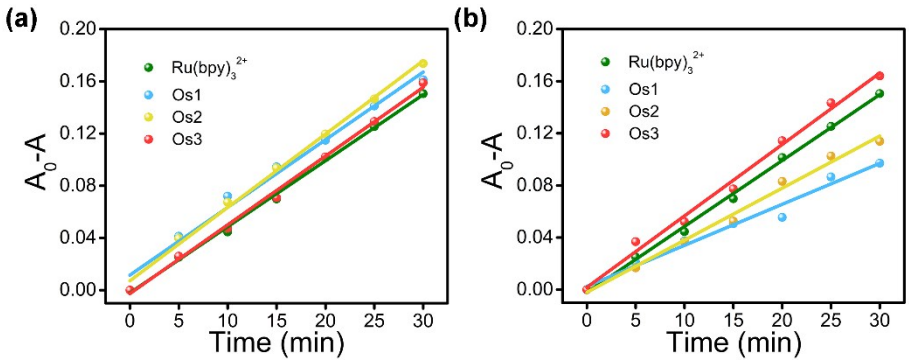

Figure S17. Changes in absorbance of RNO at 440 nm against irradiation time in the presence of $Ru(bpy)_3^{2+}$ or **Os1-Os3** in histidine-PBS solution. The irradiation time interval was 5 min. The light source was a 465 nm LED- lamp (a) and a 633 nm LED-lamp (b).

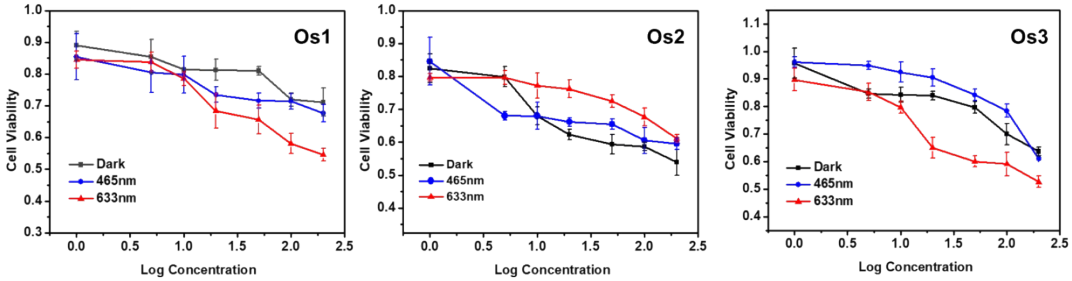

Figure S18. Growth curves for the LO2 cells treated with **Os1**, **Os2** or **Os3** for 4 h in the dark or followed by irradiation with 465 nm (13 mW cm^{-2}, 1 h) or 633 nm light (20 mW cm^{-2}, 1 h), and then incubated for a further 43 h. The cells were transferred to fresh medium before irradiation.

Table S1. Data of the HOMO-LUMO values of **Os1-Os3**.

Complex	HOMO-LUMO
Os1	9.64 eV
Os2	5.38 eV
Os3	4.70 eV

Table S2. The IC_{50} values of **Os1-Os3** towards Hep-G2 and LO2 cells in the dark and upon irradiation.

Cell lines	Complex	IC_{50} (μM)		
		Dark	465 nm	633 nm
Hep-G2	**Os1**	> 100	71.83±3.32	> 100
	Os2	> 100	43.47±2.48	58.18±0.48
	Os3	> 100	1.23±0.12	4.05±0.05
LO2	**Os1**	> 100	> 100	> 100
	Os2	> 100	> 100	> 100
	Os3	> 100	> 100	> 100

Table S3. The TON values of the osmium complexes for photo-oxidation of NADH.

Complex	Condition	TON
Os1	Dark	0.076±0.0035
	465 nm	11.35±0.014
	633 nm	6.44±0.20
Os2	Dark	0.16±0.028
	465 nm	7.03±0.13
	633 nm	3.41±0.078
Os3	Dark	0.14±0.035
	465 nm	11.40±0.17
	633 nm	11.13±0.14