Electronic Supplementary Information for

Visible-light harvesting iridium complexes as singlet oxygen sensitizers for photooxidation of 1,5-dihydroxynaphthalene

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Experimental Section

General.

All the chemicals used in synthesis are analytical pure and were used as received. 1,5-dihydroxynaphthalene (**DHN**) was purchased from Sun Chemical Technology (Shanghai, P. R. China) Co,. Ltd. and was used after recrystallization in ethanol. Solvents were dried and distilled for synthesis. NMR spectra were recorded on a 400 MHz Varian Unity Inova NMR spectrophotometer. ^{13}C NMR spectra were recorded on the same instrument (100 MHz) with total proton decoupling. Mass spectra were recorded with Q-TOF Micro MS spectrometer. 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).

Synthesis of the sensitizers

All the sensitizers were synthesized according to the procedures reported by us previously.[1] The sensitizers were synthesized by using cyclometalated Ir(III) chlorido-bridged dimers $[Ir\text{-}(ppy)_2Cl]_2$ and the relative ligands with refluxing for 5-6 h in CH_2Cl_2 / MeOH (2:1, v/v) mixed solvents. The ligands were synthesized by using the aldehydes (such as 7-diethylamino-2-oxo-2H-chromene-3-carboxyldehyde), ammonium acetate and 1,10-phenanthroline-5,6 -dione to reflux for 6h in acetic acid.

Photooxidation details

Phtooxidation was carried out according to a modified literature method.[2]

A acetonitrile / 2-propanol (4:1, v/v) mixed solvent containing **DHN** (1.5×10^{-4} M) and a sensitizer (10 mol % *vs*. **DHN**) was put into a two neck round bottom flask (25 mL), and oxygen was bubbled through the solution for 10 min. The solution was then irradiated using a 35 W xenon lamp through a cut off filter (0.72 M $NaNO_2$ solution, which is transmitant for light with wavelength $\lambda > 385$ nm). UV-vis absorption spectra were recorded at intervals of 2 – 5 min. The **DHN** consumption was monitored by a decrease in the absorption at 301 nm, and the concentration of **DHN** was calculated by using its molar extinction coefficient (ε = 7664 M^{-1} cm^{-1}). On the other hand, 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 (ε = 3811 M^{-1} cm^{-1}), and the yield of Juglone was obtained by dividing the concentration of Juglone with the initial concentration of **DHN**.[2] The photostability experiments were carried out using the same method except without the substrate DHN (for the sensitizers) or without sensitizers (for DHN).

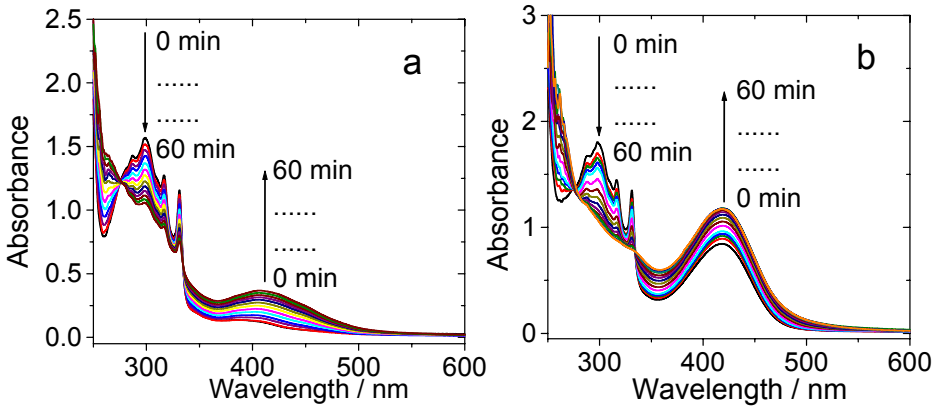

Fig. S1 UV-vis absorption spectral change for the photooxidation of **DHN** (1.5×10^{-4} M) using complexes (a) **Ir-2** and (b) **Ir-4** as sensitizers, in acetonitrile / 2-propanol (4:1, v/v) mixed solvent, 1.5×10^{-5} M, 20°C. Irradiated with 35 W xenon lamp (20 mW cm^{-2} in the photoreactor. The UV light with wavelength shorter than 385 nm was blocked by 0.72 M $NaNO_2$ solution).

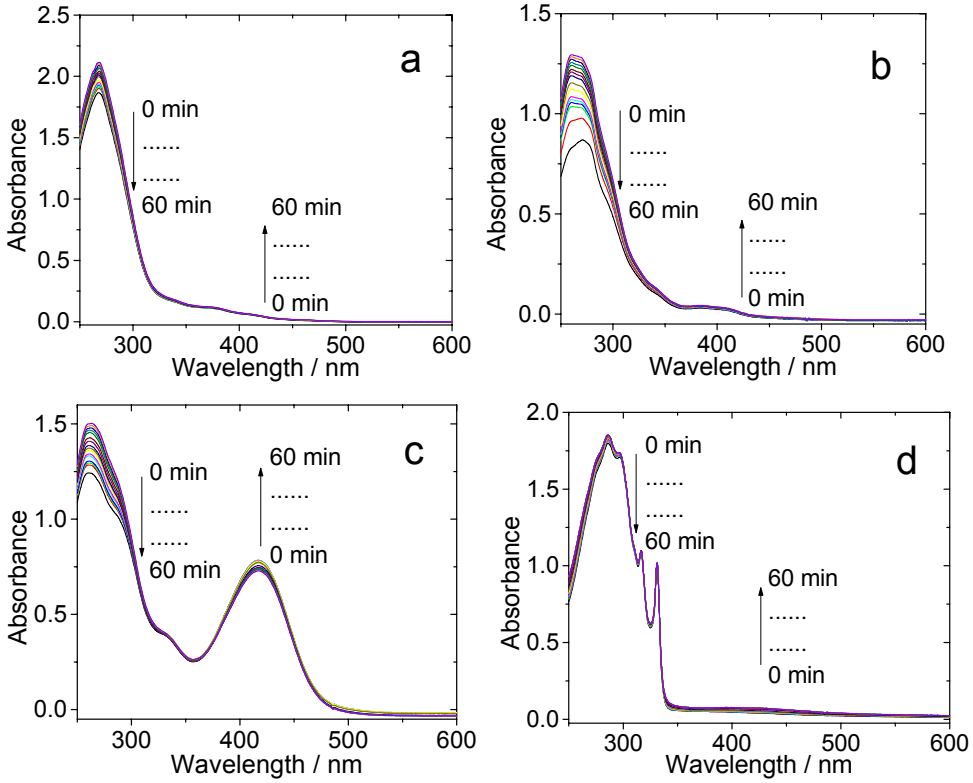

Fig. S2 UV-vis absorption spectral change of complexes (a: **Ir-1**, b: **Ir-2** and c: **Ir-4,** 1.5×10^{-5} M) and the substrate **DHN** (d, 1.5×10^{-4} M) upon irradiation ($\lambda > 385$ nm) in acetonitrile / 2-propanol (4:1, v/v) mixed solvent, 20°C. Irradiated with 35 W xenon lamp (with an intensity in the photo-reactor of 20 mW cm^{-2}. The UV light with wavelength shorter than 385 nm was blocked by 0.72 M $NaNO_2$ solution).

Reference

1 J. Sun, W. Wu, H. Guo and J. Zhao, *Eur. J. Inorg. Chem.*, 2011, 3165.

2 S. Takizawa, R. Aboshi and S. Murata, *Photochem. Photobiol. Sci.*, 2011, **10**, 895.