Supplementary Information

Photofunctions of iridium(III) complexes in vesicles: long-lived excited states and visible-light sensitization for hydrogen evolution in aqueous solution

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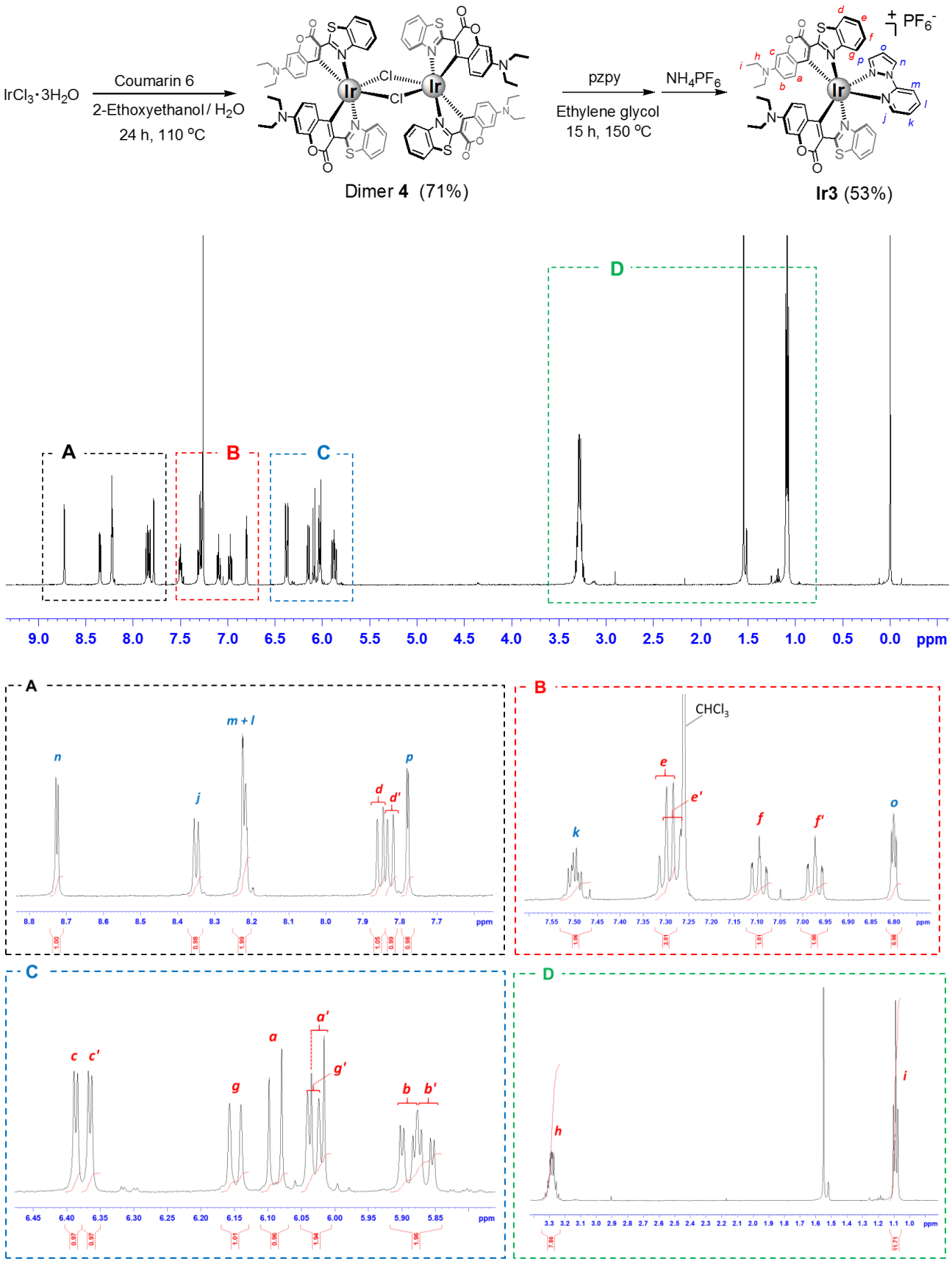

Fig. S1 Synthetic scheme and ^{1}H NMR spectrum of **Ir3** in $CDCl_3$

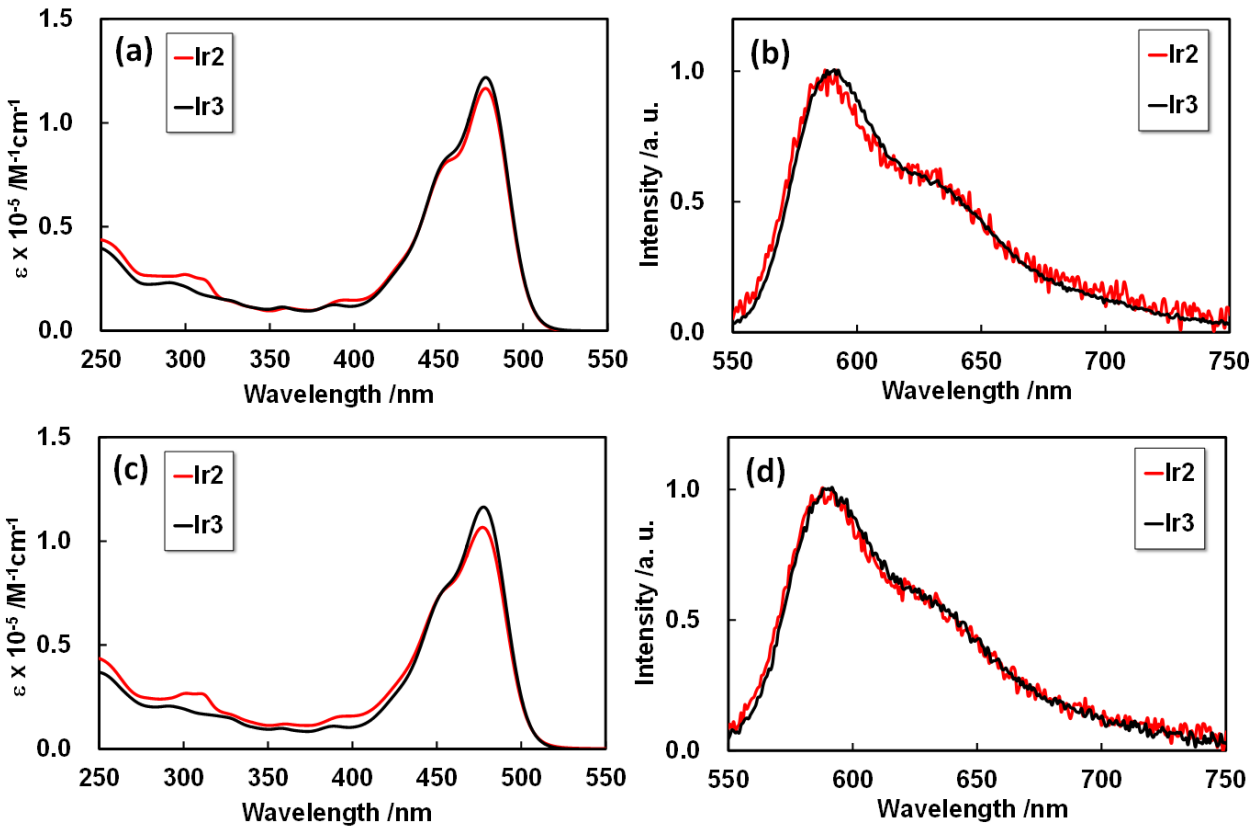

Fig. S2 UV-vis absorption and phosphorescence spectra of **Ir2** and **Ir3**. (a) UV-vis absorption spectra in CH_3CN. (b) Phosphorescence spectra in CH_3CN (excited at 478 nm). (c) UV-vis absorption spectra in CH_3CN–pH 4.5 acetate/acetic acid buffer solution (1:1 v/v). (d) Phosphorescence spectra in CH_3CN–pH 4.5 acetate/acetic acid buffer solution (1:1 v/v) (excited at 477–478 nm).

Table S1 Phosphorescent properties of **Ir2** and **Ir3** at 77 K[a]

Complex	λ_{em} /nm[b]	Φ[c]
Ir2	578, 630, 690	0.92
Ir3	579, 630, 693	0.84

[a] In 2-MeTHF, excited at 481 nm. [b] Emission maxima. [c] Emission quantum yield.

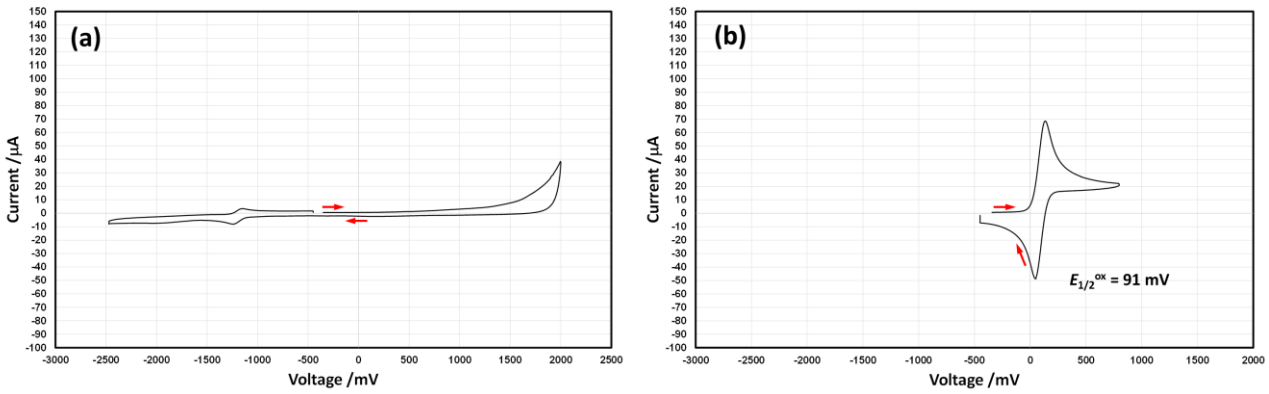

Fig. S3 Cyclic voltammograms of (a) the blank solution and (b) ferrocene recorded at a 100 mV/s scan rate (in deaerated CH_3CN, *vs.* $Ag/AgNO_3$). In the blank solution, a weak reversible wave was observed at approximately –1.2 V most probably due to residual oxygen.[1]

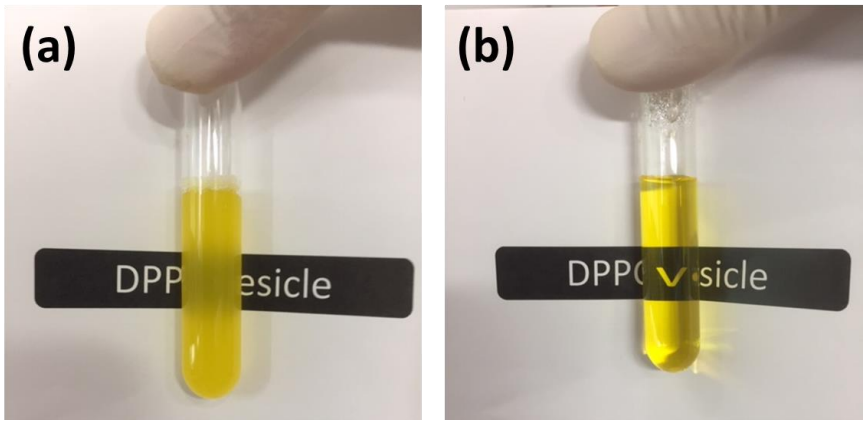

Fig. S4 Photographs of the DPPC vesicle solution containing **Ir2** (a) before and (b) after the ultrasonic process

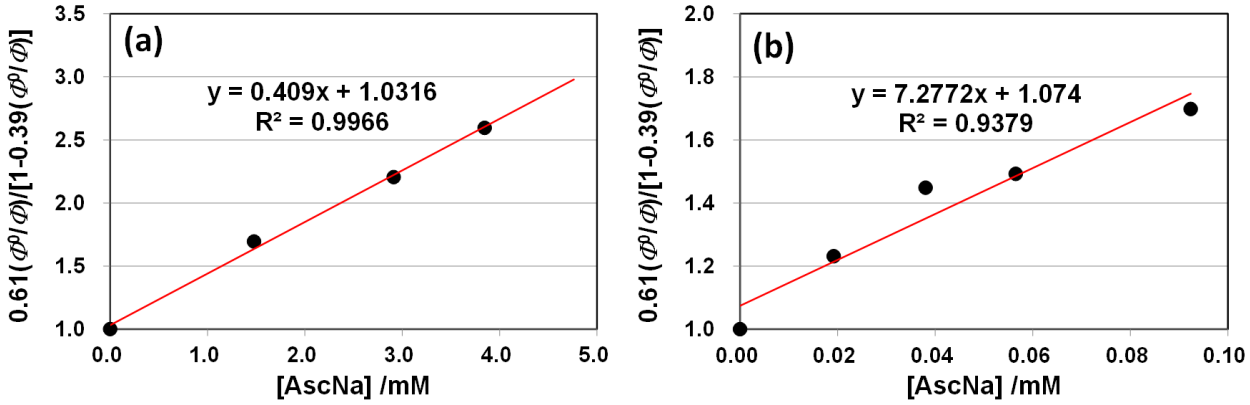

Fig. S5 (a) Modified Stern–Volmer plot for quenching of the phosphorescence from **Ir2** (excitation: 477 nm) with AscNa in vesicle solution ([**Ir2**] = 11 μM). (b) Modified Stern–Volmer plot for quenching of the phosphorescence from **Ir3** (excitation: 475 nm) with AscNa in vesicle solution ([**Ir2**] = 11 μM). The least-squares analyses of the plots yield quenching constants, K_{SV}, of 409 M^{-1} and 7280 M^{-1}, respectively.

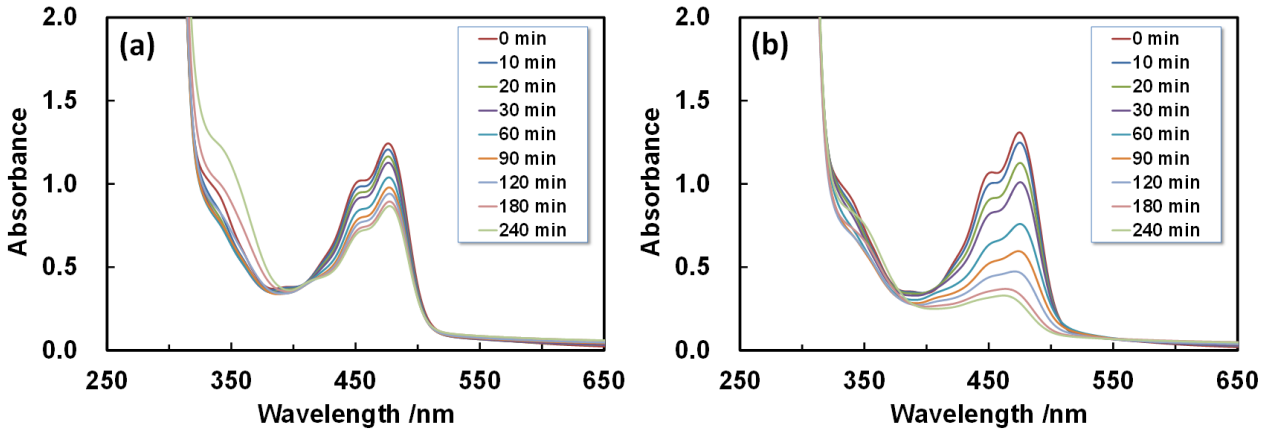

Fig. S6 Changes observed in the absorption spectra during the photochemical H_2 evolution using (a) the **Ir2**-embedded DPPC vesicles and (b) the **Ir3**-embedded DPPC vesicles. Conditions: AscNa (100 mM)/DPPC vesicles with **Ir2** or **Ir3** (11 μM)/**NiP** (0.05 mM), λ > 440 nm.

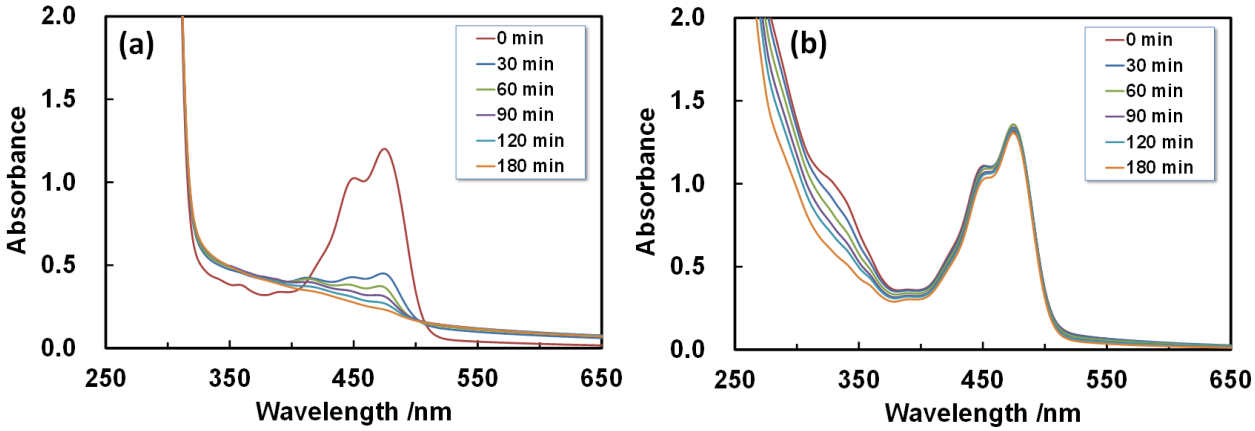

Fig. S7 Changes observed in the absorption spectra during the irradiation (> 440 nm) of the **Ir3**-embedded vesicles only with (a) AscNa (100 mM) or (b) **NiP** (0.05 mM).

Reference

1. N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, *J. Chem. Educ.*, 2018, **95**, 197.