

Supporting Information

Efficient Photochemical Production of Hydrogen in Aqueous Solution by Simply Incorporating a Water-insoluble Hydrogenase Mimic into Hydrogel

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Materials.

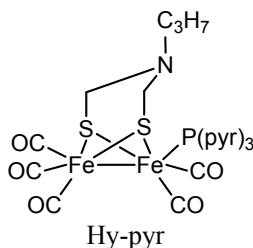
Reagents were purchased from Acros, Alfa Aesar, or Beijing Chemicals and used without further purification unless otherwise noted. Milli-Q deionized water (Millipore) was used in the PVP-gel preparation and the light-driven hydrogen production experiments. THF was dried with sodium, and distilled under a N₂ atmosphere. All solvents used for spectroscopic measurements were spectral grade.

Instruments.

¹H NMR (400 MHz) spectra were obtained on a Bruker Avance II-400 spectrometer with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. ESI mass spectra were recorded on a Waters LCT Premier XE apparatus. Absorption and emission spectra were obtained on a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively. The electrochemical experiments were determined by using glassy carbon

electrodes. Cyclic voltammetric measurement was recorded on CHI600C. The transient absorption spectra were performed on an Edinburgh LP 920 pump-probe spectroscopic setup. The analysis of hydrogen production was carried out on a Shimadzu GC-2014 with a TCD detector.

Synthesis and characterization of the hydrogenase mimic (Hy-pyr).



Hy-pyr was synthesized and purified according to the literature procedures.^{1, 2} A solution of $[\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6]$ (2.0 g, 5.8 mmol) in dry THF (100 mL) was precooled to $-78\text{ }^\circ\text{C}$, and then treated with LiBHET_3 (11.6 mL, 1 mol L^{-1} in THF). After the mixture was stirred for 10 min, CF_3COOH (11.6 mmol) and $\text{C}_3\text{H}_7\text{N}(\text{CH}_2\text{OH})_2$ (7.4 g, 62 mmol) were added in order. The mixture was warmed to room temperature for additional 12 h. A crude product was obtained by removal of the solvent, which was purified by using flash chromatography (petroleum ether/methylene chloride = 10/1) to give a dark red solid $[\{(\mu\text{-SCH}_2)_2\text{NC}_3\text{H}_7\}\text{Fe}_2(\text{CO})_6]$ (2.3 g, 92%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 0.80 (t, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.61 (t, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.51 (s, 4H, $-\text{NCH}_2\text{S}$). MS (ESI-TOF) m/z : found 429.8812 ($\text{M}+\text{H}^+$), calcd. m/z 429.8805 ($\text{M}+\text{H}^+$).

The CO-removing reagent $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.16 g, 1.4 mmol) was added to the solution of $[\{(\mu\text{-SCH}_2)_2\text{NC}_3\text{H}_7\}\text{Fe}_2(\text{CO})_6]$ (0.6 g, 1.4 mmol) in CH_3CN (50 mL), and the mixture was stirred at room temperature for 10 min. Ligand $\text{P}(\text{pyr})_3$ (0.32 g, 1.4 mmol) was added to the mixture. The reaction solution was refluxed for 6 h. After solvent was removed on a rotary evaporator, the crude product was purified by using flash chromatography (petroleum ether/methylene chloride = 10/1) to give a dark red solid (0.35 g).

IR (KBr) $\nu(\text{cm}^{-1})$: 2053 (CO), 2010 (CO), 1982 (CO). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ = 0.65 (t, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.07 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.08 (t, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.58 (s, 2H, $-\text{NCH}_2\text{S}$), 3.02 (s, 2H, $-\text{NCH}_2\text{S}$), 6.38 (s, 6H, pyr), 6.89 (s, 6H, pyr). MS (ESI-TOF) m/z: found 630.9635 ($\text{M}+\text{H}^+$), calcd. m/z 630.9625 ($\text{M}+\text{H}^+$).

PVP-gel production.

An aqueous solution of 10% PVP in the average molecular weight of 1,300,000 was placed in a Petri dish. Irradiation was carried out using a 500 W high pressure mercury lamp to make the PVP cross-link. The mercury lamp was placed longwise 5 cm distant from top of the solution. After 8 h of irradiation and 24 h of vacuum drying to remove the water, the xerogel was separated from the Petri dish.

Hy-pyr/PVP preparation.

The Hy-pyr/PVP catalyst used in hydrogen production system was prepared by the following procedure. A solution of Hy-pyr in methanol (5 μM , 2 mL) was added into 100 mg xerogel particles. After all the liquid was sucked up into gel, the dried Hy-pyr/PVP catalyst was obtained by evaporating the solvent from the swollen gel.

Photocatalytic hydrogen generation.

All H_2 photoproduction experiments were performed in a Pyrex reactor with 10 mL sample solution and a magnetic stir. The sample solutions were purged with Nitrogen for 30 min prior to irradiation. A 300 W Xe lamp was used as the visible light source with filters cutting off the light below 400 nm and above 780 nm. The generated photoproduct of hydrogen was quantified by GC analysis using a 5 Å molecular sieve column, a TCD detector, and N_2 carrier gas with methane as an internal standard. An Ophir Nova II power meter was used to measure the light intensity.

Electrochemical experiment.

A three-electrode system (a 3 mm glass carbon working electrode, a platinum wire counter electrode, and a nonaqueous Ag/Ag⁺ reference electrode) was used to measure the cyclic voltammograms. The working electrode was polished with a 0.05 μm alumina paste and sonicated for 10 min before use. The electrolyte solution with 0.1 M n-Bu₄NPF₆ was purged with argon for 30 min before measurement.

Estimation of the free energy change (ΔG) for different electron transfer routes.

The ΔG_a of direct electron transfer from the excited photosensitizer *Ru(bpy)₃²⁺ to Hy-pyr involved in an electron transfer process was estimated by the equation:

$$\Delta G_a = E(D^{\bullet+}/D) - E(A/A^{\bullet-}) - E_{0,0} - e^2/r\epsilon - e^2/2(1/r_+ + 1/r_-)(1/\epsilon' - 1/\epsilon)$$

$E(D^{\bullet+}/D)$ and $E(A/A^{\bullet-})$ are the oxidation potential of electron donor Ru(bpy)₃³⁺/Ru(bpy)₃²⁺ and the reduction potential of electron acceptor (Fe^IFe^I/Fe^IFe⁰), respectively. $E_{0,0}$ represents the excited state energy of Ru(bpy)₃²⁺ here. The $e^2/r\epsilon$ represents the Coulombic energy associated with bringing separated radical ions at a distance r in a solvent of dielectric constant ϵ (37.5, acetonitrile). The distance between the donor and the acceptor (r) is about 80 Å. The term of $e^2/2(1/r_+ + 1/r_-)(1/\epsilon' - 1/\epsilon)$ is the Born correction to the solvation energy, which depends on the radius of the donor cation (r_+) and the acceptor anion (r_-). To estimate the Born correction to the solvation energy, we set r_+ and r_- equal to 6 and 6 Å, respectively, by assuming that both donor and acceptor are spherical ($\epsilon' = 80.1$, water). The obtained free energy change data are summarized in supplementary Table S1.

The ΔG_b of the electron transfer from the reduced photosensitizer Ru(bpy)₃⁺ to Hy-pyr involved in an electron transfer process was estimated by the following equation:

$$\Delta G_b = E(D/D^{\bullet-}) - E(A/A^{\bullet-}) - e^2/r\epsilon - e^2/2(1/r_+ + 1/r_-)(1/\epsilon' - 1/\epsilon)$$

$E(D/D^{\bullet-})$ and $E(A/A^{\bullet-})$ are the reduction potential of electron donor Ru(bpy)₃²⁺/Ru(bpy)₃⁺ and electron acceptor (Fe^IFe^I/Fe^IFe⁰), respectively. The obtained free energy change data are also listed in Table S1.

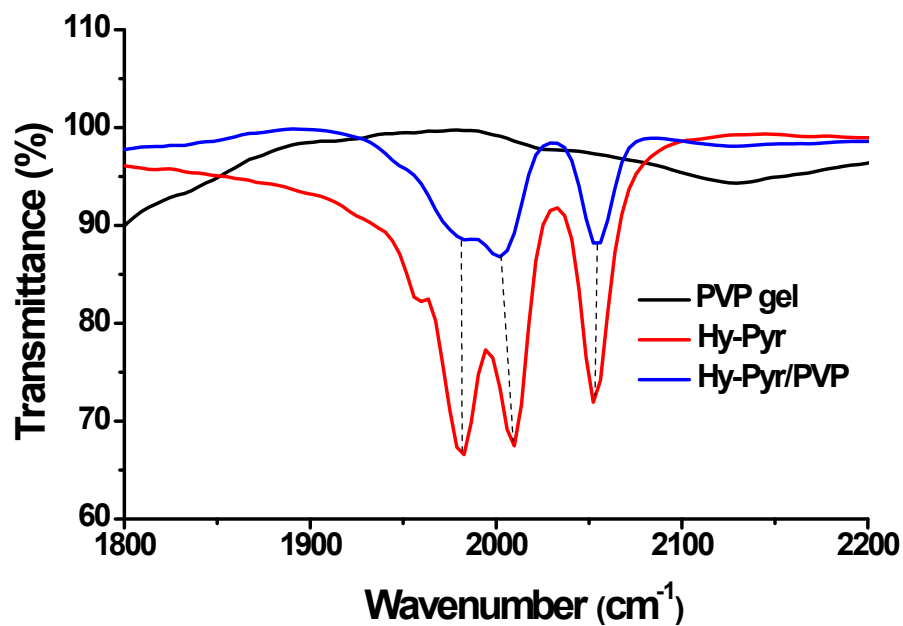


Figure S1. Infrared spectra of PVP gel (black), Hy-pyr (red) and Hy-pyr/PVP (blue).

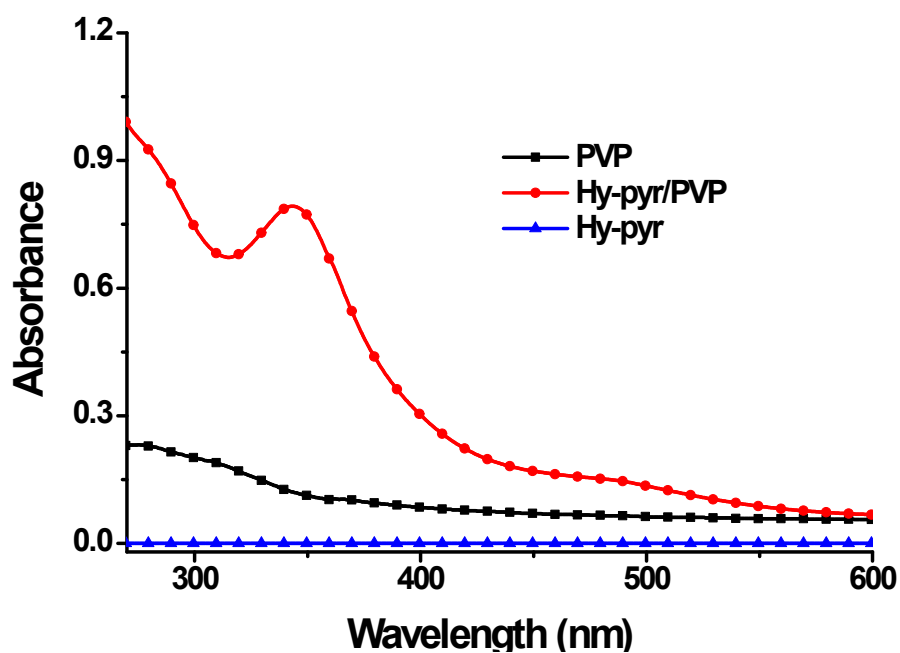


Figure S2. UV-Vis absorption spectra of the aqueous dispersions of the PVP hydrogel (10 mg/mL, black square), Hy-pyr (5×10^{-5} M, blue triangle) and Hy-pyr/PVP ($[\text{Hy-pyr}] = 1 \times 10^{-4}$ M, $[\text{PVP hydrogel}] = 10$ mg/mL, red circle).

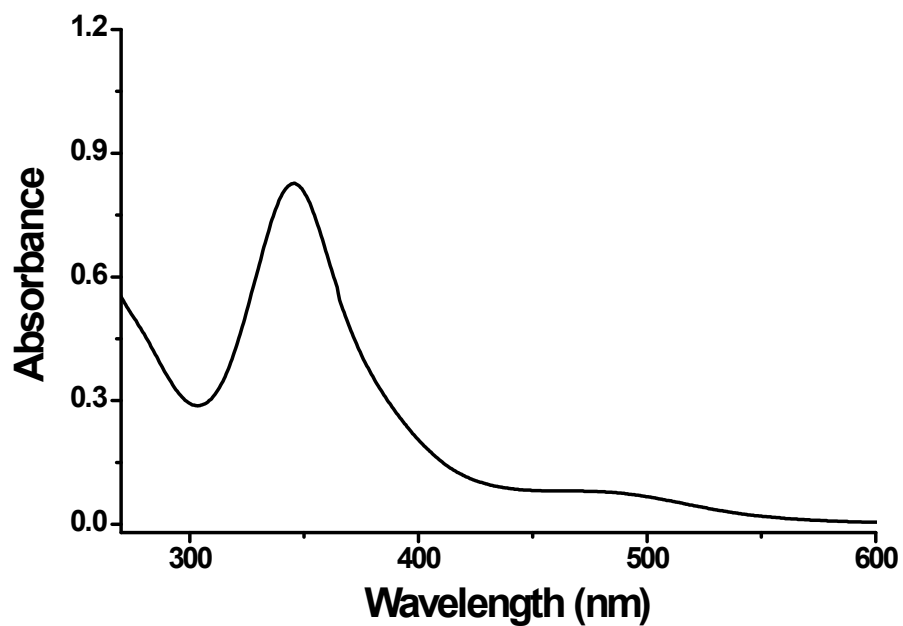


Figure S3. UV-Vis absorption spectrum of Hy-pyr (5×10^{-5} M) in CH₃CN.

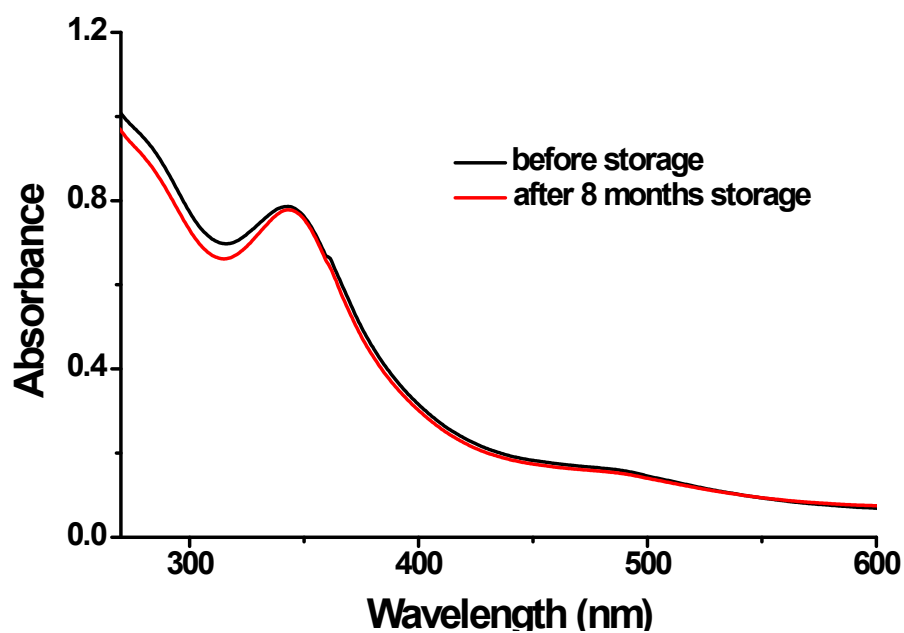


Figure S4. UV-Vis absorption spectra of the aqueous dispersion of Hy-pyr/PVP (Hy-pyr, 5×10^{-5} M). black: fresh prepared Hy-pyr/PVP; red: Hy-pyr/PVP after storage in a refrigerator (4 °C) for 8 months.

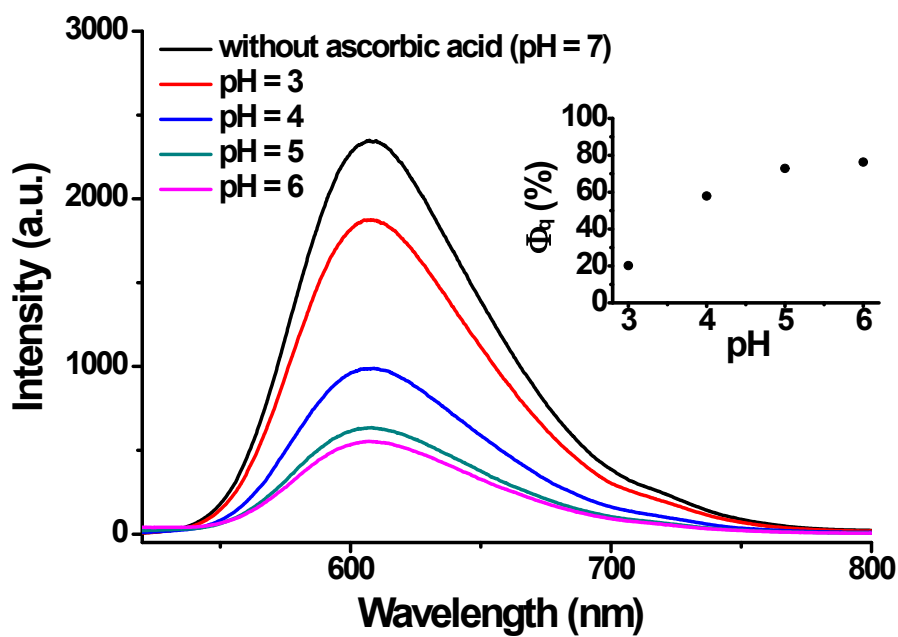


Figure S5. Emission spectra of aqueous solutions of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (5×10^{-5} M) in the absence and presence of ascorbic acid (0.2 M) at different pH values, $\lambda_{\text{ex}} = 450$ nm. Inset: the luminescence quenching efficiency (Φ_q) of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ by ascorbic acid at different pH values.

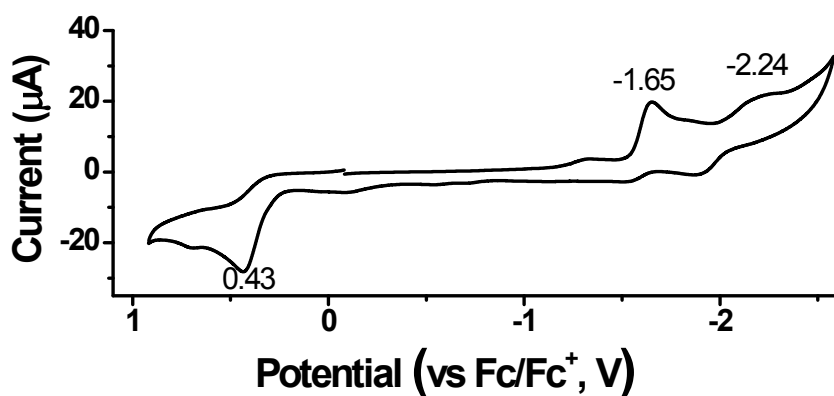


Figure S6. Cyclic voltammogram of Hy-pyr (1 mM) in CH_3CN with 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as the electrolyte at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ under Ar atmosphere.

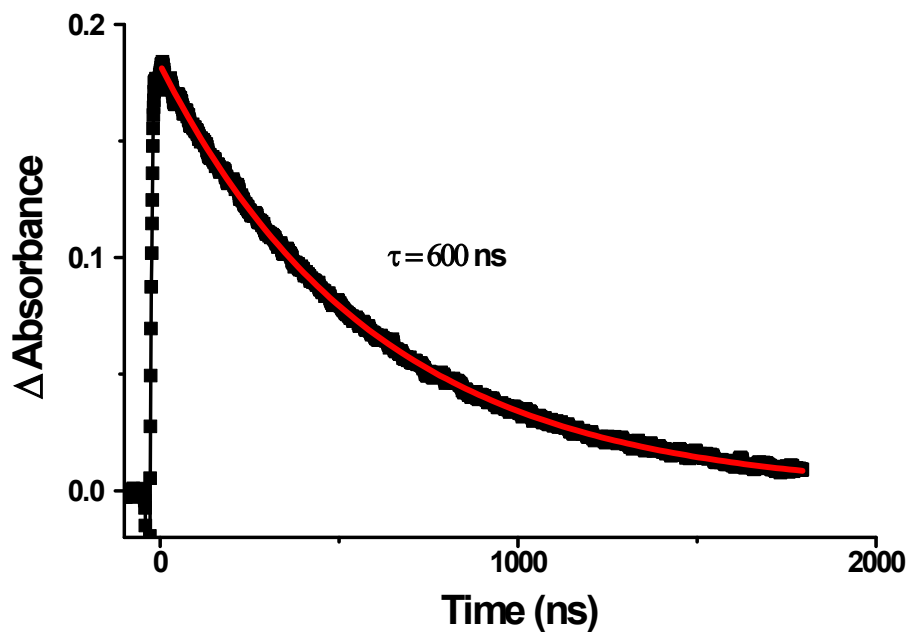


Figure S7. Kinetic trace at 360 nm obtained following laser flash photolysis of a deoxygenated aqueous solution containing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (5×10^{-5} M) and Hy-pyr/PVP ($[\text{Hy-pyr}] = 1 \mu\text{M}$, $[\text{PVP Hyrogel}] = 10$ mg/mL) at pH = 4. $\lambda_{\text{ex}} = 450$ nm.

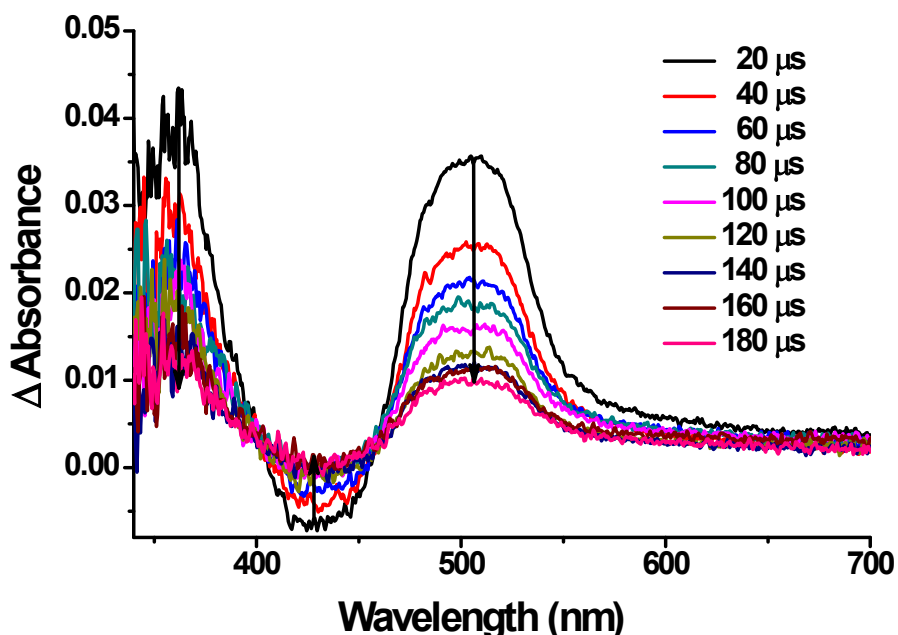


Figure S8. Transient absorption spectra obtained between 20 μs and 180 μs following laser flash photolysis of a deoxygenated aqueous solution containing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (5×10^{-5} M), ascorbic acid (0.2 M), Hy-pyr/PVP ($[\text{Hy-pyr}] = 1 \times 10^{-4}$ M, $[\text{PVP Hyrogel}] = 10$ mg/mL) at pH = 4. $\lambda_{\text{ex}} = 450$ nm.

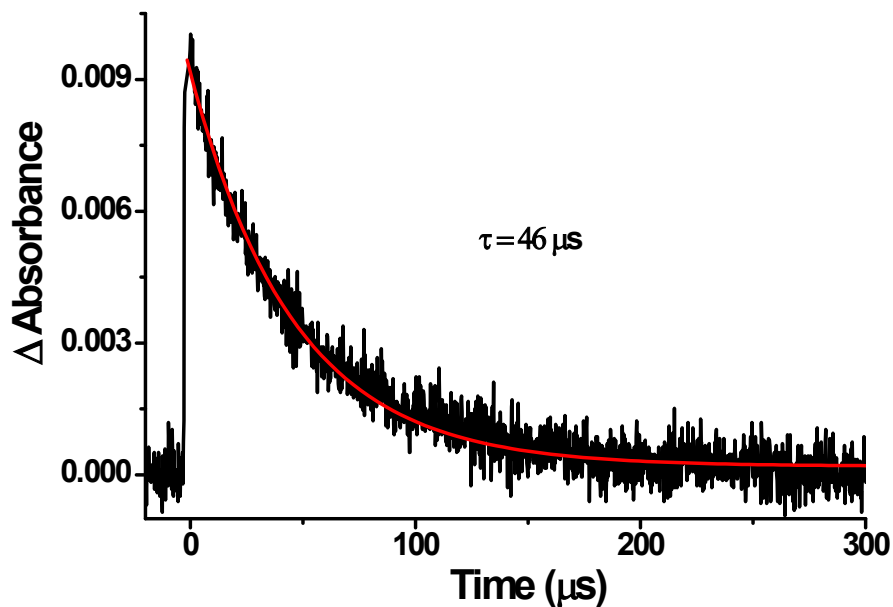


Figure S9. Kinetic trace at 505 nm obtained following laser flash photolysis of a deoxygenated aqueous solution containing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (5×10^{-5} M) and ascorbic acid (0.2 M) at pH = 4. $\lambda_{\text{ex}} = 450$ nm.

Table S1. Free energy change for the direct oxidative quenching of photosensitizer (ΔG_a) and the quenching of reduced photosensitizer by Hy-pyr (ΔG_b) in CH_3CN and in water.

	in CH_3CN	in water
ΔG_a (eV)	0.68	0.64
ΔG_b (eV)	-0.05	-0.09

1. J. D. Lawrence, H. X. Li and T. B. Rauchfuss, *Chem. Commun.*, 2001, 1482-1483.
2. Y. Na, M. Wang, J. X. Pan, P. Zhang, B. Akermark and L. C. Sun, *Inorg. Chem.*, 2008, **47**, 2805-2810.