Supporting Information

Photoinduced hydrogen evolution by a pentapyridine cobalt complex: elucidating some mechanistic aspects.

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Synthesis and characterization

[Co(II)(Py5)Cl]Cl (1). **1** was obtained following a slightly adapted literature procedure [R. J. M. Klein Gebbink, R. T. Jonas and T. D. P. Stack, *Inorg.Chem.*, 2002, **41**, 4633]. **Py5** (50.0 mg, 0.10 mmol) and $CoCl_2 \cdot 6H_2O$ (23.8 mg, 0.10 mmol) were dissolved in methanol (15 mL) and refluxed under Ar atmosphere. The reaction was followed by thin layer chromatography (SiO_2, CH_2Cl_2/MeOH = 95/5, R_f = 0.52 and 0.02 for **Py5** and **1**, respectively), until complete consumption of the ligand. The pink solution was concentrated in vacuum and a pink microcrystalline solid was precipitated by addition of diethyl ether. The solid was filtered, washed thoroughly with cold diethyl ether and dried under vacuum. Yield: 54.0 mg (89.2%). ESI-MS: m/z calcd. for $C_{29}H_{25}N_5O_2ClCo$ ($\mathbf{1}^+$) 569.1, found 569.1.

Table S1. Photolysis data at different catalyst concentration and at pH 4: turnover numbers (TONs), turnover frequencies (TOFs), and initial rates.[a]

[**1**] (μM)	TON	TOF (min^{-1})	Initial rate (μmol min^{-1})[b]
10	100	4.8	0.24
25	111	3.9	0.49
50	187	8.1	2.03
75	181	5.7	2.13
100	169	5.8	2.92

[a] Data referred to experiments shown in Figure 2 of the main article obtained upon continuous visible irradiation ($\lambda > 400$ nm) of 1 M acetate buffer pH 4 solutions (5 mL) containing 0.5 mM $Ru(bpy)_3^{2+}$, 0.1 M ascorbic acid, and **1** (10-100 μM); [b] initial rates are calculated from the slope in the linear part of the kinetic traces.

Table S2. Photolysis data at different pH and at 50 μM **1**: turnover numbers (TONs), turnover frequencies (TOFs), and rates.[a]

pH	TON	TOF (min^{-1})	Initial rate (μmol min^{-1})[b]
3	143	4.8	1.20
4	187	8.1	2.03
5	205	7.2	1.80
6	98	2.8	0.70
7	72	1.0	0.25

[a] Data referred to experiments shown in Figure S1 obtained upon continuous visible irradiation ($\lambda >$ 400 nm) of solutions (5 mL) containing 0.5 mM $Ru(bpy)_3^{2+}$, 0.1 M ascorbic acid, and **1** 50 μM at different pH (1 M acetate buffer for pH 3, 4, and 5, and 1 M phosphate buffer for pH 6 and 7); [b] initial rates are calculated from the slope in the linear part of the kinetic traces.

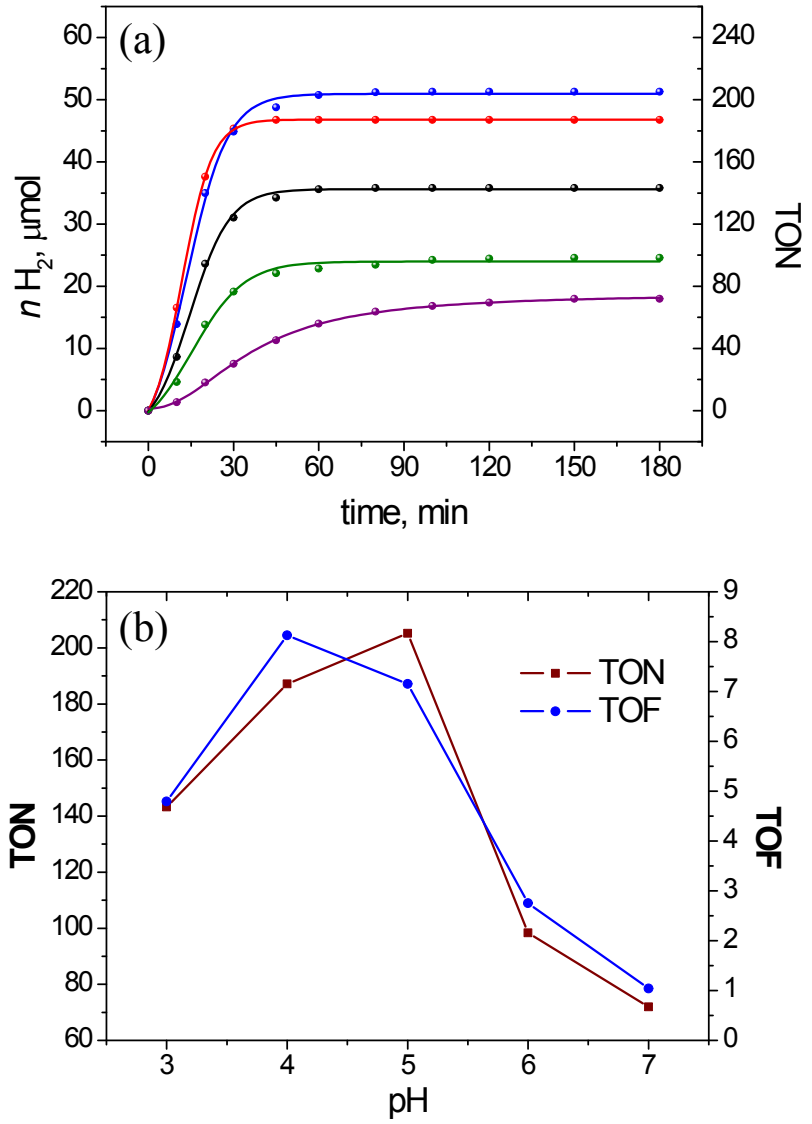

Figure S1. (a) Hydrogen evolution kinetics obtained upon continuous visible irradiation ($\lambda > 400$ nm) of solutions (5 mL) containing 0.5 mM $Ru(bpy)_3^{2+}$, 0.1 M ascorbic acid, and 50 µM **1** in 1 M acetate buffer at pH 3 (black trace), pH 4 (red trace), pH 5 (blue trace), and 1 M phosphate buffer at pH 6 (green trace), and pH 7 (purple trace); (b) plot of TON and TOF as a function of the pH.

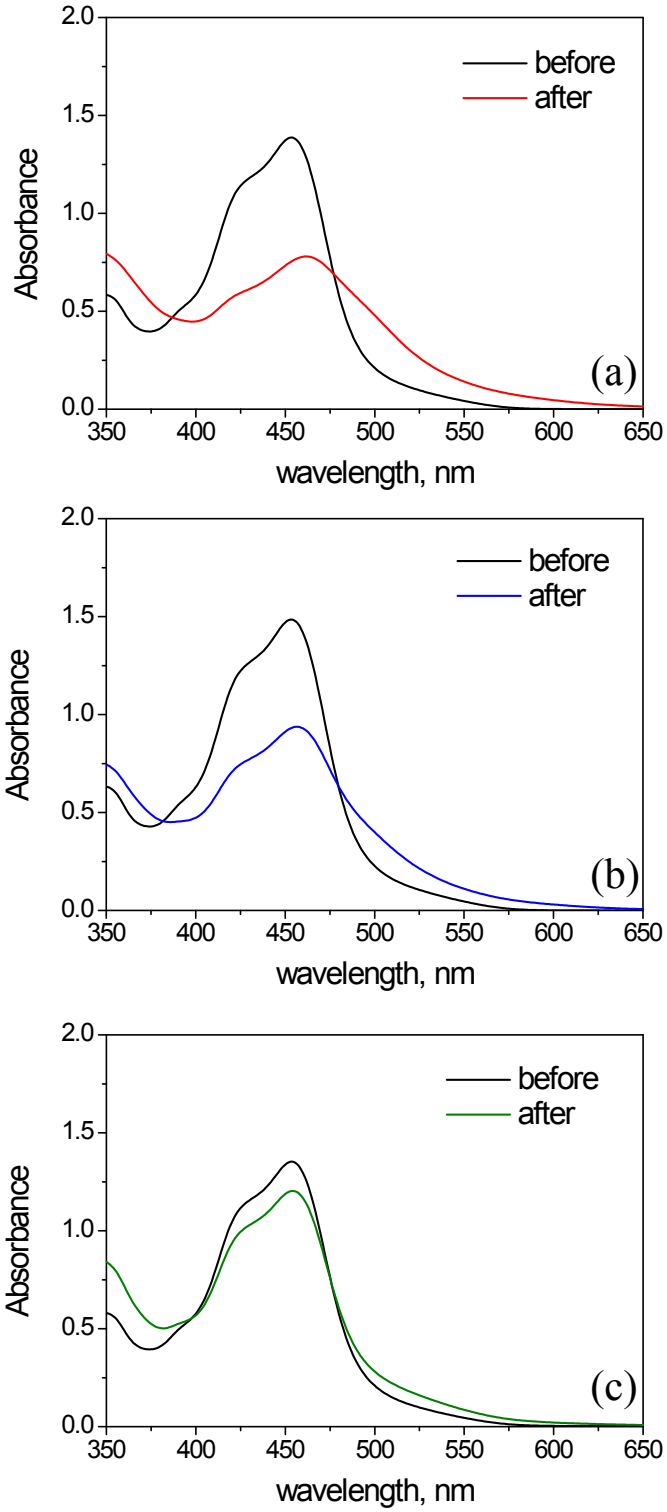

Figure S2. Comparison of absorption spectra before/after photolysis of solutions (5 mL) containing 0.5 mM $Ru(bpy)_3^{2+}$, 0.1 M ascorbic acid, and 50 μM **1** at (a) pH 4, (b) pH 5, and (c) pH 6.

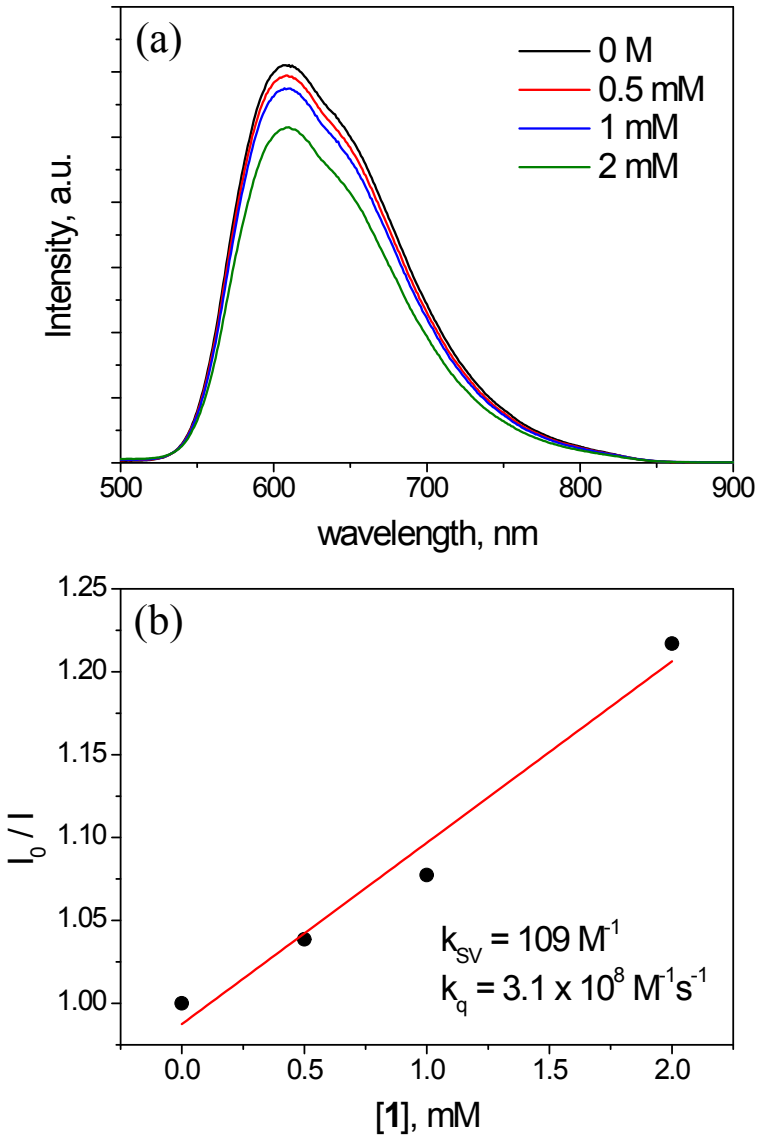

Figure S3. (a) Photoluminescence spectra (excitation at 400 nm) of solution containing 50 μM $Ru(bpy)_3^{2+}$ in 1 M acetate buffer at pH 4 after addition of different aliquots of **1** (0-2 mM); (b) Stern-Volmer plot of quenching by **1**.

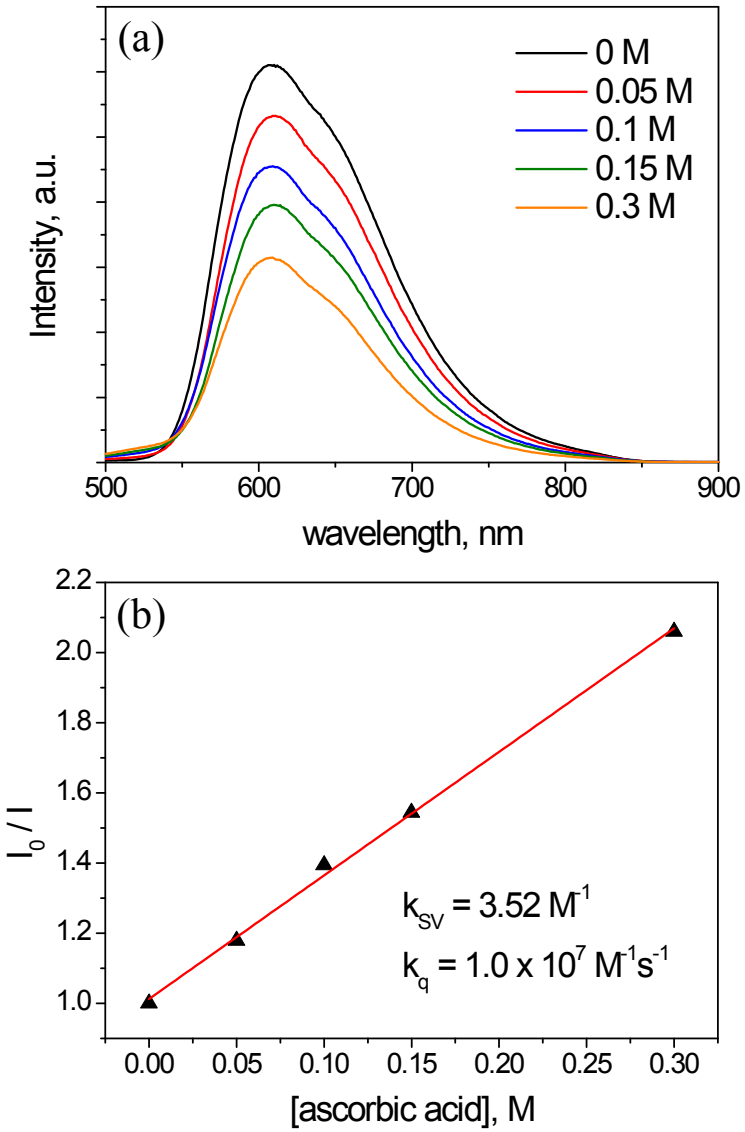

Figure S4. (a) Photoluminescence spectra (excitation at 400 nm) of solution containing 50 μM $Ru(bpy)_3^{2+}$ in 1 M acetate buffer at pH 4 after addition of different aliquots of ascorbic acid (0-0.3 M); (b) Stern-Volmer plot of quenching by ascorbic acid.

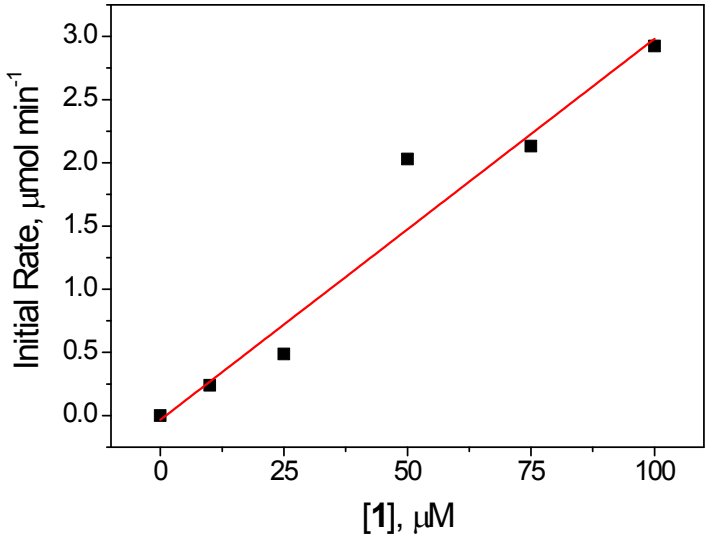

Figure S5. Plot of the initial rate of hydrogen evolution vs. catalyst concentration obtained from the kinetic traces of Figure 2 of the main article. The initial rates are calculated from the slope in the linear part of the kinetic traces.