Supporting Information

Efficient photocatalytic hydrogen generation from water by a cationic cobalt(II) porphyrin

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Materials and Methods

Materials. Acetonitrile for electrochemical studies was of spectroscopic grade, while for photophysical and photolysis experiments Milli-Q Ultrapure water and related buffer were used, all the other reagents were of reagent grade quality, and used as received. $Ru(bpy)_3Cl_2·6H_2O$, ascorbic acid and 5,10,15,20-tetrakis (4'-pyridyl) porphyrin (**TPyP**) were purchased from Sigma Aldrich. Insertion of cobalt(II) inside the **TPyP** porphyrin core, and methylation of the four peripheral pyridyl groups of Zn(II)TPyP and Co(II)TPyP, were performed following slightly adapted literature procedures, see below.[S1,S2]

NMR. [1]H spectra were recorded on a *Varian 500* (500 MHz) or on a *JEOL Eclipse 400FT* (400 MHz) spectrometer. All spectra were run at room temperature; ^{1}H chemical shifts were referenced to the peak of residual non-deuterated solvent (δ = 7.26 ppm for $CDCl_3$, 2.50 ppm for DMSO-d_6) or to TMS (δ = 0 ppm) for D_2O.

Mass Spectrometry. Electrospray Ionization (ESI) measurements were performed on a *Perkin Elmer APII* at 5600 eV by Dr. Fabio Hollan, Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy.

Electrochemical Meaurements. Cyclic Voltammetry (CV) measurements were carried out with a PC-interfaced *Eco Chemie Autolab/Pgstat 30* Potentiostat. Argon-purged 10^{-4} M sample solutions in acetonitrile, containing 0.1 M $LiClO_4$, or in 1 M phosphate buffer at pH 7 were used. A conventional three-electrode cell assembly was adopted: a saturated calomel electrode (SCE Amel) and a platinum electrode, both separated from the test solution by a frit, were used as reference and counter electrodes, respectively; a glassy carbon electrode was used as the working electrode.

Steady-state Absorption/Emission Measurements. UV-Vis absorption spectra were recorded on a *Jasco V-570 UV/Vis/NIR* or on a *V-550 UV/Vis* spectrophotometer. Emission spectra were

taken on a *Horiba-Jobin Yvon Fluoromax-2* spectrofluorimeter, equipped with a *Hamamatsu R3896* tube.

Nanosecond Laser Flash Photolysis. Nanosecond transient measurements were performed with a custom laser spectrometer comprised of a *Continuum Surelite II* Nd:YAG laser (FWHM 6-8 ns) with frequency doubled, (532 nm, 330 mJ) or tripled, (355 nm, 160 mJ) option, an *Applied Photophysics* xenon light source including a mod. 720 150 W lamp housing, a mod. 620 power controlled lamp supply and a mod. 03-102 arc lamp pulser. Laser excitation was provided at 90° with respect to the white light probe beam. Light transmitted by the sample was focused onto the entrance slit of a 300 mm focal length *Acton SpectraPro 2300i* triple grating, flat field, double exit monochromator equipped with a photomultiplier detector (*Hamamatsu R3896*) and a *Princeton Instruments PIMAX II* gated intensified CCD camera, using a *RB Gen II* intensifier, a ST133 controller and a PTG pulser. Signals from the photomultiplier (kinetic traces) were processed by means of a *LeCroy 9360* (600 MHz, 5 Gs/s) digital oscilloscope.

Photolysis Apparatus. The hydrogen evolution experiments were carried out upon continuous visible light irradiation with a 175 W xenon *CERMAX* arc-lamp (cut-off filter at 400 nm) of a reactor (a 10 mm pathlength pyrex glass cuvette with head space obtained from a round-bottom flask) containing the solution. The measuring cell is sealed during the photoreaction: the head to which cell is attached has indeed four ports, closed with Swagelok® connections, two of them are part of a closed loop involving GC gas inlet and sample vent in order to analyze head space content without an appreciable gas consumption, and the other two are for the degassing procedure (input and output).

Gas Chromatography. The gas phase of the reaction vessel was analyzed on an *Agilent Technologies* 490 microGC equipped with a 5 Å molecular sieve column (10 m), a thermal conductivity detector, and using Ar as carrier gas. 5 mL from the headspace of the reactor are

sampled by the internal GC pump and 200 nL are injected in the column maintained at 60°C for separation and detection of gases. The unused gas sample is then reintroduced in the reactor in order to minimize its consumption along the whole photolysis. The amount of hydrogen was quantified through the external calibration method. This procedure was performed, prior to analysis, through a galvanostatic (typically 1 mA) electrolysis of a 0.1 M H_2SO_4 solution in an analogous cell (same volume) equipped with two Pt wires sealed in the glass at the bottom of the cell. A 100% faradaic efficiency was assumed leading to a linear correlation between the amount of H_2 evolved at the cathode and the electrolysis time.

Hydrogen Evolution Experiments. In a typical experiment, samples of 5 mL were prepared in 20 mL scintillation vials by mixing appropriate aliquots of 1 M phosphate buffer, of a 5 mM Ru(bpy)$_3$Cl$_2$·6H$_2$O solution in 1 M phosphate buffer, of a 0.1 mM **CoP** mother solution in 1 M phosphate buffer and further adding **AscH** (as solid). The solution was then put in the reactor, degassed by bubbling Ar for 30 min, and thermostated at 15°C. The cell was then irradiated under continuous vigorous stirring of the solution. The gas phase of the reaction was analyzed through GC and the amount of hydrogen quantified.

Synthesis and characterization
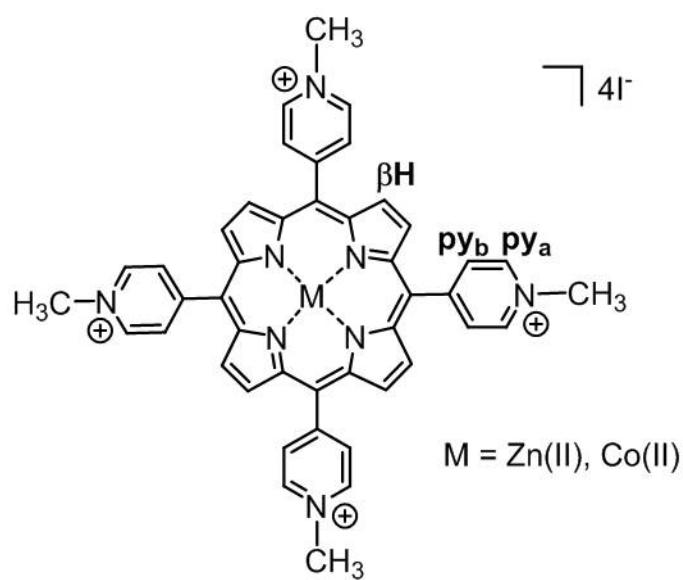
Chart S1.

5,10,15,20-tetrakis (4'-pyridyl) zinc(II) porphyrin − Zn(II)TPyP. TPyP (49.5 mg, 0.080 mmol) is dissolved in chloroform (30 mL) and stirred for 16 hours with an excess of $Zn(CH_3COO)_2 \cdot 2H_2O$ (43.9 mg, 0.20 mmol), dissolved in a minimum amount of methanol. The violet product is precipitated by adding methanol to the concentrated reaction mixture, filtered, washed thoroughly with methanol and dried under vacuum. Yield: 51.9 mg (95.1%). UV-Vis. (DCM, λ, nm) 427 (Soret), 560, 599 (Q bands). ^{1}H-NMR (500 MHz, $CDCl_3$ + 40 μL pyridine-d_5, δ, ppm) 8.94 (d, $J = 5.8$ Hz, 8H, py$_a$H), 8.83 (s, 8H, βH), 8.07 (d, $J = 5.8$ Hz, 8H, py$_b$H).

5,10,15,20-tetrakis (4'-pyridyl) cobalt(II) porphyrin − Co(II)TPyP. TPyP (53.7 mg, 0.087 mmol) is dissolved in chloroform (30 mL) and stirred for 16 hours with an excess of $Co(CH_3COO)_2 \cdot 4H_2O$ (54.0 mg, 0.22 mmol) dissolved in a minimum amount of methanol. The reaction is quenched by addition of deionized water (30 mL). A purple product precipitates after cooling the mixture. The precipitated is filtered, washed thoroughly with methanol and dried under

vacuum. Yield: 44.8 mg (76.3%). UV-Vis. (DCM, λ, nm) 425 (Soret), 544 (Q band). ESI-MS m/z calcd. for $C_{40}H_{24}N_8Co$ ($[M]^+$) 675.1, found 675.2.

5,10,15,20-tetrakis (1-methylpyridinium-4'-yl) zinc(II) porphyrin – [Zn(II)NMeTPyP^{4+}][I$^-$]$_4$. Zn(II)TPyP (27.3 mg, 0.040 mmol) is treated in DMF (5 mL) with a large excess of methyl iodide (0.125 mL, 2 mmol) for 2 hours at refluxing temperature. After addition of diethyl ether, a violet solid precipitates and the unreacted CH_3I stays in the diethyl ether phase. The product is filtered, washed with cold diethyl ether, recrystallized with a water/ethanol mixture and dried under vacuum. Yield: 33.8 mg (84.7%). UV-Vis. (H_2O, λ, nm) 436 (Soret), 564, 605 (Q bands).^{1}H-NMR (500 MHz, D_2O, δ, ppm) 9.33 (d, $J = 6.1$, 8H, py$_a$H), 9.16 (s, 8H, βH), 9.01 (d, $J = 6.1$, 8H, py$_b$H), 4.85 (s, 12H, CH_3). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm) 9.43 (d, $J = 4.3$ Hz, 8H, py$_a$H), 9.09 (s, 8H, βH), 8.92 (d, $J = 4.8$ Hz, 8H, py$_b$H), 4.72 (s, 12H, CH_3).

5,10,15,20-tetrakis (1-methylpyridinium-4'-yl) cobalt(II) porphyrin – [Co(II)NMeTPyP^{4+}][I$^-$]$_4$ – CoP. Co(II)TPyP (30.4 mg, 0.045 mmol) is treated in DMF (5 mL) with a large excess of methyl iodide (0.140 mL, 2.25 mmol) for 2 hours at refluxing temperature. After addition of diethyl ether, a purple solid precipitates and the unreacted CH_3I stays in the diethyl ether phase. The product is filtered, washed with cold diethyl ether, recrystallized with a water/ethanol mixture and dried under vacuum. Yield: 27.6 mg (83.4%). ESI-MS m/z calcd. for $C_{44}H_{36}N_8Co^{4+}$ ($[M-4I]^+$) 183.8, found 183.7. UV-Vis (Figure S3). (H_2O, λ, nm) 433 (Soret), 544 (Q band).

Chloro(4-Ethyl-pyridine)bis(dimethylglyoximate) cobalt(III). Co(dmgH)$_2$Cl(EtPy) was synthesized according to literature procedure.[S3]

Calculation of the electron transfer rate constant

The rate of the electron transfer reaction

$$Ru(I) + \textbf{CoP} \rightarrow Ru(II) + \textbf{CoP}^- \tag{1}$$

can be described as follows:

$$v = k\,[Ru(I)][\textbf{CoP}] = k_{obs}\,[Ru(I)] \tag{2}$$

(under pseudo-first order kinetic conditions : $[\textbf{CoP}] \gg [Ru(I)]$)

where k is the «bimolecular rate constant» and:

$$k_{obs} = k\,[\textbf{CoP}] \tag{3}$$

The evolution of $[Ru(I)]$ in time can be monitored by laser flash photolysis:

$$[Ru(I)] = [Ru(I)]_0 \exp(-k_{obs}\,t) \tag{4}$$

and obtaining the k_{obs} value from an exponential fitting of the kinetic traces. By plotting k_{obs} vs. $[\textbf{CoP}]$ and according to eq 3, the slope is k, i.e., the «bimolecular rate constant».

However, it must be considered that recombination of the reduced sensitizer with oxidized **AscH** is in competition with electron transfer to **CoP** (eq 1), therefore electron transfer rates from Ru(I) to **CoP** are calculated as follows:
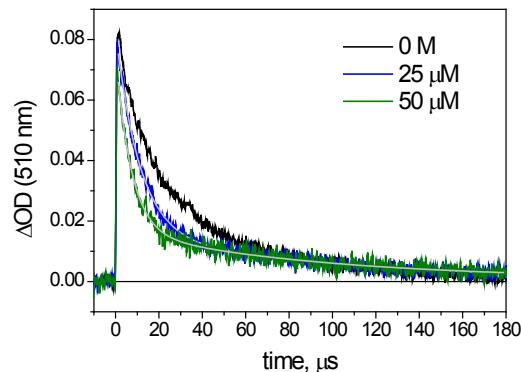
- no **CoP** (black trace): $\tau_0 = 37$ μs

- 25 μM **CoP** (blue trace):

$$\tau_1 = 11 \text{ μs } (80\%), \tau_2 = 115 \text{ μs } (20\%) \text{ with } k_{obs} = 1/\tau_1 - 1/\tau_0$$

- 50 μM **CoP** (green trace):

$$\tau_a = 7 \text{ μs } (80\%), \tau_b = 90 \text{ μs } (20\%) \text{ with } k_{obs} = 1/\tau_a - 1/\tau_0$$

The kinetic traces of 25-50 μM **CoP** solutions are always fitted with bi-exponential functions, the longer component (accounting for the 20% in both cases) is ascribed to the decay of the reduced **CoP** and is therefore not considered in the calculation.
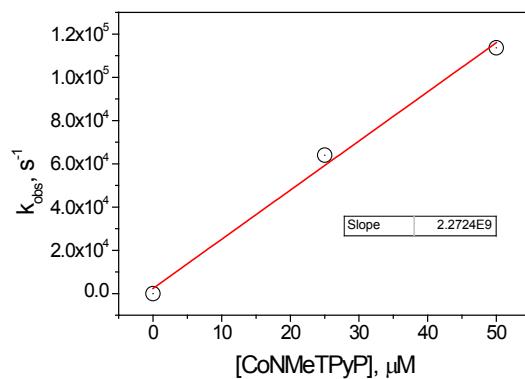
$$k = 2.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

References

[S1]   M. Perrée-Fauvet, C. Verchère-Béaur, E. Tarnaud, G. Anneheim- Herbelin, N. Bône and A. Gaudemer, *Tetrahedron*, 1996, **52**, 13569.

[S2]   B. Steiger, C. Shi and F. C. Anson, *Inorg. Chem.*, 1993, **32**, 2017.

[S3]   G. N. Schrauzer, *Inorg. Synth.*, 1968, **11**, 61.
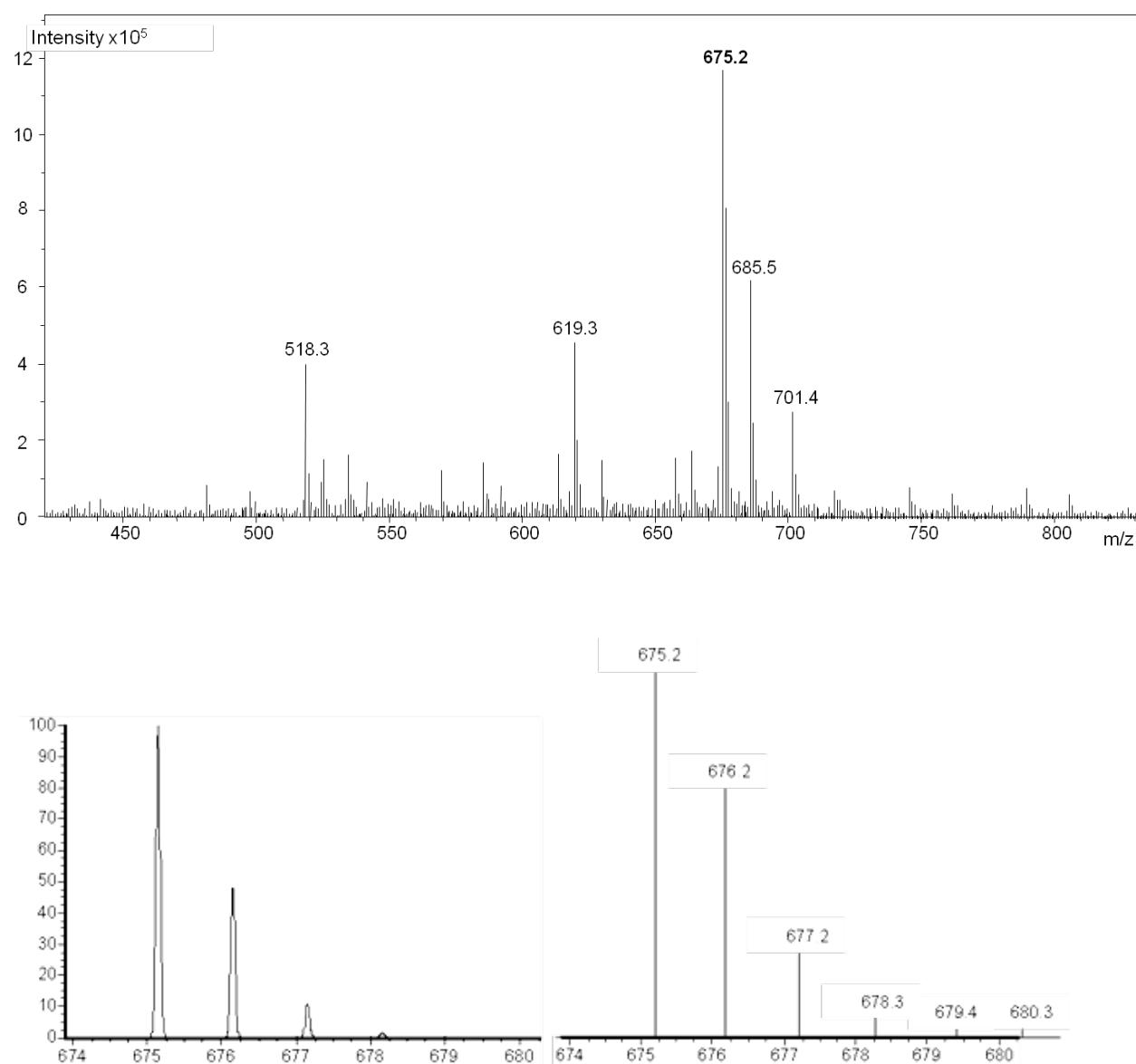
Figure S1. Top: ESI-MS spectrum of **Co(II)TPyP**; m/z calcd. for $C_{40}H_{24}N_8Co$ ([M]$^+$) 675.1, found

675.2. Bottom, left: isotopic distribution calculated of the [M]$^+$ molecular peak (program IsoPro3);

bottom, right: experimental isotopic distribution calculated of the [M]$^+$ molecular peak.
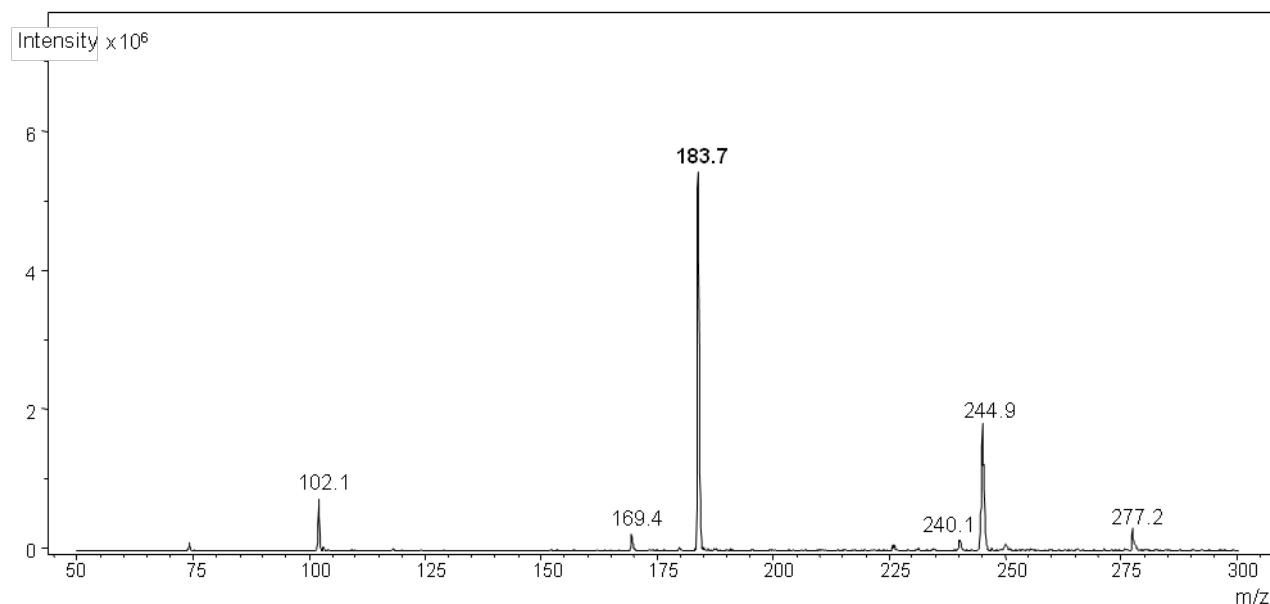
Figure S2. ESI-MS spectrum of **CoP**; m/z calcd. for $C_{44}H_{36}N_8Co^{4+}$ ($[M-4I]^{4+}$) 183.8, found 183.7.
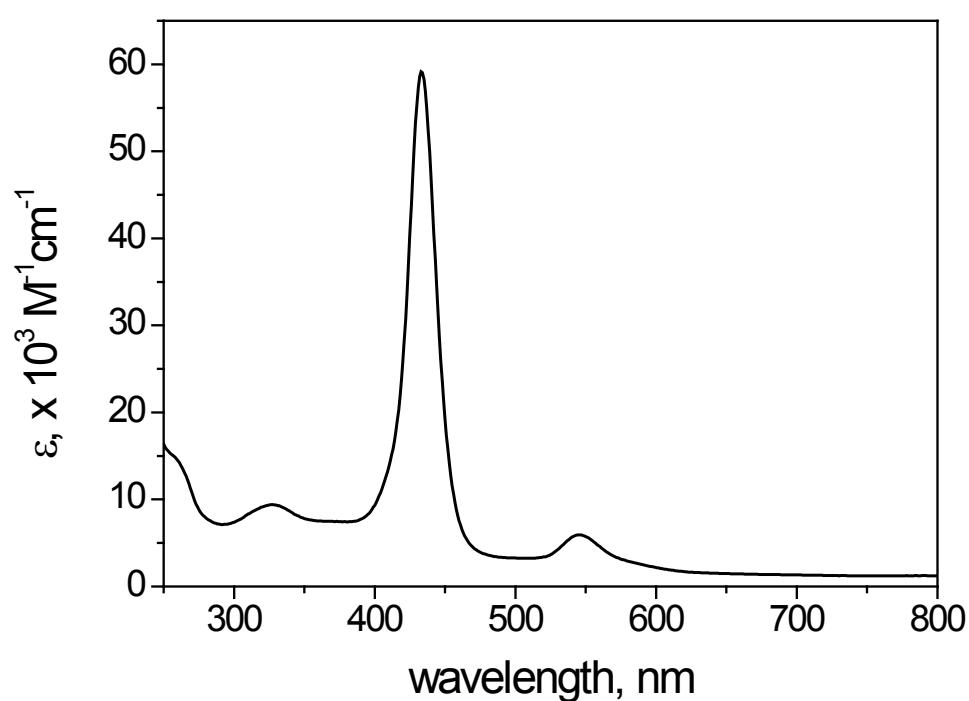
**Figure S3.** Electronic absorption spectrum of **CoP** in water.
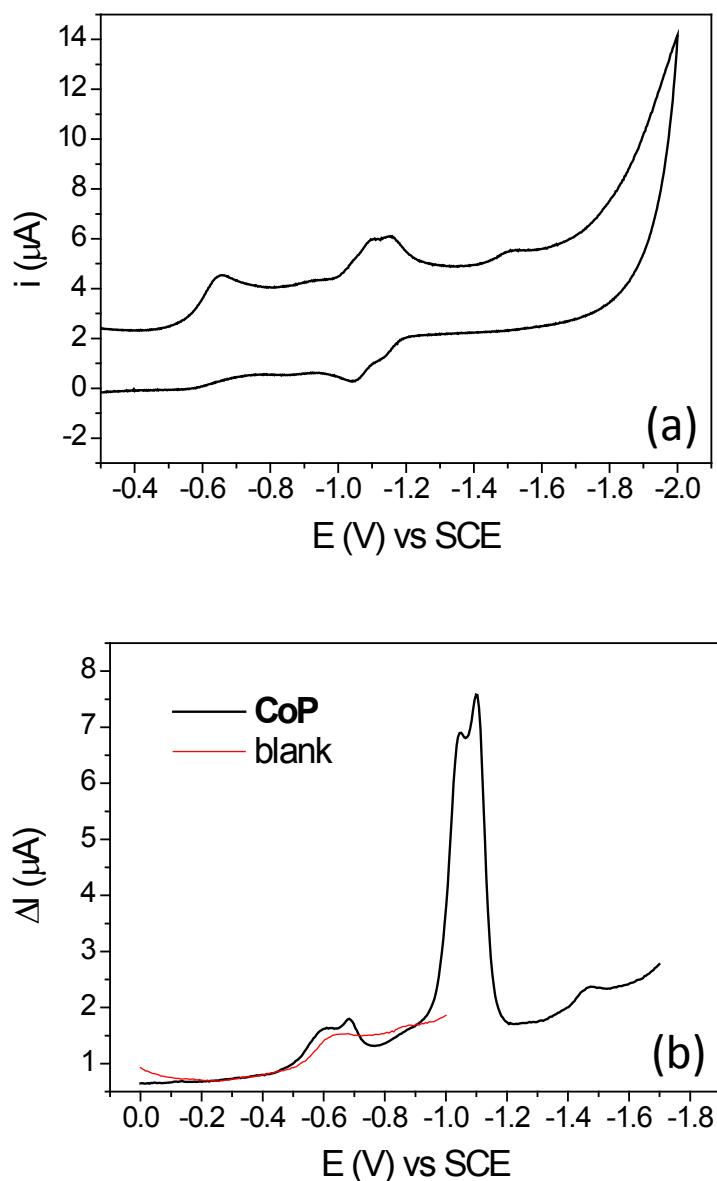
Figure S4. (a) Cyclic voltammetry (CV) of 0.1 mM **CoP** solution in acetonitrile (0.1 M LiClO$_4$, scan rate 100 mV/s, room temperature). (b) Differential pulsed voltammetry (DPV) of 0.1 mM **CoP** solution in acetonitrile (0.1 M LiClO$_4$, ΔE = 20 mV, room temperature), compared with blank. Reduction of dioxygen (inevitably present as residual traces in our working conditions) show up as a distinguishable peak, very close to the first **CoP** reduction, in the DPV measurements. In the CV measurements, it certainly contributes, together with **CoP** reduction, to the intensity of the first unresolved cathodic process.
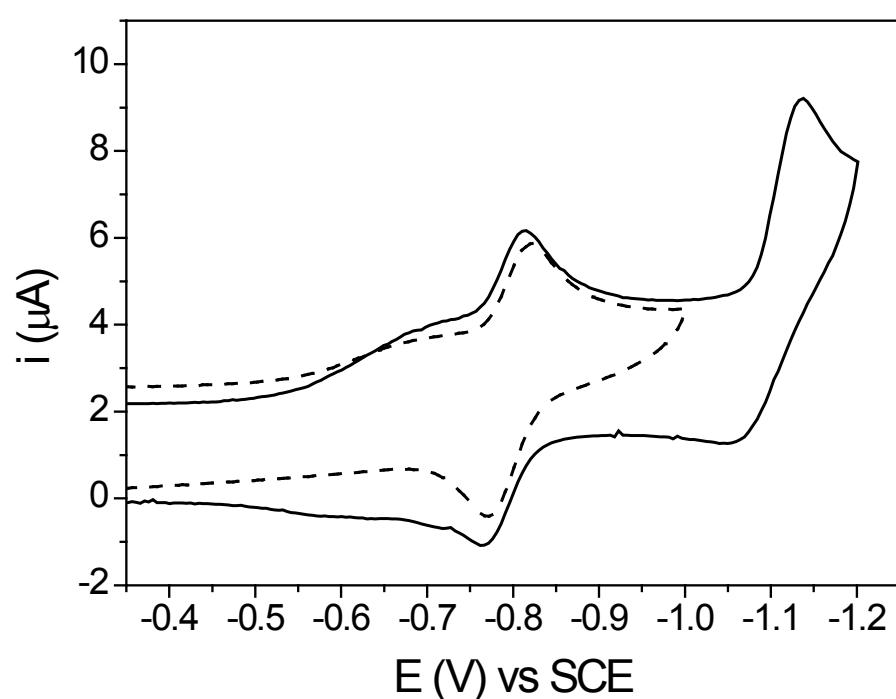
Figure S5. Cyclic voltammetry of 0.1 mM Zn(II)NMeTPyP^{4+} solution in acetonitrile (0.1 M LiClO$_4$, scan rate 100 mV/s, room temperature).
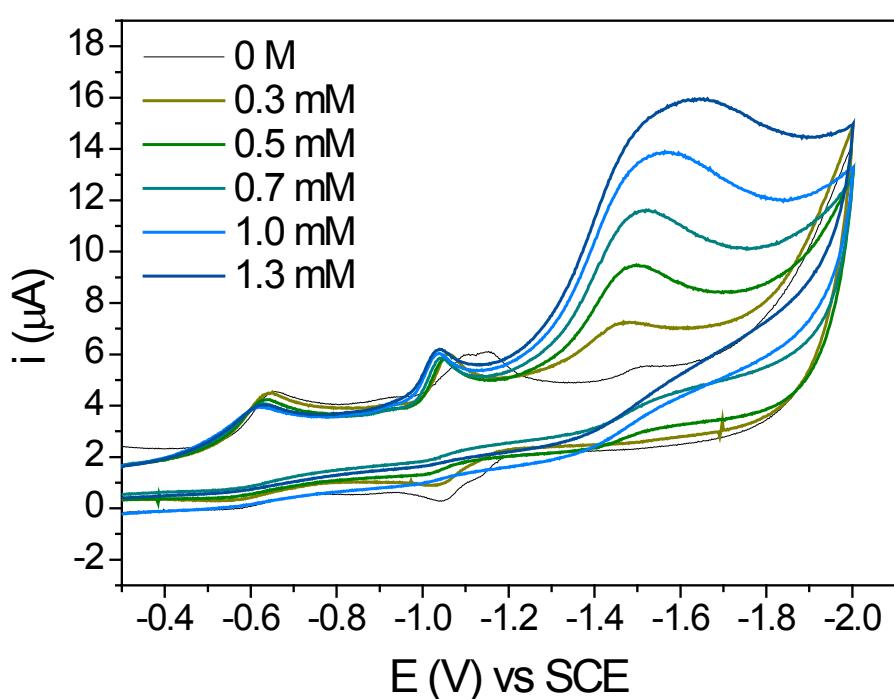
Figure S6. Cyclic voltammetry of 0.1 mM **CoP** solution in acetonitrile (0.1 M LiClO$_4$, scan rate 100 mV/s, room temperature) upon addition of different amount of benzoic acid (0-1.3 mM).
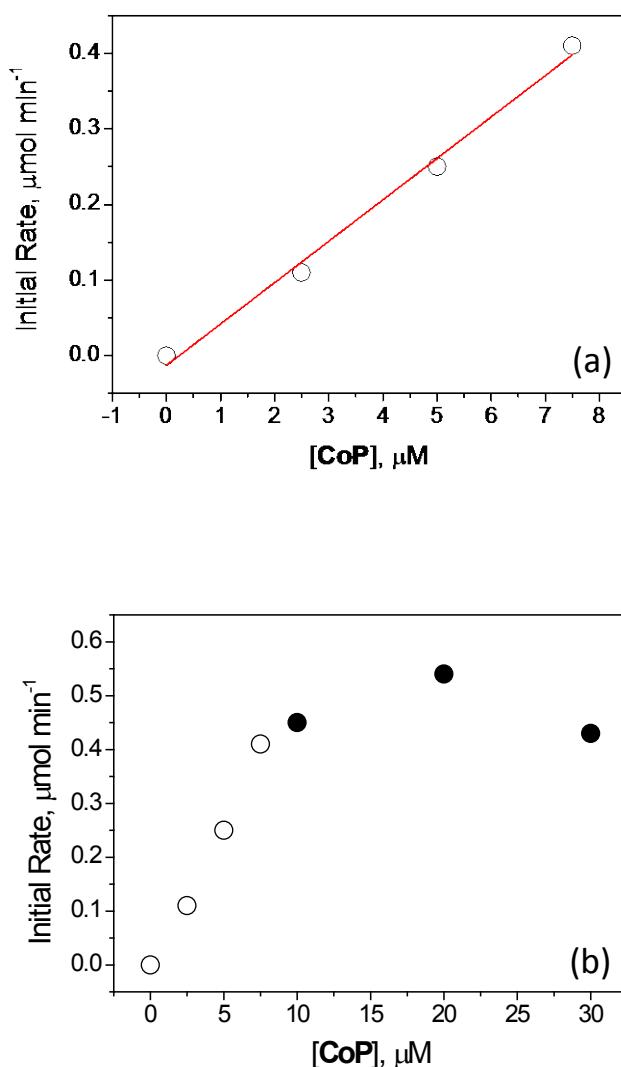
Figure S7. Plots of initial rate of hydrogen production (calculated in the linear part of the kinetic after the induction period) vs **CoP** concentration: (a) 0-7.5 μM and (b) 0-30 μM.
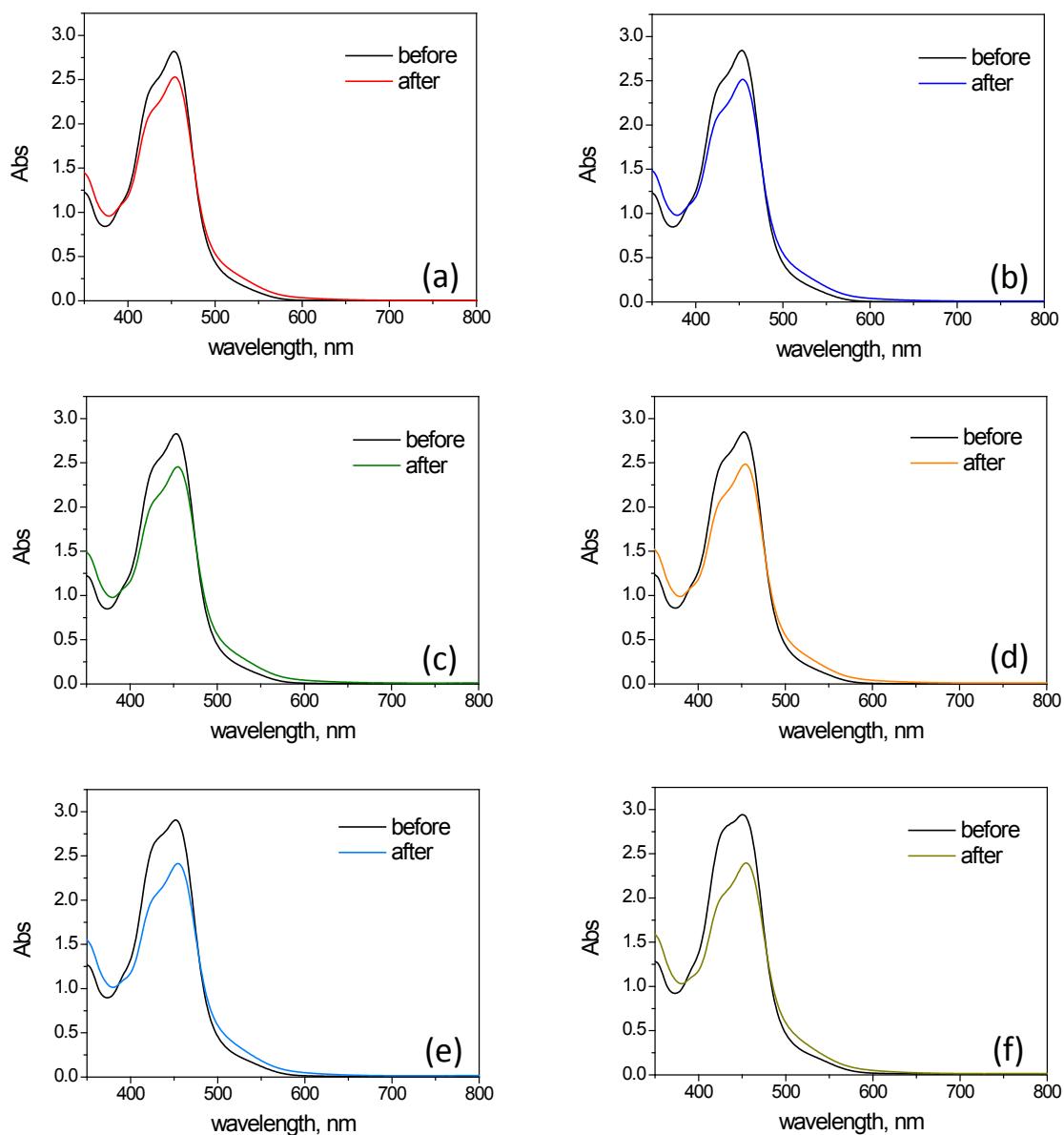
Figure S8. Comparison of absorption spectra before/after photolysis of solution containing 1 mM

Ru(bpy)$_3$$^{2+}$, 0.1 M **AscH** and (a) 2.5 μM (4 h), (b) 5.0 μM (4 h), (c) 7.5 μM (4 h), (d) 10 μM (4 h),

(e) 20 μM (4 h 30 min), and (f) 30 μM (5 h) **CoP** in 1 M phosphate buffer at pH 7.

Figure S9. Kinetic of hydrogen evolution upon irradiation of solutions containing 1 mM Ru(bpy)$_3{}^{2+}$, 0.1 M **AscH**, and 5 μM **CoP** (black trace) or 5 μM cobaloxime (red trace) in 1 M phosphate buffer at pH 7.

Figure S10. Kinetic of hydrogen evolution upon irradiation of solutions containing 1 mM Ru(bpy)$_3$$^{2+}$, 0.1 M **AscH**, and 2.5 μM **CoP** (red trace) or 100 μM cobaloxime (black trace) in 1 M phosphate buffer at pH 7.
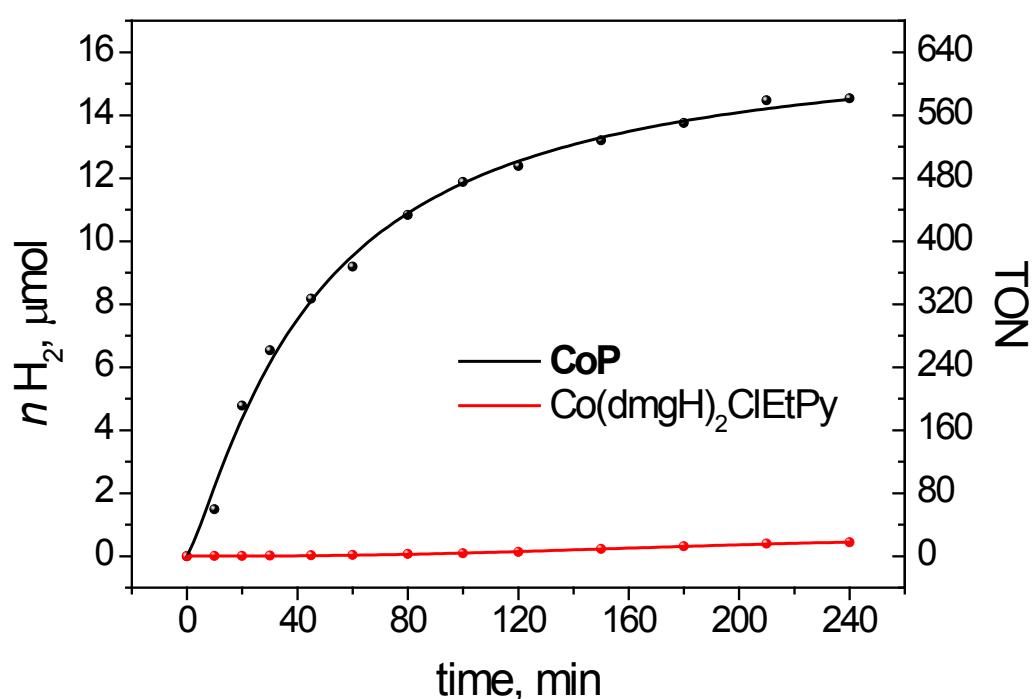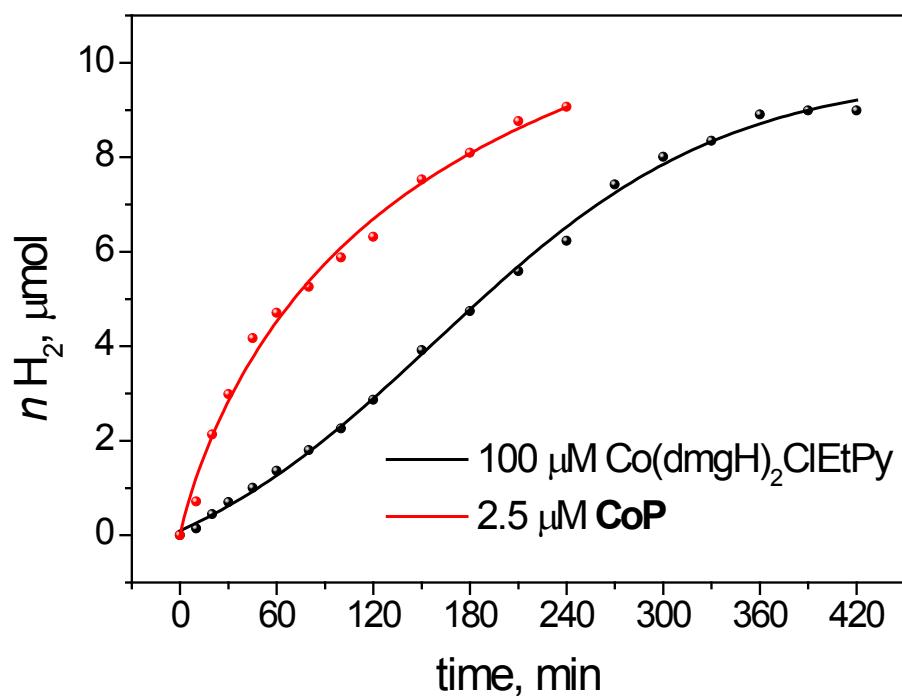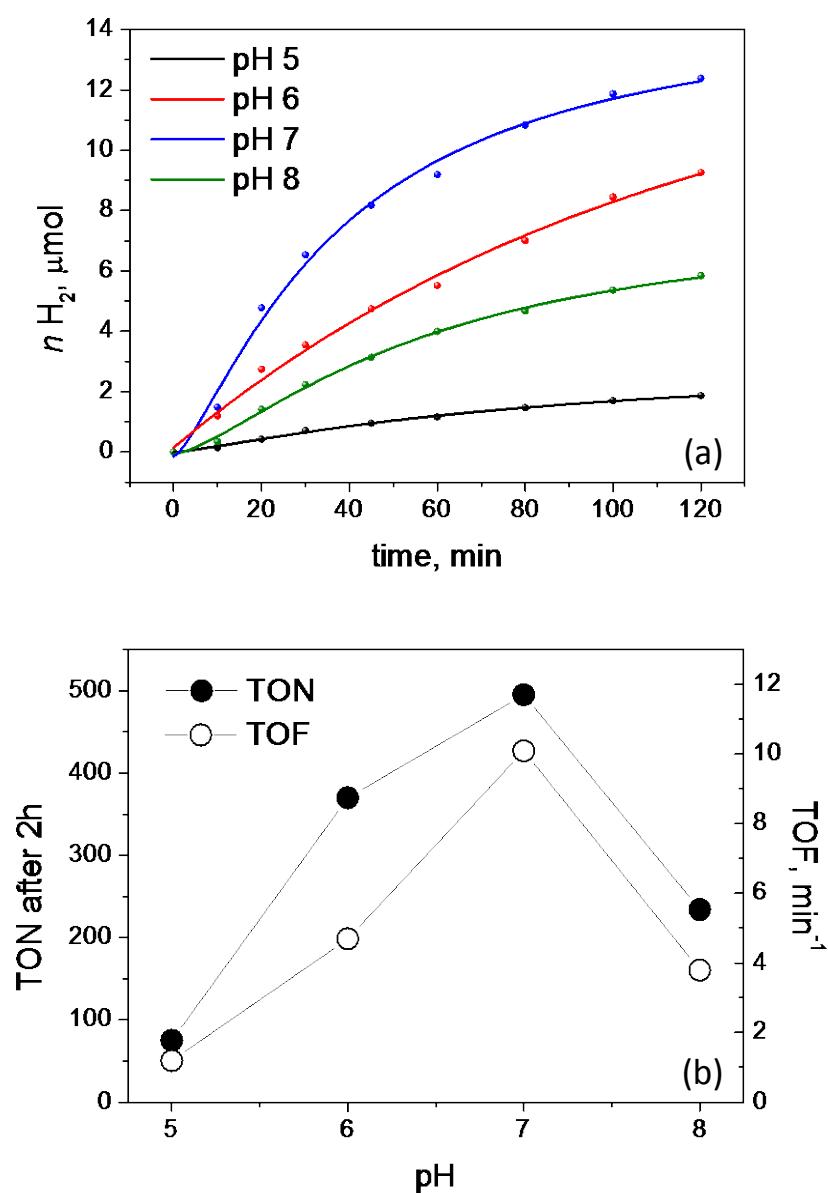
Figure S11. (a) Kinetic of hydrogen evolution upon irradiation of solutions containing 1 mM Ru(bpy)$_3^{2+}$, 0.1 M **AscH**, and 5.0 μM **CoP** in 1 M phosphate buffer at different pH; (b) plot of TON and TOF vs. pH.
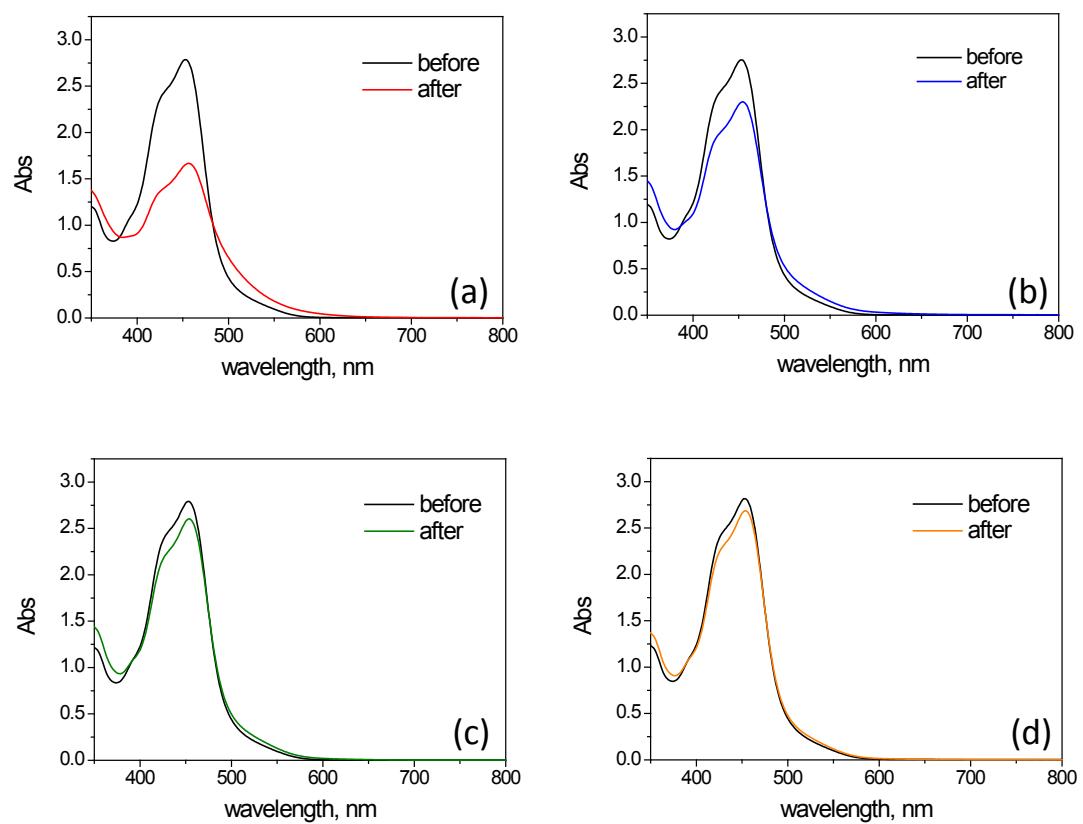
Figure S12. Comparison of absorption spectra before and after 2 h photolysis of solution containing 1 mM Ru(bpy)$_3$$^{2+}$, 0.1 M **AscH**, and 5.0 μM **CoP** in 1 M phosphate buffer at (a) pH 5, (b) pH 6, (c) pH 7, and (d) pH 8.

Figure S13. (a) Photoluminescence spectra (excitation at 450 nm) of solution containing 50 μM Ru(bpy)$_3$$^{2+}$ in 1 M phosphate buffer at pH 7 after addition of different aliquots of **AscH** (0-0.3 M); (b) Stern-Volmer plot of quenching by **AscH**.
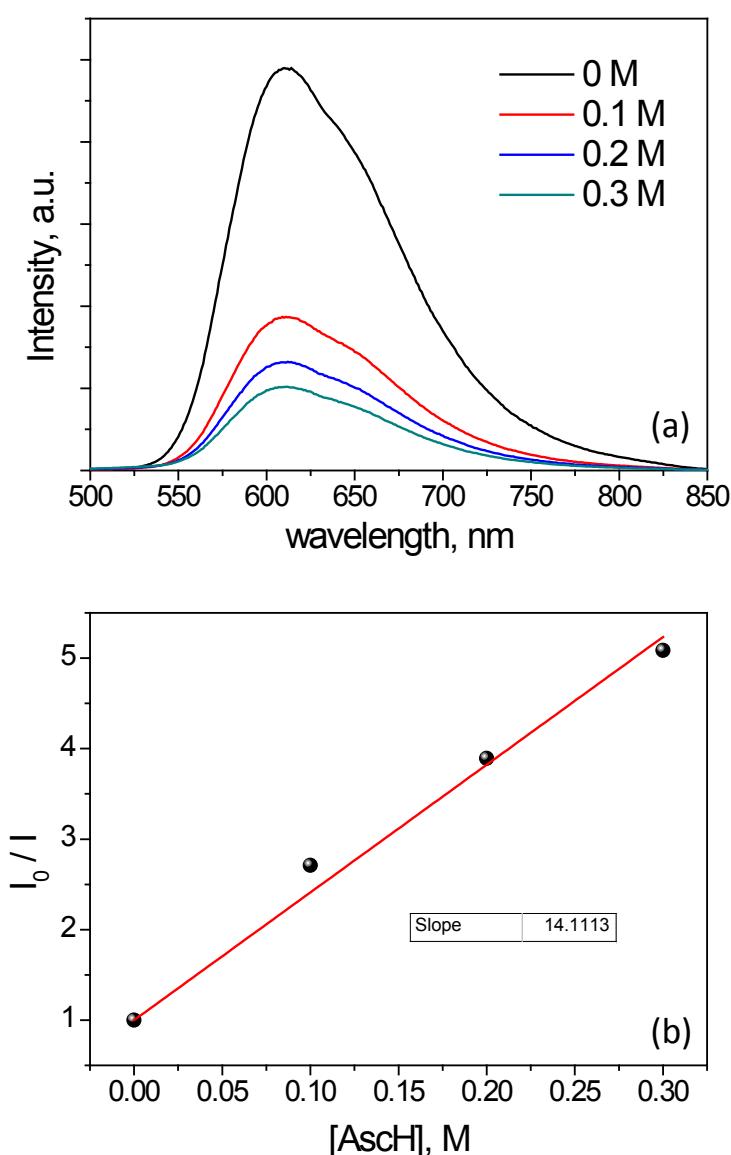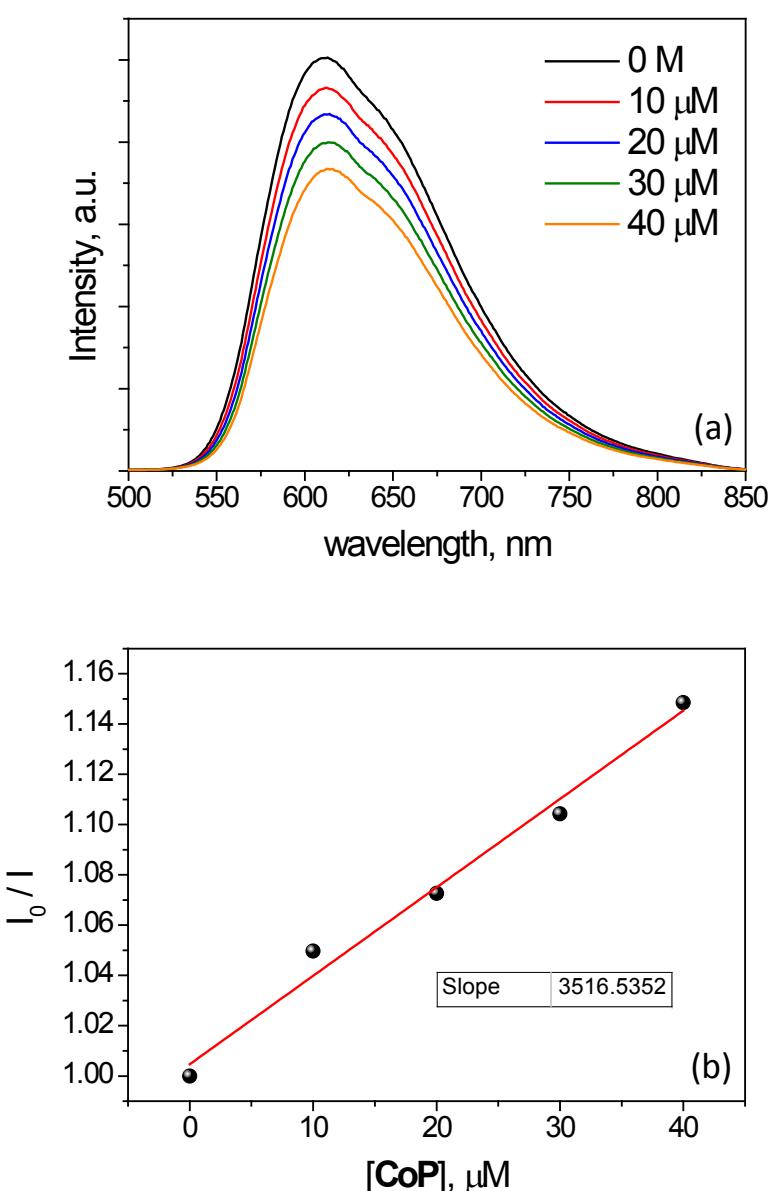
Figure S14. (a) Photoluminescence spectra (excitation at 470 nm) of solution containing 50 μM Ru(bpy)$_3^{2+}$ in 1 M phosphate buffer at pH 7 after addition of different aliquots of **CoP** (0-40 μM); (b) Stern-Volmer plot of quenching by **CoP** (inner filter correction applied).
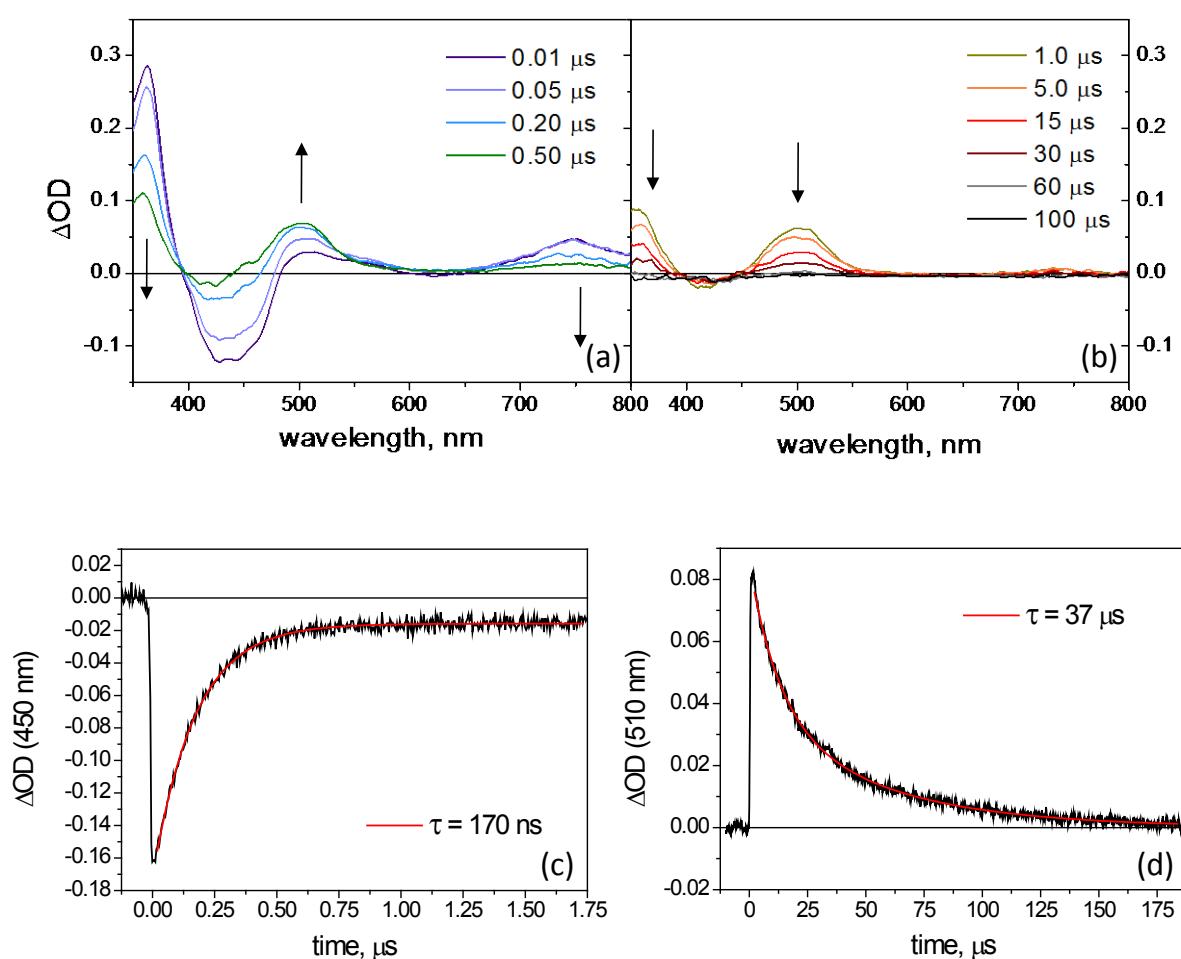
Figure S15. Laser flash photolysis of a solution containing 0.1 mM $Ru(bpy)_3^{2+}$ and 0.1 M **AscH** in 1 M phosphate buffer at pH 7: (a) transient absorption spectra between 0.01-0.50 μs time-delay (reductive quenching by **AscH**), (b) transient absorption spectra between 1.0-100 μs time-delay (charge recombination), (c) kinetic analysis at 450 nm, and (d) kinetic analysis at 510 nm.
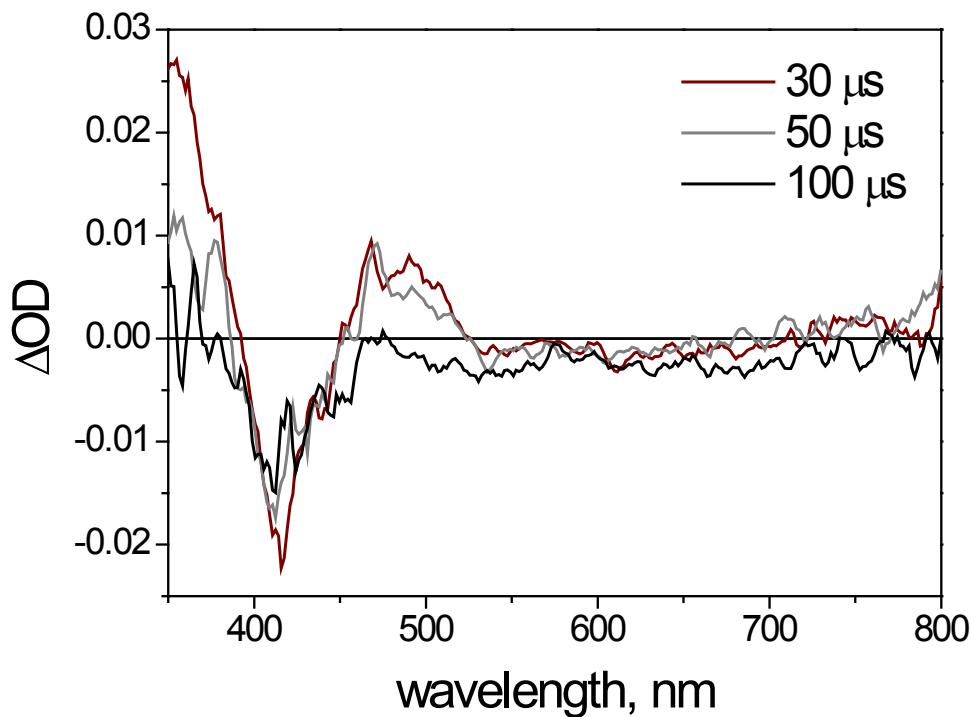
Figure S16. Zoom of transient spectra of Figure 3a of the main article: transient spectra at 30, 50, and 100 μs time delay obtained by laser flash photolysis of a solution containing 0.1 mM Ru(bpy)$_3$$^{2+}$, 0.1 M **AscH**, and 25 μM **CoP** in 1 M phosphate buffer at pH 7.