Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary material

Title:

Photocatalytic Hydrogen Production from a noble metal free system based on a water soluble porphyrin derivative and a cobaloxime catalyst

Authors:

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Materials

The dye $[ZnTMPyP]^{4+}Cl^{-}_{4}$ (**1**)[S1] and the complex $[Co^{III}(dmgH)_2pyCl]$ (**2**)[S2] were synthesized according to the literature. All other chemicals were purchased from the usual commercial sources and used as received.

Experimental details

Hydrogen production experiments. For photoinduced hydrogen evolution, each sample was prepared in a 20 mL Schlenck flask. The components were dissolved in 10 mL of Acetonitrile/10% TEOAaq (1:1 v/v). Prior to sample preparation, the 10% TEOAaq solution was adjusted to the desired pH using HCl_{conc}. The sample flask was sealed with a Suba-seal septum and degassed by bubbling nitrogen through the solution for 15 min at room temperature. The samples were irradiated with a 500 W Xexon lamp using a cut-off filter designed to remove all light with λ < 440 nm. The amounts of hydrogen evolved were determined by gas chromatography (external standard technique) using a Shimadzu GC-2010 plus chromatograph with a TCD detector and a molecular sieve 5 Å column (30 m °— 0.53 mm). Control experiments were run under the same conditions as the hydrogen evolution experiments with the removal of one of the components of the hydrogen generating samples.
For some control experiments a filter assembly was used consisting of a narrow band-pass filter at 572nm (bandwidth about 10nm FWHM) and a colour-glass filter KG5. The colour-glass filter transmits almost everything between 330 and 700nm but blocks the deep UV and IR radiation of the lamp. Extra care was taken to prevent stray UV light from reaching the sample by covering the area around the filter assembly with a large black carton. For the experiments with ascorbate as sacrificial donor the conditions were as follows: Hydrogen production upon irradiation (λ>440nm) of solution (1:1 acetonitrile/water solution of 0.2 M ascorbic acid adjusted to pH=4 using NaOH) containing **1** (4.0×10^{-5}M) and **2** (4.9×10^{-4}M).

Absorption and Emission Spectra. UV-Vis absorption spectra were measured either on a Shimadzu UV-1700 or on a Shimadzu MultiSpec 1501 diode array spectrophotometer using 10 mm path-length cuvettes. The emission spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range: 200-850 nm). The emission lifetime of **1** in $MeCN/H_2O$ 1:1 at pH 7 was determined by the Time Correlated Single Photon Counting technique using an Edinburgh Instruments mini-tau lifetime spectrophotometer equipped with an EPL 405 pulsed diode laser, at 406.0 nm with a pulse width of 71.52 ps and a pulse period of 200 ns, and a high speed red-sensitive photomultiplier tube (H5773-04) as detector.

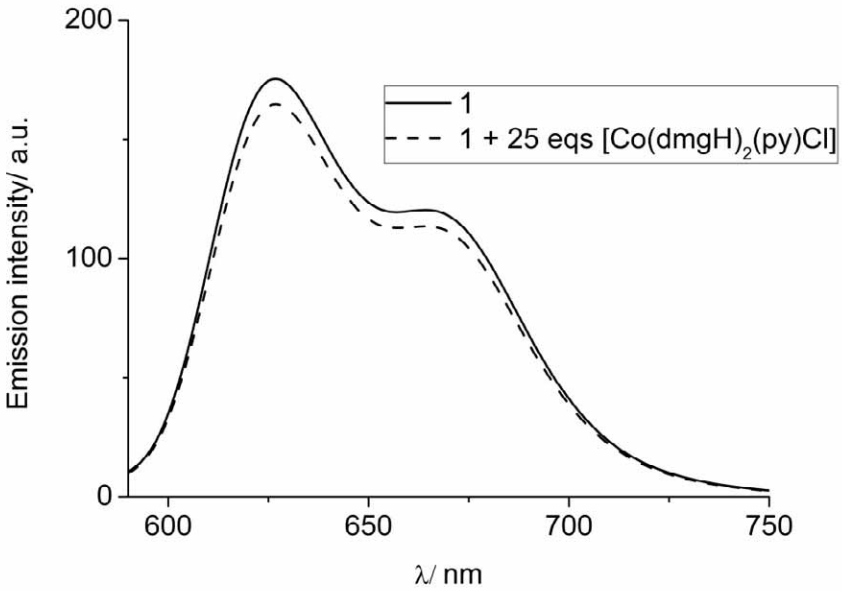

Figure S1: Emission spectra of **1** in MeCN/H_2O 1:1 (2 x 10^{-5} M) after excitation at 580 nm before and after the addition of 25 equivalents of $[Co(dmgH)_2(py)Cl]$.

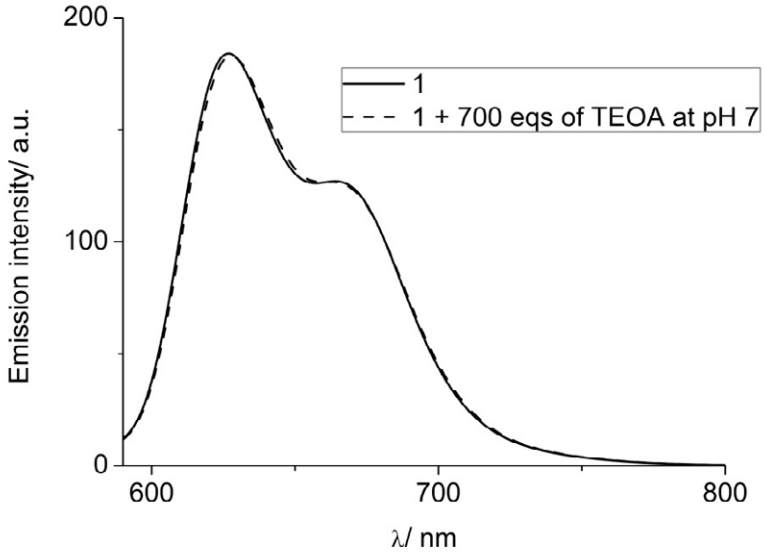

Figure S2: Emission spectra of **1** in MeCN/H_2O 1:1 (2 x 10^{-5} M), after excitation at 580 nm, before and after the addition of 700 equivalents of triethanolamine at pH 7.

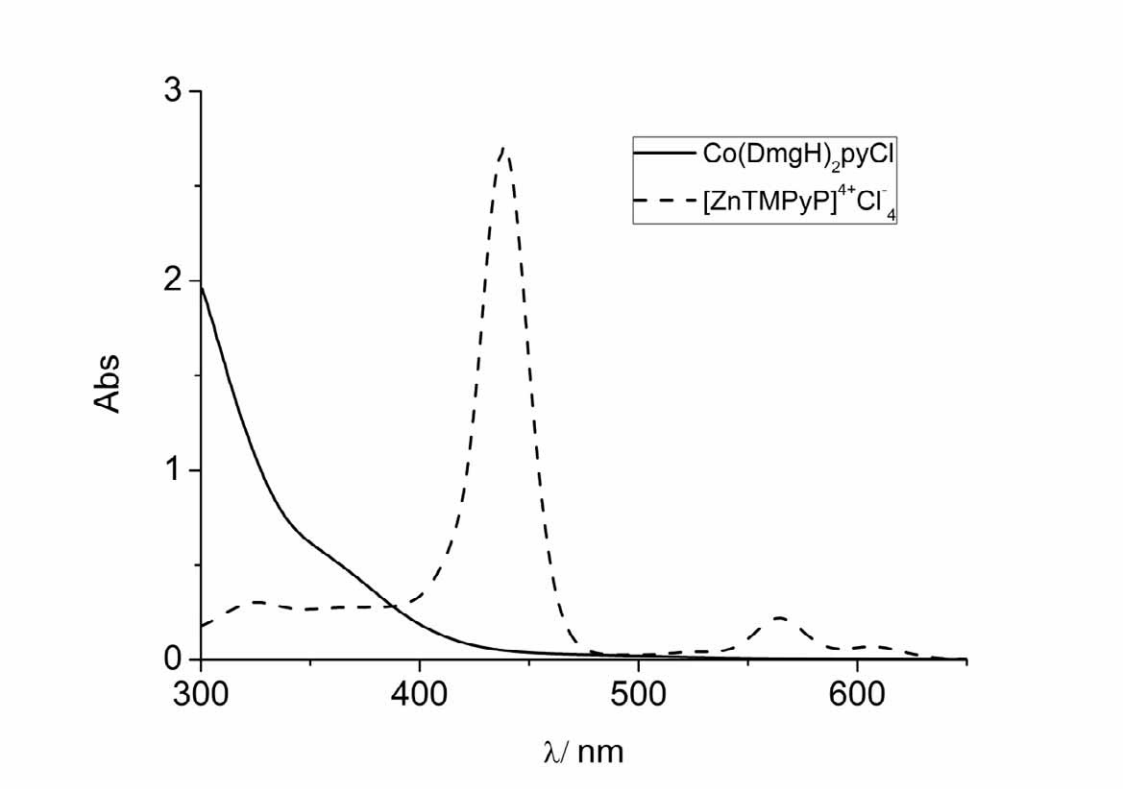

Figure S3: Absorption spectra of 1 (2.0 x 10^{-5} M) and 2 (4.9 x 10^{-4} M) in 1:1 acetonitrile/water containing 5 % v/v triethanolamine at pH 8.

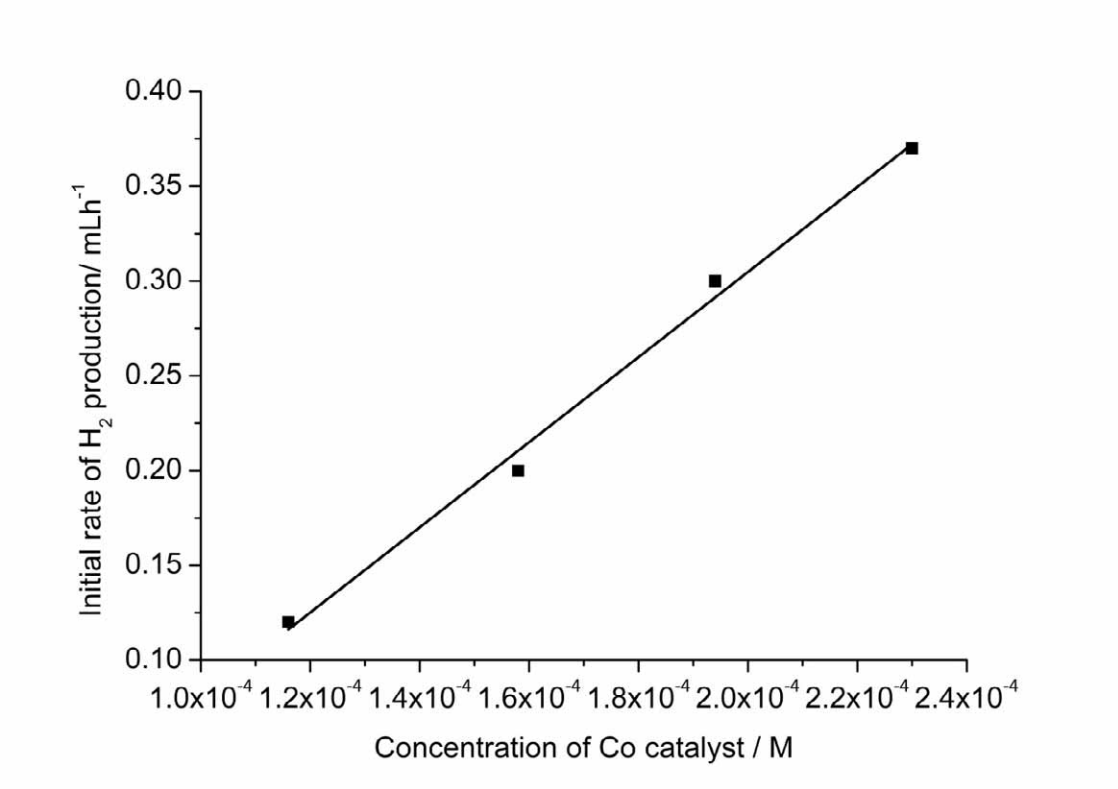

Figure S4: Effect of varying the concentration of the Co catalyst (2) on the initial rate of H_2 production upon irradiation (λ > 440 nm) of solutions (1:1 acetonitrile/water) containing 1 (4.0 x 10^{-5} M) and TEOA [5% (v/v)].

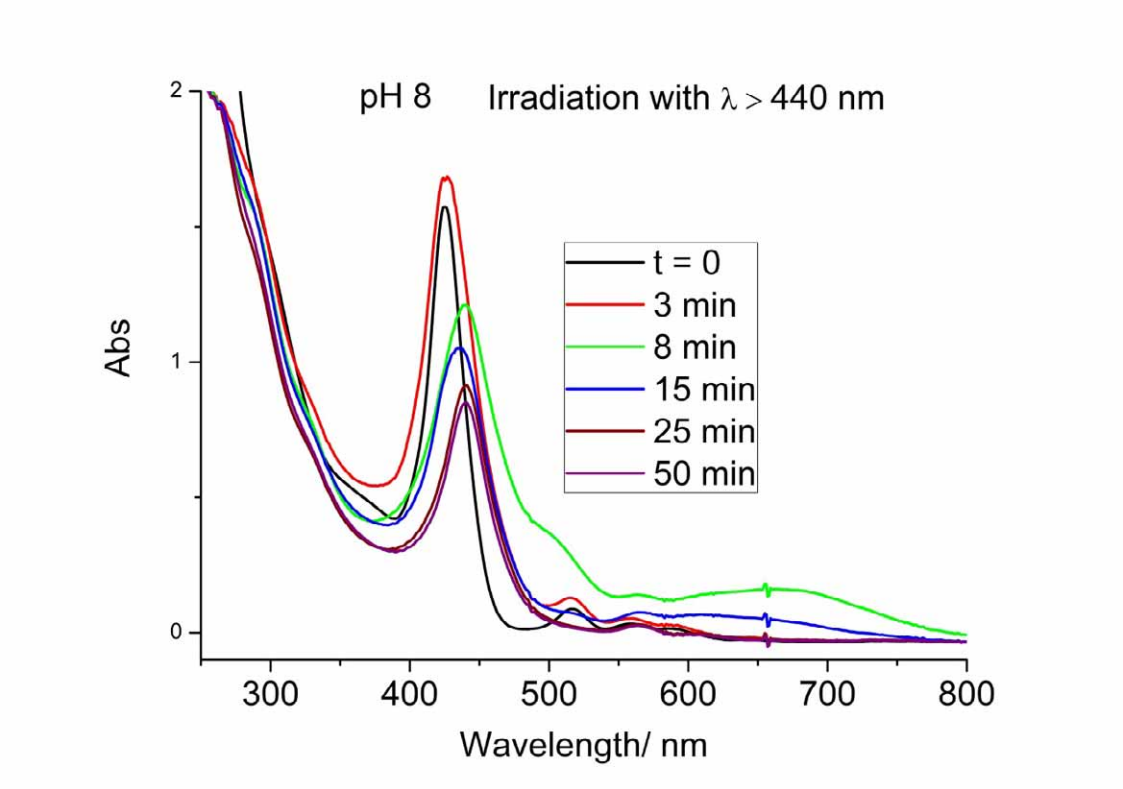

Figure S5: UV-Vis spectra at pH8, before and after irradiation of degassed solutions (1:1 acetonitrile/water) containing $[H_2TMPyP]^{4+}(Cl^-)_4$ (1.0 x 10^{-5} M), **2** (4.9 x 10^{-4} M) and TEOA [5% (v/v)].

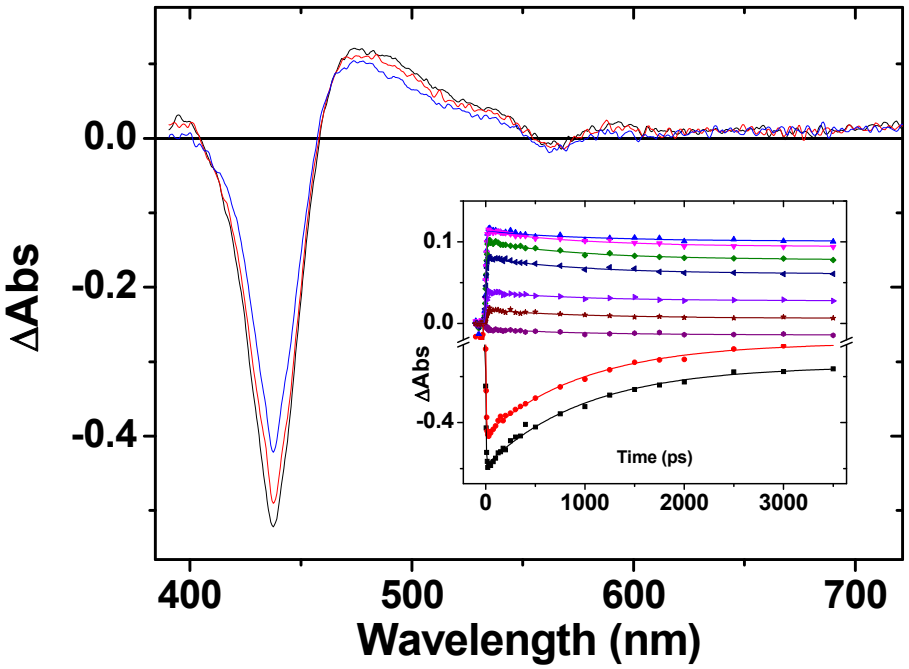

Figure S6: Picosecond transient absorption spectrum of system {**1**, **2**, TEOA, Water : MeCN at pH 7 } at 40 ps (black), 400 ps (red) and 3500 ps (blue) following 438 nm excitation. Inset: Symbols, Picosecond kinetic traces at several representative wavelengths (433, 443, 565, 596, 535, 504, 494, 484, 474 nm, bottom to top on the inset). Solid lines: the results of global exponential fit of the data convoluted with the instrument response function, which yield a single-exponential decay component (1.0 ± 0.1 ns) which gives rise to a long-lived signal.

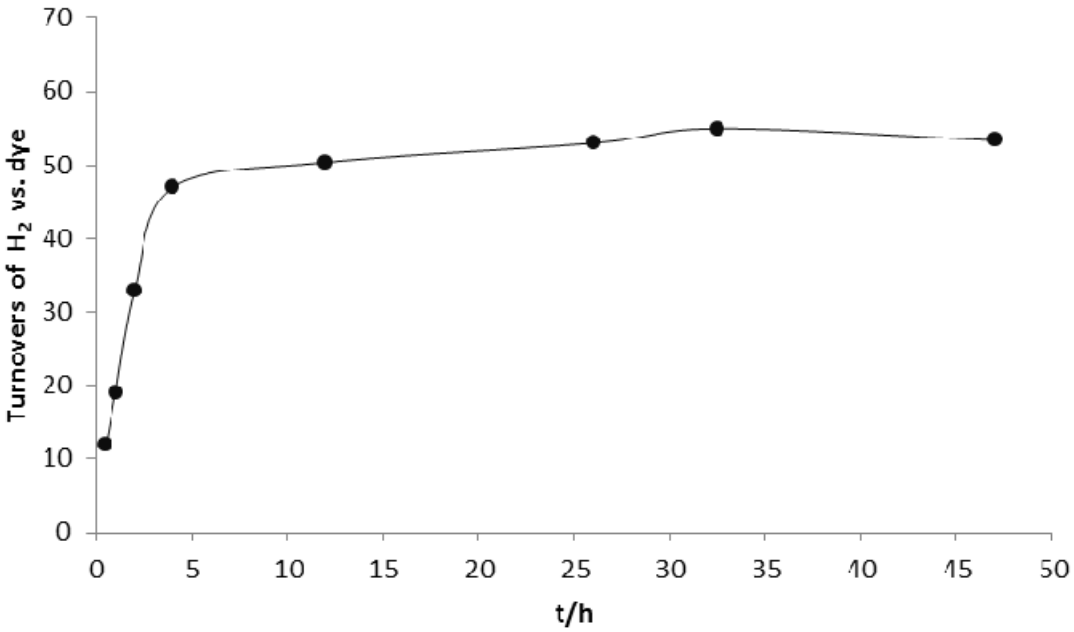

Figure S7: Plot of hydrogen production upon irradiation (λ > 440 nm) of solutions (1:1 acetonitrile/water) containing 1 (4.0×10^{-5} M), 2 (4.9×10^{-4} M) and ascorbate [0.2 M] at pH 4.

References

S1. Christensen, P. A.; Harriman, A.; Porter, G.; Neta, P. *J. Chem. Soc. Farad. Trans. 2* **1984**, *80*, 1451.

S2. Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.