Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information for

Photocatalytic generation of hydrogen from water using a cobalt pentapyridine complex in combination with molecular and semiconductor nanowire photosensitizers

Yujie Sun, [a,c] Jianwei Sun, [a,d] Jeffrey R. Long, [a,d,e]* Peidong Yang, [a,e]* and Christopher J. Chang [a,b,c]*

[a]*Department of Chemistry and the* [b]*Howard Hughes Medical Institute, University of California, Berkeley, California 94720, United States;* [c]*Chemical Sciences Division,* [d]*Joint Center for Artificial Photosynthesis (JCAP),* [e]*Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

Table S1 Crystallographic data for $[(CF_3PY5Me_2)Co(NCCH_3)](CF_3SO_3)_2$ (**1-CH_3CN**).

Empirical formula	$C_{38}H_{33}CoF_9N_8O_6S_2$
Formula weight	991.77
Temperature	173 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C12/c1
Unit cell dimensions	a = 23.898(3) Å, α = 90.00(0)° b = 15.593(2) Å, β = 109.468(2)° c = 23.950(3) Å, γ = 90.00 (0)°
Volume	8414.39 (66) $Å^3$
Z	8
Density (calculated)	1.566
Absorption coefficient	0.603
F(000)	4040
Crystal size	$0.2 \times 0.1 \times 0.1$ mm^3
Theta range for collection	2.61° to 25.42°
Index ranges	$-28 \le h \le 29, -18 \le k \le 18, -28 \le l \le 28$
Reflections collected	7767
Independent reflections	6502
Completeness to max	99.8%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least squares on F^2
Data/restrains/parameters	7767/269/655
Goodness-of-fit[a]	1.051
Final R indices[b] [I > 2d(I)]	R_1 = 0.0542, wR_2 = 0.1627
R indices[b] (all data)	R_1 = 0.0639, wR_2 = 0.1627
Largest diff. peak and hole	1.25, -0.69 e $Å^{-3}$

[a] $\mathrm{GooF} = [\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$

[b] $R_1 = \sum \big||F_o| - |F_c|\big| / \sum |F_o|, \quad wR_2 = \left\{\sum\left[w(F_c^2 - F_o^2)^2\right] / \sum\left[w(F_o^2)^2\right]\right\}^{1/2}$

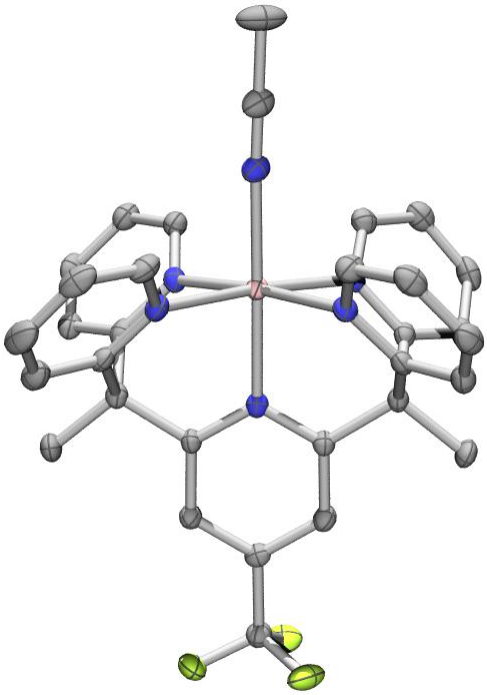

Fig. S1 X-ray crystal structure of the complex [**1-CH$_3$CN**](CF$_3$SO$_3$)$_2$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, CF$_3$SO$_3^-$ anions, and CH$_3$CN solvent molecules are omitted for the sake of clarity.

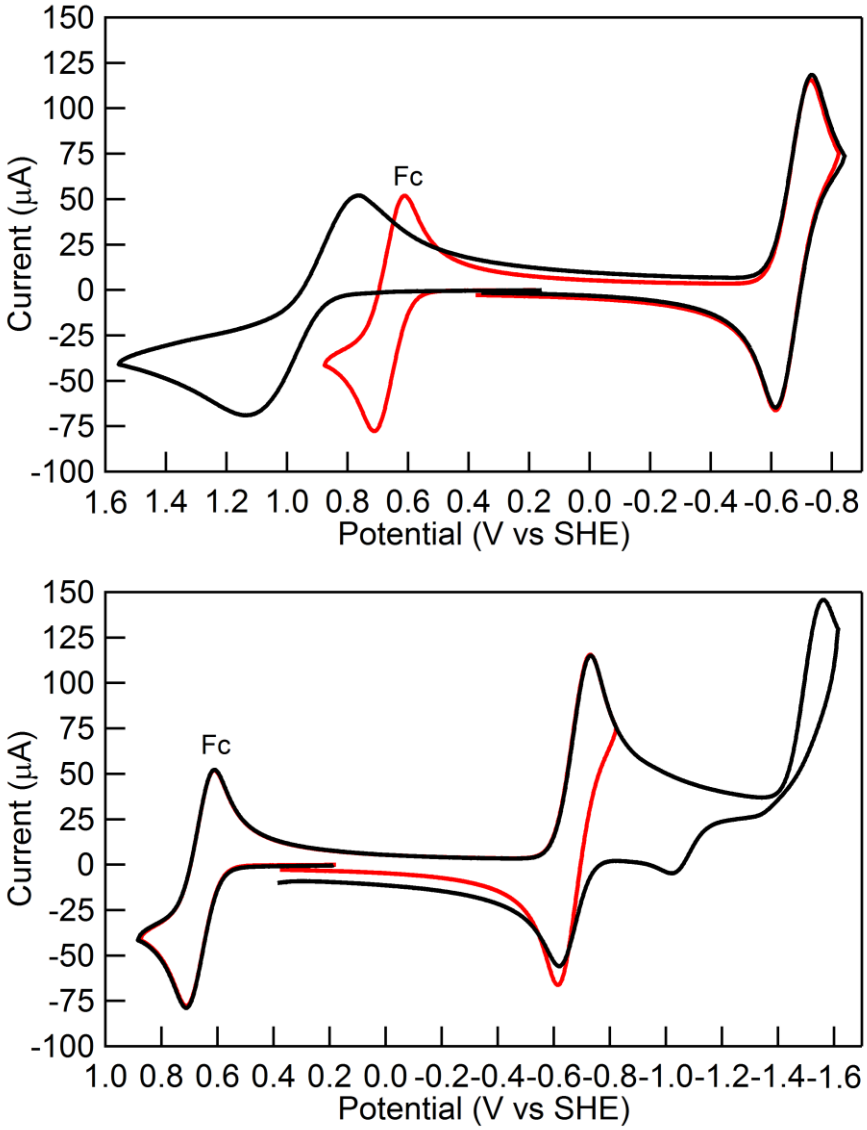

Fig. S2 Cyclic voltammograms of **1-CH_3CN** in 0.1 M Bu_4NPF_6 CH_3CN with (red) and without (black) the internal reference ferrocene ($E_{Fc}^{+/0}$ = 0.64 V vs SHE; scan rate: 100 mV/s).

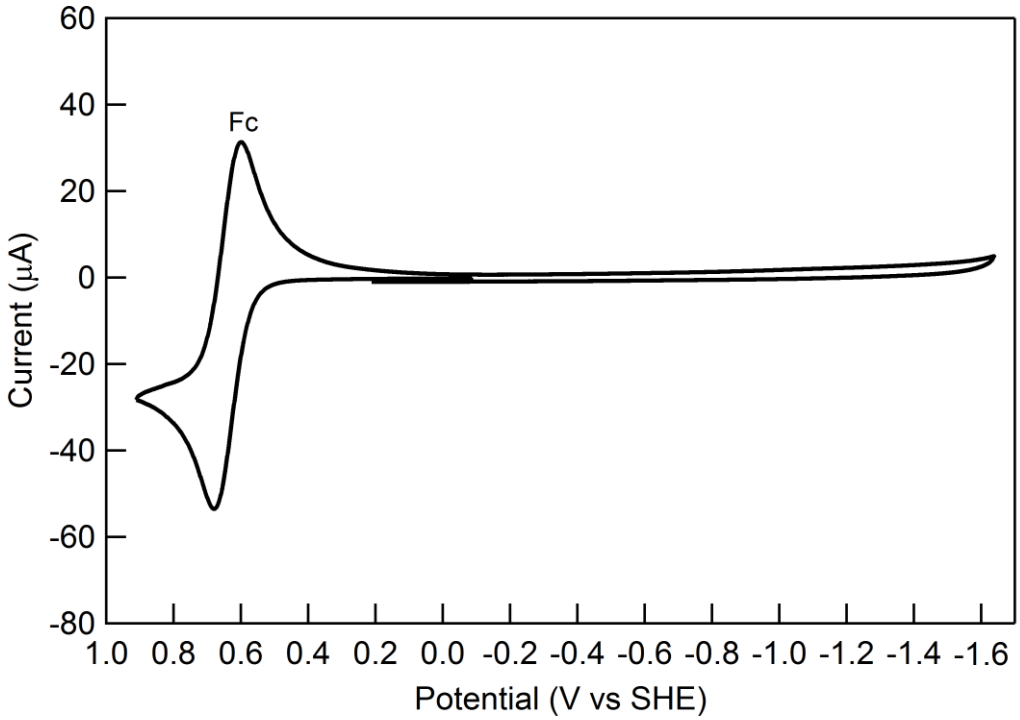

Fig. S3 Cyclic voltammogram of 0.2 mM CF_3PY5Me_2 in 0.1 M Bu_4NPF_6 CH_3CN and the ferrocene peak ($E_{Fc}^{+/0}$ = 0.64 V vs SHE) included as the reference (scan rate: 100 mV/s).

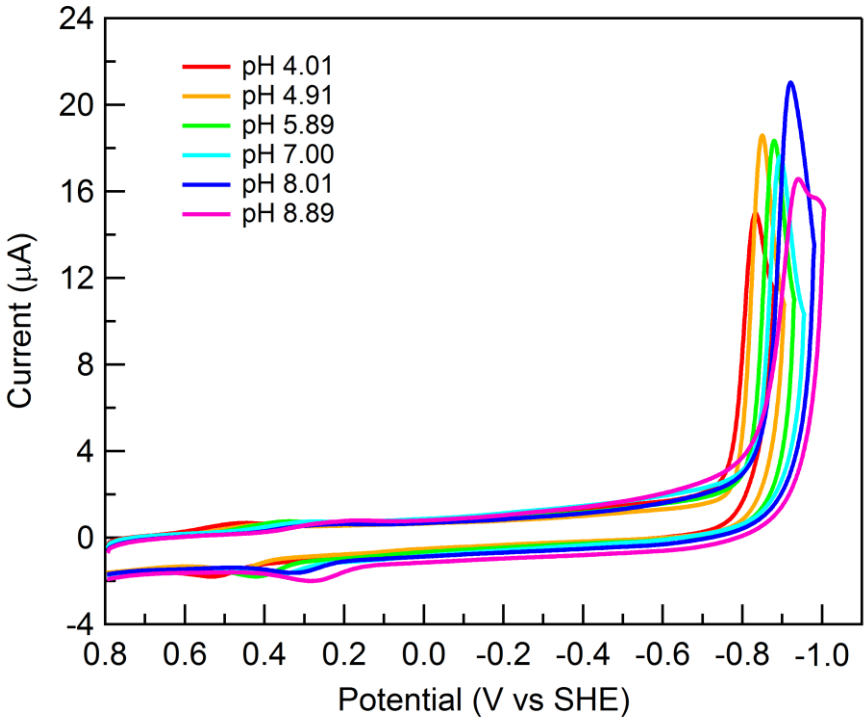

Fig. S4 Cyclic voltammograms of **1** at different pHs (scan rate: 100 mV/s).

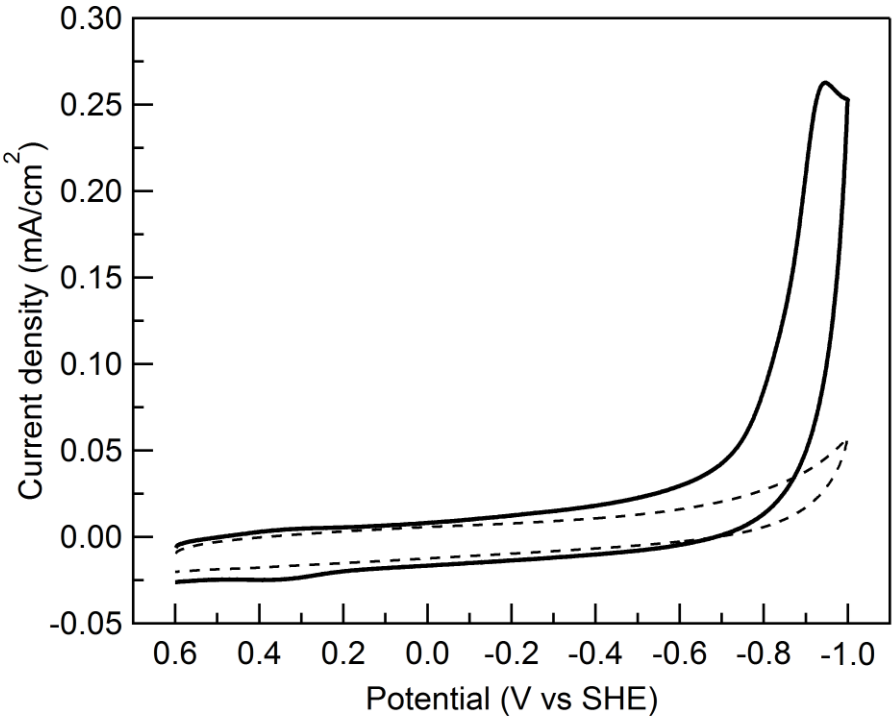

Fig. S5 Cyclic voltammogram of 0.1 mM (solid) and 0 mM (dashed) **1** in 0.2 M $NaClO_4$ (scan rate: 100 mV/s)

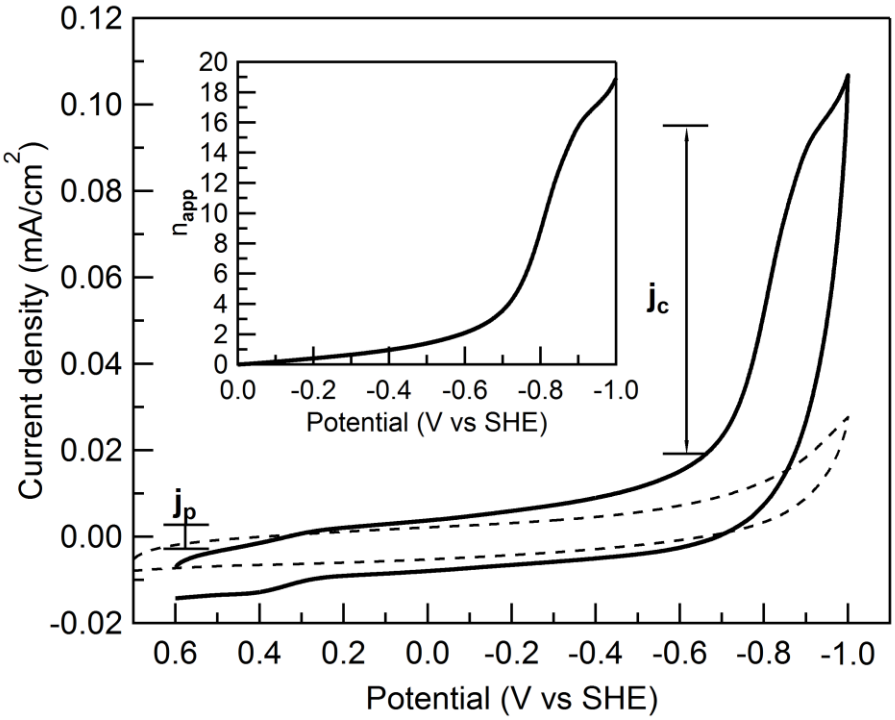

Fig. S6 Rotating disk electrode voltammogram of 0.1 mM (solid) and 0 mM (dashed) **1** in 0.2 M $NaClO_4$ (rotation rate: 400 rpm; scan rate: 25 mV/s)

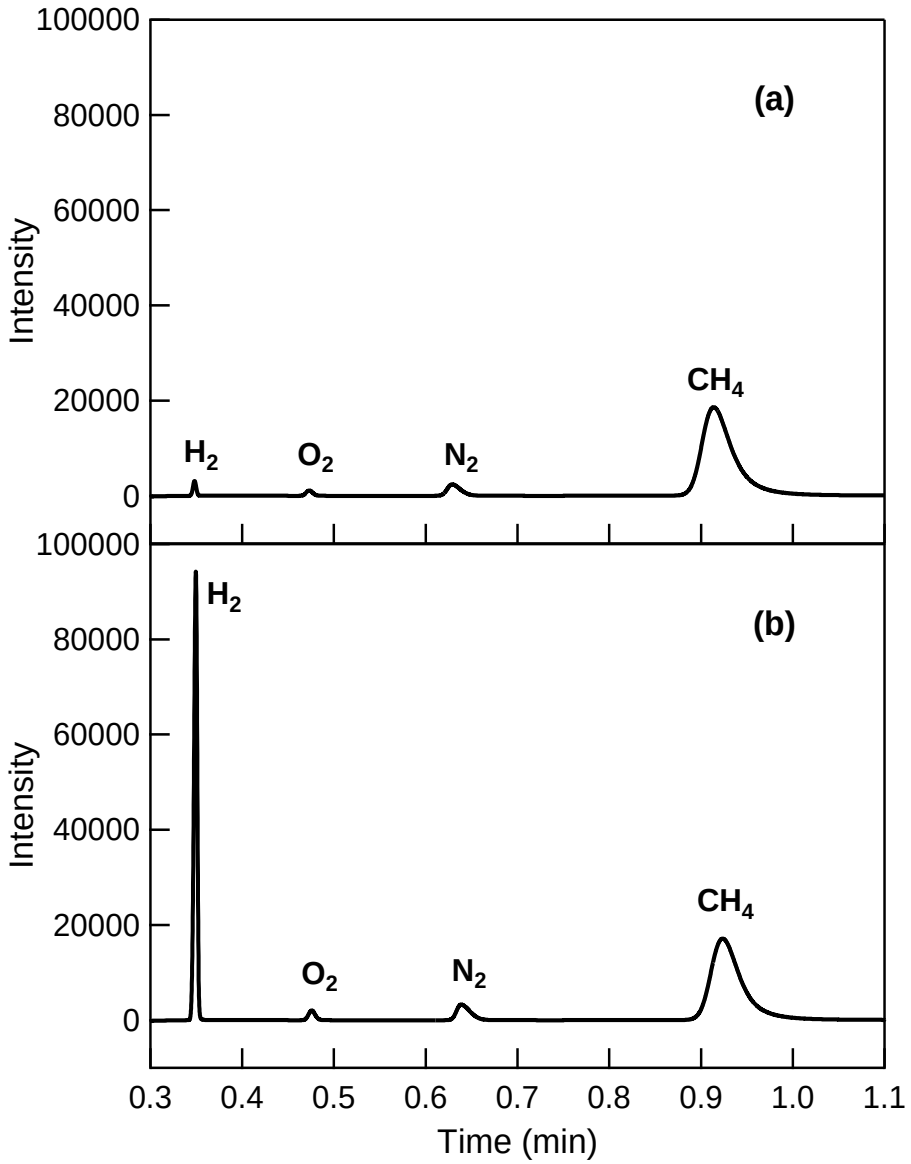

Fig. S7 Gas chromatograms of 0 μM (a) and 50 μM (b) **1**, 0.2 mM $[Ru(bpy)_3]Cl_2$, and 0.1 M ascorbic acid in 1.0 M phosphate buffer of pH 7 after 8 h of illumination with $\lambda_{irr} \geq 455$ nm.

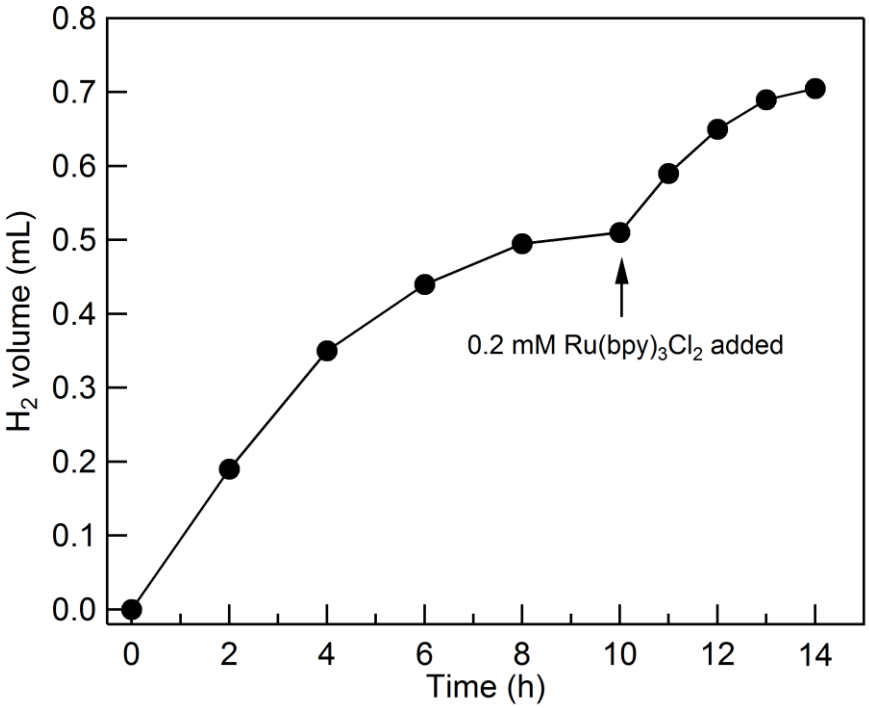

Fig. S8 Photocatalytic hydrogen evolution over time as measured by gas chromatography for aqueous solutions containing 50 μM 1, 0.2 mM $[Ru(bpy)_3]Cl_2$, and 0.1 M ascorbic acid in 1.0 M phosphate buffer of pH 7. After 10 h photolysis, another 0.2 mM was added ($\lambda_{irr} \geq 455$ nm).

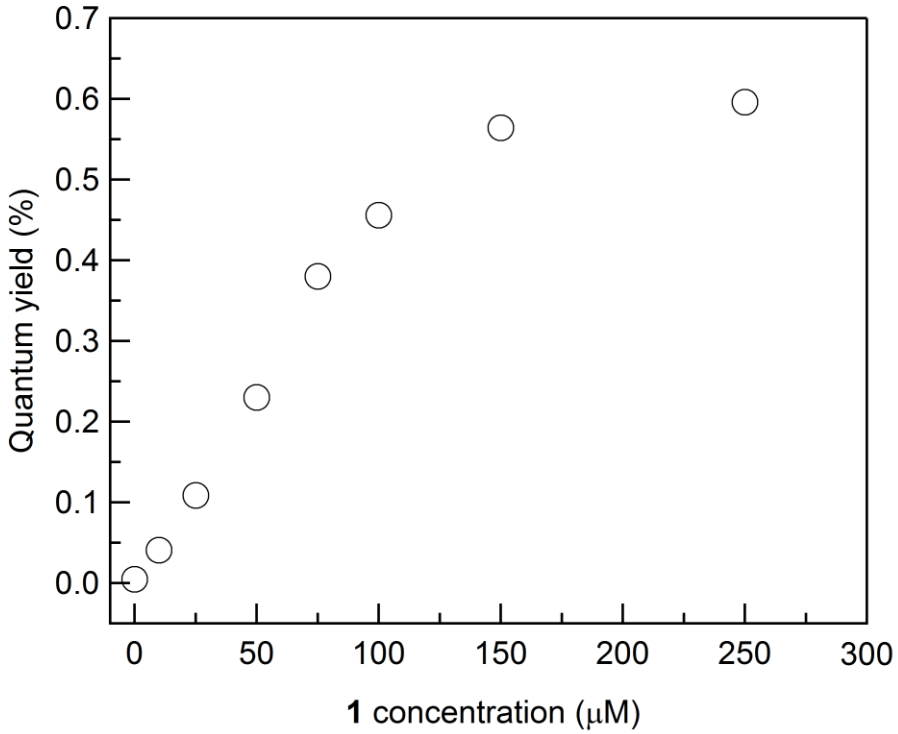

Fig. S9 Quantum yield of hydrogen evolution versus catalyst concentration with 0.2 mM $[Ru(bpy)_3]Cl_2$ and 0.1 M ascorbic acid in 1.0 M phosphate buffer of pH 7 ($\lambda_{irr} \geq 455$ nm).

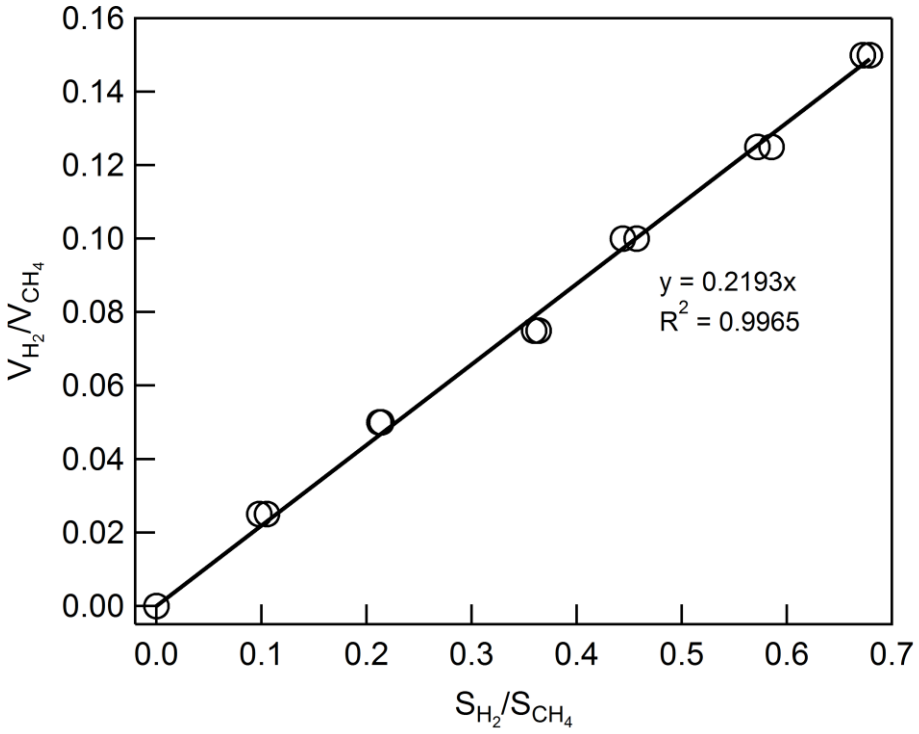

Fig. S10 Calibration curve used for H_2 quantification by gas chromatography using CH_4 (4 mL) as an internal standard (V: gas volume; S: integrated area of the peak signal in the gas chromatogram).