**Electronic Supplementary Information** 

## Photocatalytic Hydrogen Evolution Using a Ru(II)-Bound Heteroaromatic Ligand as a Reactive Site

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## **Experimental Section**

**Synthesis of <sup>15</sup>N-labelled 1,10-phenanthroline-5,6-dioxime.** The labelled compound was synthesized according to the literature methods.<sup>1</sup> <sup>15</sup>N-enriched hydroxylamine hydrochloride (supplied by CIL) was used to form the <sup>15</sup>N-labelled oxime groups.

Synthesis of <sup>15</sup>N-labelled 5,6-diamino-1,10-phenanthroline. The labelled compound was synthesized according to the literature methods.<sup>1</sup> <sup>15</sup>N-Labelled 1,10-phenanthroline-5,6-dioxime was used as the starting compound to form the <sup>15</sup>N-labelled amino groups. <sup>1</sup>H NMR (DMSO- $d_6$ ):  $\delta$  8.77 (dd, J = 4.1, 1.3 Hz, 2H; phen-H2 and phen-H9), 8.48 (dd, J = 8.4, 1.3 Hz, H2; phen-H4 and phen-H7), 7.60 (dd, J = 8.4, 4.2 Hz, H2; phen-H3 and phen-H8), 5.31 (s, 1H; NH), 5.11 (s, 1H; NH).

Synthesis of <sup>15</sup>N-labeled  $[Ru^{II}(bpy)_2(tpphz)](ClO_4)_2$  ((1-<sup>15</sup>N)·(ClO\_4)\_2). The labelled compound was synthesized according to the literature methods for the non-labelled analog.<sup>2</sup> <sup>15</sup>N-Labelled 5,6-diamino-1,10-phenanthroline was reacted with  $[Ru^{II}(bpy)_2(1,10-phenanthroline-5,6-dione)](PF_6)_2$  to afford  $[Ru^{II}(bpy)_2(^{15}N-tpphz)](PF_6)_2$  $((1-{}^{15}N)\cdot(PF_6)_2)$ , in which the two nitrogen atoms of the pyrazine moiety were  ${}^{15}N$ -labelled. To a solution of  $(1-^{15}N)$  (PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN, excess NaClO<sub>4</sub> was added as solids. Addition of an aliquot of water afforded precipitation of the perchlorate salt. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ 9.42 (dd, J = 8.2, 1.8 Hz, 2H; tpphz-Ha), 9.19 (dd, J = 8.2, 0.9 Hz, 2H; tpphz-Ha'), 8.62 (d, *J* = 8.0 Hz, 2H; bpy-H3), 8.58 (d, *J* = 8.0 Hz, 2H; bpy-H3'), 8.29 (dd, *J* = 5.0, 1.1 Hz, 2H; tpphz-Hc'), 8.24 (t, J = 5.2 Hz, 4H; tpphz-Hc and bpy-H6), 8.18 (td, J = 8.0, 1.4 Hz, 2H; bpy-H4), 8.05 (td, *J* = 8.0, 1.4 Hz, 2H; bpy-H4'), 7.94 (dd, *J* = 5.5, 0.9 Hz, 2H; bpy-H6'), 7.83 (dd, J = 8.2, 5.0 Hz, 2H; tpphz-Hb), 7.69 (dd, J = 7.9, 4.3 Hz, 2H; tpphz-Hb'), 7.54 (ddd, J = 5.5, 1.4, 0.9 Hz, 2H; bpy-H5), 7.39 (ddd, J = 5.5, 1.4, 0.9 Hz, 2H; bpy-H5'). <sup>15</sup>N NMR (CD<sub>3</sub>OD):  $\delta$  308.22 (s). MS (ESI): m/z calcd: 400.07  $[M - 2ClO_4]^{2+}$ ; found: 400.07.

Ion-Exchange from  $(1^{-15}N) \cdot (ClO_4)_2$  to  $(1^{-15}N) \cdot Cl_2 \cdot (1^{-15}N) \cdot (ClO_4)_2$  was dispersed in H<sub>2</sub>O using a ultrasonic bath sonicator and ion-exchange resin DOWEX MATATHON A2 (Cl<sup>-</sup> form) was added to the suspension. The mixture was stirred to dissolve the dispersed

perchlorate salt for 5 min, and the resin was removed by filtration.  $(1-{}^{15}N)\cdot Cl_2$  was obtained by removal of the solvent under vacuum.

**Electrochemical measurements of 1**·( $ClO_4$ )<sub>2</sub>. Cyclic and differential-pulse voltammetry (CV and DPV) were performed in the presence of  $[(n-butyl)_4N]PF_6$  (TBAPF<sub>6</sub>, 0.1 M) as an electrolyte under an Ar atmosphere at room temperature in the dark, with use of a glassy-carbon disk as a working electrode, Ag/AgNO<sub>3</sub> as a reference electrode, and Pt wire as an auxiliary electrode.

**Determination of quantum yields of photochemical reactions.** The quantum yield of the photochemical reduction of **1** was determined in a  $CH_3OH-H_2O$  (1:1 v/v) mixed solvent in the presence of  $Et_3N$  (1.8 M) under photoirradiation at 440 nm by using a standard method<sup>3</sup> with an actinometer (potassium ferrioxalate) at room temperature. The reaction was monitored to observe the decrease of absorbance at 380 nm and the data at the initial stage, during which a linear change was observed, were used to determine the quantum yield.

**Irradiation power dependence of formation rate of 2.** The reactions were performed with the solution of  $1 \cdot (ClO_4)_2$  (25  $\mu$ M) in a CH<sub>3</sub>OH-H<sub>2</sub>O mixed solvent (1:1, v/v, 3 mL) in the presence of Et<sub>3</sub>N (1.8 M) under irradiation of white light (380 – 670 nm) at room temperature. The irradiation power was controlled by a ND-filter equipped to the light source unit. Absorption changes at 380 nm were monitored at every second during the initial period, and from the slope, the initial rates, *v*, were determined.

**Concentration dependence of the formation rate of 2.** The reactions were performed with the solution of  $1 \cdot (ClO_4)_2$  (10, 25, 40, 50 and 60  $\mu$ M) in a CH<sub>3</sub>OH-H<sub>2</sub>O mixed solvent (1:1, v/v, 3 mL) in the presence of Et<sub>3</sub>N (1.8 M) under irradiation of white light (380 – 670 nm) at room temperature. Absorption changes at 380 nm were monitored at every second during the initial period, and from the slope, the initial rates, *v*, were determined.

**Kinetic isotope effect on formation rates of 2.** The reactions were performed at room temperature with the solution of  $1 \cdot (ClO_4)_2$  (25  $\mu$ M) in CH<sub>3</sub>OH-H<sub>2</sub>O (1:1, v/v) or CD<sub>3</sub>OD-D<sub>2</sub>O (1:1, v/v) mixed solvents (3 mL) in the presence of Et<sub>3</sub>N (1.8 M) under light

irradiation at 420 nm. Absorption changes at 380 nm were monitored at every second during the initial period, and from the slope, the initial rates, *v*, were determined.

**DFT calculations**. Theoretical calculations on **2** were performed by using the Gaussian 09 program package.<sup>4</sup> In the ground state, complex **2** is in the singlet state. Restricted density functional theory (RDFT) calculations were carried out with the B3LYP functional.<sup>5,6</sup> SDD basis<sup>7</sup> for Ru atoms and  $6-311+G^{**}$  basis<sup>8</sup> for H, C, and N atoms are used.

## **Reference and Notes**

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**Table S1.** Summary of electron donors employed in this work: The first oxidation potentials  $(E_{ox})$  of electron donors, quenching efficiencies (*Eff*) for phosphorescence of **1**, and the initial rates  $(v_{H2})$  of the photocatalytic hydrogen evolution under photoirradiation  $(380 - 670 \text{ nm})^a$ 

entry	electron donor	$E_{\rm ox}$ , V vs. SCE	Eff	$v_{\rm H2}$ , nmol h <sup>-1</sup>
1	$Et_3N$	+0.80 <sup>b</sup>	76% <sup>d</sup>	$8.2^{d}$
2	N-ethylmorpholine	>+1 <sup>b</sup>	$12\%^{d}$	$1.5^{d}$
3	oxalic acid	+0.98 <sup>b</sup>	61% <sup>e</sup>	$1.5^{e}$
4	L-ascorbic acid	+0.15 <sup>b</sup>	89% <sup>f</sup>	0.25 <sup>f</sup>
5	ferrocene	+0.05°		0.3 <sup>g</sup>

<sup>*a*</sup>[1] = 25  $\mu$ M for all measurements. <sup>*b*</sup> In CH<sub>3</sub>OH/phosphate buffer (pH 7.0) (1 : 1 v/v). <sup>*c*</sup> In a CH<sub>3</sub>OH/water mixed solvent (4 : 1, v/v) with 0.1 M tetramethylammonium chloride as an electrolyte. <sup>*d*</sup> In a CH<sub>3</sub>OH/H<sub>2</sub>O mixed solvent (1 : 1, v/v, 3 mL) with an electron donor (1 mL, 1.8 M). <sup>*e*</sup> In a CH<sub>3</sub>OH/phosphate buffer (pH 6.0) mixed solvent (1 : 1, v/v, 4 mL) with an electron donor (1.1 M). <sup>*f*</sup> In a CH<sub>3</sub>OH/phosphate buffer (pH 7.0) mixed solvent (1 : 1 v/v, 4 mL) with an electron donor (0.025 M). <sup>*g*</sup> In CH<sub>3</sub>OH/water (4 : 1 v/v) with an electron donor (0.025 M).

substrate	product	yield, %	TON
С <sup>С</sup> н	ССОН	1.2	6.2
NC	NC	1.0	5.6
MeO	МеО	0.9	5.3
	OH	2.5	14
	_	None	_
	—	None	_

*Table S2.* Photocatalytic hydrogenation of various organic substrates (0.14 M) with **1** (0.26 mM) in CD<sub>3</sub>OD in the presence of Et<sub>3</sub>N (0.21 M) as a sacrificial reductant <sup>*a*</sup>

 $^a$  Reactions were performed under Ar atmosphere at 298 K for 12 h. Irradiation wavelength: 380 – 670 nm.

*Table S3.* Cartesian coordinate of the optimized structure of **2** shown in Fig. 4 at the B3LYP Level. Units are in Angstrom

atom	Х	Y	Z
С	-5.375139	3.301190	0.462150
С	-4.400207	2.303411	0.608100
Ν	-4.120773	1.432427	-0.406061
С	-4.807487	1.544829	-1.562913
С	-5.787610	2.514681	-1.774038
С	-6.078866	3.412665	-0.739234
С	-3.606004	2.112628	1.840996
Ν	-2.716788	1.076814	1.806367
С	-1.956232	0.839827	2.896224
С	-2.040621	1.601994	4.061527
С	-2.951327	2.665470	4.105605
С	-3.739763	2.919210	2.980738
Ru	-2.644526	0.004136	0.007899
Ν	-1.022388	-1.230473	0.531599
С	0.197547	-0.673264	0.248403
С	1.430775	-1.335079	0.503149
С	1.355025	-2.647446	1.042500
С	0.115342	-3.199798	1.322571
С	-1.055501	-2.458465	1.060327
С	2.675132	-0.663491	0.232093
С	2.675842	0.605787	-0.342473
С	1.432691	1.252382	-0.672003
С	0.198670	0.626284	-0.343103
Ν	-1.020368	1.200890	-0.592258
С	-1.051564	2.405924	-1.171227
С	0.120614	3.091464	-1.552509
С	1.359539	2.519337	-1.311337

Ν	3.881386	1.239762	-0.642761
С	5.116919	0.604515	-0.314978
С	5.116402	-0.643745	0.248601
N	3.880323	-1.308609	0.508853
С	6.348075	1.283922	-0.614299
С	7.592119	0.685780	-0.245701
С	7.591727	-0.647066	0.355166
С	6.347221	-1.318774	0.559347
N	8.779659	-1.203744	0.677554
С	8.788957	-2.426031	1.189629
С	7.619230	-3.195111	1.405149
С	6.393367	-2.635717	1.086012
С	6.394707	2.550537	-1.252703
С	7.620822	3.159799	-1.460031
С	8.790107	2.488710	-1.025715
N	8.780309	1.295748	-0.448654
Ν	-2.815937	-1.067532	-1.784965
С	-2.089181	-0.855346	-2.902677
С	-2.237045	-1.618432	-4.061019
С	-3.177911	-2.656151	-4.067780
С	-3.931031	-2.884953	-2.913726
С	-3.733217	-2.079176	-1.782760
С	-4.483634	-2.247223	-0.519567
Ν	-4.138286	-1.386045	0.482699
С	-4.781106	-1.480105	1.666093
С	-5.779843	-2.421171	1.916278
С	-6.138825	-3.308736	0.893842
С	-5.480804	-3.216243	-0.334759
Н	-6.913617	-4.055259	1.048673
Η	-3.321469	-3.274222	-4.950344
Н	7.697630	4.126154	-1.951193

Η	7.695424	-4.203218	1.803782
Η	-3.045921	3.283489	4.994795
Η	-6.836833	4.181772	-0.863918
Η	-2.030363	2.837265	-1.354449
Н	0.033198	4.056788	-2.042287
Η	2.259095	3.032405	-1.637158
Н	2.252942	-3.232981	1.214433
Η	0.026388	-4.202185	1.730846
Н	-2.034443	-2.873128	1.278447
Н	5.488997	3.036413	-1.607501
Η	9.767385	2.950419	-1.167717
Η	9.766041	-2.838767	1.441271
Η	5.487472	-3.223115	1.214878
Η	-1.264110	0.007161	2.825458
Η	-1.404019	1.362481	4.908412
Η	-4.449249	3.739340	2.994268
Η	-5.588464	3.985417	1.276167
Η	-6.306372	2.557057	-2.727417
Η	-4.554427	0.833153	-2.341743
Η	-4.476888	-0.777003	2.434252
Η	-6.260773	-2.449669	2.889791
Η	-5.746705	-3.892839	-1.139644
Η	-4.661730	-3.686200	-2.897711
Η	-1.624207	-1.400007	-4.930820
Н	-1.370846	-0.043334	-2.860892
Η	3.889170	2.245826	-0.520401
Н	3.888429	-1.882797	1.343876



*Fig. S1* Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of  $1 \cdot (ClO_4)_2$  (1 mM) in MeCN containing TBAPF<sub>6</sub> (0.1 M) as an electrolyte at room temperature.



*Fig. S2* Phosphorescence spectra of  $1 \cdot (ClO_4)_2$  (25  $\mu$ M,  $\lambda_{ex} = 424$  nm) in water-MeOH (1:1, v/v, black line) and in water-MeOH-Et<sub>3</sub>N (3:3:2, v/v/v, red line) mixed solvents at room temperature.



*Fig. S3* (a) Stern-Volmer plot for  $1 \cdot (ClO_4)_2$  (25  $\mu$ M) in a water-MeOH mixed solvent (1:1, v/v) as a function of the concentration of Et<sub>3</sub>N. The slope indicates that  $k_q \tau_0$  is 0.23 M<sup>-1</sup>. (b) A decay curve of phosphorescence intensity of  $1 \cdot (ClO_4)_2$  (25  $\mu$ M,  $\lambda_{ex} = 408$  nm,  $\lambda_{em} = 620$  nm) in a water-MeOH mixed solvent (1:1, v/v, red,  $\tau_0 = 16.7$  ns) and prompt (grey).



*Fig. S4* DPVs of triethylamine (11 mM, red), triethanolamine (11 mM, purple), L-ascorbic acid (1.0 mM, orange), oxalic acid (1.0 mM, blue line) and *N*-ethylmorpholine (11 mM, green line) in a MeOH-phosphate buffer mixed solvent (1:1, v/v).



*Fig. S5* UV-vis spectral changes at room temperature before (light blue) and after (red) photoirradiation (380 – 670 nm) for 30 min to the solution of  $1 \cdot (ClO_4)_2$  (25  $\mu$ M) in a water-MeOH mixed solvent (1:1, v/v), containing a reductant: (a) EtMor (1.8 M), (b) Ox (1.1 M), and (c) As (0.025 M). Before the photoirradiation, the pH value of each solution was measured with a digital pH meter. The pH value of the solution containing EtMor (1.8 M) was 10.2, that containing Ox (1.1 M) was 0.8, and that containing As was 3.5.



*Fig. S6* Emission spectra of **1** (25  $\mu$ M) in CH<sub>3</sub>OH/H<sub>2</sub>O (1 : 1, v/v) containing oxalic acid (63  $\mu$ M) (red line) and after pohotoirradiation (380 – 670 nm) for 12 h (blue line). Excitation wavelength: 449 nm.



*Fig.* S7 UV-vis spectral change of  $1 \cdot (ClO_4)_2$  (25 mM) under photoirradiation (380 – 670 nm) in a water-MeOH mixed solvent (1:1, v/v), containing oxalic acid (1.1 M) (a), *N*-ethylmorpholine (1.8 M) (b) and triethanolamine (1.8 M) (c) as reductants, at room temperature. The isosbestic points are indicated by red circles.



*Fig. S8* UV-vis spectral change of  $1 \cdot (ClO_4)_2$  (300  $\mu$ M) in the presence of Me<sub>4</sub>NCl (0.1 M) as an electrolyte in a CH<sub>3</sub>OH-borate buffer (pH 9.5) mixed solvent (1:1, v/v), applying a continuous voltage at -1.4 V *vs*. Ag/AgCl at room temperature in the dark under Ar atmosphere: before electrolysis (light blue trace) and after electrolysis for 6 h (red trace). The UV-vis measurements were preformed in a quartz cell with 2 mm path length. Working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/AgCl.



*Fig. S9* <sup>1</sup>H NMR spectrum of  $2 \cdot (ClO_4)_2$  generated by photoirradiation to  $1 \cdot (ClO_4)_2$  (300  $\mu$ M) with white light (380 – 670 nm) for 4 h in the presence of 5 equiv of Et<sub>3</sub>N in CD<sub>3</sub>OD (a), and that after exposure of the solution of  $2 \cdot (ClO_4)_2$  to dioxygen (10  $\mu$ L) (b).



*Fig. S10* UV-vis spectra of 1 M NaI in acetonitrile (2 mL, black line) and after addition of a photochemical reaction solution (100  $\mu$ L) of  $1 \cdot (ClO_4)_2$  (red line). The reaction solution was prepared as follows: a solution of  $1 \cdot (ClO_4)_2$  (25  $\mu$ M) in a CH<sub>3</sub>OH/H<sub>2</sub>O (1 : 1 v/v) mixed solvent in the presence of Et<sub>3</sub>N (1 mL) was irradiated with white light (380 – 670 nm) for 8 h under Ar, and then O<sub>2</sub> was introduced to the cell with continuous flow for 10 min. After stirring the mixture for 5 min, the UV-vis spectrum was measured to obtain the red trace.



*Fig. S11* UV-vis spectra of  $[TiO(TPyPH_4)]^{4+}$  (5  $\mu$ M) in 0.5 M HClO<sub>4</sub> (2 mL, black line) and after addition of a photochemical reaction solution (40  $\mu$ L) of  $1 \cdot (ClO_4)_2$  (red line). The reaction solution was prepared as follows: a solution of  $1 \cdot (ClO_4)_2$  (25  $\mu$ M) in a CH<sub>3</sub>OH/H<sub>2</sub>O (1 : 1 v/v) mixed solvent in the presence of Et<sub>3</sub>N (1 mL) was irradiated with 380 – 670 nm for 4 h under Ar, and then O<sub>2</sub> was introduced to the cell with continuous flow for 10 min. After stirring the mixture for 5 min at room temperature, the UV-vis spectrum was measured to obtain the red trace.



*Fig. S12* A plot of the initial rates (v) of the formation of  $2 \cdot (ClO_4)_2$  from  $1 \cdot (ClO_4)_2$  through a photochemical process against the initial concentration of **1**. The reactions were done in a CH<sub>3</sub>OH-H<sub>2</sub>O mixed solvent (3 mL, 1 : 1, v/v) in the presence of Et<sub>3</sub>N (1 mL) under irradiation of white light (380 – 670 nm) at room temperature.



*Fig. S13* Size distribution observed by dynamic light scattering (DLS) measurements (a) before and (b) after 10 min photoirradiation (380 - 670 nm) to the solution of  $1 \cdot (\text{ClO}_4)_2$  (25  $\mu$ M) in a water-CH<sub>3</sub>OH-Et<sub>3</sub>N mixed solvent (1 : 1 : 1, v/v/v) at room temperature.



*Fig. S14* <sup>1</sup>H NMR spectral change of  $3 \cdot (ClO_4)_2$  (0.20 mM) with Et<sub>3</sub>N (1.0 mM) in a CD<sub>3</sub>OD-D<sub>2</sub>O mixed solvent (1:1, v/v): (a) before and (b) after photoirradiation (380 – 670 nm) at room temperature.

<sup>1</sup>H NMR of the photochemical product **6** in (b) (CD<sub>3</sub>OD : D<sub>2</sub>O = 1 : 1):  $\delta$  8.74 (d, *J* = 8.0 Hz, 2H; taptp-Ha), 8.68-8.59 (m, 6H; taptp-Hd', bpy-H3 and bpy-H3'), 8.16 (t, *J* = 8.0 Hz, 2H; bpy-H4), 8.10-8.03 (m, 5H; taptp-Hb' and bpy-H4'), 7.95 (d, *J* = 5.8 Hz, 2H; bpy-H6), 7.86 (d, *J* = 6.0 Hz, 2H; bpy-H6'), 7.83-7.77 (m, 4H; taptp-Hc and taptp-Ha'), 7.68-7.58 (m, 4H; taptp-Hb and taptp-Hc'), 7.53 (t, *J* = 8.0 Hz, 2H; bpy-H5), 7.35 (t, *J* = 8.0 Hz, 2H; bpy-H5'). The assignment of the signals was made with use of <sup>1</sup>H-<sup>1</sup>H COSY.



*Fig. S15* UV-vis spectral changes of  $2 \cdot (ClO_4)_2$  in a water: MeOH mixed solvent (1:1, v/v) in the dark at room temperature: (a) 0 - 10 h (every 2 h) and (b) 10 - 26 h (every 2 h).



*Fig. S16* <sup>1</sup>H NMR spectral change of  $2 \cdot (ClO_4)_2$  in CD<sub>3</sub>OD at room temperature in the dark. Complex  $2 \cdot (ClO_4)_2$  was generated by photoirradiation (380 – 670 nm, for 4 h) to  $1 \cdot (ClO_4)_2$  (300  $\mu$ M) in the presence of 5 equiv Et<sub>3</sub>N in CD<sub>3</sub>OD at room temperature. The red signals in the spectra at 0 and 86 h are derived from the protons attached to the reduced tpphz ligand in **2** (0 h) and the tpphz ligand in **1** (86 h), respectively.



*Fig. S17* The rate of H<sub>2</sub> evolution catalysed by  $1 \cdot (ClO_4)_2$  (25  $\mu M$ ) in a CH<sub>3</sub>OH-H<sub>2</sub>O mixed solvent (1:1, v/v, 3 mL) in the presence of Et<sub>3</sub>N (1.8 M) and 70% HClO<sub>4</sub> (10, 30, 50 and 80  $\mu L$ ) under photoirradiation (380 – 670 nm) at room temperature.



*Fig. S18* (a) CVs and (b) DPVs of **1** in MeCN/H<sub>2</sub>O (2:1 v/v) containing TBAPF<sub>6</sub> (0.10 M) as an electrolyte at room temperature.

Comment: The reduction peak current observed at -1.25 V in DPVs is estimated to be two times larger than that at +0.94 V due to the Ru(II/III) potential as a 1e<sup>-</sup> oxidation process. Thus, the reduction wave at -1.25 V was assigned as a 2e<sup>-</sup> transfer process of **1** to form [Ru(bpy)<sub>2</sub>(tpphz-H<sup>•</sup>)]<sup>2+</sup> via a PCET process followed by the formation of **2**.



*Fig. S19* Gas chromatograms of (a) a solution containing  $1 \cdot (ClO_4)_2$  (0.26 mM), Et<sub>3</sub>N (0.21 M) and benzaldehyde (1.4 mM) in CH<sub>3</sub>OH and (b) after photoirradiation for 7 days. The solution was diluted with CH<sub>3</sub>CN upon the measurements. Gas chromatograms of the authentic samples of benzaldehyde (c) and benzyl alcohol (d) in CH<sub>3</sub>CN.



*Fig. S20* Time-course of turnover numbers of hydrogenation of benzaldehyde to benzyl alcohol catalysed by  $1 \cdot (ClO_4)_2$  in CD<sub>3</sub>OD upon photoirradiation (380 – 670 nm) at room temperature in the presence of Et<sub>3</sub>N as a function of time. [ $1 \cdot (ClO_4)_2$ ]: 0.26 mM. [Et<sub>3</sub>N]: 0.21 M. [benzaldehyde]: 0.14 M.



*Fig. S21* A picture of the reaction setup for the photoelectrochemical hydrogen evolution catalysed by **1**.