Electronic supplementary information (ESI)

Mechanism of a one-photon two-electron process in photocatalytic hydrogen evolution from ascorbic acid with a cobalt chlorin complex

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Experimental section

**Materials.** Chemicals were purchased from commercial source and used without purification. Ru(bpy)$_3$SO$_4$ and Co$^{II}$(Ch) were synthesized according to literature procedure.$^{1,2}$ Ascorbic acid (AscH$_2$) and acetic acid (CH$_3$COOH) were obtained from Wako Pure Chemical Industries. Sodium ascorbate (AscHNa), anhydrous acetonitrile (MeCN) for stopped-flow measurements, tris(4-bromophenyl)ammoniumyl hexachloroantimonate ((p-BrC$_6$H$_4$)$_3$N$^+$SbCl$_6$) and decamethylcobaltocene (Co(Cp)$^+$)$_2$) were obtained from Sigma Aldrich. CH$_3$COOD was obtained from Tokyo Chemical Industry, Co. Ltd (TCI). MeCN for photocatalytic H$_2$ evolution was obtained from Nacalai tesque. Deuterated oxide (D$_2$O, 99%) was obtained from Cambridge Isotope Laboratories. D$_2$ gas (99.5%) was commercially obtained from Sumitomo Seika Chemicals Co., Ltd. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore, Direct-Q 3 UV).

**Absorption/emission measurements.** UV-Vis spectroscopy was carried out on a Hewlett-Packard 8453 diode array spectrophotometer at room temperature using quartz cells (light path length = 1 cm). Emission spectroscopy was carried out on a Shimadzu RF-5300PC fluorescence spectrometer at room temperature using quartz cells (light path length = 1 cm).

**Nanosecond laser flash photolysis.** Laser flash photolysis experiments were performed using a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at $\lambda$ = 450 nm with the power of 0.5 mJ per pulse. The transient absorption measurements were performed using a continuous wave xenon lamp (150 W) and a photomultiplier (Hamamatsu 2949) as a probe light and a detector, respectively. The output from a photomultiplier was recorded on a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz).

**Quantum yield determination.** A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photocatalytic hydrogen evolution. Typically, a square quartz cuvette (light path length = 1 cm) that contained a substrate solution (2.0 mL) of [Ru(bpy)$_3$]$^{2+}$ (2.0 mM), AscH$_2$ (0.8 M), AscHNa (0.3 M) and Co$^{II}$(Ch) (50 µM) was irradiated with monochromatised light of $\lambda$ = 450 nm from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, [Ru(bpy)$_3$]$^{2+}$ absorbed essentially 99% incident light of $\lambda$ = 450 nm (Abs$_{450nm}$ = 7). The light intensity of monochromatised light of $\lambda$ = 450 nm was determined as $7.4 \times 10^{-10}$ einstein s$^{-1}$. The photochemical reaction was monitored using a Shimadzu GC-14B gas chromatography. The quantum yield of the amount of evolved H$_2$ was determined using the comparative method.$^{3}$

**Photocatalytic H$_2$ evolution.** A mixed solution (2.0 mL) of water/MeCN (1:1 v/v) containing [Ru(bpy)$_3$]$^{2+}$ (2.0 mM), AscH$_2$ (0.8 M), AscHNa (0.3 M) and Co$^{II}$(Ch) was flushed with Ar gas. The solution was then irradiated by a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a colour filter glass (Asahi Techno Glass) transmitting $\lambda$ > 420 nm at room temperature. The distance between the lamp and sample cell was 30 cm. 25 µL from the headspace of the reaction vessel (3.0 mL) was injected in a Shimadzu GC-14B gas chromatography (detector: TCD, column temperature: 50 °C, column: active carbon with the particle size of 60-80 mesh, carrier gas: N$_2$ gas) to determine the amount of evolved H$_2$. The amount of gas was quantified through calibration curves.

**Photocatalytic H$_2$ evolution in D$_2$O.** A mixed solution (2.0 mL) of water/MeCN (1:1 v/v) or D$_2$O/MeCN (1:1 v/v) containing [Ru(bpy)$_3$]$^{2+}$ (2.0 mM), AscH$_2$ (0.8 M), AscHNa (0.3 M) and Co$^{II}$(Ch) was flushed with Ar gas. The solution was then irradiated by a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a colour filter glass (Asahi Techno Glass) transmitting $\lambda$ > 420 nm at room temperature. The distance between the lamp and sample cell was 22 cm. Amount of hydrogen evolved from H$_2$O/MeCN mixed solution was quantified using
a Shimadzu GC-14B gas chromatography. Hydrogen evolved in D$_2$O/MeCN mixed solution was detected using a Shimadzu GC-8A gas chromatography [detector, TCD; column temperature, 77 K (liquid N$_2$); column, Hydro Isopack (2.0 m, 4.0 m i.d., GTR TEC Co., Ltd.); carrier gas, Ne] to analyse H$_2$, HD and D$_2$ gases.

**Kinetic measurements.** Kinetic measurements for fast reactions with short half-lifetimes were performed on a UNISOKU RSP-601 stopped-flow spectrophotometer with an MOS-type highly selective photodiode array at 298 K using a Unisoku thermostated cell holder. When stopped-flow measurements were carried out under deaerated conditions, deaerated MeCN with a stream of N$_2$ was transferred by means of a glass syringe to a spectrometer cell that was purged with a stream of N$_2$ in advance. Rate constant of the reaction of [Co(Ch)]$^-$ with CH$_3$COOH in MeCN at 298 K was determined by monitoring the appearance of the absorption band due to the corresponding [Co$^{III}$(Ch)]$^+$ ($\lambda_{\text{max}} = 652$ nm). [Co(Ch)]$^-$ was prepared by mixing Co$^{II}$(Ch) and Co(Cp*)$_2$ in anhydrous MeCN inside a globe box. Rate constant of the reaction of [Co$^{III}$(Ch)]$^+$ with AscHNa in air-saturated H$_2$O/MeCN mixed solutions at 298 K was determined by monitoring the decay of the absorption band due to the corresponding [Co$^{III}$(Ch)]$^+$.

**Emission lifetime measurements.** Time-resolved emission decay measurements were performed on a Horiba FluoroMax-4 spectrofluorophotometer. The time resolved emission decays were measured using a 200 ps pulse laser diode emitting at 450 nm.

**Electrochemical measurements.** Cyclic voltammetry (CV) measurements were performed on an ALS 630B electrochemical analyser and voltammograms were measured in a N$_2$-saturated H$_2$O/MeCN mixed solution (1:1 v/v) containing 0.10 M Na$_2$SO$_4$ as a supporting electrolyte at room temperature. A conventional three-electrode cell was used with a glassy carbon working electrode (surface area of 0.3 mm$^2$) and a platinum wire as the counter electrode. The glassy carbon-working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The potentials were measured with respect to the saturated calomel electrode (SCE) reference electrode. Redox potentials were determined using the relation $E_{1/2} = (E_{pa} + E_{pc})/2$.

**Spectroelectrochemical measurements.** UV-visible spectroelectrochemical experiments were performed with a home-built thin-layer quartz cell (light path length = 1 mm) that had a light transparent platinum net working electrode. Potentials were applied and monitored with an ALS 730D electrochemical analyser. The potentials were measured with respect to the Ag/AgNO$_3$ (1.0 x 10$^{-2}$ M) reference electrode. All potentials (vs Ag/AgNO$_3$) were converted to values vs SCE by adding 0.29 V.$^{S4}$

**References**


Fig. S1 Cyclic voltammograms of (a) AscHNa (5.0 mM) and (b) Co(II)(Ch) (1.0 mM) in a N2-saturated H2O/MeCN mixed solution (1:1 v/v) containing 0.10 M Na2SO4; sweep rate: 0.1 V s⁻¹.
**Fig. S2** Time courses of \( \text{H}_2 \) evolution in the photocatalytic reduction of proton in an Ar-saturated \( \text{H}_2\text{O}/\text{MeCN} \) mixed solution (1:1 v/v) containing \([\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}\) (2.0 mM), \(\text{Co}^{\text{II}}(\text{Ch})\) (0.10 mM) and \(\text{AscH}_2\), \(\text{AscHNa}\) (0.9 M, 0.2 M) (red), (0.8 M, 0.3 M) (blue), (0.7 M, 0.4 M) (green), (0.6 M, 0.5 M) (purple) under visible light irradiation (\(\lambda > 420 \text{ nm}\)) at 298 K.

**Fig. S3** Fluorescence spectrum of \([\text{Ru}(\text{bpy})_3]^{2+}\) in an Ar-saturated \(\text{H}_2\text{O}/\text{MeCN} \) mixed solution (1:1 v/v) before and after addition of \(\text{AscH}_2\) (0.80 M) and \(\text{AscHNa}\) (0.30 M) at 298 K.
**Fig. S4** UV-vis absorption spectra of $[{\text{Ru(bpy)₃}}]^{2+}$ (33 µM, black line) and Co²⁺(Ch) (17 µM, red line) in a H₂O/MeCN mixed solution (1:1 v/v).

**Fig. S5** (a) Fluorescence spectrum of $[{\text{Ru(bpy)₃}}]^{2+}$ with various concentration of AscHNa in a deaerated H₂O/MeCN mixed solution (1:1 v/v). (b) Stern-Volmer plot. (c) Fluorescence decay profile (excitation at 450 nm) at 600 nm of $[{\text{Ru(bpy)₃}}]^{2+}$ in a deaerated H₂O/MeCN mixed solution (1:1 v/v).
Fig. S6 (a) First-order plots for the rate of electron transfer from $[\text{Ru(bpy)}_3]^+$ to $\text{Co}^{II}(\text{Ch})$. (b) Plot of $k_{\text{obs}}$ of electron transfer from $[\text{Ru(bpy)}_3]^+$ to $\text{Co}^{II}(\text{Ch})$ vs. $[\text{Co}^{II}(\text{Ch})]$. 

Fig. S7 (a) UV-vis absorption spectral changes of $\text{Co}^{II}(\text{Ch})$ (150 µM) in the electrolysis at $-1.7$ V (vs. SCE) in deaerated MeCN containing TBAPF$_6$ (0.10 M) using a quartz cuvette (light path length = 1 mm) at 298 K. (b) UV-vis absorption spectra of $[\text{Co}(\text{Ch})]^-$ (15 µM) formed by electron-transfer reduction of $\text{Co}^{II}(\text{Ch})$ (15 µM) with $\text{Co}($Cp$)_2$ (300 µM) in deaerated MeCN at 298 K. The black and red lines show the spectra before and after addition of $\text{Co}($Cp$)_2^+$, respectively.
(a) Time profiles of absorbance at 652 nm due to $[\text{Co}^{III}(\text{Ch})]^+$ generated by the addition of various concentrations of $\text{CH}_3\text{COOH}$ to the solution of $[\text{Co}^I(\text{Ch})]$ (30 µM) in deaerated MeCN at 298 K. (b) First-order plots for the formation of $[\text{Co}^{III}(\text{Ch})]^+$.

Fig. S9 Plot of $k_{obs}^{-1}$ vs. $[\text{CH}_3\text{COOH}]^{-1}$. 
Fig. S10 Plots of $k_{\text{obs}}$ for the rate of the formation of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ vs. $[\text{CH}_3\text{COOH}]$ and $[\text{CH}_3\text{COOD}]$.

Fig. S11 (a) First-order plots for the rate of electron transfer from [AscHNa] to $[\text{Co}^{\text{III}}(\text{Ch})]^+$. (b) Plot of $k_{\text{obs}}$ of electron transfer from [AscHNa] to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ vs. [AscHNa].