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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. $Ru(bpy)_3SO_4$ and $Co^{II}(Ch)$ were synthesized according to literature procedure.[S1,S2] Ascorbic acid ($AscH_2$) and acetic acid (CH_3COOH) were obtained from Wako Pure Chemical Industries. Sodium ascorbate (AscHNa), anhydrous acetonitrile (MeCN) for stopped-flow measurements, tris(4-bromophenyl)ammoniumyl hexachloroantimonate ($(p\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^{-}$) and decamethylcobaltocene ($Co(Cp^*)_2$) were obtained from Sigma Aldrich. CH_3COOD was obtained from Tokyo Chemical Industry, Co. Ltd (TCI). MeCN for photocatalytic H_2 evolution was obtained from Nacalai tesque. Deuterated oxide (D_2O, 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 λ = 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 λ = 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 λ = 450 nm ($Abs_{450nm} \approx 7$). The light intensity of monochromatised light of λ = 450 nm was determined as 7.4×10^{-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.[S3]

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 λ > 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 ℃, 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_2O. A mixed solution (2.0 mL) of water/MeCN (1:1 v/v) or D_2O/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 λ > 420 nm at room temperature. The distance between the lamp and sample cell was 22 cm. Amount of hydrogen evolved from H_2O/MeCN mixed solution was quantified using a Shimadzu GC-14B gas chromatography. Hydrogen evolved in D_2O/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 $[Co^{I}(Ch)]^{-}$ with CH_3COOH in MeCN at 298 K was determined by monitoring the appearance of the absorption band due to the corresponding $[Co^{III}(Ch)]^{+}$ (λ_{max} = 652 nm). $[Co^{I}(Ch)]^{-}$ 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_2O/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_2O/MeCN mixed solution (1:1 v/v) containing 0.10 M Na_2SO_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 $Ag/AgNO_3$ (1.0×10^{-2} M) reference electrode. All potentials (vs $Ag/AgNO_3$) were converted to values vs SCE by adding 0.29 V.[S4]

References

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[S2] K. Mase, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.*, 2013, **135**, 2800.

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[S4] C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, *Mercel Dekker*, *New York*, 1970.

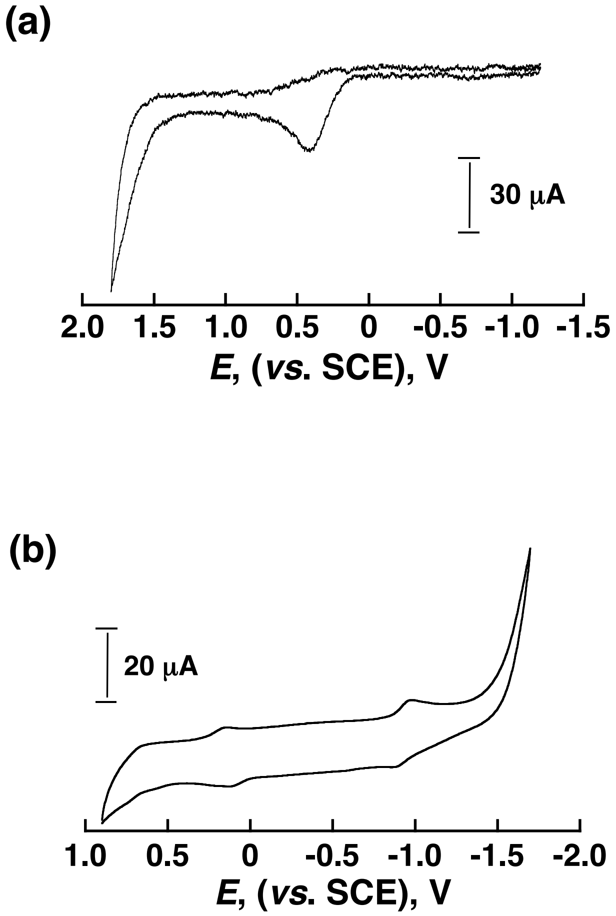

Fig. S1 Cyclic voltammograms of (a) AscHNa (5.0 mM) and (b) $Co^{II}(Ch)$ (1.0 mM) in a N_2-saturated H_2O/MeCN mixed solution (1:1 v/v) containing 0.10 M Na_2SO_4; sweep rate: 0.1 V s^{-1}.

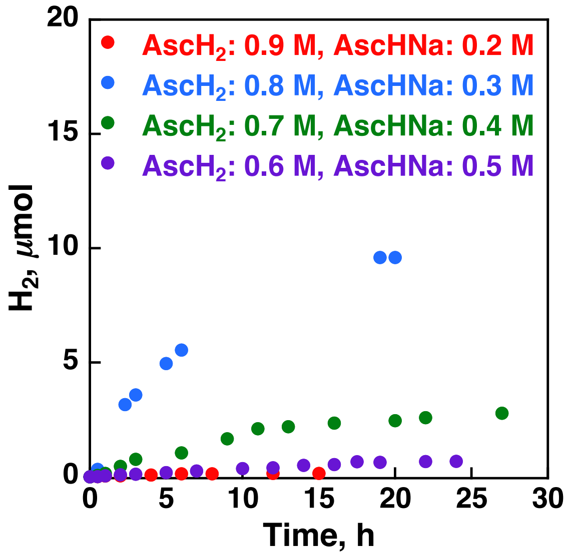

Fig. S2 Time courses of H_2 evolution in the photocatalytic reduction of proton in an Ar-saturated H_2O/MeCN mixed solution (1:1 v/v) containing $[Ru^{II}(bpy)_3]^{2+}$ (2.0 mM), Co^{II}(Ch) (0.10 mM) and $AscH_2$, AscHNa (0.9 M, 0.2 M) (red), (0.8 M, 0.3 M) (blue), (0.7 M, 0.4 M) (green), (0.6 M, 0.5 M) (purple) under visible light irradiation (λ > 420 nm) at 298 K.

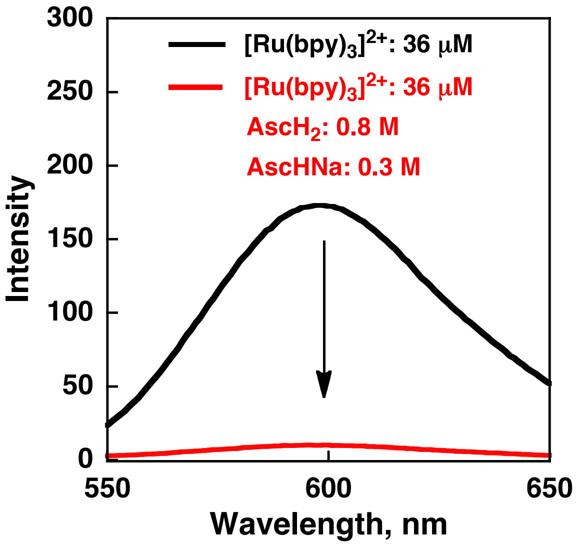

Fig. S3 Fluorescence spectrum of $[Ru(bpy)_3]^{2+*}$ in an Ar-saturated H_2O/MeCN mixed solution (1:1 v/v) before and after addition of $AscH_2$ (0.80 M) and AscHNa (0.30 M) at 298 K.

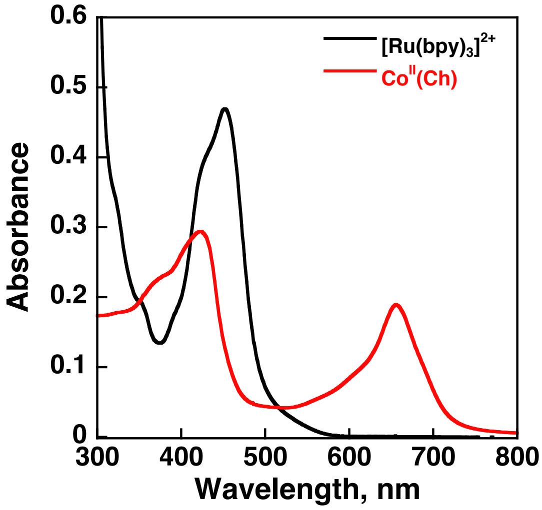

Fig. S4 UV-vis absorption spectra of $[Ru(bpy)_3]^{2+}$ (33 μM, black line) and $Co^{II}(Ch)$ (17 μM, red line) in a H_2O/MeCN mixed solution (1:1 v/v).

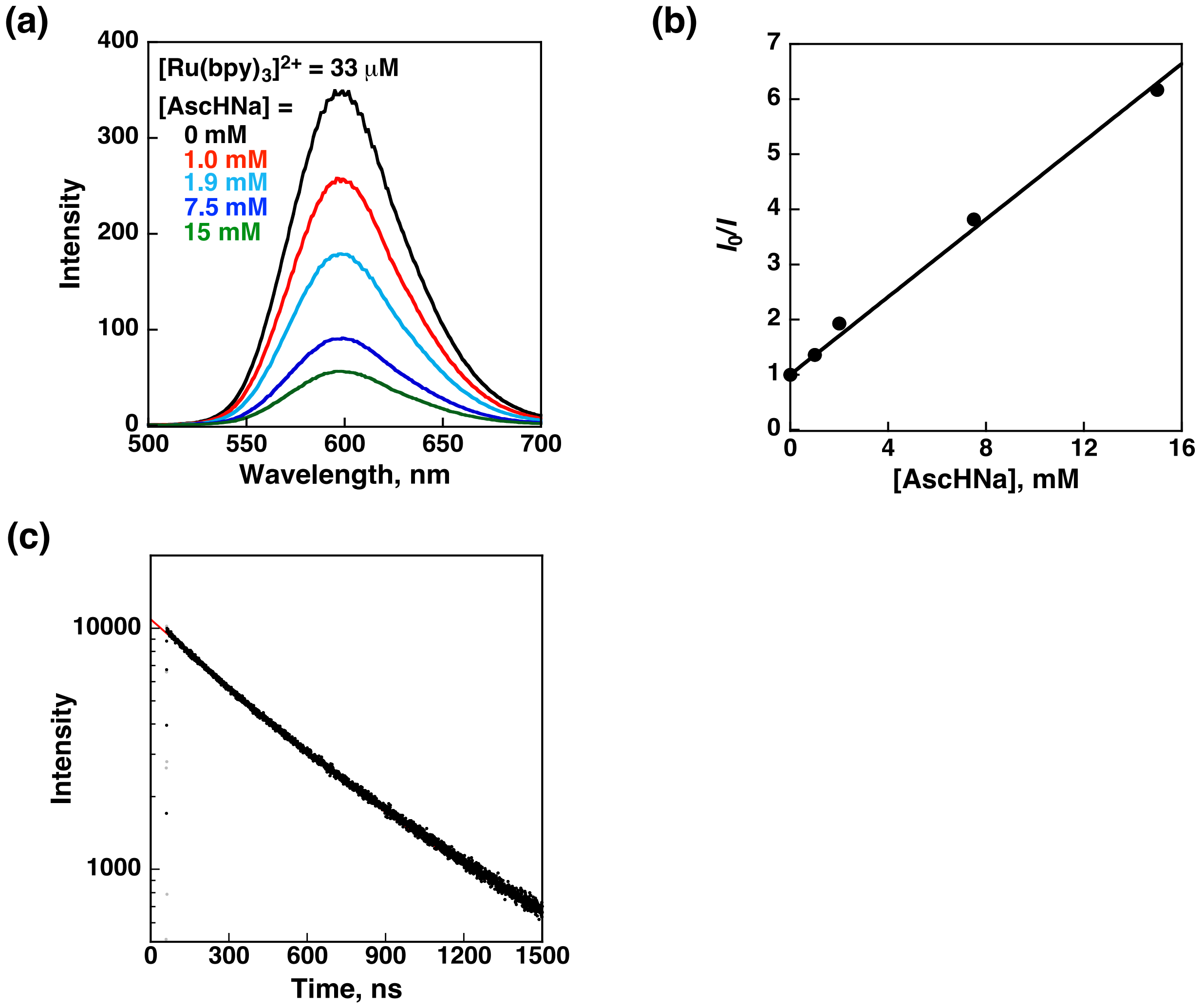

Fig. S5 (a) Fluorescence spectrum of $[Ru(bpy)_3]^{2+*}$ with various concentration of AscHNa in a deaerated H_2O/MeCN mixed solution (1:1 v/v). (b) Stern-Volmer plot. (c) Fluorescence decay profile (excitation at 450 nm) at 600 nm of $[Ru(bpy)_3]^{2+}$ in a deaerated H_2O/MeCN mixed solution (1:1 v/v).

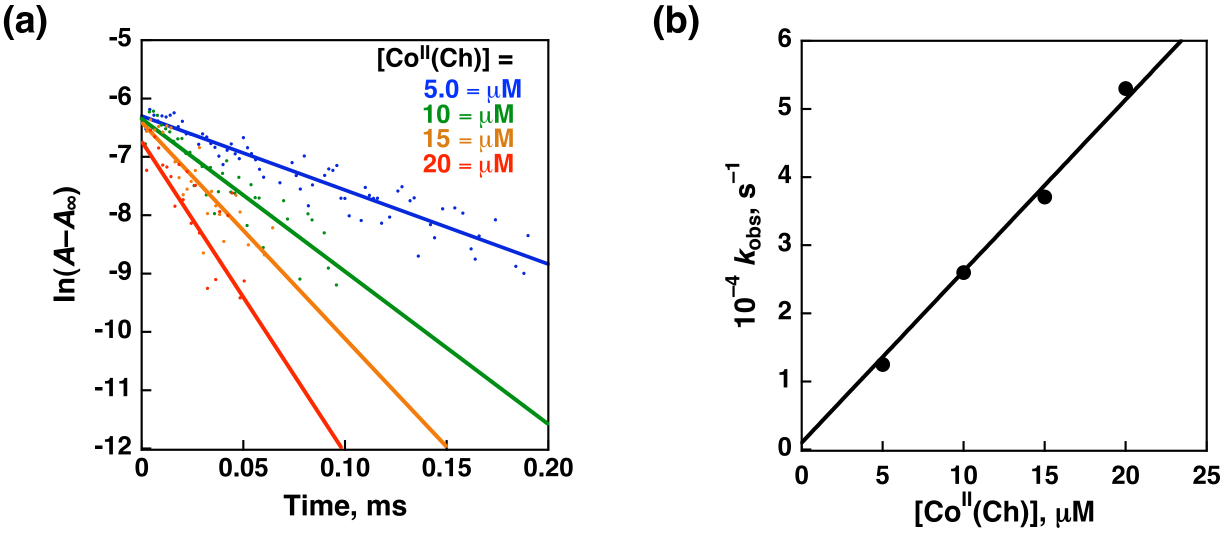

Fig. S6 (a) First-order plots for the rate of electron transfer from $[Ru(bpy)_3]^+$ to $Co^{II}(Ch)$. (b) Plot of k_{obs} of electron transfer from $[Ru(bpy)_3]^+$ to $Co^{II}(Ch)$ *vs*. $[Co^{II}(Ch)]$.

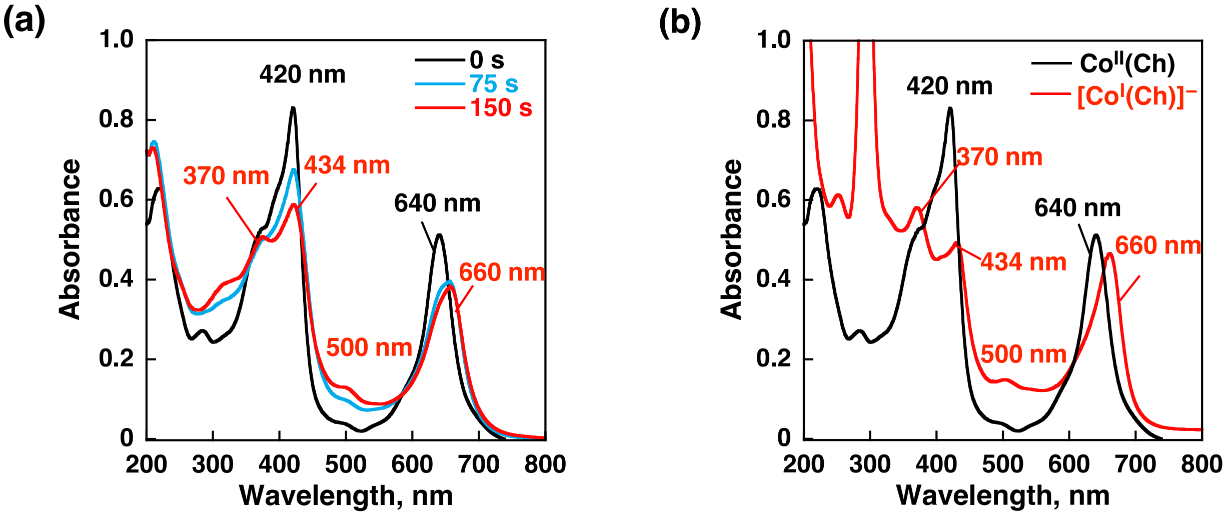

Fig. S7 (a) UV-vis absorption spectral changes of $Co^{II}(Ch)$ (150 μM) in the electrolysis at –1.7 V (*vs*. SCE) in deaerated MeCN containing $TBAPF_6$ (0.10 M) using a quartz cuvette (light path length = 1 mm) at 298 K. (b) UV-vis absorption spectra of $[Co^{I}(Ch)]^-$ (15 μM) formed by electron-transfer reduction of $Co^{II}(Ch)$ (15 μM) with $Co(Cp^*)_2$ (300 μM) in deaerated MeCN at 298 K. The black and red lines show the spectra before and after addition of $Co(Cp^*)_2$, respectively.

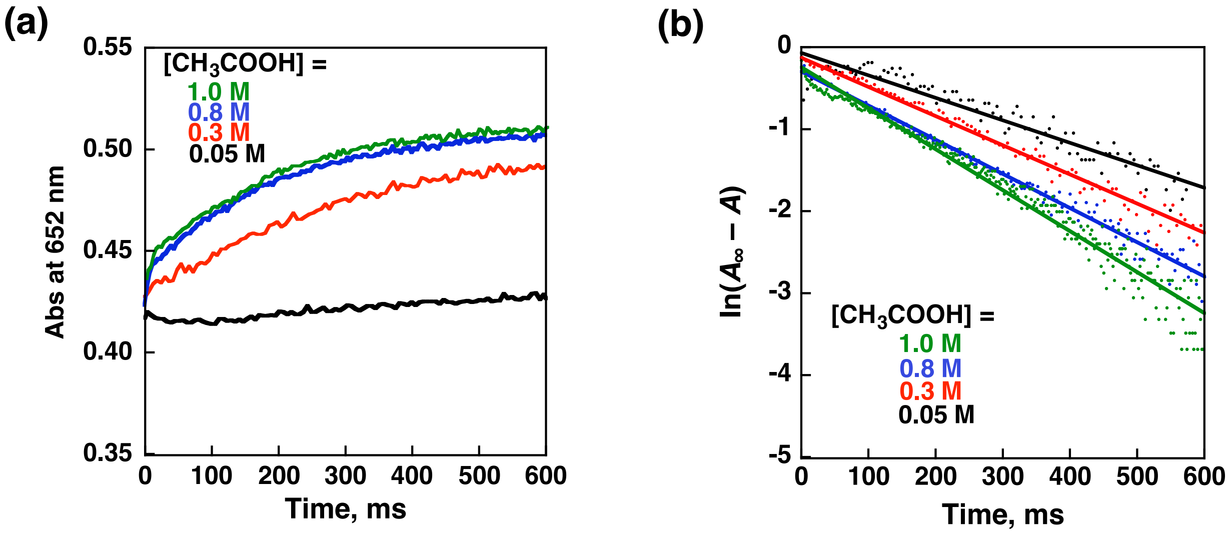

Fig. S8 (a) Time profiles of absorbance at 652 nm due to $[\mathrm{Co^{III}(Ch)}]^+$ generated by the addition of various concentrations of CH_3COOH to the solution of $[\mathrm{Co^{I}(Ch)}]^-$ (30 μM) in deaerated MeCN at 298 K. (b) First-order plots for the formation of $[\mathrm{Co^{III}(Ch)}]^+$.

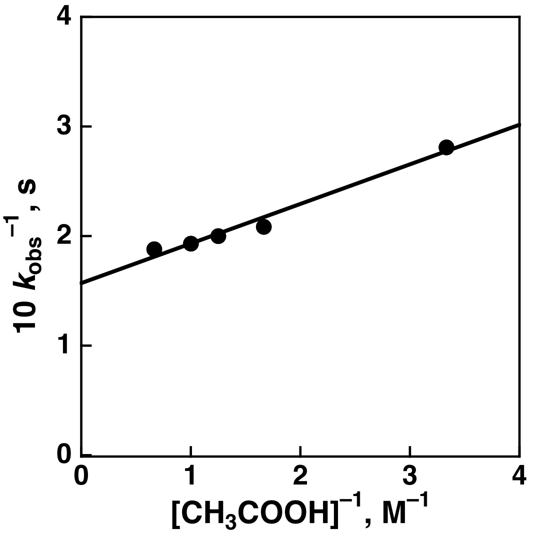

Fig. S9 Plot of k_{obs}^{-1} *vs*. $[CH_3COOH]^{-1}$.

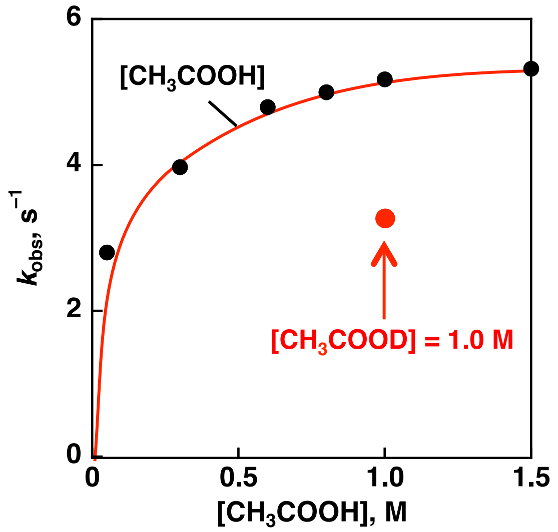

Fig. S10 Plots of k_{obs} for the rate of the formation of [Co^{III}(Ch)]$^+$ *vs*. [CH_3COOH] and [CH_3COOD].

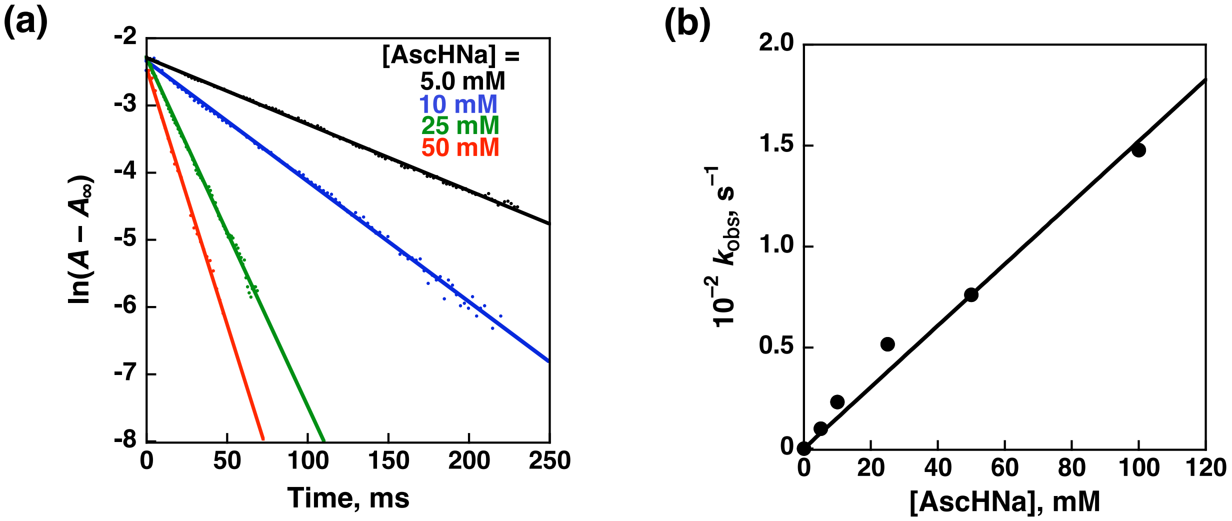

Fig. S11 (a) First-order plots for the rate of electron transfer from [AscHNa] to [Co^{III}(Ch)]$^+$. (b) Plot of k_{obs} of electron transfer from [AscHNa] to [Co^{III}(Ch)]$^+$ *vs*. [AscHNa].