

Electronic supplementary information (ESI)

Photocatalytic reduction of CO₂ and H₂O to CO and H₂ with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes

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Experimental section

Materials. Chemicals were purchased from commercial source and used without purification. $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3](\text{PF}_6)_2$ and $\text{Co}^{\text{II}}(\text{Ch})$ were synthesized according to literature procedure.^{S1,S2} Triethylamine (TEA) was obtained from Wako Pure Chemical Industries. TEA was refluxed with acetic anhydrous, then distilled, refluxed with KOH and again distilled. (*p*- BrC_6H_4) $_3\text{N}^+\text{SbCl}_6^-$, anhydrous acetonitrile (MeCN) for stopped-flow measurements, decamethylcobaltocene ($\text{Co}(\text{Cp}^*)_2$) and Multi-walled carbon nanotubes (MWCNTs) (L 6-9 nm \times 5 μm , > 95%) were obtained from Sigma Aldrich. MWCNTs was heated at 450 °C in air for 15 min to remove the amorphous carbon. The obtained powder was then shaken in aq HCl (2.0 M) at room temperature for 2 h. These procedures were repeated one more time to obtain the purified MWCNTs. Purification of water (18.2 M Ω 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 1 cm cells (light path length = 1 cm). Emission spectroscopy was carried out on a Shimadzu RF-5300PC fluorescence spectrometer at room temperature using 1 cm cells (light path length = 1 cm).

Quantum yield determination. A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photocatalytic hydrogen evolution. Typically, a 3.0 mL sample cell (light path length = 1 cm) that contained a substrate solution (2.0 mL) of $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$ (2.0 mM), TEA (0.50 M), $\text{Co}^{\text{II}}(\text{Ch})$ (10 μM) and MWCNTs (1.0 mg) was irradiated with monochromatised light of $\lambda = 450$ nm from LED lamp. Under the conditions of actinometry experiments, $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$ absorbed essentially 99% incident light of $\lambda = 450$ nm ($\text{Abs}_{450\text{nm}} \approx 7$). The light intensity of monochromatised light of $\lambda = 450$ nm was determined as 1.8×10^{-8} einstein s^{-1} . The photochemical reaction was monitored using a Shimadzu GC-17A gas chromatography. The quantum yield of the amount of evolved CO was determined using the comparative method.^{S3}

Photocatalytic CO and H₂ evolution. A mixed solution (2.0 mL) of MeCN/H₂O (95:5 v/v) containing $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$ (2.0 mM), TEA (0.5 M) and $\text{Co}^{\text{II}}(\text{Ch})$ was flushed with CO₂ 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. 100 μL from the headspace of the reaction vessel (3.0 mL) was injected in a Shimadzu GC-17A gas chromatograph [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 19095PMS0, 30 m \times 0.53 mm) at 313 K] equipped with a thermal conductivity detector to determine the amount of evolved CO and H₂. The amount of gas was quantified through calibration curves.

Electrochemical measurements. Cyclic voltammetry (CV) measurements of $\text{Co}^{\text{II}}(\text{Ch})$ and TEA were performed on an ALS 630B electrochemical analyser and voltammograms were measured in deaerated MeCN (2.0 mL) containing 5% (v/v) H₂O in the presence of 0.1 M TBAPF₆ as a supporting electrolyte at room temperature. A conventional three-electrode cell was used with a glassy carbon (GC) working electrode (surface area of 7.1 mm²) 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 Ag/AgNO₃ (1.0 \times 10⁻² M) reference electrode. All potentials (*vs.* Ag/AgNO₃) were converted to values *vs.* saturated calomel electrode (SCE) by adding 0.29 V.^{S4}

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.

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 condition, deaerated MeCN with a stream of N₂ was transferred by means of a glass syringe to a spectrometer cell that was already purged with a stream of N₂. Rate constant of the reaction of [Co^I(Ch)]⁻ with CO₂ in MeCN containing 5% (v/v) H₂O at 298 K was determined by monitoring the decay of the absorption band due to the corresponding [Co^{III}(Ch)(CO₂)]⁺ (λ_{\max} = 660 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 TEA in deaerated MeCN containing 5% (v/v) H₂O at 298 K was determined by monitoring the decay of the absorption band due to the corresponding [Co^{III}(Ch)]⁺ (λ_{\max} = 652 nm).

IR measurements. IR spectra were recorded on a Jasco FT/IR-6200 spectrometer. The IR spectrum of the compound under CO/N₂ (P/P) was obtained after bubbling CO/N₂ (P/P) using gas blender (KOFLOC GASBLENDER GB-3C) through the solution for 10-15 min.

References

- [S1] C. Turro, J. M. Zaleski, Y. M. Karabatsos and D. G. Nocera, *J. Am. Chem. Soc.*, 1996, **118**, 6060.
- [S2] K. Mase, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.*, 2013, **135**, 2800.
- [S3] (a) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London Ser. A.*, 1956, **235**, 518; (b) j. G. Calvert, J. N. Pitts, *Photochemistry*, Wiley, New York, 1966, p. 783
- [S4] C. K. Mann and K. K. Barnes, In *Electrochemical Reactions in Non-aqueous Systems*; MerceL Dekker: New York, 1970.

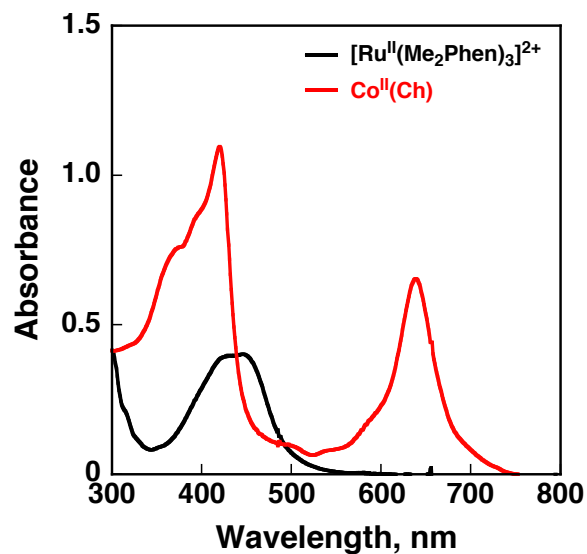


Fig. S1 UV-vis absorption spectra of $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$ (28 μM , black line) and $\text{Co}^{\text{II}}(\text{Ch})$ (20 μM , red line) in MeCN containing 5% (v/v) H_2O .

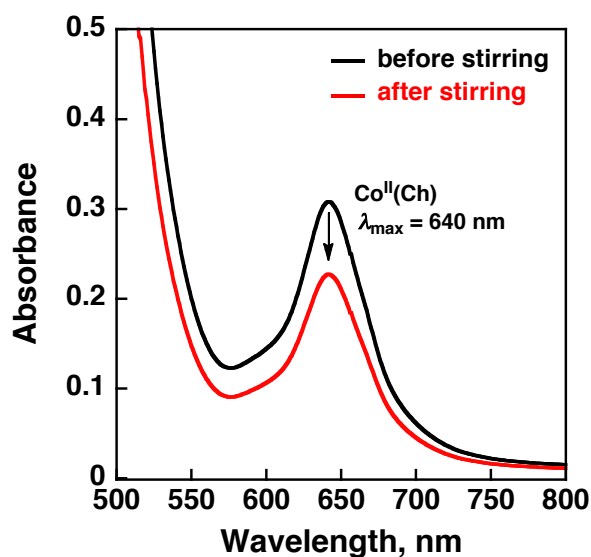


Fig. S2 UV-vis absorption spectra before and after stirring a CO_2 -saturated MeCN solution of $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$ (2.0 mM), $\text{Co}^{\text{II}}(\text{Ch})$ (10 μM), TEA (0.50 M) and MWCNTs (1.0 mg) containing 5% (v/v) H_2O for 9 h under dark.

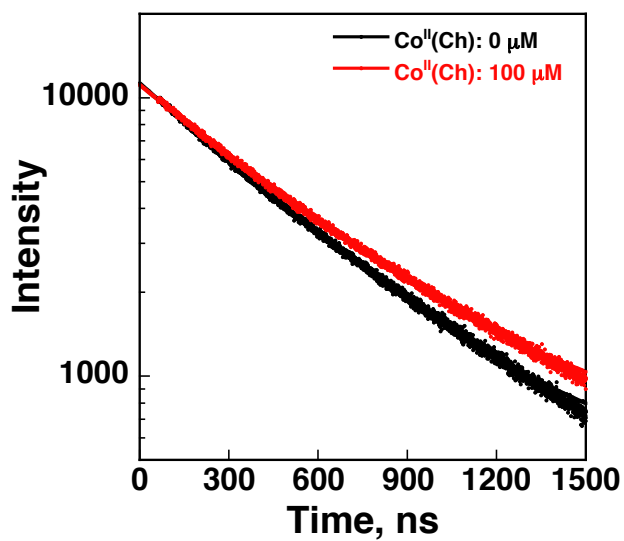


Fig. S3 Emission decay profiles of $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$ (8.8 μM) in the absence (black line) and presence of $\text{Co}^{\text{II}}(\text{Ch})$ (100 μM , red line) in deaerated MeCN containing 5% (v/v) H_2O at 298 K.

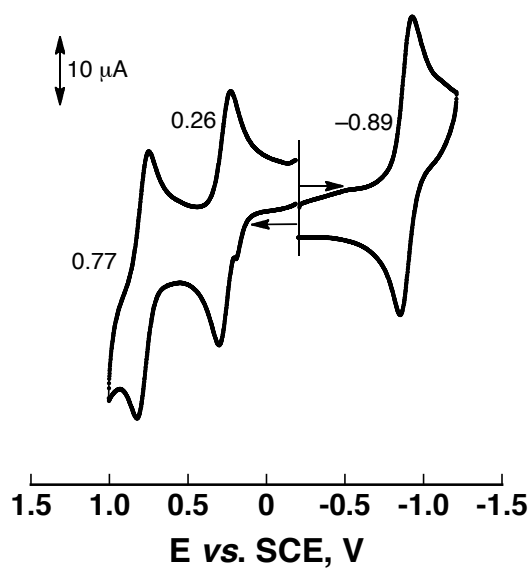


Fig. S4 Cyclic voltammogram of $\text{Co}^{\text{II}}(\text{Ch})$ (1.0 mM) in N_2 -saturated MeCN containing 5% (v/v) H_2O in the presence of TBAPF_6 (0.10 M); sweep rate: 0.1 V s^{-1} .

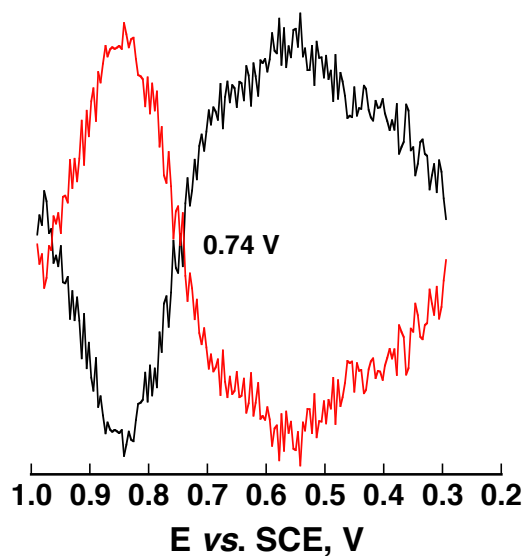


Fig. S5 SHACV of TEA (2.0 mM) in N₂-saturated MeCN containing 5% (v/v) H₂O in the presence of TBAPF₆ (0.10 M).

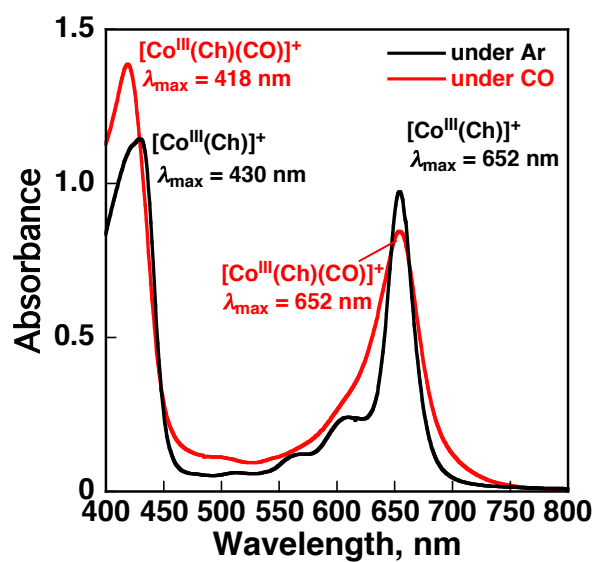


Fig. S6 UV-vis absorption spectra of [Co^{III}(Ch)]⁺ (20 μM) in N₂-saturated (black line) and CO/N₂-saturated (3:22 P/P) MeCN containing 5% (v/v) H₂O.

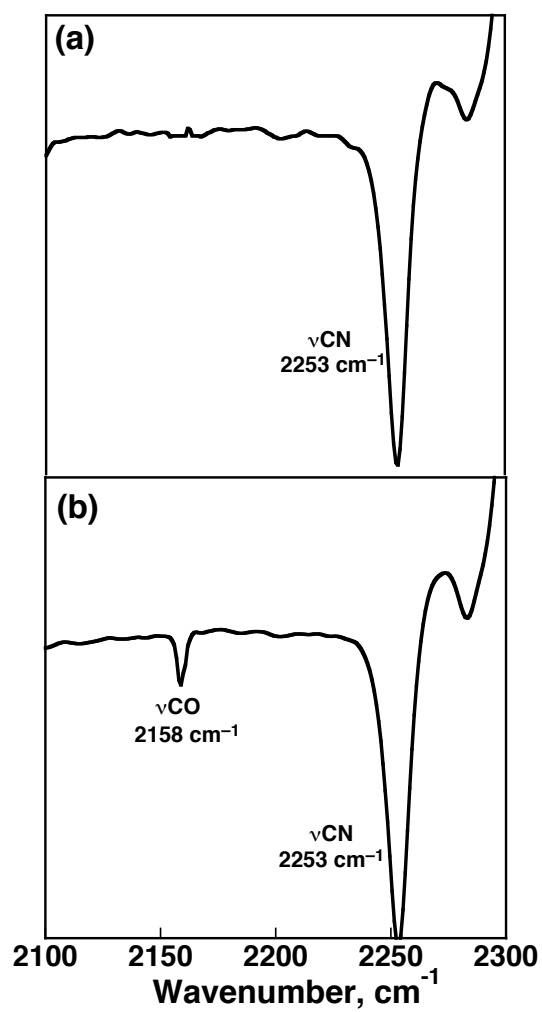


Fig. S7 FT-IR spectra of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ (460 μM) in (a) N_2 -saturated and (b) CO/N_2 -saturated (3:22 P/P) MeCN containing 5% (v/v) H_2O .

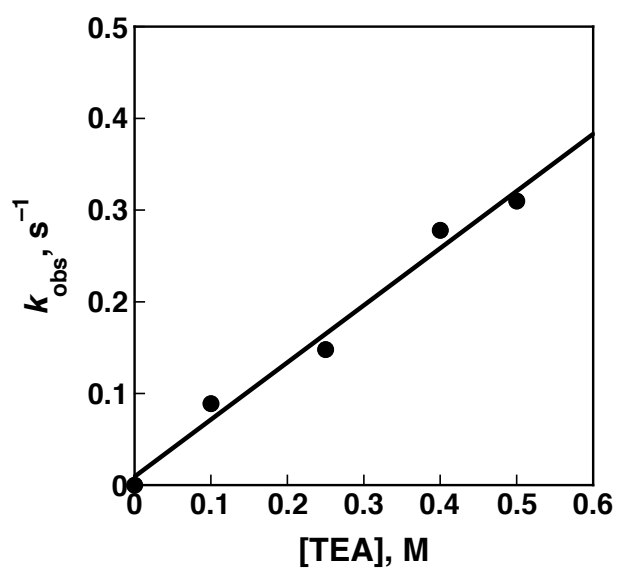


Fig. S8 Plot of k_{obs} vs. $[\text{TEA}]$.