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Electronic Supplementary Information

A Cobalt-NHC Complex as an Improved Catalyst for Photochemical Hydrogen Evolution from Water

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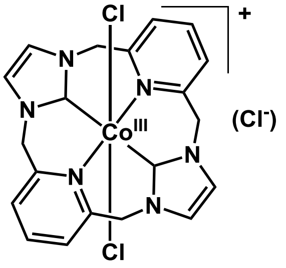
Experimental Section

Materials

All solvents and reagents were of the highest quality available and were used as received. Cobalt nanoparticles with the average particle size of 28 nm (Ionic Liquids Technologies) were used as received. **Co(dmgBF$_2$)$_2$**$\cdot$2H_2O (**2**$\cdot$2H_2O),[1] **LH$_2$**(PF_6)$_2$,[2] [Ru(bpy)$_3$]$Cl_2\cdot 6H_2O$,[3,4] [N,N’-dimethyl-4,4’-bipyridinium]I_2 ((MV)I_2),[5] [4,4’-dimethyl-N,N’-propylene-2,2’-bipyridinium]Br_2 ((DQ1)Br_2),[6] and [N,N’-propylene-2,2’-bipyridinium]Br_2 ((DQ2)Br_2)[6] were prepared as previously described.



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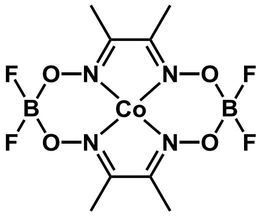
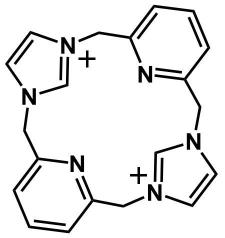


Co(dmgBF$_2$)$_2$ (2)



LH$_2^{2+}$

Synthesis of [Co(L)Cl_2]Cl$\cdot$2H_2O (1$\cdot$2H_2O). The suspension of **LH$_2$**(PF_6)$_2$ (0.815 g, 1.3 mmol) and Ag_2O (0.692 g, 3.0 mmol) in acetonitrile (10 mL) were heated at 70 °C for 24 h. After cooling to room temperature, the solution was filtered for the removal of the unreacted Ag_2O. The filtrate was evaporated to a total volume of ca. 1 mL followed by addition of water (20 mL) to give Ag(I)-NHC complex, which was reported to have a composition of [Ag_2L_2](PF_6)$_2$.[7,8] This was once collected by filtration, dried in vacuo, and finally redissolved in dry acetonitrile (400 mL) followed by addition of $CoCl_2\cdot 6H_2O$ (0.963 g, 1.5 mmol). This mixture was stirred at room temperature overnight, during which AgCl deposited. Without removing AgCl by filtration, the mixture was evaporated under reduced pressure to a total volume of ca. 20 mL followed by addition of NBu_4Cl (5.01 g, 18.0 mmol).

The resulting green precipitate was collected by filtration and washed with acetonitrile (10 mL x 3). This crude product was redissolved in a minimum amount of water (ca. 10 mL) followed by filtration for the removal of insoluble materials, such as the remaining AgCl. The filtrate was then evaporated to dryness to give another crude product which must be further purified by recrystallization from hydrochloric acid. The following procedures were crucial to obtain the compound axially ligated with two chloride ions. The solid was redissolved in 0.1 M HCl solution (50 mL) and heated at 80 °C overnight. This was evaporated to a total volume of ca. 2 mL followed by adding a large excess of acetone (300 mL). The green product deposited was collected by filtration. This was further recrystallized from 0.1 M HCl to afford the final product as a green powder (yield: 18 mg, 2.6%). ^{1}H NMR (DMSO-d6/TMS, ppm; see also Fig. S8): δ 5.89 (d, *J* = 15.9 Hz, 4H), 6.19 (d, *J* = 16.2 Hz, 4H), 7.70 (d, *J* = 7.7 Hz, 4H), 8.05 (t, *J* = 7.5 Hz, 2H), 8.27 (s, 4H); ESI-TOF MS (see also Fig. S9): m/z = 471.00 $[Co(\mathbf{L})Cl_2]^+$ (calcd for $C_{20}H_{18}Cl_2N_6Co$: 471.02); Elemental analysis calcd for $C_{20}H_{20}N_6Cl_3Co{\cdot}2H_2O$ (543.72): C 44.18, H 4.08, N 15.46; found: C 43.90, H 4.06, N 15.45.

Synthesis of $[Ru(bpy)_3](NO_3)_2{\cdot}3H_2O$. An aqueous solution of $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (1.634 g, 2.182 mmol) was passed through an anion-exchange column containing IRA-402BL (the NO_3^- form) to give the product as a red solid. This was recrystallized from water and dried in vacuo (yield: 1.234 g, 72.3%). Elemental analysis calcd for $C_{30}H_{24}N_8O_6Ru{\cdot}3H_2O$ (747.68): C 48.19, H 4.04, N 14.99; found: C 48.10, H 3.74, N 14.98.

Synthesis of $MV(NO_3)_2$. This was prepared in the same manner as $[Ru(bpy)_3](NO_3)_2{\cdot}3H_2O$ using $(MV)I_2$ (6.581 g, 14.95 mmol) as a starting material to afford the product as a white powder (yield: 2.066 g, 44.5%). Elemental analysis calcd for $C_{12}H_{14}N_4O_6$ (310.26): C 46.45, H 4.55, N 18.06; found: C 46.34, H 4.59, N 18.03.

Synthesis of DQ1(NO_3)$_2$·2H_2O. This was prepared in the same manner as [Ru(bpy)$_3$](NO_3)$_2$·3H_2O using (DQ1)Br_2 (1.004 g, 2.601 mmol) as a starting material to afford the product as a white powder (yield: 0.295 g, 29.4%). Elemental analysis calcd for $C_{15}H_{18}N_4O_6$·2H_2O (386.36): C 46.63, H 5.74, N 14.50; found: C 46.52, H 5.76, N 14.40.

Synthesis of DQ2(NO_3)$_2$·H_2O. This was prepared in the same manner as [Ru(bpy)$_3$](NO_3)$_2$·3H_2O using (DQ2)Br_2 (2.281 g, 6.369 mmol) as a starting material to afford the product as a white powder (yield: 0.624 g, 28.8%). Elemental analysis calcd for $C_{13}H_{14}N_4O_6$·H_2O (340.29): C 45.88, H 4.74, N 16.46; found: C 45.77, H 4.74, N 16.41.

Measurements

UV-vis spectra were recorded on Shimadzu Multispec-1500, UV-2450SIM, and UV-2600 spectrophotometers. ^{1}H NMR spectra were acquired on a JEOL JNM-ESA 600 spectrometer. ESI-TOF mass spectra were recorded on a JEOL JMS-T100LP spectrometer. Cyclic and square wave voltammograms were recorded on an ALS 602DKM electrochemical analyzer (BAS). Bulk electrolysis was performed on an ALS 1100C electrochemical analyzer (BAS). Photochemical hydrogen evolution experiments were carried out using the automated system developed in our group, as described elsewhere.[9,10] The photoirradiation was carried out by an ILC Technology CERMAX LX-300 300 W Xe lamp equipped with a CM-1 cold mirror which reflects lights in the range of $400 < \lambda < 800$ nm.

Electrochemical Generation of MV^{+}•.

An aqueous solution of MV^{+}• was prepared by the published method[11] with minor modifications as follows. The bulk electrolysis was carried out using a porous carbon fiber electrode supplied from

BAS as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) (0.241 V vs. NHE) as the reference electrode. The working compartment was separated from other electrodes using an agar KNO_3 salt bridge. Electrolysis at -0.9 V vs. SCE was carried out for a solution of 10 mM $MV(NO_3)_2$ in an aqueous acetate buffer solution (0.03 M CH_3COOH and 0.07 M CH_3COONa; pH 5.0; 40 mL) containing 0.1 M KNO_3 as an additional supporting electrolyte. The electrolysis was continued until the reduction yield reached 63% based on the coulometric analysis during the electrolysis. The $MV^{+\bullet}$ concentrations were spectrophotometrically confirmed at 550 nm where the absorptivity of dimer is exactly double that of monomer ($\varepsilon_{\mathrm{monomer}} = {}^{1}/_{2}\varepsilon_{\mathrm{dimer}} = 8800\ M^{-1}cm^{-1}$).[12] The $MV^{+\bullet}$ and MV^{2+} concentrations in the resulting solution were 6.3 and 3.7 mM, respectively. Finally, 16 mL of this solution was mixed with an aqueous acetate buffer solution (0.03 M CH_3COOH and 0.07 M CH_3COONa; pH 5.0; 4 mL) in the absence (blank) and presence of 0.5 mM $\mathbf{1}\cdot 2H_2O$. All these procedures were carried out inside an N_2-based glovebox (Takasugi Seisakusho, Japan), which was specially designed and made for spectrophotometry.

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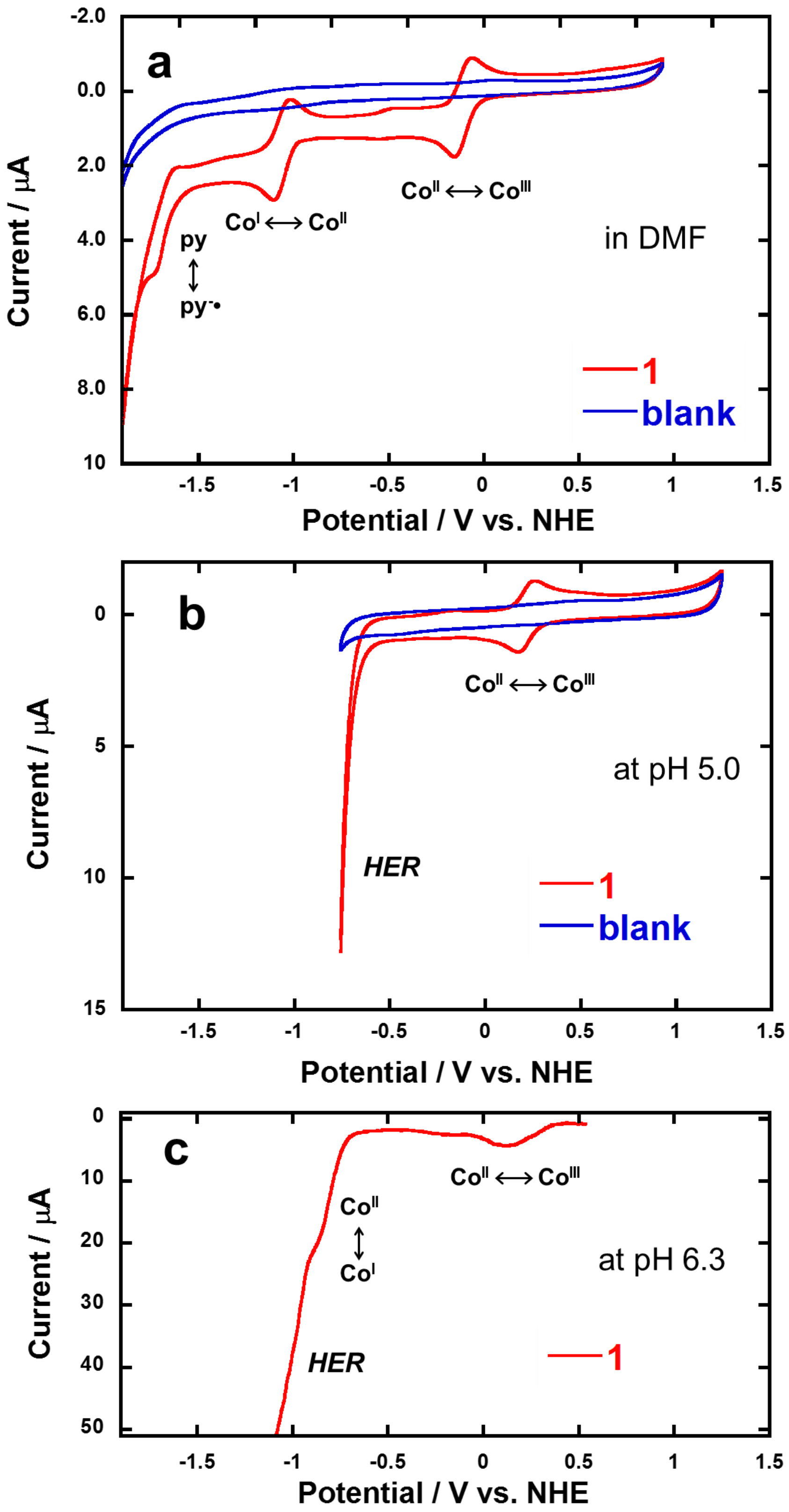

Fig. S1 Captions are given in next page.

Fig. S1 (Continued). (a) Cyclic voltammograms of **1**·$2H_2O$ (0.5 mM) in DMF containing 0.1 M NBu_4PF_6 (tetra(*n*-butyl)ammonium hexafluorophosphate) as a supporting electrolyte, recorded at a scan rate of 100 mV/s under Ar, using a three electrode system consisting of a platinum working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode. The potentials were corrected by employing the ferrocene/ferrocenium (Fc/Fc^+) couple as an internal standard, in which the Fc/Fc^+ couple was considered to be 0.550 V vs. NHE.

(b) Cyclic voltammograms of **1**·$2H_2O$ (0.1 mM) in an aqueous acetate buffer solution (0.03 M CH_3COOH and 0.07 M CH_3COONa; pH 5.0) containing 0.1 M KCl as a supporting electrolyte at a scan rate of 100 mV/s under Ar, where a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE; 0.241 V vs. NHE) were employed.

(c) A square wave voltammogram (SWV) of **1**·$2H_2O$ (0.5 mM) in an aqueous non-buffered solution (pH 6.3) containing 0.1 M KNO_3 as a supporting electrolyte under Ar, using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode. A shoulder attributable to the Co(II)/Co(I) couple is observed at around -0.85 V vs. NHE.

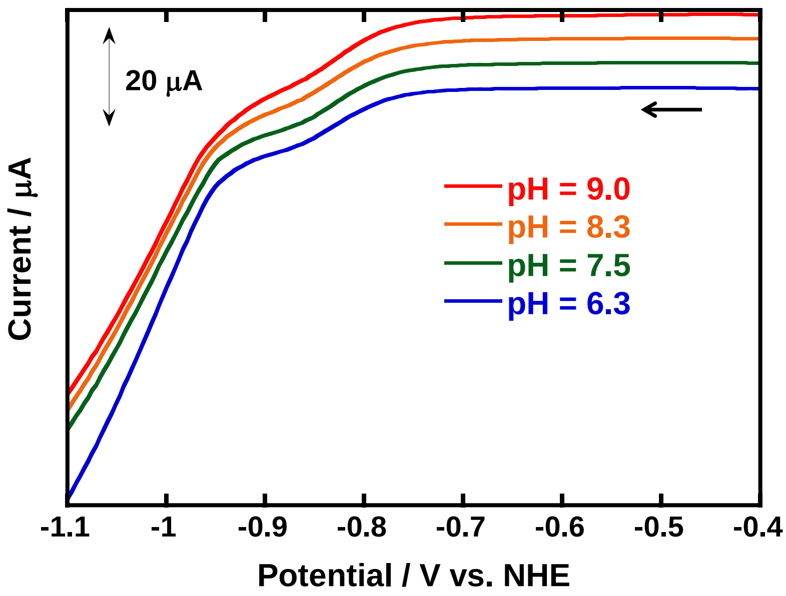

Fig. S2 SWVs of **1**·2H_2O (0.5 mM) in an aqueous 0.1 M KNO_3 solution under Ar atmosphere, using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode, where the pH of each solution was adjusted simply by adding KOH without using any buffer reagents.

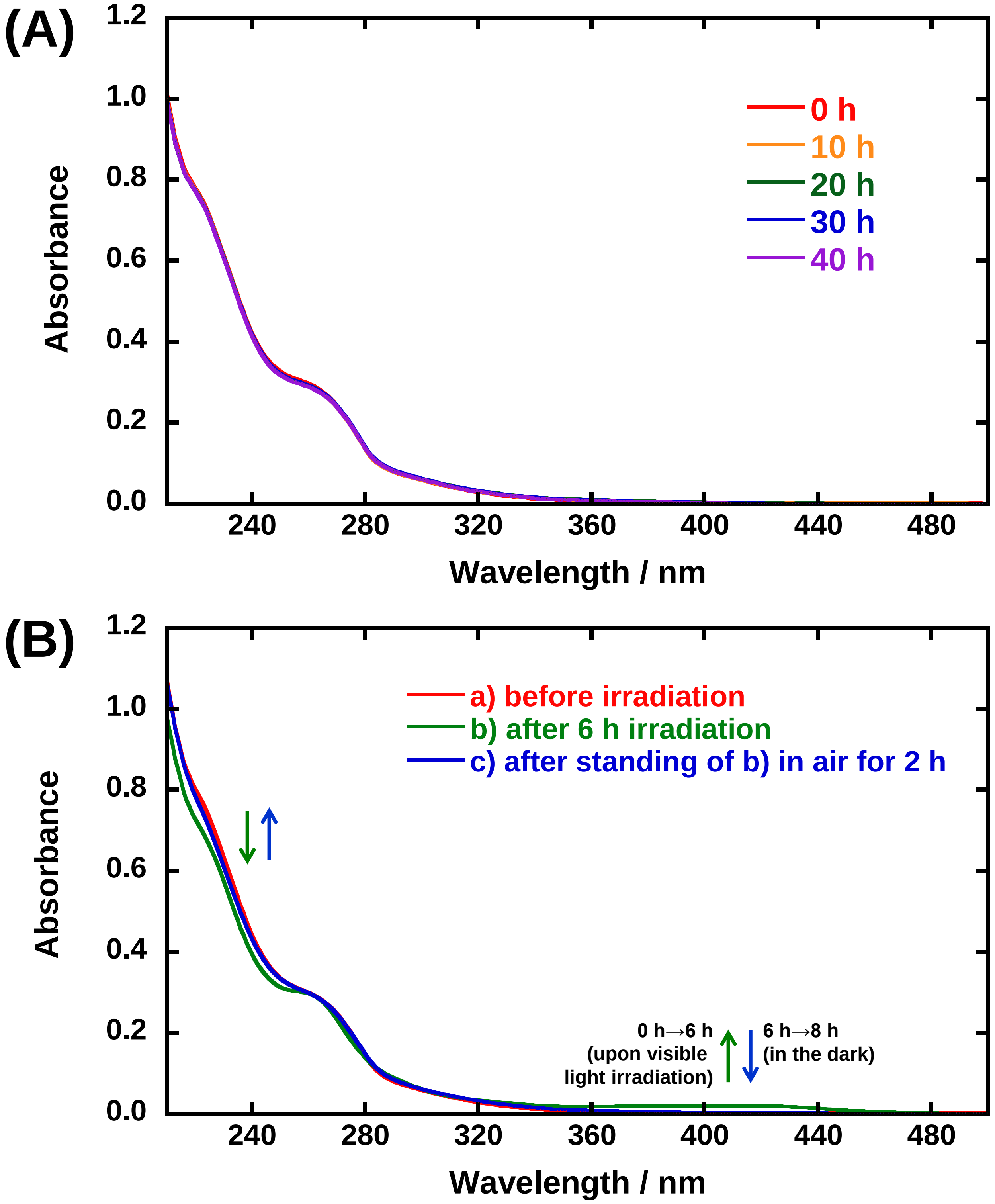

Fig. S3 Captions are given in next page.

Fig. S3 (A) The time-course of UV-vis absorption spectra of **1**·$2H_2O$ (0.04 mM) in water at 20 °C in air. (B) a) UV-vis absorption spectrum of **1**·$2H_2O$ (0.04 mM) in water at 20 °C under Ar, b) UV-vis absorption spectrum of **1**·$2H_2O$ (0.04 mM) in water after the irradiation of 300 W Xe lamp for 6 h at 20 °C under Ar, c) UV-vis absorption spectrum of **1**·$2H_2O$ (0.04 mM) in water after standing of b) in air for 2 h at 20 °C. The light source used for Bb) is same to that used for the H_2 evolution experiments reported in this manuscript.

These confirm the thermal and photochemical stability of Co-NHC complex **1** in aqueous media. In (A), spectral changes over 40 h are almost meaningless, which well demonstrates the high stability of the complex toward hydrolysis in aqueous media. In (B), the absorption feature changes, giving rise to a slight decrease in absorbance at the 240-nm shoulder together with a clear appearance of a new band at 400 nm. The new species generated is probably assigned as a photoreduced species, such as a Co(II) species, as these spectral changes reversed to afford the original spectral feature after exposure to air. We assume that partial photoreduction occurs but the reduced species can be quantitatively recovered to the original Co(III) species in air. Since the original spectral feature could be perfectly recovered at the end of the above experiments, the photodegradation of **1** is considered negligible under these photolysis conditions.

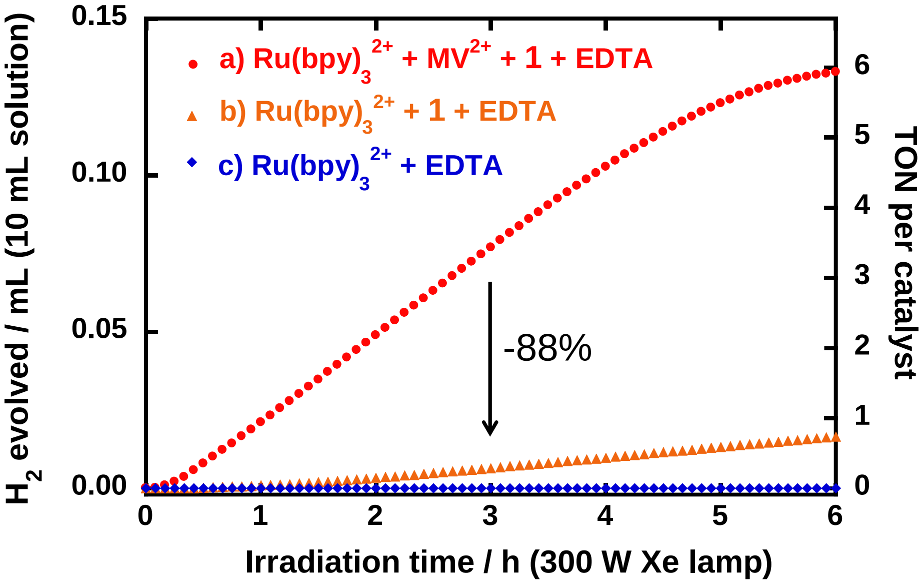

Fig. S4 Photochemical H_2 production from an aqueous acetate buffer solution (0.03 M CH_3COOH and 0.07 M CH_3COONa; pH 5.0; 10 mL) containing EDTA (30 mM; disodium salt) and $[Ru(bpy)_3](NO_3)_2 \cdot 3H_2O$ (0.04 mM), a) with $MV(NO_3)_2$ (2.0 mM) and **1**$\cdot 2H_2O$ (0.1 mM), b) with **1**$\cdot 2H_2O$ (0.1 mM), or c) without acceptor and catalyst, under Ar atmosphere at 20 ˚C.

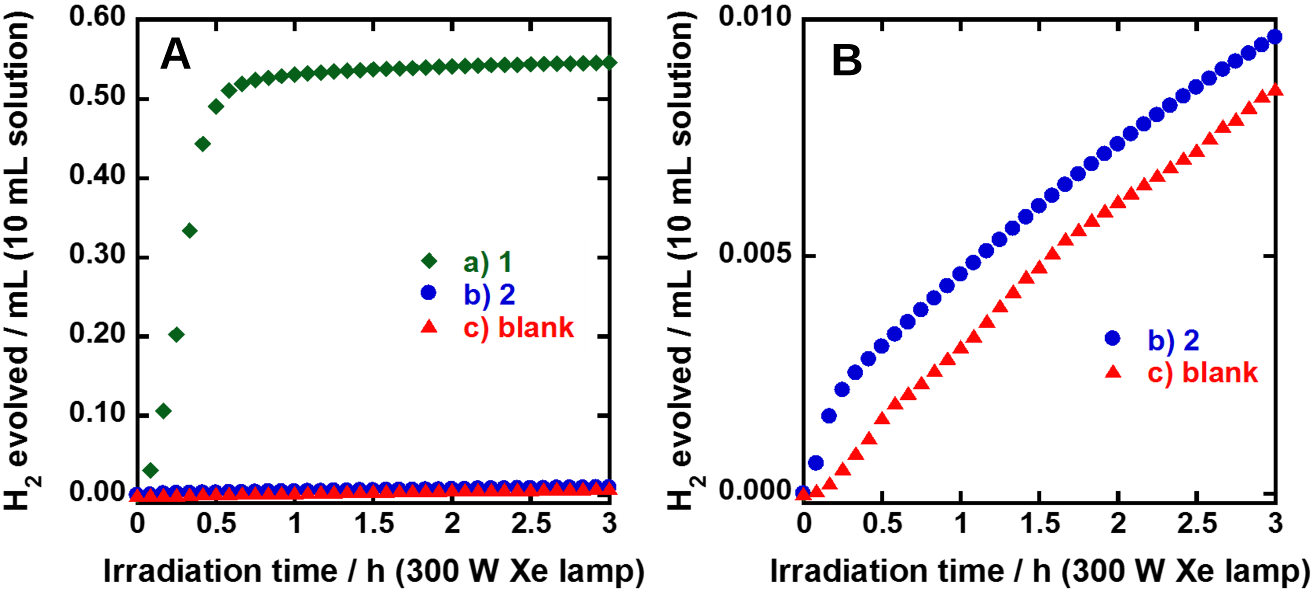

Fig. S5 (A) Photochemical H_2 production from an aqueous acetate buffer solution (0.03 M CH_3COOH and 0.07 M CH_3COONa; pH 5.0; 10 mL) containing EDTA (30 mM; disodium salt), $[Ru(bpy)_3](NO_3)_2 \cdot 3H_2O$ (0.04 mM), and $DQ1(NO_3)_2$ (2.0 mM), in the presence of a) **1**$\cdot 2H_2O$ (0.1 mM), b) **2**$\cdot 2H_2O$ (0.1 mM), or c) no catalyst, under Ar atmosphere at 20 ˚C. Fig. S5B shows the magnifications of the curves for Fig. S5Ab), c).

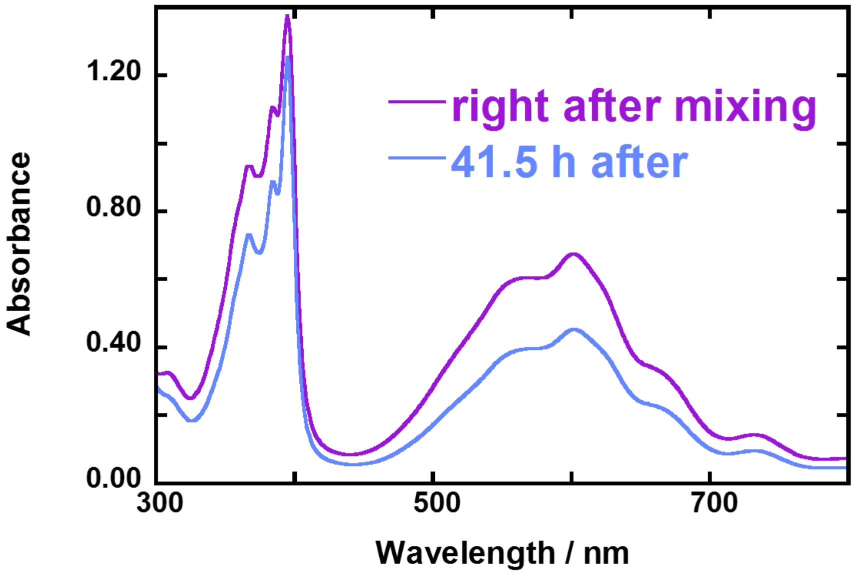

Fig. S6 The decay of absorption bands of MV^{+}• during the experiment in Fig. 5 (blank). Absorption spectra were measured for the two sampling time; (a) right after mixing and (b) 41.5 h after mixing. For each measurement, 1 mL was taken out from the mixture and was mixed with 7 mL of an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa, and 0.1 M KNO_3; pH 5.0) to give 8-fold dilution, which was required to diminish the maximum absorbance of each spectrum to be lower than 1.4 with use of a quartz cuvette having an optical path length of 1 mm. All these procedures were carried out inside an N_2-based glovebox.

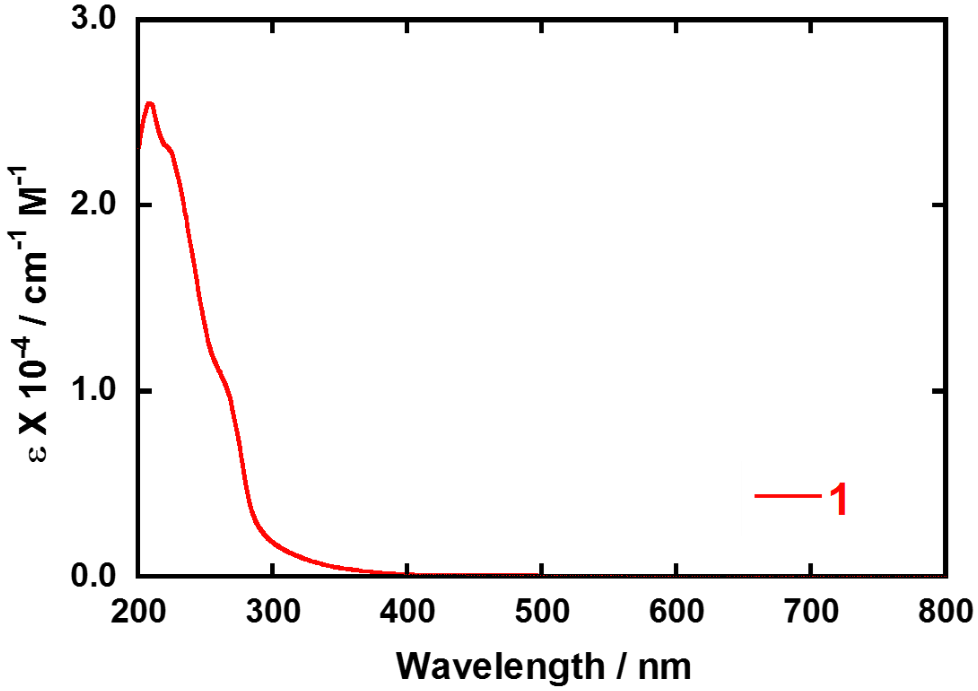

Fig. S7 UV-vis absorption spectrum of **1**·2H_2O in water at 20 °C.

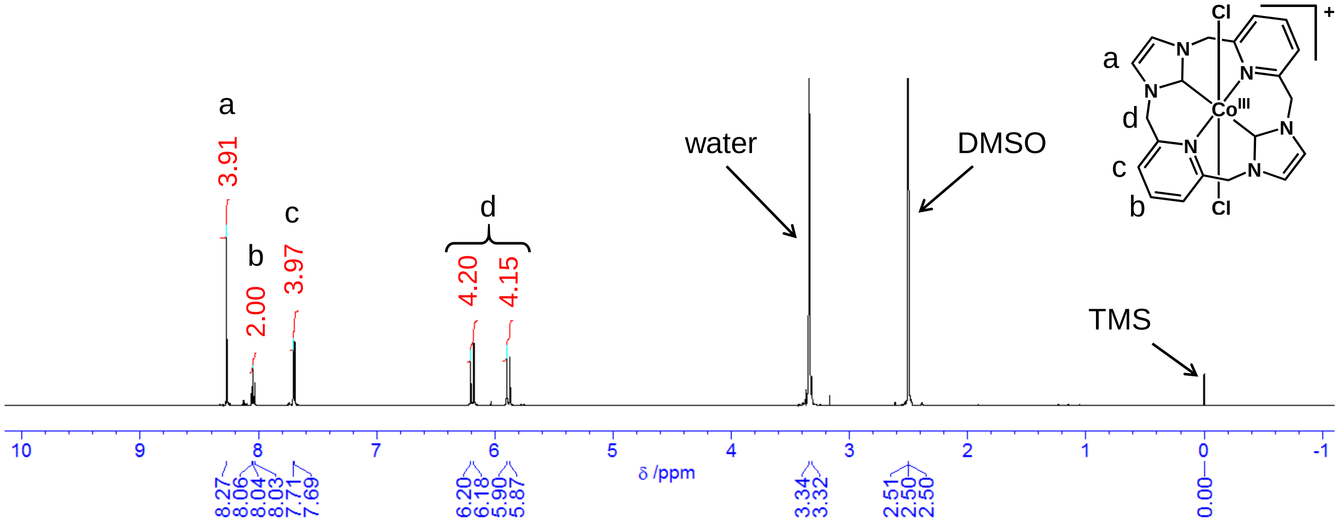

Fig. S8 ^{1}H NMR spectrum (600 MHz) of **1**·$2H_2O$ (DMSO-d6; TMS as an internal standard).

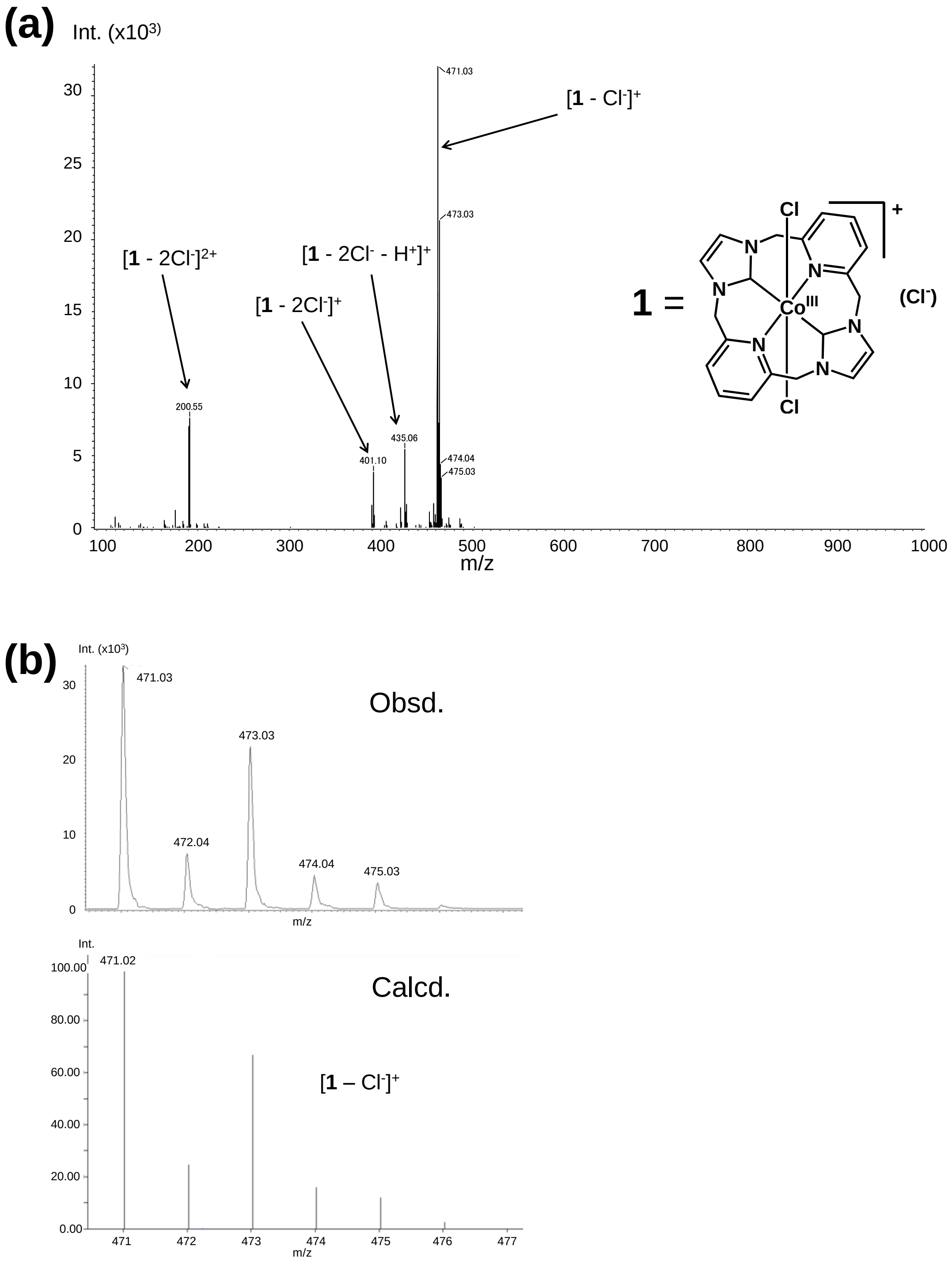

Fig. S9 a) ESI-TOF mass spectrum of **1**·$2H_2O$ in methanol. b) Comparison of the isotopic distribution patterns of the observed and calculated peaks at 471.03 (471.02, [**1** – $Cl^-]^+$) m/z.