Photocatalytic CO_2 reduction using a Mn complex as a catalyst

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Supporting Information

Experimental details

Reagents. 1,4-Dihydronicotinamide (BNAH) was synthesized according to literature.[1] Acetonitrile (MeCN) was distilled three times over P_2O_5 and then distilled over CaH_2 just prior to use. Dimethylformamide (DMF) and dimethylacetoamide (DMA) were dried over molecular sieves of size 4 Å and distilled at reduced pressure. Triethanolamine (TEOA) was distilled at reduced pressure. Tetraethylammonium tetrafluoroborate was dried in vacuo at 100 °C overnight before use. All other reagents and solvents were of high purity and commercially obtained from Kanto Chemical Co. Inc., Wako Pure Chemical Industries, Ltd. and Aldrich Chemical Company.

Synthesis of ***$Ru(dmb)_3(PF_6)_2$***. A photosensitizer, $Ru(dmb)_3(PF_6)_2$ (dmb = 4,4′-dimethyl-2,2′-bpyridine) was synthesized from *cis*-$[Ru(dmb)_2Cl_2]$ (91.7 mg, 0.169 mmol) and dmb (46.5 mg, 0.255 mmol) according to literature[2] and further purified by column chromatography on basic alumina (Activity I; Merck KGaA) with a MeCN–CH_2Cl_2 (1:1 v/v) mixed eluent, ion-exchange chromatography (CM Sephadex™ C-25) with an acetone/H_2O (1:1 v/v) mixed eluent containing NH_4PF_6 and recrystallization from acetone/Et_2O several times. Yield: 55.2 mg (34.6%). A ^{1}H-NMR spectrum (300 MHz, acetone-d_6) agreed well with reported values.[3] ESI-MS: m/z = 327 ($[M - 2PF_6^-]^{2+}$). Elemental Anal. Calcd (%) for $C_{36}H_{36}N_6P_2F_{12}Ru$: C, 45.82; H, 3.85; N, 8.91. Found: C, 45.71; H, 3.91; N, 8.68.

Synthesis of ***$Mn(bpy)(CO)_3Br$***. The Mn complex was synthesized according to literature[4] with the following improvement. An Et_2O solution (40 mL) containing 2,2′-bipyridine (bpy: 58.8 mg, 0.38 mmol) and $[Mn(CO)_5Br]$ (99.8 mg, 0.36 mmol; Stream Chemicals Inc.) was refluxed for 3 h. $Mn(bpy)(CO)_3Br$ was obtained as orange powders by filtration, washed with Et_2O and dried in vacuo. All steps were performed in dark. Yield: 99.8 mg (72.2%). A ^{1}H-NMR spectrum (300 MHz, acetone-d_6) agreed well with reported values.[4] FT-IR (CH_2Cl_2): ν(CO)/cm^{-1}, 2028, 1938, 1923. Elemental Anal. Calcd (%) for $C_{13}H_8BrMnN_2O_3$: C, 41.63; H, 2.15; N, 7.47. Found: C, 41.59; H, 2.33; N, 7.44.

Photocatalytic reaction. A 4-mL DMF-TEOA (4:1 v/v) solution containing $[Ru(dmb)_3]^{2+}$ (0.05

mM), Mn(bpy)(CO)$_3$Br (0.05 mM) and BNAH (0.1 M) in a quartz cubic cell (1 cm pass length; 11 mL volume) was bubbled with CO_2 for 30 min. The sample solution was irradiated using an Ushio 500-W Xe short arc lamp (BA-H500, UXL-500D-O and XB-50101 AA) with a 480 nm band-pass filter (FWHM: 10 nm) purchased from Asahi Spectra Co. and a $CuSO_4 \cdot 5H_2O$ aqueous solution (20 gL^{-1}, 5 cm pass length) filter. Neutral density (ND) glass filters were used to adjust the light intensity (4.3×10^{-8} einstein s^{-1}). The temperature of the reaction solution was maintained at 25±0.1 °C using an IWAKI CTS-134A cooling thermo pump during the irradiation. The incident light intensity was determined using a $K_3[Fe(C_2O_4)_3]$ actinometer.[5] The amount of formic acid in the reaction solution with diluted water was analysed by a capillary electrophoresis system (Otsuka Electronics Co. CAPI-33001) with a buffer solution (pH 6.0) consisting of quinolinic acid, hexadecyltrimethylammonium hydroxide and 2-amino-2-hydroxymethyl-1,3-propanediol as the electrolyte. The gaseous products, *i.e.* CO and H_2, were analysed using GC-TCD (GL science GC323) with an active carbon column. Quantum yields for formic acid formation (Φ_{HCOOH}) were calculated as the number of formic acid molecules formed, divided by the number of absorbed photons. Turnover numbers (TON) for the product were calculated as the number of the products divided by the number of catalyst. UV-Vis absorption spectral changes of the reaction solution during the photoirradiation were recorded on a Photal MCPD-2000 photo-diode-array spectrometer. Particle size analysis of a solution after photoirradiation was performed using an Otsuka Electronics Co. ELSZ-1000ZS zeta-potential and particle size analyser. To record FT-IR spectral changes of the reaction solution during the photoirradiation, a 4 mL DMF-TEOA (4:1 v/v) solution containing $[Ru(dmb)_3]^{2+}$ (1 mM), Mn(bpy)(CO)$_3$Br (1 mM) and BNAH (0.1 M) was introduced into an IR cell (UNISOKU USP-2031IR-A and USP-CL-T1; 0.1 mm path length) after bubbling with CO_2 for 30 min, and then irradiated using an Asahi Spectra Co. 300 W Xe short arc lamp (MAX-302) with a 480 nm band-pass filter (FWHM: 10 nm) purchased from Asahi Spectra Co. at a controlled temperature (25 °C) using the cooling thermo pump. The GC-MS experiments were performed using $^{13}CO_2$ (99 atom% ^{13}C, Cambridge Isotope Laboratories). A quartz cubic cell was deaerated using the freeze-pump-thaw method, and then $^{13}CO_2$ (69.2 kPa) was introduced. After photoirradiation, the products in the reaction solution were extracted with ethyl acetate. The organic phase was washed with diluted H_2SO_4, and analysed by GC-MS (Shimadzu GCMS-QP2010 Ultra) with a TC-WAX column. A control experiment using ordinal CO_2 rather than $^{13}CO_2$ was also performed. Figure S1 shows the GC-MS chromatograms of the peaks at m/z = 47 (a and c), 46 (b and d) and 45 (e). The results of the control experiment indicated that the peak ratio between $[HCOOH]^+$ and $[COOH]^+$, which is a fragment peak of HCOOH, was 1:0.81. By applying this data to analyse the results of the $^{13}CO_2$ experiment (Fig. S1 a and b), the production ratio between $H^{13}COOH$ and $H^{12}COOH$ was determined as 19.3:80.7.

General measurements. IR spectra were recorded on a JASCO FT/IR-610 spectrometer at 1-cm^{-1} resolution. UV-Vis absorption spectra were recorded on a JASCO V-565 spectrometer. ^{1}H NMR spectra were recorded on an AL300 NMR spectrometer. ESI-MS analysis was conducted using a Shimadzu LCMS-2010 mass spectrometer with an electrospray ionization unit. Cyclic voltammograms were measured in DMF containing a complex (0.5 mM) and Et_4NBF_4 (0.1 M) as a supporting electrolyte under Ar atmosphere using a BAS CHI720D electrochemical analyser with a glassy-carbon working electrode (diameter, 3 mm), a Ag/$AgNO_3$ (0.01 M) reference electrode and a Pt counter electrode at a scan rate of 200 mV s^{-1}.

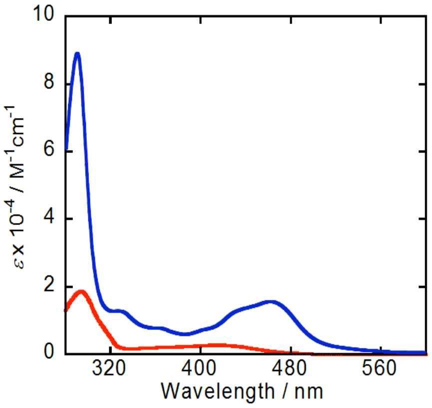

Fig. S1 UV-Vis absorption spectra of $Mn(bpy)(CO)_3Br$ (red) and $Ru(dmb)_3(PF_6)_2$ (blue) in DMF.

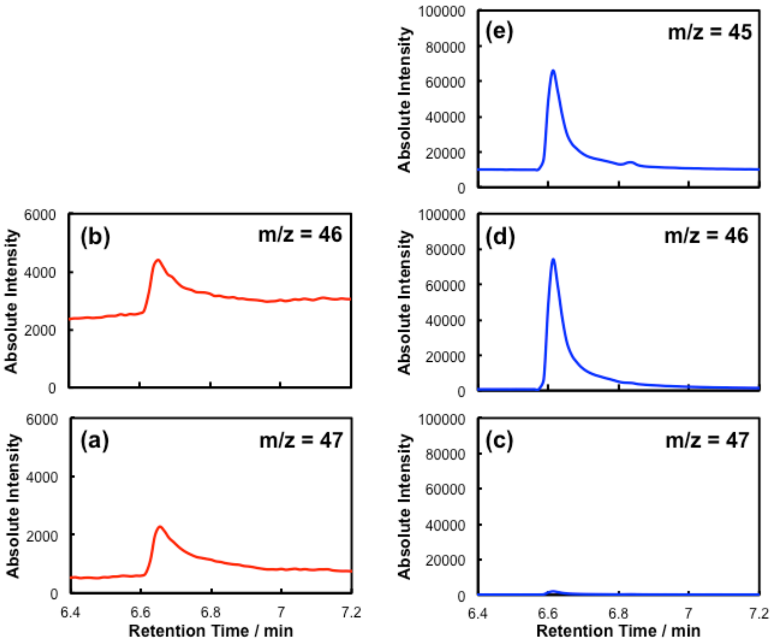

Fig. S2 GC-MS chromatograms of the peaks related to formic acid: photocatalytic reactions under $^{13}CO_2$ (a and b) and ordinal CO_2 atmospheres (c, d and e).

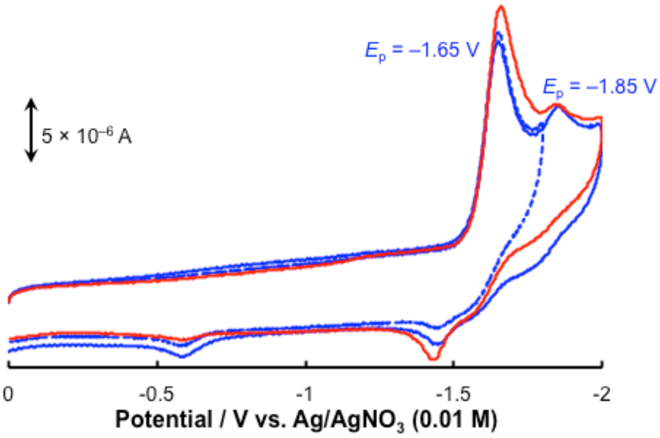

Fig. S3 Cyclic voltammograms of Mn(bpy)$(CO)_3$Br (0.5 mM) in a DMF solution containing Et_4NBF_4 (0.1 M) as a supporting electrolyte under Ar (blue) and CO_2 (red) atmosphere. Scan rate was 200 mV/s.

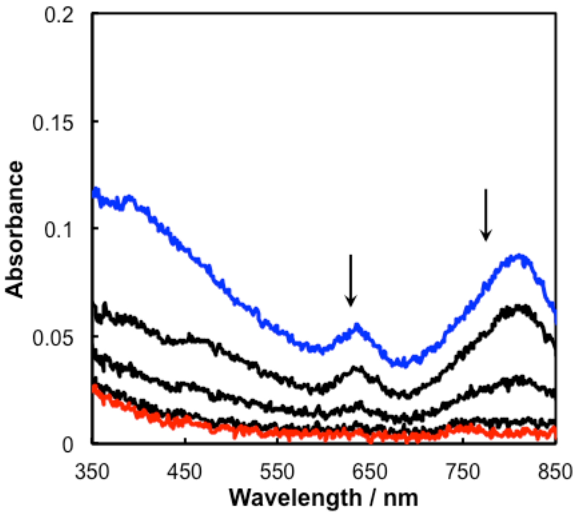

Fig. S4 Spectral changes of [Mn(bpy)$(CO)_3$]$_2$ in a DMF-TEOA (4:1 v/v) mixed solution during a 480 nm light irradiation under Ar atmosphere. The dimer was generated *in situ* by 436-nm light irradiation to a solution containing Mn(bpy)$(CO)_3$Br (0.05 mM). The spectra were taken every 20 min. Arrows indicates decrease in absorption during irradiation.

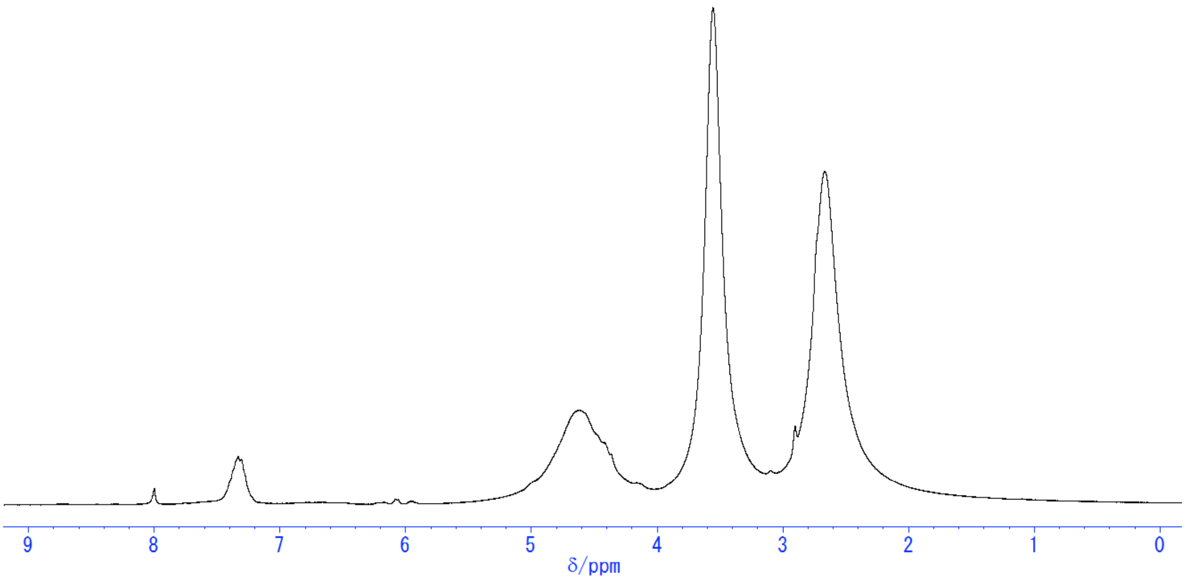

Fig. S5 ^{1}H NMR spectrum of the photocatalytic reaction solution after 20 h irradiation. The solvent was a d_7-DMF-TEOA (4:1 v/v) solution.

References

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