Photocatalytic CO\textsubscript{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.\textsuperscript{1} Acetonitrile (MeCN) was distilled three times over P\textsubscript{2}O\textsubscript{5} and then distilled over CaH\textsubscript{2} just prior to use. Dimethylformamide (DMF) and dimethylacetamide (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)\textsubscript{3}(PF\textsubscript{6})\textsubscript{2}. A photosensitizer, Ru(dmb)\textsubscript{3}(PF\textsubscript{6})\textsubscript{2} (dmb = 4,4′-dimethyl-2,2′-bpyridine) was synthesized from cis-[Ru(dmb)\textsubscript{2}Cl\textsubscript{2}] (91.7 mg, 0.169 mmol) and dmb (46.5 mg, 0.255 mmol) according to literature\textsuperscript{2} and further purified by column chromatography on basic alumina (Activity I; Merck KGaA) with a MeCN–CH\textsubscript{2}Cl\textsubscript{2} (1:1 v/v) mixed eluent, ion-exchange chromatography (CM Sephadex\textsuperscript{TM} C-25) with an acetone/H\textsubscript{2}O (1:1 v/v) mixed eluent containing NH\textsubscript{4}PF\textsubscript{6} and recrystallization from acetone/Et\textsubscript{2}O several times. Yield: 55.2 mg (34.6%). \textsuperscript{1}H-NMR spectrum (300 MHz, acetone-d\textsubscript{6}) agreed well with reported values.\textsuperscript{3} ESI-MS: m/z = 327 ([M – 2PF\textsubscript{6}]\textsuperscript{2+}). Elemental Anal. Calcd (%) for C\textsubscript{36}H\textsubscript{36}N\textsubscript{6}P\textsubscript{2}F\textsubscript{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)\textsubscript{3}Br. The Mn complex was synthesized according to literature\textsuperscript{4} with the following improvement. An Et\textsubscript{2}O solution (40 mL) containing 2,2′-bipyridine (bpy: 58.8 mg, 0.38 mmol) and [Mn(CO)\textsubscript{5}Br] (99.8 mg, 0.36 mmol; Stream Chemicals Inc.) was refluxed for 3 h. Mn(bpy)(CO)\textsubscript{3}Br was obtained as orange powders by filtration, washed with Et\textsubscript{2}O and dried in vacuo. All steps were performed in dark. Yield: 99.8 mg (72.2%). \textsuperscript{1}H-NMR spectrum (300 MHz, acetone-d\textsubscript{6}) agreed well with reported values.\textsuperscript{4} FT-IR (CH\textsubscript{2}Cl\textsubscript{2}): \nu(CO)/cm\textsuperscript{-1}, 2028, 1938, 1923. Elemental Anal. Calcd (%) for C\textsubscript{13}H\textsubscript{8}BrMnN\textsubscript{2}O\textsubscript{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)]\textsuperscript{2+} (0.05
mM), Mn(bpy)(CO)3Br (0.05 mM) and BNAH (0.1 M) in a quartz cubic cell (1 cm pass length; 11 mL volume) was bubbled with CO2 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 CuSO4·5H2O 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 Kα[Fe(C₂O₄)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 H₂, were analysed using GC-TCD (GL science GC323) with an active carbon column. Quantum yields for formic acid formation (ΦHCOOH) 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)₃Br (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 CO₂ 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 using¹³CO₂ (99 atom%¹³C, Cambridge Isotope Laboratories). A quartz cubic cell was deaerated using the freeze-pump-thaw method, and then¹³CO₂ (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 H₂SO₄, and analysed by GC-MS (Shimadzu GCMS-QP2010 Ultra) with a TC-WAX column. A control experiment using ordinal CO₂ rather than¹³CO₂ 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 the¹³CO₂ experiment (Fig. S1 a and b), the production ratio between H¹³COOH and H¹³COOH 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\(_4\)NBF\(_4\) (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\(^{-1}\).

![Graph](image1)

**Fig. S1** UV-Vis absorption spectra of Mn(bpy)(CO)\(_3\)Br (red) and Ru(dmb)(PF\(_6\))\(_2\) (blue) in DMF.

![Graph](image2)

**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).

![Cyclic voltammograms of Mn(bpy)(CO)$_3$Br (0.5 mM)](image1)

Fig. S3  Cyclic voltammograms of Mn(bpy)(CO)$_3$Br (0.5 mM) in a DMF solution containing Et$_4$NBF$_4$ (0.1 M) as a supporting electrolyte under Ar (blue) and CO$_2$ (red) atmosphere. Scan rate was 200 mV/s.

![Spectral changes of [Mn(bpy)(CO)$_3$]$_2$](image2)

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


