Highly efficient visible-light-driven CO_2 reduction to CO using a Ru(II)–Re(I) supramolecular photocatalyst in an aqueous solution

Akinobu Nakada,[a] *Kazuhide Koike,*[b,c] *Kazuhiko, Maeda,* [a] *and Osamu Ishitani**[,a,c]

[a]Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-NE-1 O-okayama, Meguro-ku, Tokyo 152-8550, Japan.

[b]National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba 305-8569, Japan

[c]CREST, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Supporting Information

General Procedure

IR spectra were measured at 1 cm^{-1} resolution with a JASCO FT/IR-610 spectrophotometer. UV–vis absorption spectra were measured with a JASCO V-565 spectrophotometer. Emission spectra were measured at 298 ± 0.1 K with a JASCO FP-6500 spectrofluorometer. Emission lifetimes were measured with a Horiba FluoroCube 1000U-S time-correlated single-photon-counting system (the excitation source was a nano-LED 460, and the instrument response was less than 1 ns).

^1H NMR spectra were measured in a CD_3OD solution using a JEOL ECA400II (400 MHz) system. Electrospray ionization−mass spectroscopy (ESI−MS) was performed with a Shimadzu LCMS-2010A system using HPLC-grade MeOH as a mobile phase.

Cyclic voltammograms were measured in an aqueous solution containing Na_2SO_4 (0.1 M) as a supporting electrolyte; the voltammograms were collected using an ALS/CHI CHI-760ES electrochemical analyzer with a glassy-carbon disk working electrode (3 mm diameter), a Pt counter electrode, and an Ag/AgCl reference electrode. For mononuclear model complexes, cyclic voltammetry was conducted in MeCN containing NEt_4BF_4 (0.1 M) with an $Ag/AgNO_3$ reference electrode was used instead of Ag/AgCl.

Materials

Tap water was purified using a Millipore Elix Essential 3 UV system and was used the same day. Other materials were reagent-grade quality and were used without further purification.

Synthesis

$BI(CO_2H)H$,[1] $BI^+(CO_2^-)$,[1] 4-methyl-2,2'-bipyridine (mmb),[2] and the bridging ligand (bpy-CH_2-CH_2-bpy)[2] were prepared using previously reported methods. $Re\{bpy(CH_2PO_3H_2)_2\}(CO)_3Cl$ (**Re**) was also synthesized according to the reported method.[3]

$[Ru(dmb)_2(mmb)]Cl_2\cdot5H_2O$, **Ru**. A MeOH solution (50 mL) containing $Ru(dmb)_2Cl_2\cdot2H_2O$ (31 mg, 0.057 mmol) and mmb (11 mg, 0.063 mmol) was refluxed for 16 h. After MeOH was removed by evaporation, purification was performed using an ion-exchange column (SP Sephadex C-25, MeCN−water (1:1, v/v) containing NH_4PF_6) to give $[Ru(dmb)_2(mmb)](PF_6)_2$. To the PF_6 salts, 40 mL of EtOH−H_2O (1:1, v/v) was added; the solution was subsequently treated with an Amberlite IRA-900J ion-exchange resin in Cl form.

Yield: 28 mg (0.037 mmol, 64%) Anal. Calcd for $C_{33}H_{44}Cl_2N_6O_5Ru$: C, 52.50; H, 5.54; N, 10.50. Found: C, 52.95; H, 5.12; N, 10.47. ^{1}H-NMR (400 MHz, MeOH) δ / ppm: 8.67 (d, 1H, J = 8.0 Hz), 8.56 (s, 5H), 8.08 (dd, 1H, J = 8.0 Hz, 7.4 Hz), 7.81 (d, 1H, J = 6.4 Hz), 7.61 (m, 5H), 7.45 (dd, 1H, J = 7.4 Hz, 6.4 Hz), 7.31 (m, 5H), 2.58 (s, 15H). ESI–MS (eluent: MeOH) m/z: 319 ($[M - 2Cl^-]^{2+}$).

$[Ru(dmb)_2(bpy\text{-}CH_2\text{-}CH_2\text{-}bpy)Re(CO)_3Cl]Cl_2\cdot 5H_2O$, **RuRe**. An EtOH–MeOH (1:1, v/v) solution (50 mL) containing $Ru(dmb)_2Cl_2\cdot 2H_2O$ (60 mg, 0.11 mmol) and bpy-CH_2-CH_2-bpy (110 mg, 0.32 mmol) was refluxed for 12 h. After removal of the solvent by evaporation, water was added to the residue and the remaining bpy-CH_2-CH_2-bpy was removed by filtration. An NH_4PF_6 saturated aqueous solution was added to the filtrate, and the precipitate was subsequently filtered to give $[Ru(dmb)_2(bpy\text{-}CH_2\text{-}CH_2\text{-}bpy)](PF_6)_2$. To the precipitate, an EtOH–acetone (4:1, v/v) mixed solution (50 mL) containing $Re(CO)_3Cl$ (44 mg, 0.12 mmol) was added; the resulting mixture was then refluxed for 14 h. After removal of the solvent by evaporation, the residue was separated by column chromatography on SP Sephadex C-25 using a 1:1 mixed solution of MeCN–H_2O (1:1, v/v) containing NH_4PF_6 as an eluent and $[Ru(dmb)_2(bpy\text{-}CH_2\text{-}CH_2\text{-}bpy)Re(CO)_3Cl](PF_6)_2$ was successfully isolated. To the PF_6 salts, 40 mL of EtOH–H_2O (1:1, v/v) was added; the solution was then treated with an Amberlite IRA-900J ion-exchange resin in the Cl form. Yield: 75 mg (0.059 mmol, 53%) Anal. Calcd for $C_{49}H_{52}Cl_3N_8O_8ReRu$: C, 46.17; H, 4.11; N, 8.79. Found: C, 46.17; H, 4.11; N, 8.80. FT-IR (MeCN) ν_{CO} / cm^{-1}: 2022, 1917, 1898. ESI–MS (eluent: MeOH) m/z: 557 ($[M - 2Cl^-]^{2+}$).

Photocatalytic Reaction

Photocatalytic reaction solutions were prepared in 11-mL test tubes (*i.d.* = 8 mm) by mixing the following (A) and (B) solutions: (A) a 2 mL aqueous solution containing the metal complex (0.05 mM), $BI(CO_2H)H$ (20 mM), and NaOH (0.1 M), which was bubbled with Ar for 30 min; (B) a 2-mL aqueous solution containing metal complexes (0.05 mM) and NaOH (0.1 M), which was bubbled with CO_2 for 30 min. The head space of the test tube was purged with CO_2. The solutions were irradiated using a merry-go-round irradiation apparatus at $\lambda > 500$ nm with a high-pressure Hg lump combined with a K_2CrO_4 (30% w, $d = 1$ cm) solution filter. Quantum yields of CO formation were determined by the following method. A solution prepared by the same procedures except for the concentration of the complex (0.3 mM) was placed in a quartz cubic cell (path length: 1 cm) and irradiated using an Asahi Spectra Co. Max-303 Xe lamp (300 W) combined with a 480-nm (FWHM = 10 nm) band-pass filter (Asahi Spectra Co., light intensity = 4.4×10^{-9} einstein/s). Absorbed photons were counted by a Shimadzu QYM-01 apparatus, and 99% of the irradiated photons were absorbed by the reaction solution. The temperatures of the solutions were controlled at 298 ± 2 K using an IWAKI CTS-134A constant-temperature system during irradiation. The gaseous reaction products, i.e., CO and H_2, were analyzed by a GC-TCD (GL Science GC 323). $HCOO^-$ in the liquid phase was analyzed by following procedure: Ethyl acetate (2 mL) and HCl (1 mL, 36%) were added to 2 mL of the sample solution, followed by extraction; the ethyl acetate phase was then analyzed using a GC-BID (Shimadzu Tracera).

$^{13}CO_2$ Labeling Experiment

The $^{13}CO_2$ labeling experiments were performed using 1 mL of an aqueous solution containing **RuRe** (0.05 mM) and $BI(CO_2H)H$ (10 mM) in an 8 mL test tube (*i.d.* = 1 cm). The test tube was degassed using the freeze–pump–thaw method, and then $^{13}CO_2$ (99%, 609 mmHg) was introduced into it. GC–MS analyses were conducted using a Shimadzu GCMS-QP2010 Ultra combined with an MS-5A column for the gaseous phase and a TC-WAX column for the liquid phase.

Measurement of UV–vis Absorption Spectra of Ru During Irradiation

A solution prepared by the same method for the photocatalytic reaction of **Ru** in a quartz cubic cell (path length: 1 cm) was irradiated using an Asahi Spectra Co. Max-303 Xe lamp (300 W) combined with a 480 nm (FWHM = 10 nm) band-pass filter purchased from Asahi Spectra Co. (the light intensity was 4.6×10^{-8} einstein/s). During irradiation, absorption spectra were measured using a Shimadzu QYM-01 apparatus. The temperatures of the solutions were controlled at 298 ± 2 K using an IWAKI CTS-134A constant-temperature system during irradiation.

Reference

(1) Brunet, P.; Wuest, J. D. *Can. J. Chem.* 1996, **74**, 689.

(2) Lepretre, J.-C.; Bar, B.; Chauvin, J.; Deronzier, A.; Lefebvre, B. *Inorg. Chem. Commun.* 2004, **7**, 47.

(3) Nakada, A.; Koike, K.; Nakashima, T.; Morimoto, T.; Ishitani, O. *Inorg. Chem.* 2015, **54**, 1800.

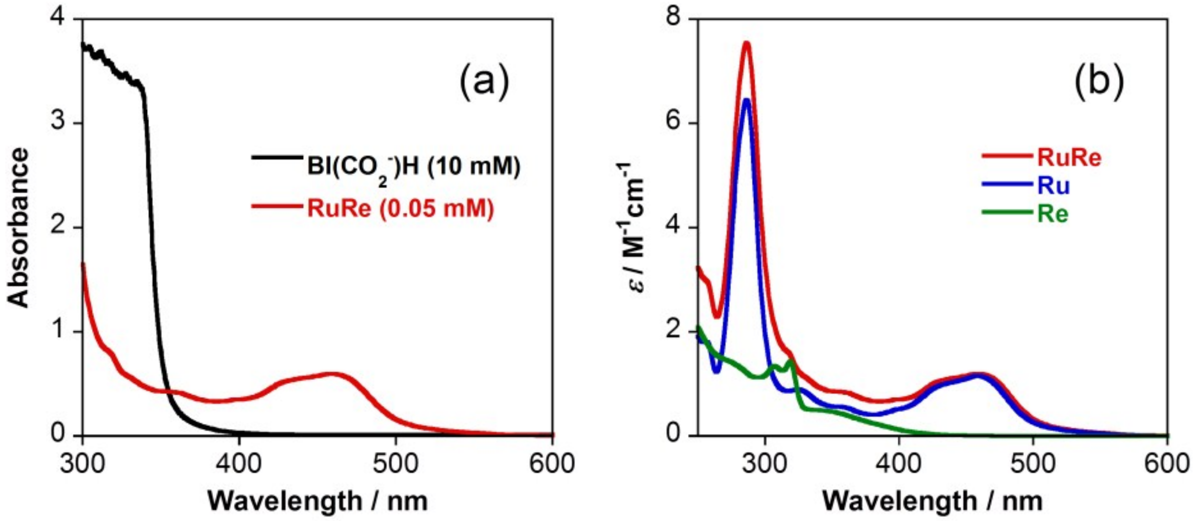

Fig. S1 (a) UV–vis absorption spectra of (a) BI(CO_2^-)H (10 mM, black) and **RuRe** (0.05 mM, red) in a NaOH (0.1 M) aqueous solution and (b) **RuRe** (red), a mononuclear model complex of the Ru(II) photosensitizer unit, $[Ru(dmb)_2(mmb)]^{2+}$ (**Ru**; dmb: 4,4'-dimethyl bipyridine; mmb: 4-methyl bipyridine, blue)**,** and a mononuclear model-complex of the Re(I) catalyst unit, Re{bpy($CH_2PO_3H_2$)$_2$}$(CO)_3$Cl (**Re**; bpy($CH_2PO_3H_2$)$_2$: 4,4'-bis(methylphosphonic acid)-2,2'-bipyridine, green) in a NaOH (0.1 M) aqueous solution.

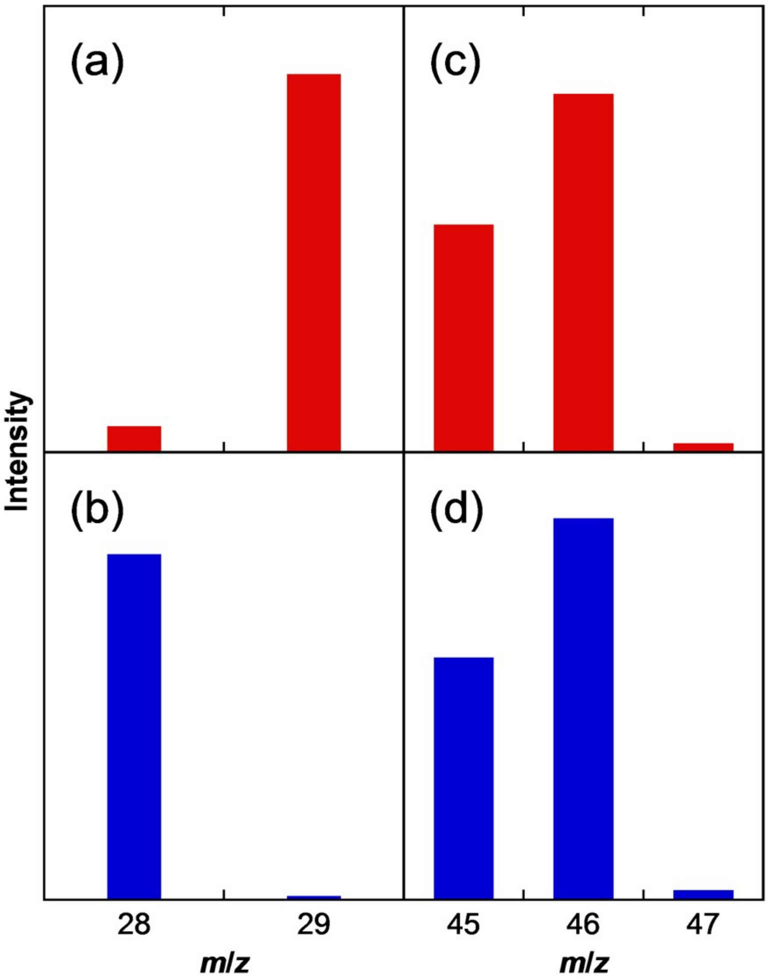

Fig. S2 (a, b) GC−mass spectra attributed to CO (a) produced under a $^{13}CO_2$ atmosphere and (b) under a $^{12}CO_2$ atmosphere after 10 h of irradiation. (c, d) GC−mass spectra attributed to the formic acid and formate produced (c) under a $^{13}CO_2$ atmosphere and (d) under a $^{12}CO_2$ atmosphere after 10 h of irradiation. NaOH (0.1 M) aqueous solutions containing **RuRe** (0.05 mM) and BI(CO_2^-)H (10 mM) were irradiated at λ > 500 nm light.

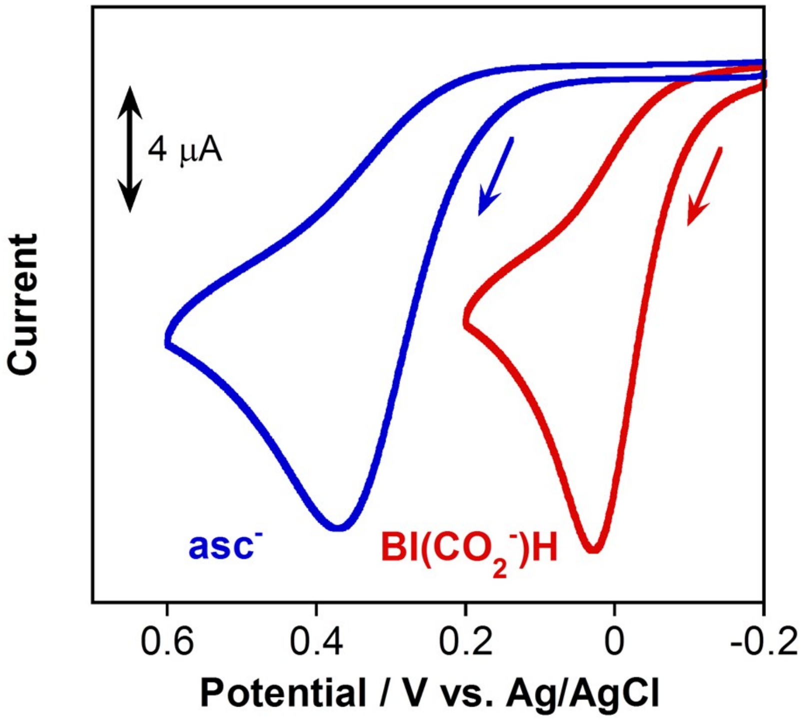

Fig. S3 Cyclic voltammograms of BI(CO_2^-)H (red) and asc$^-$ (blue) measured with an Ag/AgCl reference electrode in aqueous solutions containing Na_2SO_4 (0.1 M) as a supporting electrolyte. The scan rate was 100 mV·s^{-1}. An aqueous solution containing NaOH (0.1 M) was used for BI(CO_2^-)H.

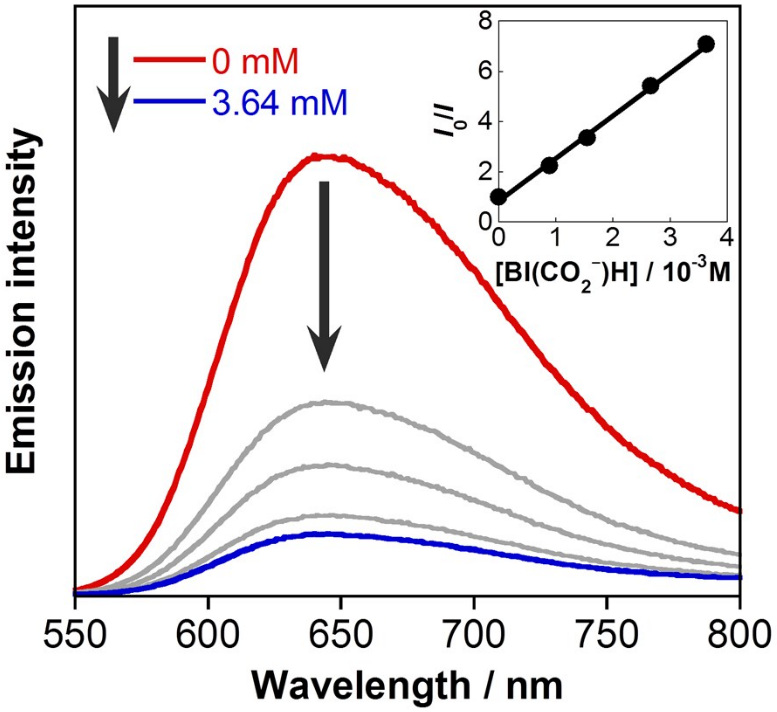

Fig. S4 Emission spectra of **RuRe** in NaOH (0.1 M) aqueous solutions containing various concentrations (0−3.64 mM) of $BI(CO_2^-)H$. The excitation wavelength was 456 nm. The inset shows the Stern−Volmer plots for the emission quenching.

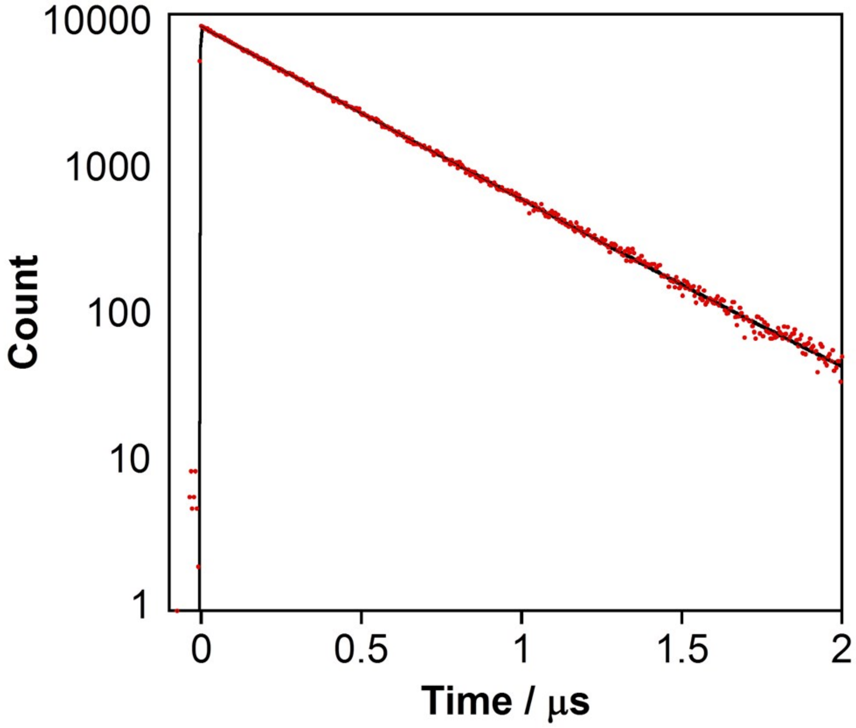

Fig. S5 Decay of emission from **RuRe** (red) excited at λ_{ex} = 456 nm and observed at λ_{em} = 630 nm in a NaOH (0.1 M) aqueous solution under an Ar atmosphere. The data was fitted with a single exponential function (black).

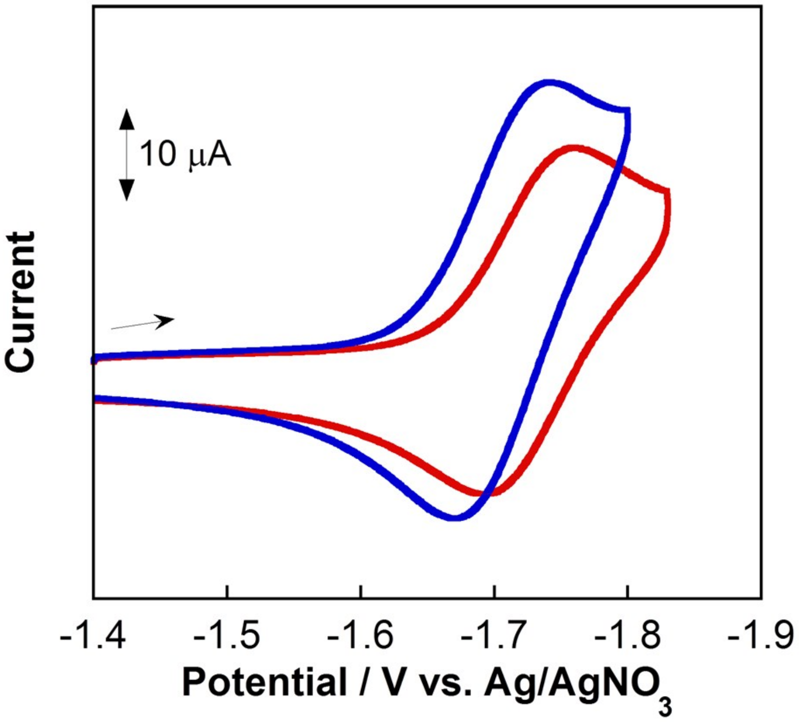

Fig. S6 Cyclic voltammograms of **Ru** (red) and Re(mmb)$(CO)_3$Cl (blue) measured with an Ag/$AgNO_3$ reference electrode in MeCN solutions containing NEt_4BF_4 (0.1 M) as a supporting electrolyte. The scan rate was 200 mV·s^{-1}.

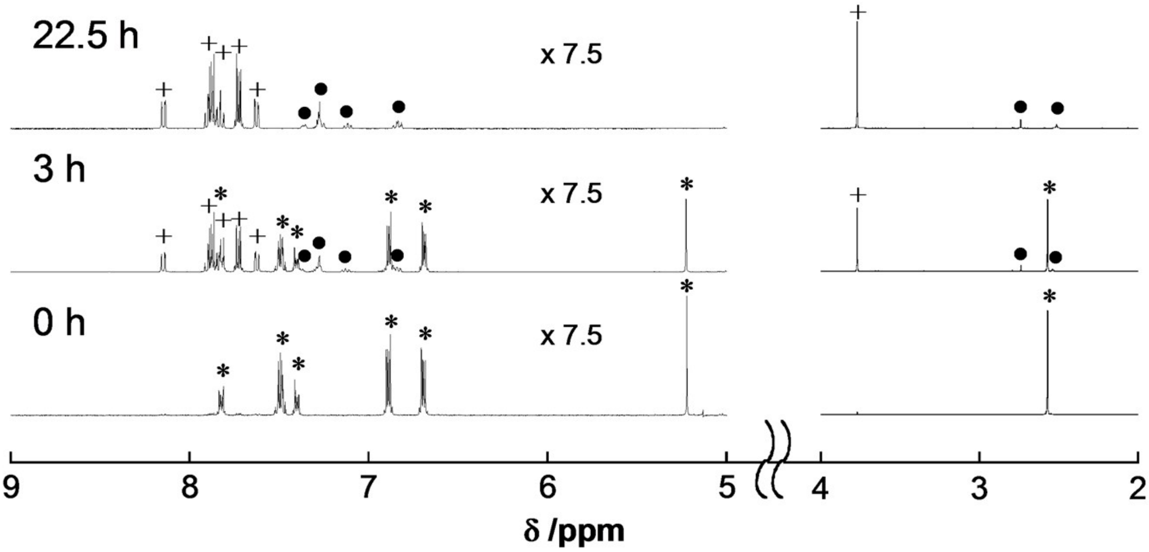

Fig. S7 ^{1}H NMR spectra of BI(CO_2^-)H (*), BI$^+$(CO_2^-) (+), and other product(s) (•) after the photocatalytic reaction: an NaOD (0.1 M)–D_2O solution containing **RuRe** (0.05 mM) and BI(CO_2H)H (10 mM) was irradiated at λ_{ex} > 500 nm under a CO_2 atmosphere (0, 3, and 22.5 h).

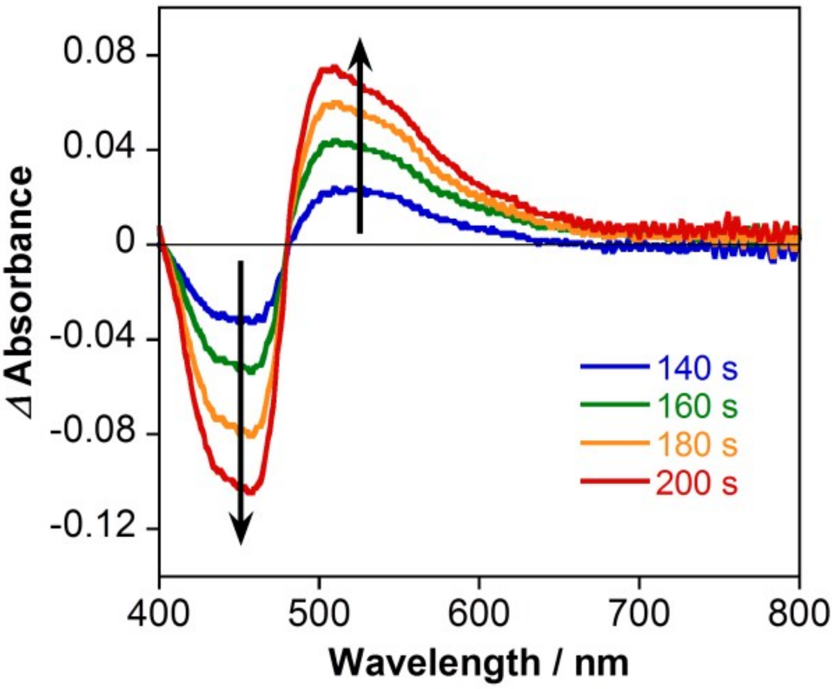

Fig. S8 Differential UV−vis absorption spectra of a NaOH (0.1 M) aqueous solution containing **Ru** (0.05 mM) and BI(CO_2^-)H (10 mM) during irradiation (140−200 s) at λ_{ex} = 480 nm (4.6×10^{-8} einstein s^{-1}).