

Supporting Information for

Photocatalytic Reduction of Low Concentration of CO₂

Takuya Nakajima,[†] Yusuke Tamaki,[†] Kazuki Ueno,[†] Eishiro Kato,[†] Tetsuya Nishikawa,[†] Kei Ohkubo,[†] Yasuomi Yamazaki,[†] Tatsuki Morimoto,^{‡§*} and Osamu Ishitani^{†*}

[†] 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.

[‡] Department of Applied Chemistry, School of Engineering, Tokyo University of Technology, 1404-1, Katakura, Hachioji, Tokyo, 192-0982, Japan.

[§] PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan.

* To whom correspondence should be addressed.

E-mail: morimotottk@teu.ac.jp, ishitani@chem.titech.ac.jp

Table of Contents

1. Materials, Methods, and Synthetic procedures
2. Supporting Figures (S1-S8)
3. Supporting References (S1-S4)

1. Materials, Methods, and Synthetic Procedures

General procedures

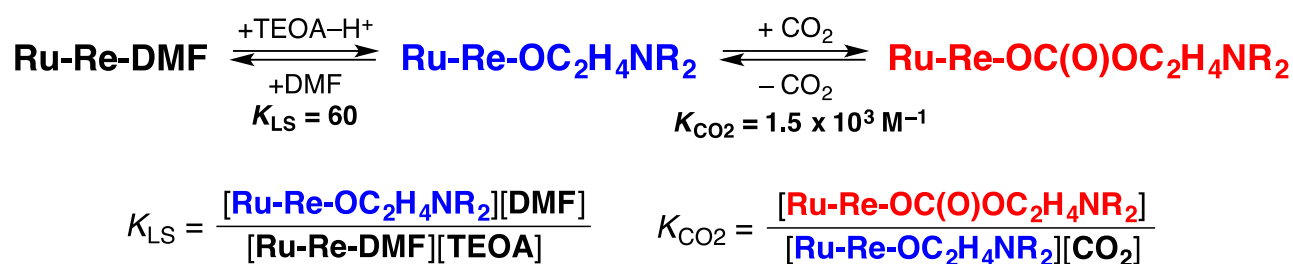
IR spectra were obtained using a JASCO FT/IR-6100 spectrometer at 1 cm^{-1} resolution. UV–Vis absorption spectra were acquired using a JASCO V-670 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained using a JEOL AL300 or a JEOL ECA400II spectrometer. CO_2 gas diluted with Ar (0.5%, 1%, 5%, 10%, and 50% CO_2 gas) was prepared from pure CO_2 (purity 99.995%) or 1% CO_2 -Ar and pure Ar using a mass flow meter.

Materials

N,N-Dimethylformamide (DMF) was dried over 4 Å molecular sieves and distilled under reduced pressure. TEOA was distilled under reduced pressure. These compounds were stored under an Ar atmosphere before use. 1,3-Dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]imidazole (BIH)^{S1} and **Ru-Re-DMF**^{S2} were prepared according to the literature. Commercially available reagents (reagent grade) were used without further purification.

Estimation of the equilibrium constants

Various amounts of a CO_2 -saturated DMF solution (the concentration of CO_2 is 0.20 M)^{S3} was added to sealed sample tubes, which were then filled with DMF–TEOA (5:1 v/v) solutions containing **Ru-Re-DMF** and **Ru-Re-OC₂H₄NR₂** (total concentrations were 3.7 mM) using a shielded syringe. The concentrations of **Ru-Re-DMF**, **Ru-Re-OC₂H₄NR₂**, and **Ru-Re-OC(O)OC₂H₄NR₂** were evaluated from the peak areas corresponding to each of the complexes in the IR spectra.^{S4} The peaks could be separated by curve fitting using a linear combination of the Gaussian function and the Lorentzian function (Figure S1). Herein, the equilibrium constants, K_{LS} and K_{CO_2} , were defined as follows:



Photocatalytic reactions

Photocatalytic systems for reducing low concentrations of CO_2

Photocatalytic reactions were conducted with a solution of **Ru-Re-DMF** and **Ru-Re-OC₂H₄NR₂** (total concentration: 0.05 mM) in DMF–TEOA (5:1 v/v, total 20 mL) containing BIH (0.1 M). Ar-based gas containing various concentrations of CO_2 was bubbled into a gas-flow cell, as shown in Figure S2. After bubbling the reaction mixture with gas for 30 min, the solution was irradiated at $\lambda_{\text{ex}} = 480\text{ nm}$ using a 300 W Xeon lamp (Asahi Spectra MAX-302). During irradiation, the gas flow (10 mL min^{-1}) was continued. The evolved CO and H_2 contained in the outlet gas were analyzed by an INFICON 3000 Micro-GC equipped with a TCD detector. The turnover numbers (TON_{CO} and TON_{H_2}) are defined as the [amount of evolved CO or H_2]/[amount of the photocatalyst]. The

reproducibility of the photocatalytic CO formation was confirmed in the case under 1% CO₂ for 5-h irradiation, and the experimental error was within 3% between two same experiments.

Measurement of quantum yield

The quantum yield for CO formation in the photocatalytic reduction of CO₂ under a pure CO₂ atmosphere was determined as follows: DMF–TEOA (5:1 v/v, 4 mL) solutions of **Ru-Re-DMF** and **Ru-Re-OC₂H₄NR₂** (total concentration: 0.05 mM) containing BIH (0.1 M) were bubbled with pure CO₂ gas in 11 mL necked quartz cubic cells (path length: 1 cm). The solutions were irradiated at $\lambda_{\text{ex}} = 480$ nm (light intensity: 5.0×10^{-9} einstein s⁻¹) using a 300 W Xeon lamp (Asahi Spectra MAX-302) with a band-pass filter for $T = 30, 60,$ and 90 min in a Shimadzu QYM-01 Photoreaction Quantum Yield Evaluation System. The evolved CO was analyzed by GC-TCD (GL science GC323), and the photon number absorbed by the reaction solution was obtained from the light intensity ($I(t)$) and absorbance at 480 nm ($A(t)$) by the equation below, which were continuously measured during the photocatalytic reaction. The (internal) quantum yield for CO formation could be estimated at 50% from the mean value of [amount of evolved CO molecules]/[amount of absorbed photons] (Figure S6).

$$\text{amount of absorbed photon} = \int_0^T I(t) \times (1 - 10^{-A(t)}) dt$$

Photochemical reduction of [Ru(dmb)₃]²⁺ by BIH in the presence of a proton source

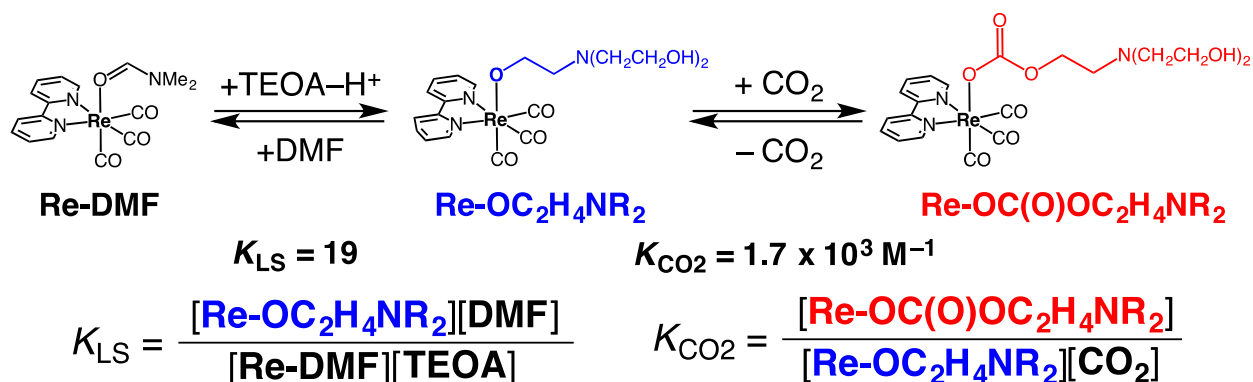
A 4 mL DMF solution containing [Ru(dmb)₃](PF₆)₂ (0.05 mM), BIH (0.1 M), and tri(*n*-propyl)ammonium hexafluorophosphate (25 mM) in a 11 mL necked quartz cubic cell (path length: 1 cm) was irradiated at 480 nm (light intensity: 5.0×10^{-8} einstein/s) under an Ar atmosphere. UV–Vis spectra were obtained using a Shimadzu QYM-01 Photoreaction Quantum Yield Evaluation System during the photoreaction to monitor formation of the one-electron-reduced species (Figure S7).

Estimation of CO₂ concentrations in a CO₂-saturated DMF-TEOA (5:1 v/v) solution and in a DMF-TEOA (5:1 v/v) solution bubbled with diluted CO₂ gas

A DMF-TEOA (5:1 v/v) mixed solution was bubbled with pure CO₂ for 20 min. This CO₂-saturated solution (1 mL) was added to a Ba(OH)₂ aqueous solution (0.025 M, 25 mL) giving precipitation of BaCO₃. The resulting solution was back-titrated with a standardized 0.100 M HCl solution, and pH was monitored by a pH meter during the titration. In order to exclude the influence of TEOA, a mixed DMF-TEOA (5:1 v/v) solution without CO₂ bubbling was also titrated. The concentration of CO₂ in the saturated DMF-TEOA (5:1 v/v) solution was determined as 0.14 M.

The equilibrated concentration of CO₂ in the mixed DMF-TEOA solution during bubbling with diluted CO₂ gas was evaluated by using a Re(I) tricarbonyl complex with a labile monodentate ligand, which can be a good indicator to monitor CO₂ concentration in a DMF solution containing TEOA.^{S4} Concentrations of CO₂ in DMF-TEOA (5:1 v/v) solutions bubbled with dilute CO₂ were obtained by using the equilibrium constants (K_{LS} and K_{CO_2}) as shown below and concentrations of three Re(I) complexes, i.e., the Re(I) complexes coordinated by deprotonated TEOA or DMF and the aminoethylcarbonato Re(I) complex. The concentrations of the complexes could be estimated

from the peak area of each Re(I) complex in the IR spectrum of the solution after bubbling with the dilute CO₂. The IR spectra of the solutions bubbled with 1%, 10%, and 100% CO₂ gas for 20 min are shown in Figure S8a-c. Based on these data, the CO₂ concentrations for the three conditions were obtained as 0.0022 M, 0.016 M, and 0.13 M, respectively. The CO₂ concentrations in the solution showed a good linearity with the partial pressure of CO₂ over the wide range of CO₂ pressure (Figure S8d).



2. Supporting Figures

Figure S1. IR spectra (black solid line) of the equilibrated mixture of **Ru-Re-DMF**, **Ru-Re-OC₂H₄NR₂**, and **Ru-Re-OC(O)OC₂H₄NR₂** (total concentration was 3.7 mM) in DMF–TEOA (5:1 v/v) with the fitting curves (green solid lines) and the corresponding components, where black, blue, and red dotted lines denote the curves of **Ru-Re-DMF**, **Ru-Re-OC₂H₄NR₂**, and **Ru-Re-OC(O)OC₂H₄NR₂**, respectively. Initial CO₂ concentrations in the solution were set at (a) 0 mM and (b) 1.1 mM.

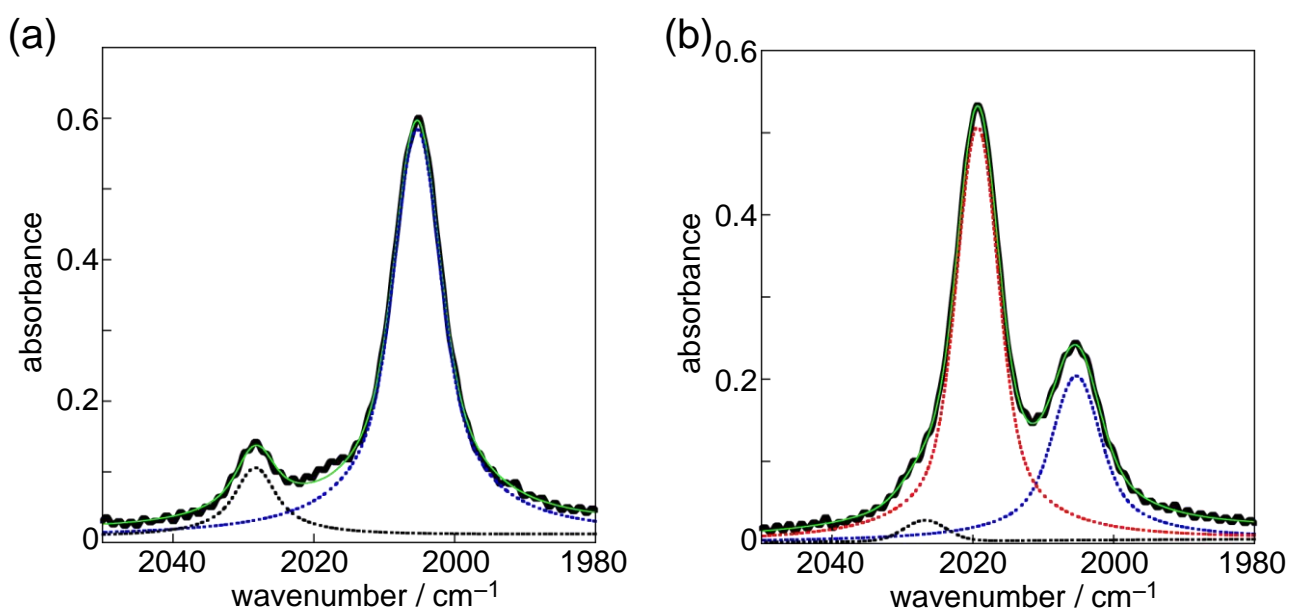


Figure S2. ^{13}C NMR spectra of **Ru-Re-OC(O)OC₂H₄NR₂** with (black line) and without (red line) ^1H decoupling under a $^{13}\text{CO}_2$ atmosphere. The three bond carbon-proton coupling with $^3J_{\text{CH}} = 3.3$ Hz confirmed the formation of **Ru-Re-OC(O)OC₂H₄NR₂** in a DMF-TEOA solution under a CO_2 atmosphere.

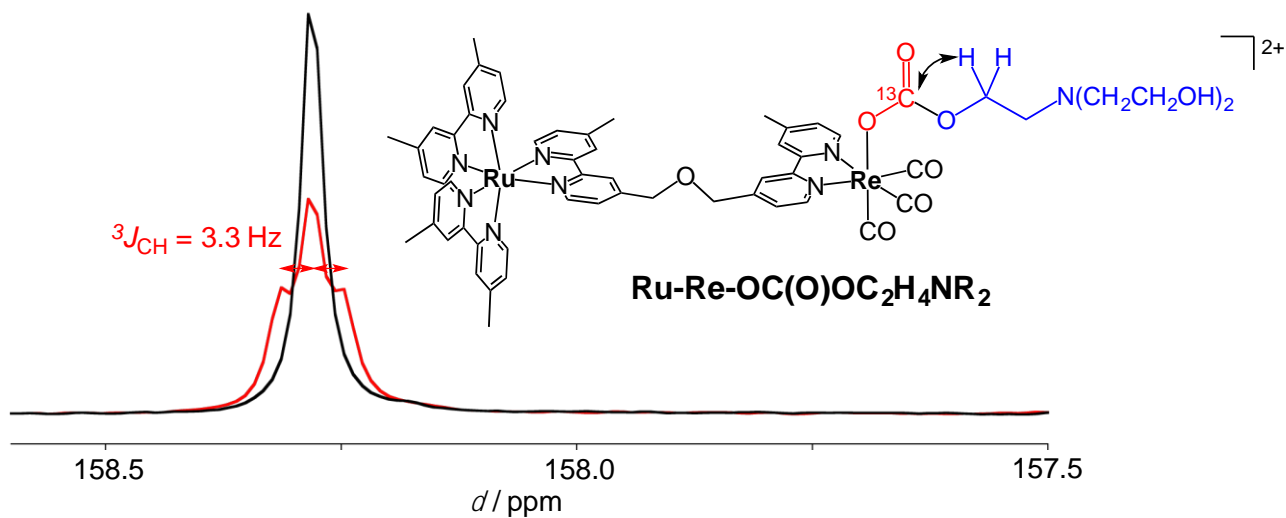


Figure S3. Gas-flow reaction system for photocatalytic reduction of CO₂.

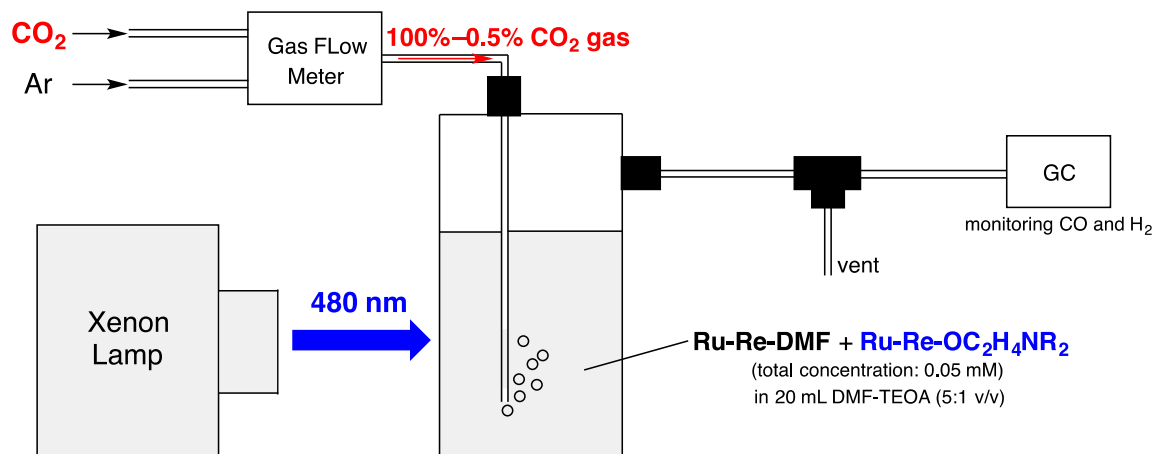


Figure S4. Turnover number (TON_{CO}) (a) and CO concentration in the outlet gas (b) for 26 h in photocatalytic reactions using **Ru-Re-DMF** and **Ru-Re-OC₂H₄NR₂** under 100% CO₂ (blue) and 10% CO₂ (green) atmosphere.

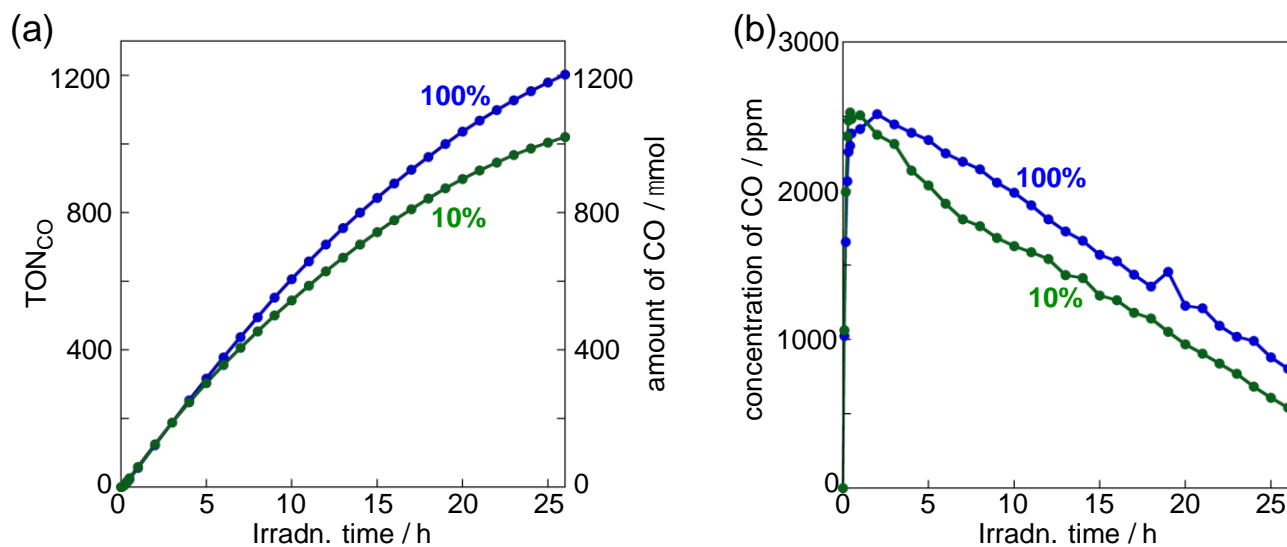


Figure S5. Turnover number (TON_{CO}) (a) and CO concentration in the outlet gas (b) for 19 h in photocatalytic reactions using **Ru-Re-DMF** and **Ru-Re-OC₂H₄NR₂** under 100% CO₂ (blue), 50% CO₂ (purple), 10% CO₂ (green), 1% CO₂ (orange), and 0.5% CO₂ (red) atmospheres.

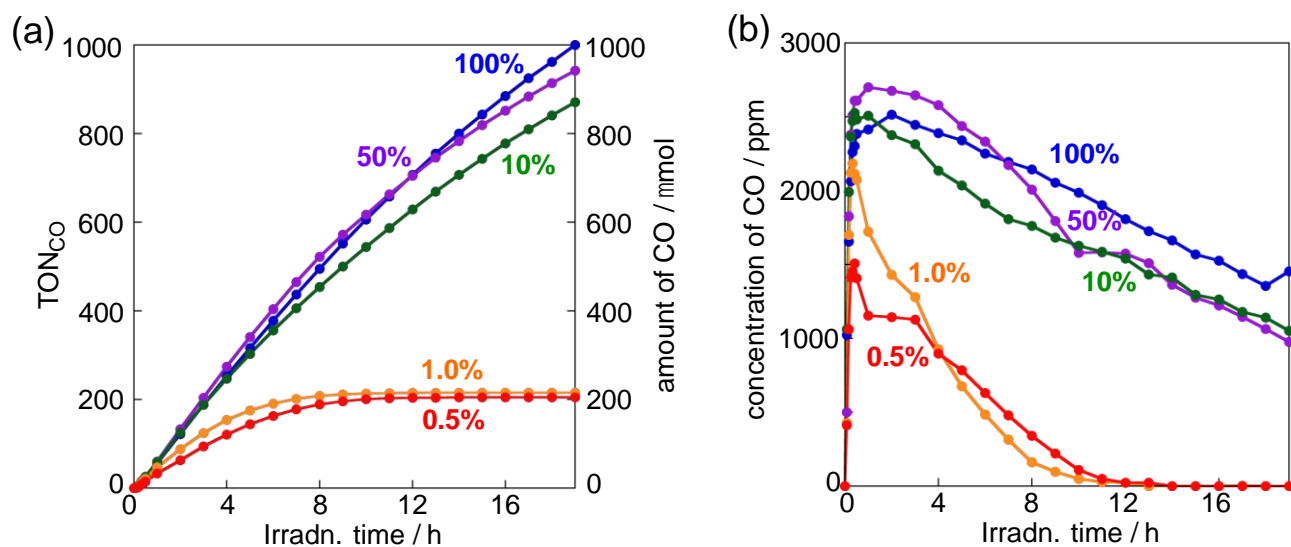


Figure S6. Measurement of the quantum yield of CO formation in the photocatalytic reduction of CO₂ using **Ru-Re-OC(O)OC₂H₄NR₂** (0.05 mM) under a 100% CO₂ atmosphere. (a) Dependence of the CO formation on amounts of absorbed photons by the reaction solution: irradiation times were 30, 60, and 90 min. (b) UV–Vis absorption spectral changes of the reaction solution during irradiation.

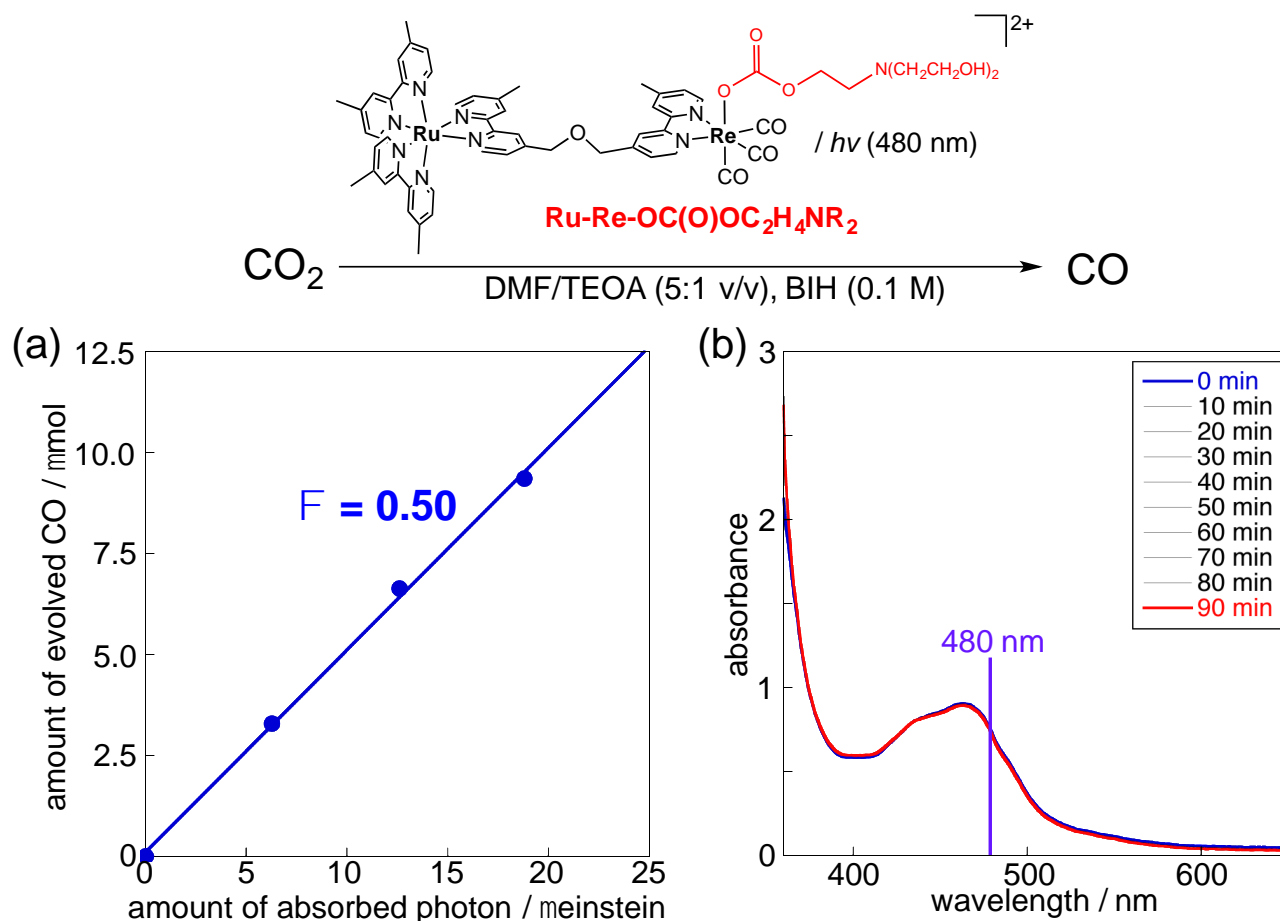


Figure S7. (a) UV–Vis absorption spectral changes of the DMF–TEOA (5:1 v/v) solution containing $[\text{Ru}(\text{dmb})_3](\text{PF}_6)_2$ (0.05 mM), BIH (0.1 M), and tri(*n*-propyl)ammonium hexafluorophosphate (25 mM) during irradiation at $\lambda_{\text{ex}} = 480$ nm (light intensity: 5.0×10^{-8} einstein/s) for 10 min and (b) differential UV–Vis absorption spectra between after and before the irradiation.

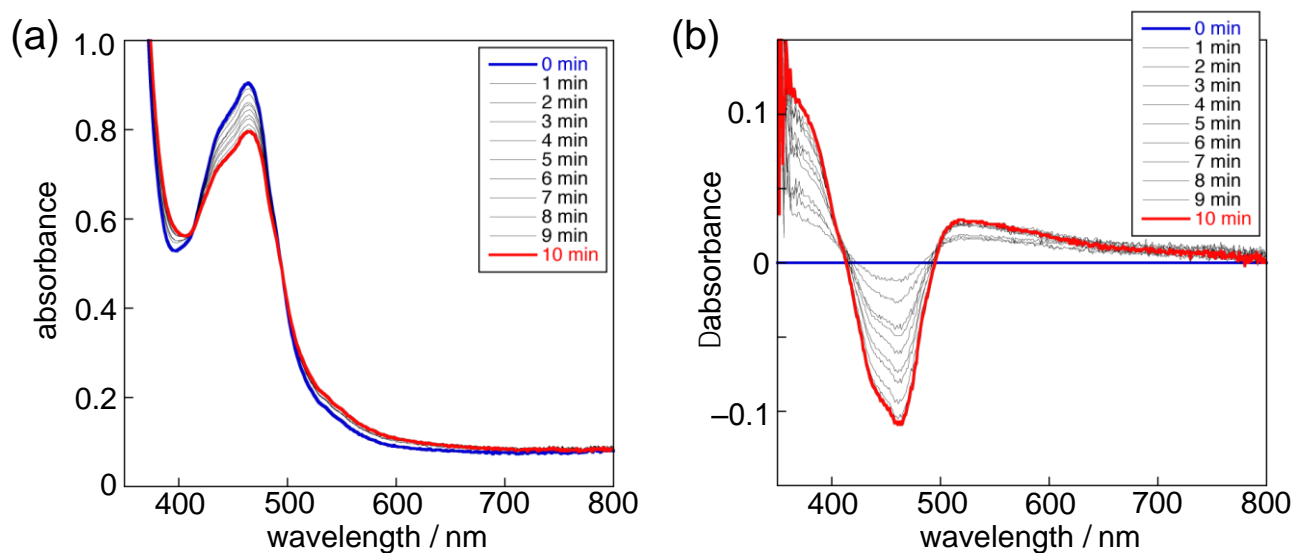
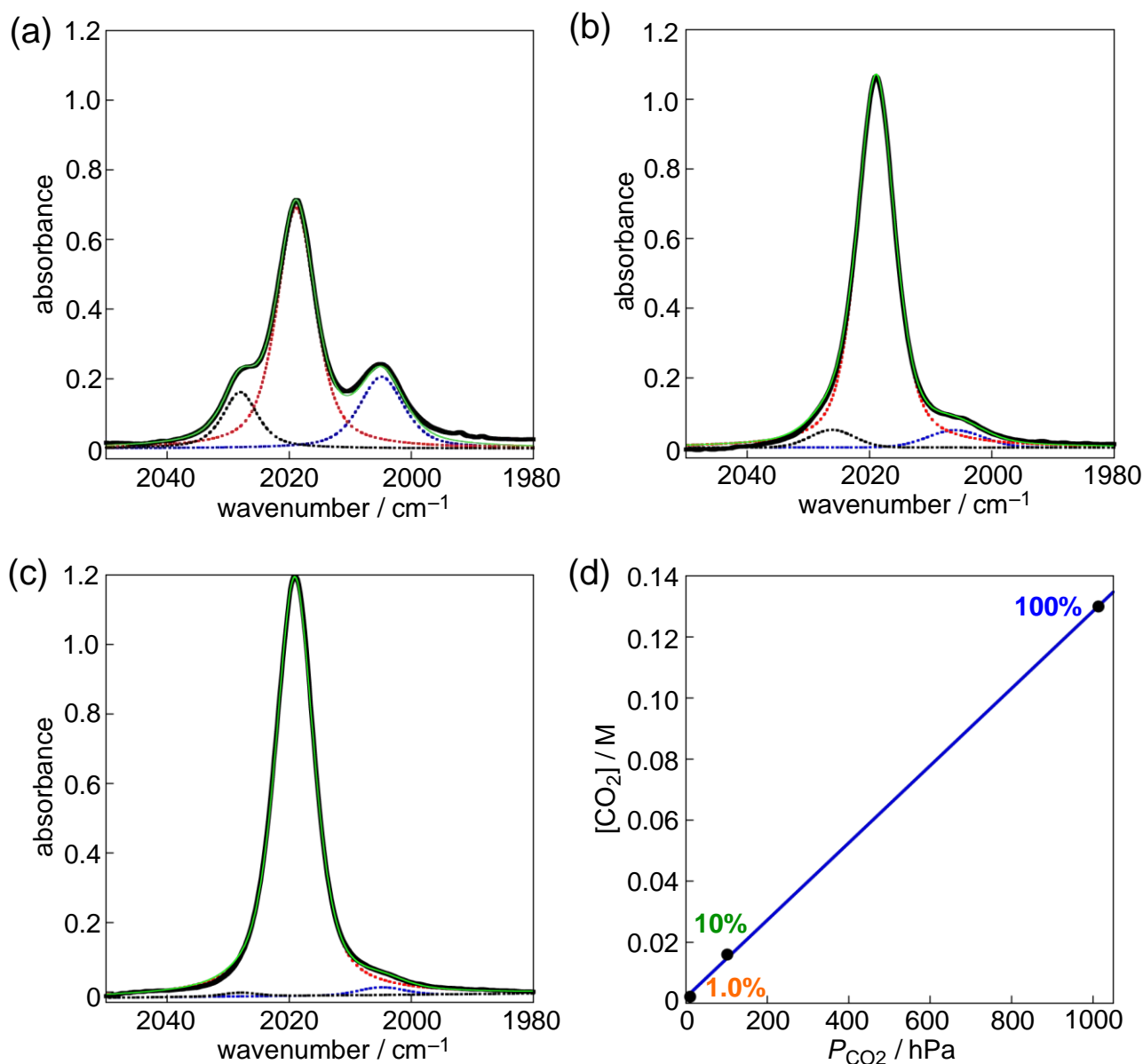


Figure S8. IR spectra (black solid lines) of the equilibrated mixture of **Re-DMF**, **Re-OC₂H₄NR₂**, and **Re-OC(O)OC₂H₄NR₂**, of which total concentration was 5.0 mM, in DMF–TEOA (5:1 v/v) by bubbling with 1% (a), 10% (b), and 100% (c) CO₂ gas. The fitting curve is shown by green solid, and the corresponding peaks attributed to **Re-DMF**, **Re-OC₂H₄NR₂**, and **Re-OC(O)OC₂H₄NR₂** were shown in black, blue, and red dotted lines, respectively. The good linearity between the CO₂ concentrations in the solution and the partial pressure of CO₂ is shown in (d).



3. Supporting References

- S1. Tamaki, Y.; Koike, K.; Morimoto, T.; Ishitani, O. *J. Catal.* **2013**, *304*, 22-28.
- S2. Kato, E.; Takeda, H.; Koike, K.; Ohkubo, K.; Ishitani, O. *Chem. Sci.* **2015**, *6*, 3003-3012.
- S3. Konno, H.; Kobayashi, A.; Sakamoto, K.; Fagalde, F.; Katz, N. E.; Saitoh, H.; Ishitani, O. *Inorg. Chim. Acta* **2000**, *299*, 155-163.
- S4. Morimoto, T.; Nakajima, T.; Sawa, S.; Nakanishi, R.; Imori, D.; Ishitani, O. *J. Am. Chem. Soc.* **2013**, *135*, 16825-16828.