

Effect of substituent groups in rhenium bipyridine complexes on photocatalytic CO₂ reduction

Yoko Ono^{1,2,*}, Jiro Nakamura¹, Masahiko Hayashi^{1,2}, Kazue Ichino Takahashi^{1,2}

¹NTT Energy and Environment Systems Laboratories, Kanagawa, Japan

²Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa, Ishikawa, Japan

Email address:

ono.yoko@lab.ntt.co.jp (Y. Ono)

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Abstract: We synthesized four different rhenium complexes, Re(bpy-R)(CO)₃Cl (bpy = 2,2'-bipyridine and R = H, CH₃, COOH, or CN), as photocatalysts that selectively reduce CO₂ to CO and investigated the effect of substituent groups (Rs) on the absorption and photocatalytic properties for CO₂ reduction under 365-nm light irradiation. The Re(bpy-R)(CO)₃Cl (R = H or CH₃ or COOH) reduced CO₂ to CO in CO₂-saturated DMF-triethanolamine solution, which was irradiated with 365-nm light. The amount of CO produced by CO₂ reduction differed, depending on the introduced Rs in the bipyridine moiety. We found that the ability of Re(bpy-R)(CO)₃Cl (R = H or CH₃ or COOH) to produce CO has a linear relationship to molar absorption coefficients of rhenium complexes at the irradiated light wavelength. Introduction of the COOH group, which has the highest molar absorption coefficient among four rhenium complexes, enhanced CO₂-to-CO reduction capacity (6.59 mol/cat-mol·2h) five times that of Re(bpy-H)(CO)₃Cl with no R.

Keywords: CO₂ Reduction, Photocatalyst, Rhenium Bipyridine Complex

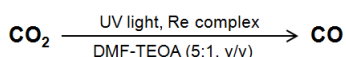
1. Introduction

Recently, much attention has been focused on photochemical CO₂ reduction using photocatalysts because it can both reduce CO₂ and produce chemicals such as CO, CH₃OH, and CH₄ as fuels [1]. The rhenium bipyridine complex Re(bpy)(CO)₃Cl (bpy = 2,2'-bipyridine) has been reported to act as a photocatalyst that photochemically reduces CO₂ to CO and/or COOH in the presence of electron donors, such as triethanolamine (TEOA), under UV light irradiation [2-18] (Scheme 1). Many researchers have focused on increasing the reaction efficiency of the photoreduction of CO₂ to CO by substituting Cl with a certain ligand. A number of studies on Re(bpy)(CO)₃L compounds (L = Br [3,12], OClO₃ [3], PPh₃ [4], {P(OEt)₃} [5], 4-Xpy(Xpy = pyridine derivatives) [6], and SCN [12]) have demonstrated that longer lifetime of the triplet state of a metal to ligand charge transfer (³MLCT) excited state enhances the rate constant for the formation of one-electron reduced intermediates, which enhances reaction efficiency. We have reported Re(bathophenanthroline)(CO)₃Cl (Re(btp)) as a CO₂ reduction photocatalyst with six times higher efficiency than that of Re(bpy)(CO)₃Cl [20]. We also found that CO was

found to be produced by both Re(btp)(CO)₃Cl degradation and CO₂ reduction and established an analytical method to determine the net amount of CO produced by CO₂ reduction by taking Re(btp)(CO)₃Cl degradation into consideration. On the other hand, as for substituent groups (Rs) introduced to bipyridine moiety, such as CH₃, OCH₃, CF₃, CH₃, C₆F₁₃(CH₂)₃, and C₈F₁₇(CH₂)₃, have been reported [6,8,9,10,15,19]. The electron-withdrawing (CH₂)₃ group of C₆F₁₃(CH₂)₃ and C₈F₁₇(CH₂)₃ greatly enhanced the lifetime of the ³MLCT state, resulting to high efficiency of CO production. Thus, Rs are one of factors that affect CO₂ reduction properties. However, a correlation between Rs and CO production is still worth investigating to enhance CO₂ reduction efficiency.

The object of the present study was mainly to clarify the effect of the R of bipyridine moieties on CO production. We synthesized four kinds of Re(bpy)(CO)₃Cl (Re(bpy-R); R = H, CH₃, COOH, or CN) as photocatalysts (Fig. 1). The CH₃ was selected as an electron-donating group, and COOH or CN was selected as an electron-withdrawing group, with the expectation that the R affects the electronic state of the bipyridine moiety and that each Re(bpy-R) exhibits different photocatalytic performance. We revealed the correlation between the ultraviolet-visible spectroscopy (UV-Vis) absorption properties and CO₂ reduction properties of those

compounds. The CO production efficiency was greatly enhanced by the novel Re(bpy-COOH).



Scheme 1. Photocatalytic CO₂ reduction to CO by Re complex.

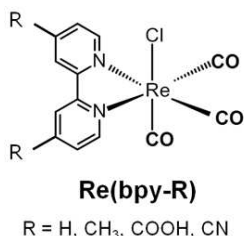


Figure 1. Chemical structure of Re(bpy-R) complexes.

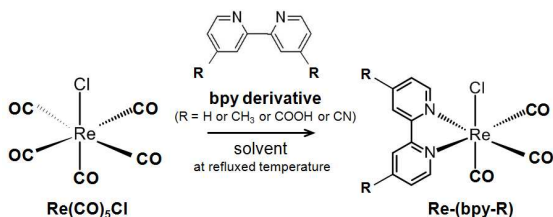
2. Experimental

2.1. Instrumentations

The UV-Vis absorption spectral measurements were performed with a Shimadzu UV-2200 spectrophotometer. The infrared (IR) spectra were recorded using a Perkin Elmer System 2000 FT-IR spectrometer. Elemental analysis was performed using a VARIO EL III analyzer. Proton-nuclear magnetic resonance (NMR) spectra were measured using a JEOL ECA-400 system. The atmospheric pressure chemical ionization (APCI) mass spectra and electrospray ionization (ESI) mass spectra were measured using a Waters LCT Premier XE instrument in the negative-ion mode. The CO amount produced by CO₂ photoreduction was analyzed using a Shimadzu GCMS-QP2010 Plus instrument equipped with an Rt-Molsieve 5A column ($L = 30$ m, $\phi = 0.32$ mm, $d = 30$ μ m).

2.2. Materials

All solvents were of high purity and used as received from Kanto Chemical Co. Rhenium pentacarbonyl chloride (Re(CO)₅Cl) and 2,2'-bipyridine (bpy) were purchased from Aldrich Chemical Co. and Kanto Chemical Co and the bpy derivatives were purchased from Tokyo Chemical Industry Co.. All reagents were used without further purification. The Re(bpy-R) was synthesized using Re(CO)₅Cl and bpy or bpy derivatives as precursors, according to a previous work [13]. The general synthetic procedure is shown in Scheme 2. The detail procedure is described in the following paragraph.



2.2.1. Synthesis of Re(bpy-H)

A solution of 2,2'-bipyridine (117 mg, 0.75 mmol) in 20 mL of toluene was added to a solution of Re(CO)₅Cl (271 mg, 0.75 mmol) in 130 mL of toluene at 110 °C. The mixture was kept at 110 °C and stirred vigorously for 3 h until the solution became a brown-orange color. The solvent was then evaporated in vacuum, and the starting materials were removed by column chromatography ($H = 300$ mm, $\phi = 25$ mm) on silica using ethyl acetate as an eluent. Then, the brown-orange compound was obtained using methanol as an eluent. After that, the solvent was removed, and the solid product was recrystallized from acetone-hexane. Yield: 78.0 mg (22.5%) Anal. Calcd for C₁₃H₈ClN₂O₃Re: C, 33.8; H, 1.7; N, 6.1; O, 10.5. Found: C, 33.6; H, 1.9; N, 5.9; O, 10.6. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 9.02$ (dd, 2H, $J = 0.9$ Hz, 5.5 Hz, bpy H^6 , H^6'), 8.77 (d, 2H, $J = 8.2$ Hz, bpy H^3 , H^3'), 8.35 (dt, 2H, $J = 1.2$ Hz, 7.9 Hz, bpy H^4 , H^4'), 7.77 (ddd, 2H, $J = 1.2$ Hz, 5.5 Hz, 7.6 Hz, bpy H^5 , H^5'). FT-IR ($\nu_{\text{CO}}/\text{cm}^{-1}$): 2024, 1921, 1899 in CH₂Cl₂. UV-Vis ($\epsilon_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 290 (12167) in DMF-TEOA (5:1, v/v). APCI-MS (m/z): 462.0 (M) in MeOH.

2.2.2. Synthesis of Re(bpy-CH₃)

A solution of 4,4'-dimethyl-2,2'-dipyridyl (138 mg, 0.75 mmol) in 50 mL of toluene was added to a solution of Re(CO)₅Cl (271 mg, 0.75 mmol) in 100 mL of toluene at 110 °C. The mixture was kept at 110 °C and stirred vigorously for 4 h until the solution became a brown-orange color. The solvent was then evaporated in vacuum, and the brown-orange compound was isolated by column chromatography ($H = 300$ mm, $\phi = 25$ mm) on silica using ethyl acetate as an eluent. After the solvent had been removed, the solid product was recrystallized from acetone-hexane. Yield: 260.0 mg (70.3%) Anal. Calcd for C₁₅H₁₂ClN₂O₃Re: C, 36.8; H, 2.5; N, 5.7; O, 9.8. Found: C, 36.8; H, 2.5; N, 5.7; O, 9.8. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 8.83$ (d, 2H, $J = 5.8$ Hz, bpy H^6 , H^6'), 8.62 (s, 2H, bpy H^3 , H^3'), 7.58 (dd, 2H, $J = 0.9$ Hz, 5.8 Hz, bpy H^5 , H^5'), 2.55 (s, 6H, bpy CH₃). FT-IR ($\nu_{\text{CO}}/\text{cm}^{-1}$): 2022, 1917, 1895 in CH₂Cl₂. UV-Vis ($\epsilon_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 290 (12167) in DMF-TEOA (5:1, v/v). APCI-MS (m/z): 490.0 (M) in MeOH.

2.2.3. Synthesis of Re(bpy-COOH)

A solution of 4,4'-dicarboxy-2,2'-dipyridyl (224 mg, 1.00 mmol) in 100 mL of ethanol was added to a solution of Re(CO)₅Cl (361 mg, 1.00 mmol) in 100 mL of ethanol at 75 °C. The mixture was kept at 75 °C and stirred vigorously for 5 h until the solution became a brown-orange color. The solvent was then evaporated in vacuum. The solid product was recrystallized from acetone-hexane. Yield: 220.6 mg (40.1%) Anal. Calcd for C₁₅H₈ClN₂O₇Re: C, 33.8; H, 1.7; N, 6.1; O, 10.4. Found: C, 33.6; H, 2.8; N, 4.3; O, 10.5. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 14.4$ (s, 1H, bpy COOH), 9.21 (d, 2H, $J = 5.8$ Hz, bpy H^6 , H^6'), 9.15 (d, 2H, $J = 0.9$ Hz, bpy H^3 , H^3'), 8.31 (dd, 2H, $J = 1.5$ Hz, 5.8 Hz, bpy H^5 , H^5'). FT-IR ($\nu_{\text{CO}}/\text{cm}^{-1}$): N.D. in CH₂Cl₂. UV-Vis ($\epsilon_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 305 (14211) in DMF-TEOA (5:1, v/v). ESI-MS (m/z): 505.0 ([M-COOH]⁻), 548.9 (M) in MeOH.

2.2.4. Synthesis of Re(bpy-CN)

A solution of 4,4'-dicyano-2,2'-dipyridyl (154 mg, 0.75 mmol) in 50 mL of toluene was added to a solution of Re(CO)₅Cl (271 mg, 0.75 mmol) in 100 mL of toluene at 110 °C. The mixture was kept at 110 °C and stirred vigorously for 3 h until the solution became a brown-orange color. The solvent was then filtered and the solid product was recrystallized from acetone-hexane. Yield: 231.1 mg (60.3%). Anal. Calcd for C₁₅H₆N₄O₃ClRe: C, 35.2; H, 1.2; N, 11.0; O, 9.38. Found: C, 35.3; H, 1.31; N, 10.8; O, 10.2. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.39 (d, 2H, *J* = 0.9 Hz, bpy H³, H^{3'}), 9.29 (dd, 2H, *J* = 0.6 Hz, 5.8 Hz, bpy H⁶, H^{6'}), 8.23 (dd, 2H, *J* = 1.5 Hz, 5.8 Hz, bpy H², H^{2'}). FT-IR (ν_{CO}/cm⁻¹): 2028, 1935, 1915 in CH₂Cl₂. UV-Vis (ε_{max}/nm (ε/M⁻¹cm⁻¹): 319 (16948) in DMF-TEOA (5:1, v/v). APCI-MS (m/z): 512.0 (M⁺), 511.0 ([M-H]⁺) in CH₃CN.

2.3. Photochemical CO₂ Reduction

Photochemical CO₂ reduction was done according to a conventional method [11]. The detail of experimental set-up was described in the previous paper [20]. The photocatalytic reaction was tested in a quartz cell (vol. = 5 mL) containing 2.0 mL of Re(bpy-R) DMF-triethanolamine (TEOA) (5:1, v/v) solution (conc. = 0.05 mM) that was stirred at room temperature during light irradiation. The solution was bubbled with CO₂ for 2 min with a flow rate of 200 mL/min and sealed with a silicon-teflon septum. As a light source, a mercury lamp (λ = 365 nm, I = 614 μW/cm²) was used for the photocatalytic reaction of CO₂. The reaction products were analyzed using gas chromatography–mass spectrometry at an arbitrary time. Moreover, during irradiation, the amount of residual Re complexes was determined by measuring the absorption maximum at the π-π* transition peak for each Re(bpy-R) [20].

3. Results and Discussion

3.1. Absorption Properties

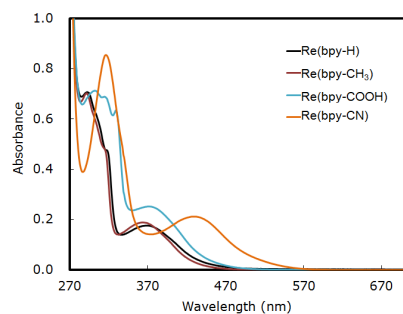


Figure 2. Steady-state absorption spectra of Re(bpy-R) complexes in DMF-TEOA (5:1, v/v) solution (conc. = 0.05 mM).

Figure 2 shows the steady-state UV-Vis absorption spectra of Re(bpy-R) complexes in DMF-TEOA solution. The spectral shapes were similar to each other and had characteristics in common with Re complexes that contain bpy derivatives as a ligand [14]. Absorption bands at around 300 to 350 nm were

assigned to the π-π* transition of the bpy moiety and those around 350 to 400 nm were assigned to the MLCT transition. The wavelength of the absorption maximum and each molar adsorption coefficient (ε) differed depending on the kinds of R. The ε of the π-π* absorption maximum for Re(bpy-COOH) was almost the same as that for Re(bpy-H) and Re(bpy-CH₃). For Re(bpy-CN), ε of both π-π* and MLCT absorption maxima were increased by about 1.2 times those for the other Re complexes, and the wavelength of the absorption maximum of the MLCT transition exhibited a long-wavelength shift of 60 nm. This wavelength shift was due to a decrease in the lowest unoccupied molecular orbital (LUMO) energy by the electron-withdrawing effect of the CN group. These results indicated that introducing electron-withdrawing groups into bpy moiety affected the electron-transition probability and highest occupied molecular orbital (HOMO)-LUMO energy levels.

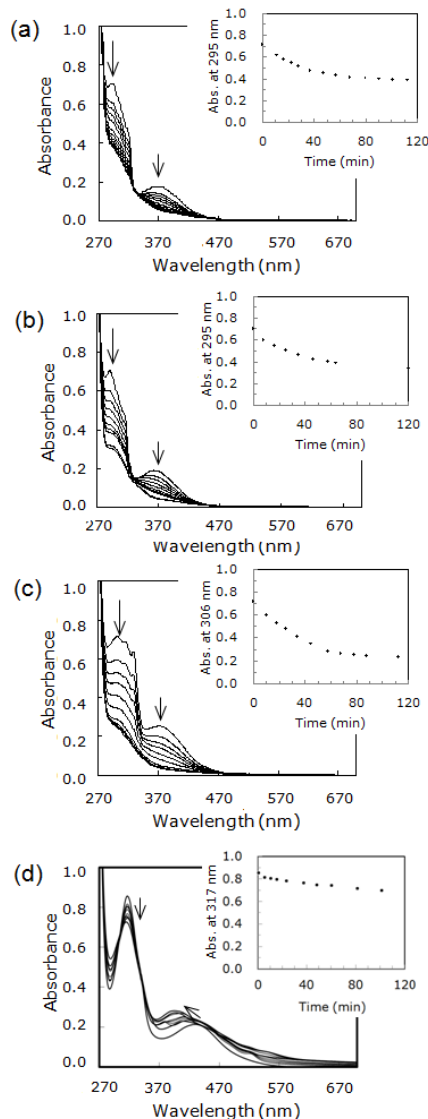


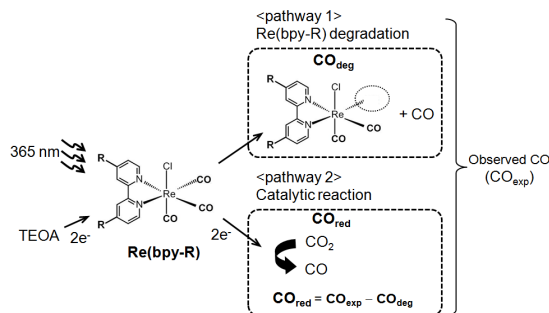
Figure 3. Ex-situ UV-Vis absorption spectral changes for (a) Re(bpy-H), (b) Re(bpy-CH₃), (c) Re(bpy-COOH), and (d) Re(bpy-CN) in DMF-TEOA (5:1, v/v) solution during 365-nm light irradiation for 2 h. Inset is absorbance at wavelength of π-π* absorption maximum vs. irradiation time plots.

Figure 3 shows ex-situ UV-Vis absorption spectral changes for Re(bpy-R) in DMF-TEOA (5:1, v/v) solution during 365-nm light irradiation for 2 h. For R = H (Fig. 3 (a)), CH₃ (Fig. 3 (b)), and COOH (Fig. 3 (c)), the absorbance intensity of both π - π^* and MLCT decreased by irradiation with 365-nm-light for 2 h. After removal of the light source, each Re(bpy-R) solution retained its absorption intensity for more than 24 h. This result suggested that light irradiation induced irreversible degradation of Re(bpy-R). On the other hand, for R = CN (Fig. 3 (d)), while the absorption intensity slightly changed, significant intensity decrease was not observed. The inset in Fig. 3 shows absorbance change at the wavelength of the π - π^* absorption maximum. This absorbance decrease was due to degradation of Re(bpy-R) by light irradiation. Therefore, the degradation rate constant (k_d) was determined for each Re(bpy-R) (R = H, CH₃, COOH) by applying the method proposed in our previous work [20]. Table 1 summarizes the k_d values for Re(bpy-R) together with the C1s group shift (ΔE_{gr}) of each R [21]. The C1s group shift is the energy shift affected by an R bounded to carbon. Each Re(bpy-R) shows a different k_d value depending on the R. It was also found that the higher the C1s group shift (ΔE_{gr}), the larger the k_d value. The results indicate that the electronic state of the R may affect the k_d of Re(bpy-R) under 365-nm light irradiation. It was indicated that the Rs of the low C1s group shift (ΔE_{gr}) may be potential candidates to prevent degradation of Re(bpy-R).

Table 1. Degradation rate constants for Re(bpy-R) under 365-nm light irradiation.

Re(bpy-R)	k_d (s ⁻¹)	ΔE_{gr} (eV) [21]
R = H	5.35×10^{-4}	0.01
R = CH ₃	3.41×10^{-4}	-0.32
R = COOH	3.87×10^{-4}	-0.15

3.1. Photocatalytic Properties



The CO was produced when Re(bpy-R) (R = H or CH₃ or COOH) in the CO₂-saturated DMF-TEOA solution was irradiated with 365-nm light. The CO formation increased depending on the irradiation time then reached the saturation point at about 120 min. When using Re(bpy-CN), on the other hand, CO formation was not observed. Since the observed CO might include not only CO from CO₂ reduction (pathway 2 in Scheme 3) but also CO from the degradation of Re(bpy-R) (pathway 1 in Scheme 3), we took the

degradation process of Re(bpy-R) into consideration. Therefore, the net amount of CO production by CO₂ reduction was determined by subtracting the CO produced by Re(bpy-R) degradation (pathway 2 in Scheme 3) from the CO observed in the reaction cell, employing a kinetic study [20].

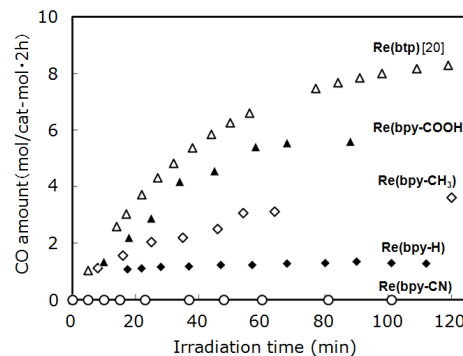


Figure 4. CO amount vs. irradiation time plots. (\blacktriangle : Re(bpy-COOH), \diamond : Re(bpy-CH₃), \blacklozenge : Re(bpy), \circ : Re(bpy-CN), Δ : Re(btp) [20]).

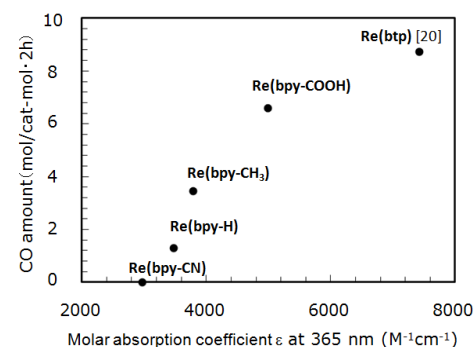


Figure 5. CO amount vs. molar absorption coefficients (ϵ) at 365-nm plots for each Re(bpy-R). Results for Re(btp) in our previous study [20] are also plotted.

Figure 4 shows the net amount of CO production by Re(bpy-R) at an arbitrary irradiation time. The results for Re(btp) [20] are plotted together. The total amount of CO production was 6.59, 3.44, 1.28, and 0 mol/cat-mol-2h for R = COOH, CH₃, H, and CN, respectively. The R, COOH or CH₃, increased CO production by about five or three times compared to R = H, respectively. To investigate the difference in CO production for each Re(bpy-R), we discuss the relationship between the absorption and photocatalytic properties. Figure 5 shows the correlation between CO amount and molar absorption coefficients at 365-nm plots for each Re(bpy-R) and Re(btp). In the range of 3000 to 5000 M⁻¹cm⁻¹, the plots indicate that the ability of Re complexes to produce CO has a linear relationship to those molar absorption coefficients. The Re complexes with a higher molar absorption coefficient exhibit higher CO production ability. This correlation is also in agreement with the results for Re(btp)(CO)₃Cl, which has ability of 8.73 mol/cat-mol-2h for CO production [20]. The high catalytic performance of Re(btp) may be due to a high molar absorption coefficient (7430 M⁻¹cm⁻¹). However, for Re(bpy-CN), which cannot

reduce CO₂ to CO, the MLCT transition band had a long-wavelength shift due to the electron-withdrawing effect of the CN group. Photocatalytic inactivity under 365-nm light irradiation is probably due to a decrease in the percentage of excited species.

For future study, there is significant value in choosing an R of a low C1s group shift and examining the irradiation-wavelength dependence on CO production for detailed understanding and enhancement of CO₂-reduction efficiency.

4. Conclusion

The substituent group R in the Re(bpy-R) significantly affects both the degradation rate constant of Re(bpy-R) and CO production ability under 365-nm light irradiation. To prevent degradation of Re(bpy-R), the Rs of the low C1s group shift (ΔE_{gr}) may be potential candidates. There is also a correlation between the ability of Re(bpy-R) to produce CO and molar absorption coefficients of each Re(bpy-R) at the irradiation wavelength. Re complexes with higher molar absorption coefficient exhibit higher CO production ability. The novel Re(bpy-COOH) produced CO at a rate of 6.59 mol/cat-mol²h, which is five times higher than that of Re(bpy-H) because of its high molar absorption coefficients at 365 nm.

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