Photocatalytic Reduction of Low Concentration of CO$_2$

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S *Supporting Information*

ABSTRACT: A novel molecular photocatalytic system with not only high reduction ability of CO$_2$ but also high capture ability of CO$_2$ has been developed using a Ru(II)−Re(I) dinuclear complex as a photocatalyst. By using this photocatalytic system, CO$_2$ of 10% concentration could be selectively converted to CO with almost same photocatalysis to that under a pure CO$_2$ atmosphere (TON$_{CO}$ > 1000, Φ_{CO} > 0.4). Even 0.5% concentration of CO$_2$ was reduced with 60% initial efficiency of CO formation by using the same system compared to that using pure CO$_2$ (TON$_{CO}$ > 200). The Re(I) catalyst unit in the photocatalyst can efficiently capture CO$_2$, which proceeds CO$_2$ insertion to the Re−O bond, and then reduce the captured CO$_2$ by using an electron supplied from the photochemically reduced Ru photosensitizer unit.

Utilization of CO$_2$ for production of energy-rich carbon compounds using solar light as an energy source has been a very attractive research field because it can solve serious global problems, i.e., energy crisis, depletion of carbon resources, and global warming.[1,2] Exhaust gases discharged from heavy industries include relatively low concentrations of CO$_2$. As a typical example, exhaust gas from fire power plants includes only 3%−13% CO$_2$ with N$_2$ as the main component;[3] however, most research on photochemical and electrochemical reduction of CO$_2$ have been conducted using pure CO$_2$ to achieve high reaction rates of the active reaction intermediates with CO$_2$.[4−12] This is problematic because condensation of CO$_2$, achieved by adsorption and desorption processes with amines and MOFs[13−16] or separation with filters,[14] is a highly energy-consuming process. If low concentrations of CO$_2$ can be directly utilized, a highly promising technology can be developed. To the best of our knowledge, there has been only one report of a visible-light driven photocatalytic reduction system for low concentrations of CO$_2$, of which catalyst was integrated into MOF as CO$_2$ adsorption active sites.[17] Although the MOF system could reduce even 5% concentration of CO$_2$ with about 1.3 times higher efficiency compared to that of the corresponding homogeneous system without MOF, its photocatalysis is not satisfactory because of low durability (TON$_{HCOOH}$ = 33.3) and low selectivity of CO$_2$ reduction (71% with H$_2$ evolution; TON$_{H_2}$ = 14.5). In natural photosynthesis, plants have acquired elaborate systems during the evolutionary process to solve the above-mentioned problem, i.e., the Hatch−Slack cycle for concentration of CO$_2$ and the Calvin cycle for CO$_2$ reductive fixation.[18] A novel photocatalytic system with a different working principle for CO$_2$ condensation is required for the development of artificial photosynthesis research.

We recently found that Re(I) complexes with deprotonated triethanolamine as a monodentate ligand can efficiently capture CO$_2$ to be converted to an aminoethylcarbonato complex, i.e., *fac*-[Re(bpy)(CO)$_3$\{OC(O)OC$_2$H$_4$N(C$_2$H$_4$OH)$_2$\}].[19,20] In addition, some *fac*-[Re(N∧N)(CO)$_3$L]-type complexes can efficiently catalyze the selective reduction of CO$_2$ to give CO.[4] If both these fascinating properties, CO$_2$ capture and reduction of CO$_2$, can be harmonized in one system, a novel photocatalytic system for reduction of low concentration CO$_2$ could be developed. Herein, we report a system with a heteronuclear bimetal complex comprising a Ru(II) redox photosensitizer and a Re(I) catalyst unit with high capability of CO$_2$ capture. We succeeded in reducing dilute CO$_2$ of which concentration was 50%−0.5% with high turnover numbers and high quantum yields.

A dinuclear complex composed of a tris-diimine Ru(II) unit as a photosensitizer and a tricarbonyl diimine Re(I) unit with a labile monodentate ligand as a catalyst, connected with a dimethylene ether (−CH$_2$OCH$_2$−) linkage (**Ru−Re−DMF** in Figure 1a), was used in this study; this complex was recently investigated as an efficient photocatalyst for CO$_2$ reduction under a pure CO$_2$ atmosphere.[20] The CO$_2$-capturing ability of the complex was examined in the presence of triethanolamine (TEOA). Addition of TEOA to a dimethylformamide (DMF) solution containing **Ru−Re−DMF** caused ligand substitution of DMF on the Re unit of **Ru−Re−DMF** with TEOA giving a Ru(II)−Re(I) complex with a deprotonated triethanolamine ligand (**Ru−Re−OC$_2$H$_4$NR$_2$**) (Process 1 in Figure 1a). An equilibrium constant (K_{LS} = 60) for ligand substitution was obtained using the FT-IR spectra, as shown in Figures 1b and S1. Introduction of CO$_2$ into a solution of **Ru−Re−DMF** and **Ru−Re−OC$_2$H$_4$NR$_2$** ([CO$_2$] = 1.1 mM) induced a drastic change in the ν_{CO} bands (2019 and 1914 cm^{-1}) in the FT-IR spectrum of the solution (Figure 1c), clearly indicating that
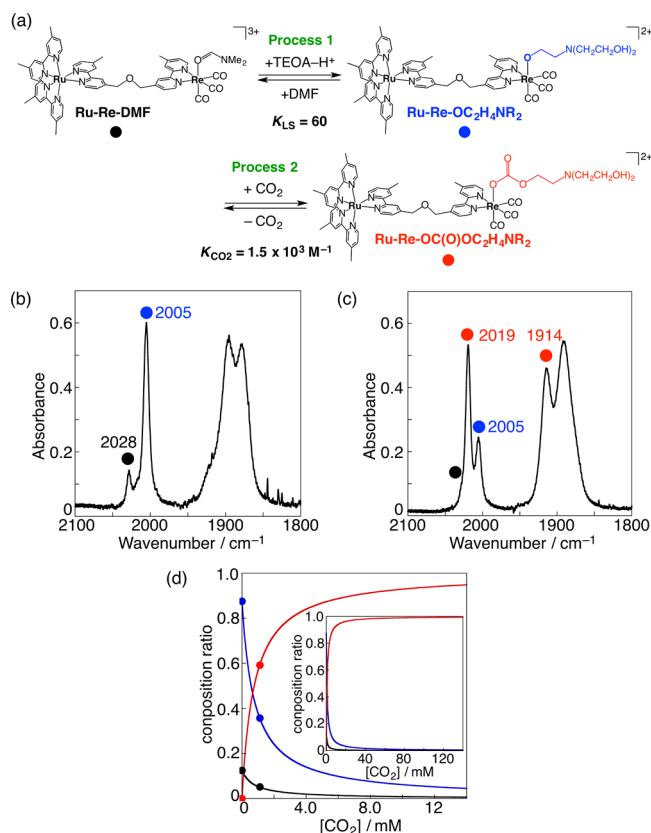
Figure 1. Ligand substitution of the dinuclear **Ru−Re−DMF** complex and the CO_2 capture behavior in a mixed solvent system of DMF and TEOA (5:1 v/v). (a) Three complexes, **Ru−Re−DMF**, **Ru−Re−OC_2H_4NR_2**, and **Ru−Re−OC(O)OC_2H_4NR_2**, observed in the mixed solvent system under a CO_2 atmosphere. (b) IR spectrum for Process 1 under an Ar atmosphere, equilibrium between **Ru−Re−DMF** and **Ru−Re−OC_2H_4NR_2**. (c) IR spectrum for Process 2 under conditions of $[CO_2]$ = 1.1 mM and equilibrium between **Ru−Re−OC_2H_4NR_2** and **Ru−Re−OC(O)OC_2H_4NR_2**. (d) Composition ratios of the complexes depending on CO_2 concentration in a solution wherein the inset shows the same figure with a wider concentration of CO_2. Black, blue, and red dots and lines in panels b, c, and d denote the complexes **Ru−Re−DMF**, **Ru−Re−OC_2H_4NR_2**, and **Ru−Re−OC(O)-OC_2H_4NR_2**, respectively.

most of the Re unit in the Ru(II)−Re(I) complexes was converted to the aminoethylcarbonato complex (**Ru−Re−OC(O)OC_2H_4NR_2**, Process 2 in Figure 1a) even in a dilute solution of CO_2 because the ν_{CO} bands are very similar to those of fac-[Re(bpy)(CO)$_3$\{OC(O)OC$_2$H$_4$N(C$_2$H$_4$OH)$_2$\}] (ν_{CO} = 2020 and 1915 cm^{-1}).[19] Identification of this CO_2 adduct was also confirmed by ^{13}C NMR measurements (Figure S2). The equilibrium constant for this CO_2 capture reaction (K_{CO2}, Process 2) was 1.5×10^3 M^{-1}, which was comparable to that of the mononuclear Re(I) complex (K_{CO2} = 1.7×10^3 M^{-1}).[19] According to this large equilibrium constant for CO_2 capture, bubbling with Ar gas containing 10% CO_2 (abbreviated as "10% CO_2 gas") converted 94% of the complex to **Ru−Re−OC(O)OC_2H_4NR_2**; moreover, the use of 1% and 0.5% CO_2 gave 65% and 48% formation yield of **Ru−Re−OC(O)-OC_2H_4NR_2**, respectively (Figure 1d).[21]

The photocatalytic ability of the Ru(II)−Re(I) complex for CO_2 reduction was investigated using a gas-flow cell with Ar-based gas containing various concentrations of CO_2 (Figure S3). As a typical run, a DMF−TEOA solution (5:1 v/v)

containing **Ru−Re−DMF** and **Ru−Re−OC_2H_4NR_2** (total concentration was 0.05 mM) as well as 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH, 0.1 M) as a sacrificial reductant[22] was bubbled with 10% CO_2 for 30 min. This solution was irradiated at λ_{ex} = 480 nm and the same gas containing 10% CO_2 was continuously bubbled into the reaction solution during irradiation. Only CO was selectively produced and H_2 was not detected (Figure 2). The turnover
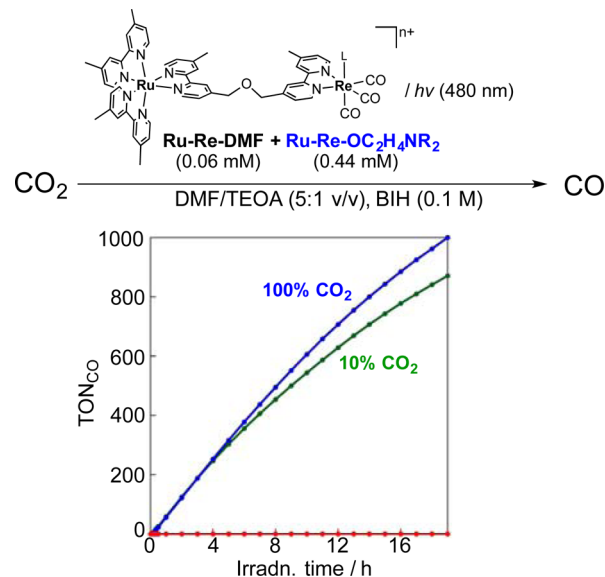
Figure 2. Photocatalytic reaction using **Ru−Re−DMF** (n = 3) and **Ru−Re−OC_2H_4NR_2** (n = 2) under a 100% or 10% CO_2 atmosphere, and turnover numbers for CO or H_2 formation (TON_{CO} or TON_{H2}) for 19 h, where blue, green, red, and orange dots denote the turnover numbers of CO formation under 100% CO_2, CO formation under 10% CO_2, H_2 formation under 100%, and H_2 formation under 10%, respectively. TON_{CO} or TON_{H2} are defined as [amount of evolved CO or H_2]/[amount of the dinuclear metal complex in solution].
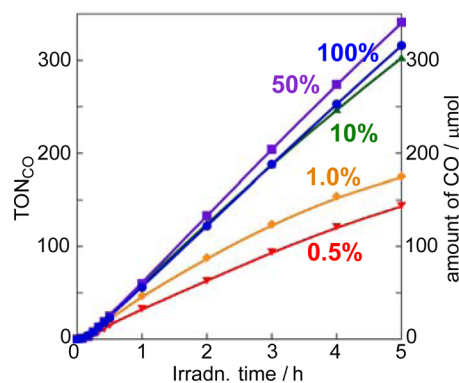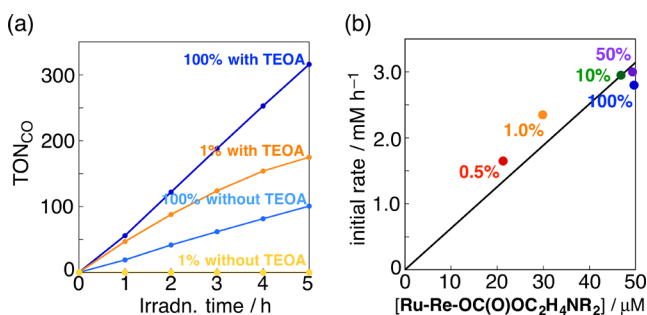

Figure 3. Photocatalytic CO formation under various concentrations of CO_2 (0.5%−100%).

numbers for CO formation (TON_{CO}) were 303 (303 μmol) and 871 (871 μmol) after 5 h and 19 h of irradiation, respectively, and increased to 1020 (1020 μmol) after 26 h of irradiation (Figure S4). It can be noted that the time course of CO formation using 10% CO_2 was similar to that of pure CO_2, particularly up to the 5 h irradiation time, as shown in Figures 2 and 3. Therefore, this photocatalytic system can supply a good method for reducing CO_2, even by using gas containing only

10% CO_2, without the use of other methods for CO_2 condensation.

Similar experiments were conducted using different concentrations of CO_2, i.e., bubbling with Ar containing 50%, 1%, or 0.5% CO_2 during irradiation (Figures 3 and S5). The time courses of CO formation were similar among the cases using 100%, 50%, and 10% CO_2 concentrations. The quantum yield of CO formation was determined as Φ_{CO} = 0.50 under a 100% CO_2 atmosphere (Figure S6), and similar values were obtained in cases with 10% CO_2. Even in cases using gas with a much lower concentration of CO_2, i.e., only 1% or 0.5%, CO was produced with about 80% and 60% efficiencies, respectively, compared to using 100% CO_2 for 1 h of irradiation. Although further irradiation lowered the photocatalytic ability, the TON_{CO} reached 215 and 205 after 19 h of irradiation, respectively (Figure S5), which are much higher than other reported systems that use relatively low concentrations of CO_2 (2.5 for CO, 33.3 for HCOOH, 14.5 for H_2 under 5% CO_2 atmosphere).[17]

For checking the function of TEOA, which is required to obtain the CO_2 adduct **Ru−Re−OC(O)OC$_2$H$_4$NR$_2$**, reference experiments without TEOA were investigated. When similar photocatalytic reactions in the absence of TEOA were conducted with pure CO_2, selective CO formation was observed, although its efficiency was about three times lower than in the presence of TEOA (Figure 4a, TON_{CO} = 101 for 5

(a)   (b)

Figure 4. Profound influence on photocatalytic CO_2 reduction by triethanolamine (a) photocatalytic reactions under 100% and 1% CO_2 atmosphere with/without TEOA. (b) Linear relationship between the initial rate of CO formation and the concentration of the CO_2-capturing complex **Ru−Re−OC(O)OC$_2$H$_4$NR$_2$**.

h of irradiation). As previously reported, TEOA works as a base for deprotonation of the one-electron oxidized form of BIH ($BIH^{+\bullet}$), which should suppress back electron transfer from the one-electron reduced form of the photocatalyst to $BIH^{+\bullet}$ as one of the obstruction processes of the photocatalytic reduction (eq 1).[22] On the other hand, when 1% CO_2 was used, formation of
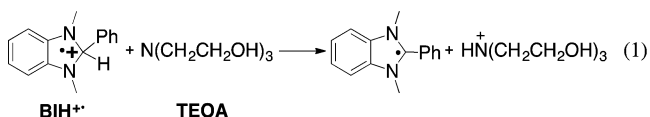
CO was not observed. This result clearly indicates that TEOA is necessary for reduction of CO_2 under a 1% CO_2 atmosphere. For determining the role of TEOA as a proton source, photocatalysis using the dinuclear complex in the presence of tri(n-propyl)ammonium hexafluorophosphate (25 mM) instead of TEOA was investigated and formation of CO was not observed. It can be noted that even in the presence of this proton source, the emission from the excited Ru unit of the

dinuclear complex was almost quantitatively quenched by BIH. The $[Ru^{II}(dmb)_3]^{2+}$ complex as a model of the photosensitizer unit of the dinuclear complex was efficiently reduced under similar reaction conditions, and the corresponding one-electron reduced species $[Ru^{II}(dmb^{-\bullet})(dmb)_2]^+$ accumulated in the reaction solution during the irradiation (Figure S7). These results clearly indicate that photochemical reduction of the dinuclear complex should proceed even in the presence of the proton source; however, as described above, in the absence of TEOA, reduction of CO_2 did not proceed under a 1% CO_2 atmosphere.

It should be also pointed out that the saturated concentration of CO_2 in the TEOA−DMF mixture (0.14 M)[21] is lower than that in pure DMF (0.20 M).[23] Therefore, from a viewpoint of the concentration of CO_2 in the reaction solution, DMF should be a better solvent than the mixture of DMF and TEOA. Moreover, the viscosity of TEOA is much higher than that of DMF. This should be also another defect of the DMF-TEOA mixed solvent for photocatalytic reactions because of the slower diffusion rates of the photocatalyst and CO_2 in the DMF-TEOA solution than in DMF. More efficient photocatalytic performance in the presence of TEOA, despite these unfavorable physical properties of TEOA, indicates that TEOA and **Ru−Re−OC(O)OC$_2$H$_4$NR$_2$** are crucial for CO_2 reduction under low concentrations of CO_2.

Figure 4b shows the correlation between the formation rate of CO in the initial stages of the photocatalytic reaction and the concentration of **Ru−Re−OC(O)OC$_2$H$_4$NR$_2$** in the reaction solution before irradiation and indicates the concentration of CO_2 in the flow gas. These results, combined with the reference experiments described above, clearly indicate that **Ru−Re−OC(O)OC$_2$H$_4$NR$_2$** mainly worked as a photocatalyst for CO_2 reduction to give CO. In other words, **Ru−Re−OC$_2$H$_4$NR$_2$** can play the role of a precursor to the photocatalyst and of a collector of CO_2 from gas containing low concentrations of CO_2; the large equilibrium constant of formation of **Ru−Re−OC(O)OC$_2$H$_4$NR$_2$** from **Ru−Re−OC$_2$H$_4$NR$_2$** and CO_2 makes the photocatalytic reduction of low concentration of CO_2 possible.

The lower durability of the photocatalyst under 1% and 0.5% CO_2 concentrations compared to those under 100%−10% (Figure S5) is another evidence for the important role of **Ru−Re−OC(O)OC$_2$H$_4$NR$_2$**, because a part of the Re complexes in solution (35% and 52% of the added Re complex under 1% and 0.5% CO_2 concentrations, respectively) was not converted to the CO_2 adduct, i.e., **Ru−Re−OC$_2$H$_4$NR$_2$** and **Ru−Re−DMF**, under 1% and 0.5% CO_2. Although these Re complexes without the aminoethylcarbonate ligand should be photochemically reduced and ligand loss from the one-electron-reduced complexes should produce the corresponding 17-electrons species of the Re(I) complex moiety. It was reported that the reaction rate of this species (mostly its solvento complex) with CO_2 was slow (k = ∼0.003 s^{-1} in THF).[24] Under low concentrations of CO_2, therefore, the slower rate of the reaction with CO_2 should cause partial decomposition of the photocatalyst, which resulted in ceasing of CO formation.

In conclusion, we developed a new photocatalytic system using a Ru−Re binuclear complex, which can reduce dilute CO_2 down to 10% CO_2 with high selectivity for CO formation (∼100%), high durability (TON_{CO} > 1000), and high efficiency (Φ_{CO} > 40%). Even under 0.5% CO_2 gas, this system can reduce CO_2 selectively to CO with ∼60% the efficiency of a system using pure CO_2. This is the first example of a molecular

photocatalyst that has the ability to concentrate and photochemically reduce CO_2. This new concept, i.e., the use of efficient CO_2 insertion reactions to metal–oxygen bond for photocatalytic reduction of CO_2, holds great potential for developing technologies for reduction of low concentrations of CO_2.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08824.

Materials, methods, and synthetic procedures (PDF)

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(21) The saturated concentration of CO_2 in DMF-TEOA was evaluated at 0.14 M by titration using with $Ba(OH)_2$ and by spectroscopic analysis using mononuclear Re(I) complex. We also confirmed the good linearity between the CO_2 concentrations in the solution and the partial pressure of CO_2 in the DMF-TEOA mixed solution. The detailed procedures and the data are shown in Supporting Information.

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