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Photochemical reduction of CO_2 with ascorbate in aqueous solution using vesicles acting as photocatalysts

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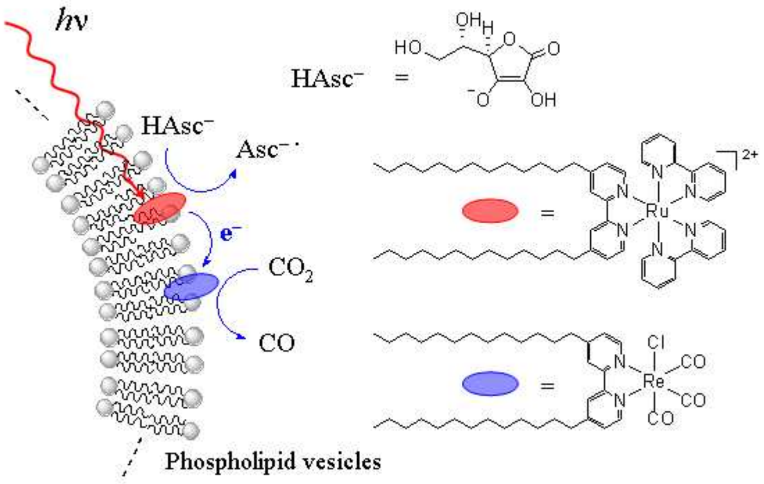
Graphical Abstract



Abstract

We report a novel system of visible-light-driven CO_2 reduction to CO in an aqueous solution, in which DPPC vesicles dispersed in the solution act as a photocatalyst using ascorbate ($HAsc^−$) as an electron source. In the vesicles metal complexes $[Ru(dtb)(bpy)_2]^{2+}$ and $Re(dtb)(CO)_3Cl$ (dtb = 4,4’-ditridecyl-2,2’-bipyridyl) are incorporated, which act as a photosensitizer and a catalyst for CO_2 reduction, respectively. The reaction is initiated with the reductive quenching of the ^{3}MLCT excited state of the Ru complex with $HAsc^−$, followed by an electron transfer from the reduced Ru complex to the Re complex to give a one-electron reduced Re species having catalytic ability for CO_2 reduction. In order to search for optimum conditions for the CO production, the dependence of the initial rate of CO formation, v_i, on the concentration of the metal complexes and $HAsc^−$ in the vesicle solution was examined. Consequently, we obtained ~ 3.5 μmol $h^{−1}$ and 190 for v_i and the turnover number for CO formation with respect to the Re catalyst, respectively. On the basis of the dependence of v_i on the incident light intensity, we have concluded that the photocatalytic reduction of CO_2 to CO with $HAsc^−$ in this system requires only one photon, and propose that $HAsc^−$ donates an electron not only to the excited state of the Ru complex, but also to the Re-CO_2 adduct involved in the catalytic cycle for CO_2 reduction.

Introduction

Photochemical reduction of CO_2 is of great interest with relation to the construction of artificial systems to convert light energy into chemical potential. Research on these systems becomes increasingly important with global interest in the shortage of fossil fuels. A number of transition metal complexes have been reported to be effective in the photocatalytic reduction of CO_2.[1-4] Among them, it has been established that rhenium(I) bipyridine complexes act as efficient photocatalysts for the selective reduction of CO_2 to CO, which were first introduced by Lehn and co-workers in 1986.[5] A photocatalytic system for the CO_2 reduction using Re(I) complexes was developed by Ishitani and co-workers on the basis of mechanistic studies,[6] and they reported that a $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ complex (bpy = 2,2'-bipyridyl) is the most effective photocatalyst for the selective reduction of CO_2 to CO with the quantum yield of 0.38 by irradiation with 365 nm light.[7]

Although the photocatalytic system for the CO_2 reduction using Re(I) complexes is of great interest from a mechanistic point of view, there are obstacles to developing it into an artificial system in which solar energy is converted into chemical potential. First of all, most Re(I) complexes do not have strong absorption in the visible region. However, this problem has been partially overcome by the introduction of polynuclear metal complexes, in which the Re(I) complex is covalently connected with a transition metal complex, such as a $[Ru(bpy)_3]^{2+}$ derivative, which acts as a redox photosensitizer. A ruthenium(II) complex $[Ru(bpy)_3]^{2+}$ has intense MLCT absorption in the visible region (λ_{max} 452 nm, log ε_{max} = 4.16 in water), and a suitable reduction potential comparable to that of Re(I) complexes, such as $Re(bpy)(CO)_3Cl$, which allows an electron transfer from a reduced Ru(II) unit to a Re(I) moiety to produce a Re species having an activity of CO_2 reduction. Thus, for example, the binuclear complex in which a $Re(dmb)(CO)_3Cl$ moiety and a $[Ru(dmb)_3]^{2+}$ moiety (dmb = 4,4'-dimethyl-2,2'-bipyridyl) are connected with a $(CH_2)_2$ group acts as an efficient photocatalyst for CO_2 reduction with the quantum yield of 0.13 by irradiation with 546 nm light.[8]

Almost all photocatalytic reduction systems of CO_2 using a Re(I) complex reported so far have been carried out in organic solvent, such as DMF, containing amines, such as triethanolamine (TEOA) and 1-benzyl-1,4-dihydronicotinamide (BNAH), that act as an electron source for CO_2 reduction. In view of the light-chemical energy conversion, the use of these sacrificial electron donors is another problem of the photocatalytic system for the CO_2 reduction using Re(I) complexes. On donating an electron, these amines decompose irreversibly to prevent a back electron transfer process and promote the CO_2 reduction process efficiently. However, systems using a sacrificial electron donor are of no significance from the viewpoint of light-chemical energy conversion, because a considerable amount of chemical energy would be lost by an irreversible decomposition of oxidized donors. Furthermore, the use of organic solvent could be disadvantageous in the future to the construction of a large photocatalytic system for CO_2 reduction.

This report describes a novel photocatalytic system for CO_2 reduction in an aqueous medium, in which vesicles containing transition metal complexes act as a photocatalyst for CO_2 reduction using ascorbate ($HAsc^-$) as an electron source. Vesicles are an approximately spherical bilayer membrane that encloses a small volume of aqueous solution, which are formed by self-organization of amphiphiles, such as phospholipids, in an aqueous medium.[9] By the use of vesicles, materials insoluble in water, which are incorporated and concentrated into the hydrophobic membrane of vesicles, can be dispersed in a bulk aqueous solution. Vesicles have been utilized for model systems to understand the nature of complex biological phenomena, such as energy transduction[10] and self-reproduction.[11] In particular, a number of systems of photoinduced electron transport across vesicle membrane mimicking natural photosynthetic systems have been reported.[12,13]

An ascorbate anion ($HAsc^{-}$, Chart 1) is an electron donor used commonly in photoinduced electron transfer experiments in an aqueous media. Although $HAsc^{-}$ is often referred to as a sacrificial electron donor, the redox behavior of $HAsc^{-}$ is completely different from that of other typical sacrificial electron donors, such as TEOA, in that its one-electron oxidized form ($Asc^{-\bullet}$), which is readily formed through deprotonation of initially formed $HAsc^{\bullet}$, has a relatively long lifetime.[14] It has been reported that a back electron transfer process occurs at the rate constant near the diffusion limit between $[Ru(bpy)_3]^{+}$ and $Asc^{-\bullet}$ that are produced by the reductive quenching of excited $[Ru(bpy)_3]^{2+}$ with $HAsc^{-}$ in an aqueous solution.[15] An encounter of the two anion radicals ($Asc^{-\bullet}$) results in disproportionation to regenerate $HAsc^{-}$ along with two-electron oxidized form, dehydroascorbate (Asc), which slowly reacts with water in an irreversible manner. Although there are a number of systems of photocatalyzed hydrogen production using $HAsc^{-}$ as an electron source in an aqueous media,[15-17] to the best of our knowledge, there are no precedents for a photocatalytic system for the selective reduction of CO_2 to CO using $HAsc^{-}$ as an electron source.[18]

[Chart 1]

Results and discussion

Design and preparation of the reaction systems

In order to construct a photochemical CO_2-reduction system in an aqueous medium using $HAsc^-$ as an electron source, we employed a well-established photocatalytic system for CO_2 reduction, which is composed of $[Ru(bpy)_3]^{2+}$ and $[Re(bpy)(CO)_3Cl]$ derivatives. The former absorbs visible light to initiate the reaction, and the latter acts as a catalytic CO_2-reduction center. It has been reported that the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ is quenched by $HAsc^-$ with a rate constant of $1{\sim}2 \times 10^7$ M^{-1} s^{-1} in an aqueous medium at pH 3~8,[15] which is comparable with that for quenching of $[Ru(dmb)_3]^{2+}$ by BNAH in DMF/TEOA (5 : 1).[19] Therefore, the system consisting of $HAsc^-$ / $[Ru(bpy)_3]^{2+}$ / $Re(bpy)(CO)_3Cl$ is also expected to act as a visible-light responding photocatalytic system for CO_2 reduction.

Furthermore, in order to disperse water-insoluble $Re(bpy)(CO)_3Cl$ derivatives in an aqueous medium and enhance an interaction between the Ru and Re complexes by the proximity effect, we incorporated both of the Ru and Re complexes into a hydrophobic membrane of phospholipid vesicles. To increase the solubility of the transition metal complexes in the vesicle membrane, we designed novel complexes having hydrophobic long alkyl groups on their bpy ligands, $[Ru(dtb)(bpy)_2](PF_6)_2$ and $Re(dtb)(CO)_3Cl$ (dtb = 4,4’-ditridecyl-2,2’-bipyridyl) (Chart 2). These complexes were prepared according to standard methods including the ligand exchange of $Ru(bpy)_2Cl_2$ and $Re(CO)_5Cl$ with dtb.

[Chart 2]

Solutions of phospholipid vesicles containing these complexes can be prepared by sonication of a suspension of these complexes and 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) in tris(hydroxymethyl)aminomethane-HCl (Tris-HCl) buffer (1.0 M, pH 7.5), followed by chromatographic separation to remove the complexes outside the vesicles. The details are described in the experimental section. By the use of a dynamic light scattering method, it was demonstrated that the solution contained particles with a diameter of 40-100 nm indicating the formation of vesicles with a unilamellar structure. Incorporation of the transition metal complexes into the vesicle solutions was confirmed by the absorption and emission spectra as shown in the following section. The concentration of the complexes in the vesicle solutions was evaluated by the UV absorptions of the complexes using their molar extinction coefficients determined in $CHCl_3$. In a typical vesicle preparation in which 0.520 μmol of each complex and 12.0 μmol of DPPC were initially used, the concentrations of $[Ru(dtb)(bpy)_2]^{2+}$ and $[Re(dtb)(CO)_3Cl]$ in the vesicle solution obtained were evaluated to be 38 μM and 40 μM, respectively, indicating that ~ 85% of the complexes employed in the vesicle preparation were incorporated into the vesicles. It should be pointed out that the dtb groups on the complexes served to increase the concentrations of the complexes incorporated into the vesicles, because no absorptions characteristic of the metal complexes could be detected in the absorption spectra of the vesicle solutions prepared by using $[Ru(bpy)_3]Cl_2$ and $Re(dmb)(CO)_3Cl$ in a similar procedure.

Photophysical and electrochemical properties of the metal complexes

The photophysical properties of the novel metal complexes were examined in homogeneous solution and DPPC vesicle solution where the complexes were incorporated in the vesicle membrane. Absorption and emission spectra of the complexes recorded in DPPC vesicle solution are shown in Fig. S1. The results are summarized in Table 1, together with those of reference complexes, $[Ru(bpy)_3]Cl_2$ and $Re(dmb)(CO)_3Cl$. As shown in the table, as well as in comparison with the data reported on the related complexes,[8,19,20] the photophysical properties of $[Ru(dtb)(bpy)_2]^{2+}$ and $Re(dtb)(CO)_3Cl$ in homogeneous solution are essentially identical to those of reference complexes, indicating that the dtb groups have a negligible effect on the electronic structure of the complexes. Absorptions appearing in the visible region at 456 and 377 nm of the Ru and Re complexes, respectively, are assigned to spin-allowed ^{1}MLCT transition. The emissions with a maximum at 592 and 573 nm of the Ru and Re complexes, respectively, correspond to the phosphorescence from their ^{3}MLCT state.

[Table 1]

Although the absorption and emission spectra of $[Ru(dtb)(bpy)_2]^{2+}$ in vesicle solution are similar to those in $CHCl_3$, the photophysical properties of $Re(dtb)(CO)_3Cl$ in vesicle solution are considerably different from those in $CHCl_3$. Rodriguez and Lima reported the solvent effect on the absorption and emission of Re(I) complexes, and established that their ^{1}MLCT absorption maximum is shifted to lower wavelength with increasing solvent polarity mainly due to stabilization of the strong dipolar ground state of the complexes.[21] On the basis of these facts, we examined the solvent effect on the absorption spectrum of $Re(dtb)(CO)_3Cl$ to determine the location of the complex in the vesicle solution. Figure S2 illustrates the absorption spectra of $Re(dtb)(CO)_3Cl$ recorded in various solvents, together with in vesicle solution. In accord with the observation by Rodriguez and Lima, a blue shift was observed in the ^{1}MLCT transition on going to solvents with increasing polarity. As shown in the figure, the position of the ^{1}MLCT transition in vesicle solution is similar to that recorded in MeOH and DMF rather than in $CHCl_3$ and cyclohexane, indicating that the metal center of Re(dtb)$(CO)_3$Cl is not located in the interior of the vesicle membrane, but close to the membrane-water interface of the vesicle. Moreover, as shown in Table 1, a large blue shift of the ^{3}MLCT emission, as well as a remarkable increase in a quantum yield for the emission, of Re(dtb)$(CO)_3$Cl is observed in vesicle solution compared with that in $CHCl_3$. It has been reported that although in some Re(I) complexes a red shift of the emission from ^{3}MLCT state is observed with increasing solvent polarity, no significant correlation between the emission maximum of Re(bpy)$(CO)_3$Cl and solvent polarity is observed.[21] Although the rigidity of the vesicle membrane might influence the properties and dynamics of the ^{3}MLCT state of the Re complex, further discussion on the excited state will not be given in this report because the Re complex acts exclusively as a catalyst for the CO_2 reduction in our system.

The electrochemical behavior of the novel metal complexes is summarized in Table 2, along with that of reference complexes. As shown in the table, the redox potentials of the novel complexes are in accord with those of reference complexes, indicating again that the dtb groups have a negligible effect on the electronic structure of the complexes. The first reversible oxidation and reduction waves of $[Ru(dtb)(bpy)_2]^{2+}$ appeared at 0.79 V and –1.79 V (*vs* Fc^+/Fc : Fc = ferrocene), respectively. Compared with similar Ru complexes reported so far,[8,19] they are assigned to the Ru(III/II) couple and the reduction of the bipyridyl ligands, respectively. For the complex Re(dtb)$(CO)_3$Cl, the irreversible oxidation wave and reversible reduction wave were observed at 0.91 V and –1.85 V (*vs* Fc^+/Fc), respectively, as reported for Re(α–diimine)$(CO)_3X$ (X = Cl, Br) type complexes in the literature.[19,22,23]

[Table 2]

Photocatalytic reduction of CO_2

In a typical run, the solution of DPPC vesicles containing both of the complexes $[Ru(dtb)(bpy)_2]^{2+}$ and $Re(dtb)(CO)_3Cl$ in a Tris-HCl buffer (pH 7.5, 3.0 mL) was placed into a quartz cell, and sodium ascorbate was added to give a vesicle solution with $HAsc^-$ (0.10 M) in an outer aqueous phase. The concentrations of the Ru and Re complexes in the solution were estimated to be 38 and 40 μM, respectively. After CO_2 was bubbled through the solution for 1 h, the pH of the solution was reduced to 6.5. Then the CO_2-saturated vesicle solution was irradiated with a 500-W xenon arc lamp through the optical filter (> 440 nm) for 2 h. By the GC analysis of the headspace of the cell, the formation of CO (6.2 μmol), along with very small amounts of H_2 (6.9 nmol) was observed. The turnover number, TON, which is defined as the ratio of moles of CO produced to moles of the catalyst used, was calculated to be 52 with respect to the Re complexes. Moreover, we confirmed that CO was not detected in the absence of light, CO_2, or $HAsc^-$. Thus, the photocatalytic reduction of CO_2 with $HAsc^-$ in aqueous solution was accomplished by using vesicles containing the complexes $[Ru(dtb)(bpy)_2]^{2+}$ and $Re(dtb)(CO)_3Cl$.

In order to gain information on the mechanism of the photocatalytic reaction and to search for optimum conditions for the CO production in this system, the dependence of the reaction efficiency on the incident light intensity and concentrations of the metal complexes and $HAsc^{-}$ was examined. The reaction efficiency is evaluated with the initial rate of CO formation, v_i, which can be determined by the amounts of CO produced after the irradiation for 2 h, because it was found that the amounts of CO increased linearly with irradiation time for at least 2 h (vide infra).

(1) Dependence on the Ru complex concentration. When the vesicle solution prepared in an identical manner to that described above, except for the absence of $[Ru(dtb)(bpy)_2]^{2+}$, was irradiated with > 440 nm, no detectable amount of CO, as well as H_2, was produced. Even in the irradiation with the shorter wavelength light (> 390 nm, 2 h), only a small amount of CO (0.022 μmol) was produced in the absence of the Ru complex. These observations suggest that the Ru complex incorporated into the vesicle membrane sensitizes the reduction of CO_2 in this photocatalytic system.

The UV-vis spectra of $[Ru(dtb)(bpy)_2]^{2+}$ and $Re(dtb)(CO)_3Cl$ in the wavelength range of > 350 nm, along with the wavelength dependence of the transmittance, $I_f(\lambda)$, of the optical filters employed in the irradiation are illustrated in Fig. S3. The relative value of the number of photons absorbed by the complex in unit time, I(rel), is estimated by the integration of $I_f(\lambda)(1 - 10^{-\varepsilon(\lambda)C_s l})$, where $\varepsilon(\lambda)$ and C_s stand for the absorption spectrum and the concentration of the complex, respectively, and l shows the length of the cell used in the irradiation experiment. Thus, the calculation of I(rel) for $[Ru(dtb)(bpy)_2]^{2+}$ and $Re(dtb)(CO)_3Cl$ under the typical irradiation conditions (C_s(Ru) = 38 μM, C_s(Re) = 40 μM) reveals that the ratio of photons absorbed by the Re complex to that by the Ru complex is 0.021 and 0.095 for the irradiation with light of > 440 nm and > 390 nm, respectively, indicating that almost all photons absorbed by the vesicle solution causes the excitation of the Ru complex. Therefore, it is concluded that the complex $[Ru(dtb)(bpy)_2]^{2+}$ works as a sensitizer to initiate subsequent reactions under the irradiation conditions of our experiments.

The concentration of the sensitizer $[Ru(dtb)(bpy)_2]^{2+}$, C_s(Ru), can affect the initial rate of CO formation, v_i, because the number of photons absorbed by the sensitizer in unit time increases with an increase in C_s(Ru). Thus, the dependence of v_i on C_s(Ru) was examined in the vesicle solutions of various C_s(Ru), which could be controlled by the ratio of the Ru complex to a constant DPPC amount in the vesicle preparation. The numerical data of v_i observed for various C_s(Ru) are shown in Table S1, along with the relative values of the number of photons absorbed by the sensitizer in unit time, I(rel). The plot of v_i against I(rel) is depicted in Fig. 1, indicating that v_i increased with an increase in C_s(Ru) up to ~ 40 μM, and remained constant above that. An approximately linear relationship between v_i and I(rel) indicates that v_i is controlled only by the number of photons absorbed by the Ru complex in unit time, and the efficiency of the CO production is almost constant in the C_s(Ru) range up to ~ 40 μM. However, the efficiency of the CO production decreased largely at the higher C_s(Ru) range. Thus, it is found that the optimal concentration of the sensitizer $[Ru(dtb)(bpy)_2]^{2+}$ for the CO production is ~ 40 μM.

[Figure 1]

The decrease in the CO production efficiency at the higher C_s(Ru) range is probably due to an increase in the rate of deactivation of the excited Ru complex through the interaction with another Ru complex in its ground state. It is pointed out that in vesicle solution the sensitizer molecules are concentrated in the vesicle membrane. Assuming that all DPPC molecules employed in the vesicle preparation are present in the vesicle solution, the fraction of the sensitizer $[Ru(dtb)(bpy)_2]^{2+}$ in the vesicle is calculated to be 3.5 mol%, indicating that the local concentration of the sensitizer in the vesicle membrane is of the order of 10^{-2} M. The decrease in the efficiency of photoinduced electron transfer in vesicles with an increase in the sensitizer concentration has been already reported.[24]

(2) Dependence on the light intensity. In order to reveal the number of photons required to produce one molecule of CO, the dependence of the initial rate of CO formation, v_i, on the incident light intensity was examined. The intensity of light incident on the vesicle solution was regulated by using three kinds of neutral density filters, and evaluated again by the integration of $I_f(\lambda)(1 - 10^{-\varepsilon(\lambda)Csl})$. The wavelength dependences of the transmittance of the neutral density filters are shown in Fig. S4. The initial rate of CO formation, v_i, decreased with a decrease in light intensity. As depicted in Fig. 2, the plots of v_i against light intensity gave a perfect straight line. A linear relationship between v_i and light intensity indicates that the photocatalytic reduction of CO_2 to CO with $HAsc^-$ in vesicle solution requires only one photon. However, two electrons are necessary for the formation of CO form CO_2. Therefore, the observation suggests that only one of the two electrons required for the reduction of CO_2 is provided by a reductant produced photochemically. The mechanism for the CO formation is discussed in detail in a subsequent section.

[Figure 2]

(3) Quenching of sensitizer phosphorescence by HAsc$^-$. In the photocatalytic system for CO_2 reduction using the Ru complex as a sensitizer reported so far, the redox process starts with reductive quenching of the ^{3}MLCT excited state of the Ru complex with a sacrificial electron donor. It is also reported that Re complexes having a structure of Re(bpy)$(CO)_3$X interact negligibly with the ^{3}MLCT excited state of the Ru complex even in dinuclear complexes in which the Ru and Re complexes are linked by a bridging ligand.[20]

Although rate constants for quenching of $[Ru(bpy)_3]^{2+}$ by ascorbate (HAsc$^-$) have been reported,[15,25] we examined the quenching process of the Ru complex with HAsc$^-$ in aqueous homogeneous solution, as well as in DPPC vesicle solution where the Ru complex was incorporated in the vesicle membrane. The Stern-Volmer plot for the quenching of emission from $[Ru(bpy)_3]^{2+}$ with HAsc$^-$ in aqueous solution is depicted in Fig. S5, indicating that the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ is effectively quenched by HAsc$^-$ with $k_q\tau = 16.6\ M^{-1}$. Considering that the lifetime of the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ was 360 ns under the conditions employed in the quenching experiment, the rate constant for quenching was determined to be $k_q = 4.6 \times 10^7\ M^{-1}\ s^{-1}$, which is in fair agreement with the values reported in aqueous media.[15,25]

The intensity of the emission from $[Ru(dtb)(bpy)_2]^{2+}$ in vesicle solution (C_s(Ru) = 46 μM in Tris-HCl buffer, pH 7.5) was also reduced by the addition of sodium ascorbate to the outer aqueous solution. Assuming that HAsc$^-$ added to the outer aqueous solution can quench the emission only from the sensitizers located in the vesicle membranes close to the outer aqueous solution, Stern-Volmer treatment of the quenching data gives the value of $k_q\tau = 12.3\ M^{-1}$ (Fig. S6). Thus, the quenching of the ^{3}MLCT excited state of $[Ru(dtb)(bpy)_2]^{2+}$ incorporated into the vesicle membranes by $HAsc^-$ added to the outer aqueous solution occurs with efficiency comparable to that in the fluid solutions. Taking into account the lifetime of the excited state of $[Ru(dtb)(bpy)_2]^{2+}$ under the conditions employed in the quenching experiment (τ = 456 ns), the rate constant for quenching in vesicle solution was calculated to be $k_q = 2.7 \times 10^7\ M^{-1}\ s^{-1}$. The free-energy change for the reductive quenching of the ^{3}MLCT excited state of $[Ru(dtb)(bpy)_2]^{2+}$ with $HAsc^-$ is estimated by the Rehm-Weller equation[26] to be −16 kcal mol^{-1}, suggesting that the quenching process proceeds by an electron transfer mechanism.[27]

Although the k_q in the vesicle solution is slightly decreased compared with that in the aqueous solution, the value is sufficiently large to initiate the photocatalytic process by the reductive quenching of the excited state of the Ru complex. It seems that the k_q value in the vesicle solution comparable to that in the aqueous solution is attributed to the position of the sensitizer $[Ru(dtb)(bpy)_2]^{2+}$ in the vesicle solution. The hydrophilic Ru center of $[Ru(dtb)(bpy)_2]^{2+}$ would be located at the membrane-water interface, facilitating an interaction between $[Ru(dtb)(bpy)_2]^{2+}$ in its excited state and $HAsc^-$ in an aqueous phase. It has been reported that rate constants for quenching of the fluorescence of pyrene derivatives incorporated into the vesicle membrane decreases considerably compared with those in homogeneous solutions.[13]

(4) Dependence on the concentration of $HAsc^-$. As mentioned in the previous section, the photocatalytic reduction of CO_2 is likely initiated by the reductive quenching of the ^{3}MLCT excited state of the Ru complex with $HAsc^-$. Thus, the initial rate of CO formation, v_i, should be dependent on the concentration of $HAsc^-$ added to the outer aqueous solution because the efficiency of quenching, η_q, which is depicted by $k_q\tau[\mathrm{HAsc}^-]/(1 + k_q\tau[\mathrm{HAsc}^-])$, is affected by the concentration of HAsc^-.

Figure 3 shows the dependence of the initial rate of CO formation, v_i, in the photocatalytic reaction on the initial concentration of HAsc^- added to the outer aqueous solution. As shown in the figure, v_i increased with an increase in the concentration of HAsc^- up to ~ 0.1 M, and further addition of HAsc^- gave no effects on v_i in practice. The enhancement of v_i with an increase in the HAsc^- concentration can be interpreted in terms of an increase in the efficiency of quenching, η_q. The data shown in Fig. 3, however, cannot be entirely explained only by this factor, because the value of η_q, which can be evaluated by using the rate constant for quenching ($k_q = 2.7 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) and the lifetime of the excited state of $[\mathrm{Ru(dtb)(bpy)_2}]^{2+}$ under the reaction conditions (τ = 538 ns), continues to increase even in the concentration range above ~ 0.1 M, e. g., η_q = 0.59 at 0.10 M and η_q = 0.93 at 0.88 M.

[Figure 3]

The cessation of increase in v_i in the concentration range above ~ 0.1 M can be attributed to an increase in the steady state concentration of the one-electron oxidized form of ascorbate ion ($\mathrm{Asc}^{-\bullet}$) formed by quenching of the excited state of $[\mathrm{Ru(dtb)(bpy)_2}]^{2+}$ with an increase in the HAsc^- concentration, which causes an increase in the rate of the back electron transfer from the reduced Ru complex, $[\mathrm{Ru(dtb)(bpy)_2}]^{+}$, to $\mathrm{Asc}^{-\bullet}$. On the basis of the mechanism proposed for the photocatalytic CO_2 reduction using Ru(II)-Re(I) dinuclear complexes,[8,19] an electron transfer occurs from $[\mathrm{Ru(dtb)(bpy)_2}]^{+}$ to the Re complex to produce $[\mathrm{Re(dtb)(CO)_3Cl}]^{-\bullet}$, which starts a catalytic cycle for CO_2 reduction. It is known that an electron transfer from the reduced Ru complex to the Re complex occurs slowly even in the Ru(II)-Re(I) dinuclear complexes, so that the reduced species of the Ru site have the lifetime of several ms.[20] On the other hand, as mentioned in the introductory part, it has been reported that the rate constant for the back electron transfer from $[Ru(bpy)_3]^+$ to $Asc^{-\bullet}$ is near the diffusion limit.[15] Thus, the electron transfer process should compete with the back electron transfer to $Asc^{-\bullet}$.

Assuming that the local concentration of $Re(dtb)(CO)_3Cl$ in the vesicle membrane is proportional to $C_s(Re)$, the efficiency of the electron transfer from $[Ru(dtb)(bpy)_2]^+$ to $Re(dtb)(CO)_3Cl$ in the vesicle membrane, η_{el}, can be depicted by $k_{el}mC_s(Re)/(\tau_s^{-1} + k_{el}mC_s(Re))$, where k_{el} and τ_s are the bimolecular rate constant for the electron transfer and the lifetime of $[Ru(dtb)(bpy)_2]^+$ in the absence of the Re complex, respectively, and $mC_s(Re)$ is the local concentration of the Re complex in the vesicle membrane. It is reasonable to think that an increase in the rate of the back electron transfer from $[Ru(dtb)(bpy)_2]^+$ to $Asc^{-\bullet}$ in the range of the higher $HAsc^-$ concentration results in the reduction of τ_s, leading to a decrease in η_{el}. Thus, in the concentration range above ~ 0.1 M an increase in the efficiency of quenching, η_q, could be compensated with a decrease in the efficiency of the successive electron transfer process, η_{el}, yielding that v_i is almost independent of the $HAsc^-$ concentration.

(5) Consumption of $HAsc^-$. In order to confirm that $HAsc^-$ added to the outer aqueous solution acts as an electron donor to reduce CO_2, the concentration of sodium ascorbate (HAscNa) of the irradiated vesicle solution was determined, and compared with that of the initial solution. The HAscNa concentration was determined by HPLC equipped with an ODS column with an eluent of a phosphate buffer containing MeCN.[28]

HAscNa was added to the aqueous solution of vesicles containing both complexes (C_s(Ru) = 43 μM and C_s(Re) = 40 μM in Tris-HCl buffer, 3.0 mL), so that the concentration of $HAsc^-$ was about 0.01 M for convenience of measurement. After bubbling of CO_2, the solution was irradiated (> 440 nm) for 2 h to produce CO (1.6 μmol) and H_2 (5.5 nmol). By the HPLC analysis, the HAscNa concentration in the vesicle solution before and after the irradiation was determined to be 10.1 mM and 9.0 mM, respectively, indicating that CO was produced in the photocatalytic reduction of CO_2 at the expense of HAscNa. The amounts of $HAsc^-$ consumed (3.3 μmol) were fairly consistent with the amounts of CO produced. If $HAsc^-$ acts as a reductant donating two electrons (vide infra), the chemical yield of CO in the photocatalytic reduction of CO_2 under the conditions described above was evaluated to be 48% on the basis of $HAsc^-$ consumed.

(6) Dependence on the Re complex concentration. As mentioned above, the Re complex $Re(dtb)(CO)_3Cl$ incorporated into the vesicle membrane acts as a catalyst for the CO_2 reduction, which can be activated by electron transfer from the reduced Ru complex. The same reaction scheme has been postulated for the photocatalytic CO_2 reduction using Ru(II)-Re(I) dinuclear complexes with bridging ligands.[8,19] Although it was reported that in the photocatalytic CO_2 reduction in a mixed solution of $[Ru(dmb)_3]^{2+}$ and $Re(dmb)(CO)_3Cl$ an increase in the concentration of the Re complex caused a decrease in the efficiency of CO_2 reduction,[19] no detailed studies have been reported on the dependence on the concentration of the catalyst. On the other hand, it is known that the photocatalytic activity for the CO_2 reduction of the Re complex, such as

Re(dmb)$(CO)_3$Br, in a DMF-TEOA solution strongly depends on the concentration of the complex.[23]

Fig. 4 shows the dependence of the initial rate of CO formation, v_i, in the photocatalytic reaction on the Re complex concentration in the vesicle solution, C_s(Re). The numerical data of v_i, along with initial amounts of the Re complex employed in the vesicle preparation, are summarized in Table S2. It is noted that on the irradiation in the absence of the Re complex, the formation of very small amounts of CO and H_2 was observed probably due to the photocatalytic activity of the Ru complex. As shown in the figure, v_i increased monotonically with an increase in C_s(Re), and reached a steady value of ~ 4 μmol h^{-1} at ~ 40 μM practically.

[Figure 4]

As mentioned in the previous section, electron transfer occurs from the reduced Ru complex, $[Ru(dtb)(bpy)_2]^+$, to Re(dtb)$(CO)_3$Cl in the vesicle membrane, which competes with the back electron transfer to $Asc^{-\bullet}$. Assuming that processes other than the electron transfer from $[Ru(dtb)(bpy)_2]^+$ to the Re complex are independent of C_s(Re), the initial rate of CO formation, v_i, would be directly proportional to the efficiency of the electron transfer from $[Ru(dtb)(bpy)_2]^+$ to the Re complex, $\eta_{el} = k_{el}mC\text{s}(\text{Re})/(\tau_s^{-1} + k_{el}mC_s(\text{Re}))$. Thus, if we write $v_i = a\eta_{el}$, where a is a proportionality constant, a linear relationship between $1/v_i$ and $1/C_s$(Re) is expected as shown in Eq. (1).

$$1/v_i = (1/a)(1 + 1/(k_{el}\tau_s mC_s(\text{Re}))) \qquad (1)$$

As shown in the inset of Fig. 4, a plot of $1/v_i$ against $1/C_s$(Re) gives a straight line as expected. These results suggest that an increase in v_i with C_s(Re) can be interpreted in terms of an increase in the efficiency of the electron transfer from the reduced Ru complex, $[Ru(dtb)(bpy)_2]^+$, to the Re complex, η_{el}. However, as C_s(Re) is increased, v_i and η_{el} increase, while turnover frequency, TOF, which is defined as the ratio of v_i to moles of the catalyst used, decreases. In fact, as C_s(Re) was increased from 5 μM to 60 μM, TOF decreased from 93 h^{-1} to 24 h^{-1} (Table S2). Thus, from a practical point of view, we select ~ 40 μM as the optimum value of C_s(Re) for the CO production in this system. At 40 μM of C_s(Re), the efficiency of the electron transfer from the reduced Ru complex to the Re complex, η_{el}, is estimated to be 0.76 on the basis of the analysis of Fig. 4.

(7) Influence of pH and buffer. The efficiency of the photocatalytic CO_2 reduction using ascorbate as an electron donor would depend on the pH of aqueous solutions. A lowering of pH is unfavorable for the electron-donating ability of ascorbate because of an increase in the one-electron redox potential of $Asc^{-\bullet}/HAsc^-$ couple and an increase in the population of the fully protonated acid, H_2Asc, the pK_a of which is 4.1. On the other hand, a decrease in the reduction potential of CO_2, as well as an increase in the concentration of CO_2 in solutions, in lower pH ranges would favor the CO_2 reduction process. Moreover, it is possible that the catalytic activity of the Re complex for the CO_2 reduction is controlled by pH because the protonation process is included in the catalytic cycle. A complicated pH dependent aspect has been reported in the photocatalytic hydrogen generation systems using $[Ru(bpy)_3]^{2+}$ as a sensitizer and ascorbate as an electron donor, in which the hydrogen yield is maximized at around pH

4 and reduced at both higher and lower pH levels.[15]

The pH dependence of the efficiency of photocatalytic CO_2 reduction in vesicle solutions was examined in the range of pH 5 ~ 7 using two different buffer solutions. The results are summarized in Table 3. As shown in the table, although the efficiency of the by-product H_2 formation increases as the pH of the solution is lowered, no significant change is observed in the efficiency of the CO production. This photocatalytic system of the CO_2 reduction in vesicle solution works in a buffer solution other than Tris-HCl, indicating that Tris molecules that are present in large quantities in the solution do not play an essential role in the photocatalytic reduction of CO_2. However, that a slight increase in the efficiency of the CO production in a Tris-HCl buffer compared with that in a phosphate buffer is attributed to the participation of Tris molecules in catalytic cycle for the CO_2 reduction with the Re complex. It has been reported that in the photocatalytic system for CO_2 reduction using Re(I) complexes, such as $Re(bpy)(CO)_3X$ (X = NCS, Cl), in a DMF-TEOA binary solvent the solvent-coordinated complexes, $Re(bpy)(CO)_3S$ (S = DMF, TEOA), participate in the catalytic cycle for CO_2 reduction.[20]

[Table 3]

(8) Dependence on irradiation time. Figure 5 shows the amount of CO, along with that of by-product H_2, produced by the irradiation of the vesicle solution under the conditions determined as optimum for the CO_2 reduction as a function of irradiation time. On the irradiation of the vesicle solution, the formation of CO started and continued at a nearly constant rate for ~ 3 h. After that the rate of CO formation decreased with the irradiation, and the formation of CO ceased practically after 15 h of irradiation. At this time, the turnover number, TON, of CO formation with respect to the Re catalyst was calculated to be 190.

[Figure 5]

To gain an insight into the dependence of CO formation on the irradiation time, the UV-vis absorption spectra were recorded in the course of the reaction (Fig. S7). The absorbance at 456 nm due to the ^{1}MLCT transition of the Ru complex started to decrease after ~ 4 h of the irradiation, indicating that the sensitizer is degraded in the course of the reaction. At the end of the irradiation, the absorbance at 456 nm disappeared almost completely, and the broad absorption band appeared in the range of 500-700 nm. Thus, the decrease in the rate of CO formation is primarily attributed to the decomposition of $[Ru(dtb)(bpy)_2]^{2+}$ incorporated into the vesicle membranes, which is probably due to the photochemical reaction of the Ru complex under the reaction conditions. It has been reported that $[Ru(bpy)_3]^{2+}$ is not stable photochemically in acidic aqueous solutions.[18,29] Nevertheless, in order to construct a robust photocatalytic system for CO_2 reduction, further studies are required to reveal the mechanism of the degradation of the sensitizer in the course of the reaction.

Mechanism of photocatalytic CO_2 reduction

On the basis of the data described above and recent investigations of photocatalytic CO_2 reduction with Re(I) complexes, we propose a mechanism for the CO formation as illustrated in Scheme 1. The reaction is initiated with the excitation of the Ru complex located in the vesicle membranes close to the outer aqueous solution. The ^{3}MLCT excited state of the Ru complex is efficiently quenched by HAsc$^-$, followed by an electron transfer from the reduced Ru complex to the Re(I) complex to give a one-electron reduced Re species (Re^0) having the catalytic ability for CO_2 reduction. A recent investigation reported that the Cl$^-$ ligand is eliminated from Re^0 forming the 17-electron species, which can react with CO_2 to give a Re-CO_2 adduct. The second electron is donated to the Re-CO_2 adduct, leading to the CO formation and the regeneration of the Re(I) complex through the coordination of Cl$^-$.

[Scheme 1]

The important point of a catalytic Re cycle for reduction of CO_2 to CO is the source of the second electron. Lehn and co-workers proposed a reaction scheme where the second electron is provided by the oxidative decomposition of the sacrificial donor TEOA.[13] On the other hand, Ishitani and co-workers postulated that another one-electron reduced Re species donates the second electron to the Re-CO_2 adduct.[30] Recently, it has been shown that this bimetallic mechanism predominates in the photocatalytic reduction of CO_2 using binuclear Re(I) complexes.[23] In our system of the photocatalytic reduction of CO_2 with HAsc$^-$ in the vesicle solution, however, the possibility that the second electron originates from another one-electron reduced Re species or the reduced Ru complex generated by reductive quenching of the excited Ru complex can be ruled out because only one photon is required for the formation of CO from CO_2 in our system. Therefore, the possible candidates for the electron donor to the Re-CO_2 adduct are HAsc$^-$ and its one-electron oxidized form (Asc$^{-\bullet}$). Although further studies are required to reveal the mechanism for the catalytic Re cycle for the reduction of CO_2 to CO, we assign the source of the second electron tentatively to $HAsc^{-}$ for the following two reasons. First, it has been reported that although the oxidation potential of $Asc^{-\bullet}$ is more negative than that of $HAsc^{-}$, the rate constant for the oxidation of $Asc^{-\bullet}$ is smaller mainly due to a substantial energy barrier to the two-electron oxidized form (Asc, Chart 1), the structure of which is highly strained having three adjacent carbonyl groups in a five-membered ring.[14] Second, it is reported that the steady state concentration of $Asc^{-\bullet}$ would be 0.2 μM under conditions for photocatalytic hydrogen production ($HAsc^{-}$ (0.1 M) / $[Ru(bpy)_3]^{2+}$ / Co(III) catalyst),[15] which is about six orders of magnitude lower than the concentration of $HAsc^{-}$ used. Thus, it is expected that the Re-CO_2 adduct encounters with $HAsc^{-}$ much more frequently compared with $Asc^{-\bullet}$ in our photocatalytic system.

As shown in Fig. 5, the evolution of CO was observed without an induction period, indicating that immediately after the irradiation a steady state is reached in the concentrations of reactive intermediates involving the reaction scheme. Thus, according to Scheme I, the initial rate of CO formation, v_i, is described by Eq. (2),

$$v_i = \alpha I \eta_q \eta_{el} \eta_{cat} \tag{2}$$

where α and I are the fraction of the Ru complexes located in the vesicle membranes close to the outer aqueous solution and the number of photons absorbed by the Ru complexes present in the vesicle solution in unit time, respectively. As mentioned in the previous sections, η_q is the efficiency of quenching of the excited Ru complex by $HAsc^{-}$ and η_{el} is the efficiency of the electron transfer from the reduced Ru complex (Ru^{I}) to the Re complex to give a one-electron reduced Re species (Re^0). Finally, η_{cat} is the efficiency of the catalytic reaction, which is expressed as the ratio of the moles of CO formed to that of Re^0 produced through the electron transfer process. Under the optimum conditions for the CO production (C_s(Ru) = C_s(Re) = ~ 40 μM, [$HAsc^-$] = 0.10 M), the efficiencies η_q and η_{el} are estimated to be 0.59 and 0.76, respectively. The quenching efficiency, η_q, is considerably smaller compared with that in the photocatalytic CO_2 reduction using the Ru(II)-Re(I) dinuclear complexes and a sacrificial electron donor ($\eta_{el} > 0.8$).[19,20] In our photocatalytic system, although we can increase η_q simply with an increase in [$HAsc^-$], an increase in [$HAsc^-$] causes a decrease in the electron transfer efficiency η_{el} probably due to an increase in the rate of back electron transfer from Ru^I to $Asc^{-\bullet}$. Therefore, it is strongly suggested that a design to suppress the back electron transfer process is necessary to enhance the total efficiency of CO formation in our photocatalytic system using $HAsc^-$ as an electron source.

Conclusions

We have developed a novel photocatalytic system for CO_2 reduction using visible light and ascorbate ($HAsc^-$) as an electron source in an aqueous solution. In this system, the photoreduction of CO_2 is catalyzed by phospholipid vesicles dispersed in the solution, which contain the Ru and Re complexes acting as a photosensitizer and a catalyst for CO_2 reduction, respectively. Under the optimum conditions for the CO production in this system, the turnover number, TON, for CO formation with respect to the Re catalyst was calculated to be 190.

On the basis of the dependence of the initial rate of CO formation on the light intensity, we have concluded that the photocatalytic reduction of CO_2 to CO with $HAsc^-$ in this system requires only one photon, and propose that $HAsc^-$ donates an electron not only to the excited Ru sensitizer, but also to the Re-CO_2 adduct involved in the catalytic cycle for CO_2 reduction. Assuming that $Asc^{-\bullet}$ formed by the one-electron oxidization of $HAsc^-$ disproportionates to $HAsc^-$ and dehydroascorbate (Asc), the overall reaction driven photochemically in this system is represented by Eq. (3).

$$CO_2 + H_2Asc \xrightarrow{h\nu} CO + Asc + H_2O \qquad (3)$$

If we use the standard reduction potentials of the CO_2/CO and Asc/H_2Asc couples,[31] it is found that this process is thermodynamically unfavorable by 31 kcal mol^{-1}, confirming that light energy can be converted into chemical potential in our photocatalytic system.

Phospholipid vesicles play an important role in this system. Incorporation of Re(dtb)$(CO)_3$Cl into vesicle membranes makes it possible for water-insoluble Re complexes acting as efficient catalysts for the selective reduction of CO_2 to CO to disperse in an aqueous media. Furthermore, the sensitizer $[Ru(dtb)(bpy)_2]^{2+}$ is also incorporated into vesicle membranes, making it favorable for an electron transfer from the reduced Ru complex to the Re complex without linking both complexes with covalent bonds. We are continuing work to enhance the total efficiency of CO_2 reduction in the photocatalytic system using vesicles as the reaction field.

Experimental

General methods

^{1}H NMR spectra were recorded on a 500 MHz spectrometer. UV-vis spectra were recorded on a JASCO V-560 spectrometer. Phosphorescence spectra were recorded on a JASCO FP-777 spectrofluorometer with a 200 nm min^{-1} scanning speed and a 1.5 nm bandwidth. Gas chromatography (GC) was performed using GC7000TF (J-Science Lab. Co., Ltd.) with a thermal conductivity detector and an activated carbon column (3 m × 3 mm). The high-performance liquid chromatography (HPLC) analyses were carried out on a JASCO 880 high-pressure liquid chromatography system equipped with an ODS column (Crestpak C18T-5, JASCO). Cyclic volammetry (CV) was carried out in nitrogen-purged MeCN using a HOKUTO DENKO potentiostat/galvanostat HAB-151 equipped with a YOKOGAWA 3025 XY recorder. Phosphorescence lifetime measurements were carried out on a compact fluorescence lifetime spectrometer (Quantaurus-Tau C11367-01, Hamamatsu Photonics). Phosphorescence quantum yields were obtained on an absolute PL quantum yield spectrometer (Quantaurus-QY C11347-01, Hamamatsu Photonics). *cis*-$Ru(bpy)_2Cl_2$,[35] $Re(dmb)(CO)_3Cl$,[36] and 4,4'-ditridecyl-2,2'-bipyridyl[37] (dtb) were synthesized according to literature procedures. 1,2-Dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) and $Re(CO)_5Cl$ were purchased from Sigma-Aldrich, and sodium ascorbate (HAscNa), tris(hydroxymethyl)aminomethane (Tris), and $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ were purchased from Tokyo Kasei Kogyo Co., Ltd. and used without purification.

Synthetic procedures

Bis(2,2'-bipyridyl)(4,4'-bistridecyl-2,2'-bipyridyl)ruthenium(II) hexafluorophosphate. $[Ru(dtb)(bpy)_2](PF_6)_2$ A mixture of *cis*-$Ru(bpy)_2Cl_2$ (29.5 mg, 60.9 μmol) and dtb (31.6 mg, 61.0 μmol) in ethanol (8 mL) was heated to reflux for 5 h under N_2 atmosphere. After cooling to room temperature, the solution was filtered and concentrated to ~ 2 mL under reduced pressure. To the solution was added a saturated solution of NH_4PF_6 in methanol (30 mL), and the solution was cooled at 0 °C. The pure product (48.3 mg, 65.0%) was obtained by filtration as an orange solid: mp 242-245 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.0 Hz, 2H), 8.33 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 1.5 Hz, 2H), 8.00 (td, *J* = 8.0, 1.0 Hz, 2H), 7.98 (td, *J* = 8.0, 1.0, 2H), 7.78 (dd, *J* = 5.5, 1.0 Hz, 2H), 7.75 (dd, *J* = 5.5, 1.0 Hz, 2H), 7.57 (d, *J* = 6.0 Hz, 2H), 7.53-7.47 (m, 4H), 7.30 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.80 (td, *J* = 8.3, 3.0 Hz, 4H), 1.69 (quin, *J* = 8.0 Hz, 4H), 1.50-1.20 (m, 40H), 0.88 (t, *J* = 7.0 Hz, 6H); Anal. Calcd for $C_{56}H_{76}N_6F_{12}P_2Ru{\cdot}0.5H_2O$: C, 54.54; H, 6.29; N, 6.81. Found: C, 54.80; H, 6.42; N, 6.34.

fac-tricarbonylchloro(4,4'-ditridecyl-2,2'-bipyridyl)rhenium(I). $Re(dtb)(CO)_3Cl$ $Re(CO)_5Cl$ (44.7 mg, 0.123 μmol) was dissolved in hot toluene (8 mL). To the solution was added dtb (61.7 mg, 0.122 μmol), and the reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in diethyl ether, and the solution was concentrated until a precipitate was formed. The pure product (56.8 mg) was obtained by filtration as a yellow solid, and the concentration of the filtrate gave an additional product (19.0 mg). The total yield was 77%: mp 126-127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 5.0 Hz, 2H), 7.95 (d, *J* = 1.0 Hz, 2H), 7.33 (dd, *J* = 5.0, 1.0 Hz, 2H), 2.79 (t, *J* = 8.0 Hz, 4H), 1.72 (quin, *J* = 8.0 Hz, 4H), 1.43-1.22 (m, 40H), 0.88 (t, *J* = 8.0 Hz, 6H); Anal. Calcd for $C_{39}H_{60}N_2O_3ClRe$: C, 56.67; H, 7.32; N, 3.39. Found: C, 56.40; H, 7.45; N, 3.28.

Vesicle preparation

A $CHCl_3$ solution of $[Ru(dtb)(bpy)_2](PF_6)_2$ (0.52 μmol), $Re(dtb)(CO)_3Cl$ (0.52 μmol), and DPPC (12.0 μmol) was evaporated under reduced pressure to form a thin film in a flask. The film was dried under vacuum overnight, and dispersed in a solution of 1.0 M Tris-HCl buffer (pH 7.5) containing 1.0 M NaCl by vortex mixing (Shibata, TTM-1). The resulting suspension was treated with ultrasonic process (Iwaki, USC-100Z38S-22) for 2 h at ~ 55 °C under Ar. The solution was developed on a column with Sephadex G-50 (Amersham Biosciences) equilibrated with a 1.0 M Tris-HCl buffer solution containing 1.0 M NaCl to remove the metal complexes outside the vesicles, and the fraction containing the lipids was collected to give a vesicle solution (11.4 mL). The concentration of the Ru complex in the vesicle solution, C_s(Ru), was evaluated by the absorbance at the wavelength of its maximal absorption and its molar extinction coefficient determined in $CHCl_3$. The concentration of the Re complex, C_s(Re), was estimated by using the vesicle solution prepared without the Ru complex and assuming that C_s(Re) is directly proportional to the amounts employed in the vesicle preparation. Dynamic light scattering studies of vesicle solutions were made on a Honeywell Microtac UPA-150.

Phosphorescence quenching studies

A vesicle solution for phosphorescence quenching studies was prepared in the same manner as that described above, except for the absence of $Re(dtb)(CO)_3Cl$. Solutions of the vesicle containing the Ru complex and various amounts of $HAsc^-$ were placed in quartz cell (10 mm × 10 mm), and their phosphorescence spectra were measured at room temperature under air on excitation at 450 nm. Relative phosphorescence intensities (F^0/F) were determined by measuring the peak of heights for the maxima, and were analyzed by the modified Stern-Volmer equation (Supporting Information).

Phosphorescence quenching studies in a homogeneous solution were carried out using a solution of $[Ru(bpy)_3]Cl_2$ in water (50 μM) at room temperature under air

Photocatalytic reactions

A vesicle solution (3.0 mL) was placed into a quartz cell (10 mm × 10 mm). To the solution was added HAscNa (30 μmol), and CO_2 was bubbled through the solution for 1 h. The solution was irradiated with a 500 W xenon arc lamp through an optical cutoff filter. The light intensity at the cell position was measured by the use of a photon counting meter (Ushio, UIT-150) and adjusted to ~ 0.8 mW cm^{-2} at 366 nm. The amounts of CO and H_2 evolved were determined by the GC analysis of the headspace of the cell (1.5 mL). The HAscNa concentration of the vesicle solution was determined by HPLC with an eluent of a KH_2PO_4-H_3PO_4 buffer (42 mM, pH 2.25) containing 7% MeCN using a UV detector (254 nm).

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Table 1 Photophysical properties of the Ru and Re complexes in $CHCl_3$ and vesicle solutions.

complex	system[a]	λ_{abs} / nm (ε_{max} / 10^4 M^{-1} cm^{-1})	λ_{em}[b] / nm	Φ_{em}[c]	τ[d] / ns
$[Ru(dtb)(bpy)_2](PF_6)_2$	$CHCl_3$	288 (8.32), 456 (1.38)	592	0.11	807
$[Ru(bpy)_3]Cl_2$	MeCN	286 (8.19), 451 (1.39)	587	0.073	575
$[Ru(dtb)(bpy)_2](PF_6)_2$	DPPC	288, 455	613	0.058	538
$Re(dtb)(CO)_3Cl$	$CHCl_3$	292 (1.79), 377 (0.35)	573	0.020	77
$Re(dmb)(CO)_3Cl$	$CHCl_3$	291 (1.73), 383 (0.35)	573	0.019	68
$Re(dtb)(CO)_3Cl$	DPPC	293, 318, 370sh	518	0.23	99 (6%), 1190 (94%)

[a] $CHCl_3$: in $CHCl_3$ solution. DPPC: in DPPC vesicle solution where the complex was incorporated in the vesicle membrane. The concentrations of the Ru and Re complexes were 41.8 and 42.4 μM, respectively. [b] λ_{ex} = 450 nm and 380 nm for the Ru and Re complexes, repectively. [c] Quantum yields for emission recorded in deareated solutions at 25 °C. [d] Lifetime of the emission recorded in deareated solutions at 25 °C. The decay profile of the Re complex emission in vesicle solution was satisfactorily analyzed by the sum of two exponential functions, each fraction of which is shown in parentheses.

Table 2 Redox potentials of the Ru and Re complexes.[a]

complex	$E_{1/2}$(oxdn) / V vs. Fc^+/Fc	$E_{1/2}$(redn) / V vs. Fc^+/Fc
$[Ru(dtb)(bpy)_2](PF_6)_2$	0.79	−1.79, −2.00, −2.20
$[Ru(bpy)_3]Cl_2$	0.92	−1.73, −1.92, −2.15
$[Ru(dmb)_3]^{2+}$[c]	0.82	−1.73, −1.94, −2.16
$Re(dtb)(CO)_3Cl$	0.91[b]	−1.85
$Re(dmb)(CO)_3Cl$	0.92[b]	−1.85
$Re(dmb)(CO)_3Cl$[c]	1.03	−1.74

[a] The values were obtained at 25 °C in acetonitrile solutions containing 0.10 M tetrabutylammoniumu perchlorate.

[b] Irreversible peak. [c] From ref. 22.

Table 3 Products of photocatalytic reduction of CO_2 in aqueous solutions of DPPC vesicles containing the Ru and Re complexes.[a]

Buffer[b]	pH[c]	C_s(Ru)[d] / μM	C_s(Re)[e] / μM	Reduction products	
				CO / μmol	H_2 / nmol
Tris-HCl	7.5 (6.5)	38	40	6.2	6.9
Tris-HCl	8.5 (7.1)	39	40	6.2	2.7
Phosphate	7.5 (6.4)	38	40	4.2	7.6
Phosphate	6.0 (5.8)	39	40	5.3	14

[a] Photoproducts obtained after the irradiation (> 440 nm) of CO_2-saturated solutions (3.0 mL) containing $HAsc^-$ (0.1 M) for 2 hr. [b] Buffer used for the preparation of vesicle solutions. Tris-HCl; tris(hydroxymethyl)aminomethane and HCl. Phosphate; KH_2PO_4 and Na_2HPO_4. [c] pH of the buffer in the vesicle preparation. The value after bubbling of CO_2 is shown in parentheses. [d] Concentration of $[Ru(dtb)(bpy)_2]^{2+}$ determined by UV-vis spectrum. [e] Concentration of $Re(dtb)(CO)_3Cl$ estimated by using the vesicle solution prepared without the Ru complex.

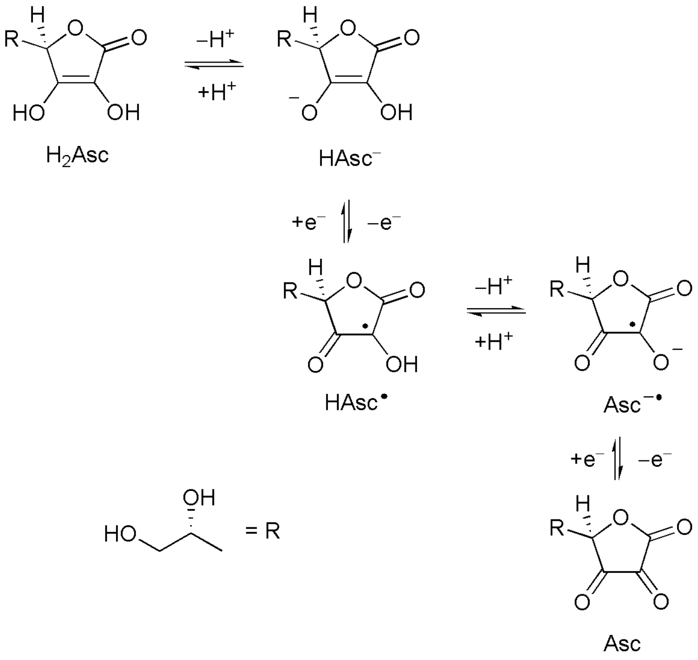
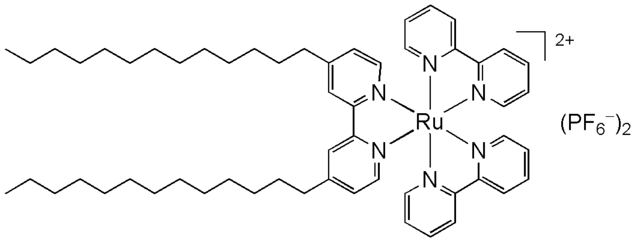
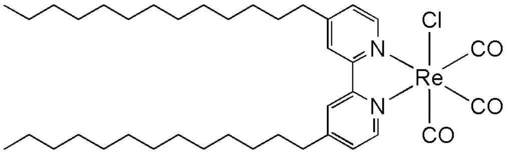


Chart 1. Chemical structure of an ascorbate anion (HAsc$^-$) and its interconversion.



$[Ru(dtb)(bpy)_2](PF_6)_2$



$Re(dtb)(CO)_3Cl$

Chart 2. Chemical structure of novel complexes having hydrophobic long alkyl groups

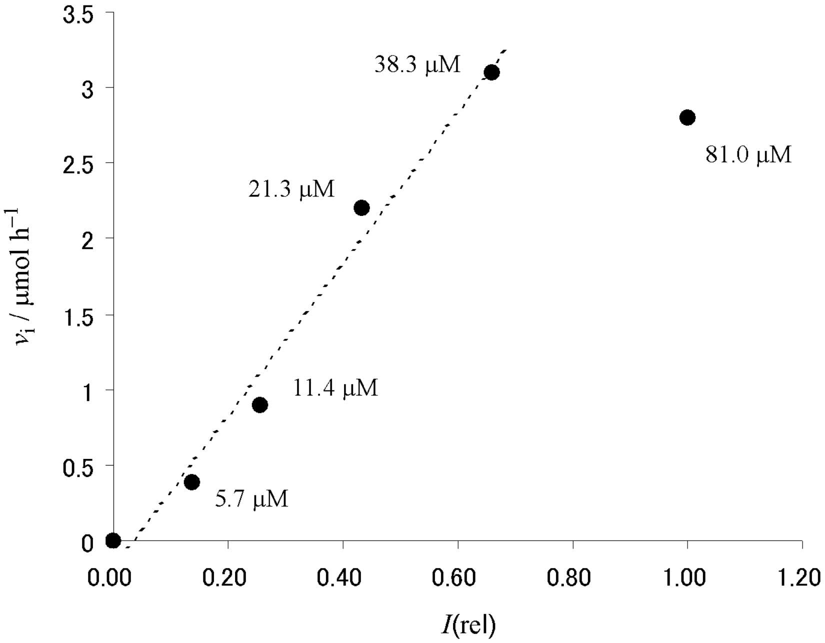


Fig. 1 Dependence of the initial rate of CO formation, v_i, on the concentration of the sensitizer $[Ru(dtb)(bpy)_2]^{2+}$, C_s(Ru), in the photocatalytic reduction of CO_2 in the vesicle solution (Tris-HCl, pH 6.5, C_s(Re) = ~ 40 µM, $[HAsc^-]$ = 0.10 M, > 440 nm). The data are presented by the plot of v_i *vs*. relative value of the number of photons absorbed by the sensitizer, I(rel), which is estimated by the integration of $I_f(\lambda)(1 - 10^{-\varepsilon(\lambda)C_sl})$ (I(rel) = 1.00 for C_s(Ru) = 81.0 µM). The values of C_s(Ru) are exhibited in the figure.

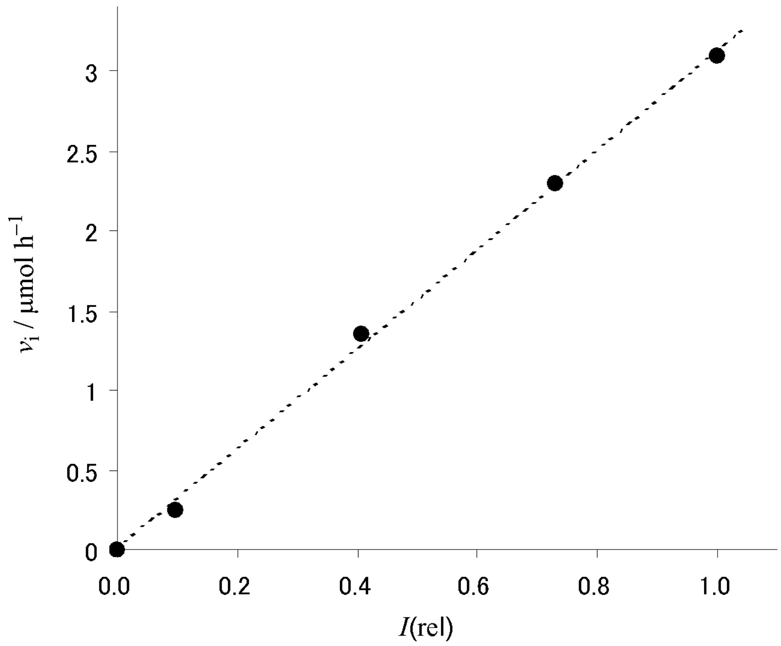


Fig. 2 Dependence of the initial rate of CO formation, v_i, on the incident light intensity in the photocatalytic reduction of CO_2 in the vesicle solution (Tris-HCl, pH 6.5, C_s(Ru) = 38 ~ 41 μM, C_s(Re) = ~ 40 μM, [HAsc$^-$] = 0.10 M, > 440 nm). The intensity of incident light was regulated by using three kinds of neutral density filters, and evaluated by the relative value of the numbers of photons absorbed by the sensitizer, I(rel), calculated by the integration of $I_f(\lambda)(1 - 10^{-\varepsilon(\lambda)C_s l})$, in which $I_f(\lambda)$ stands for the wavelength dependence of incident light (I(rel) = 1.0 for the irradiation without neutral density filters).

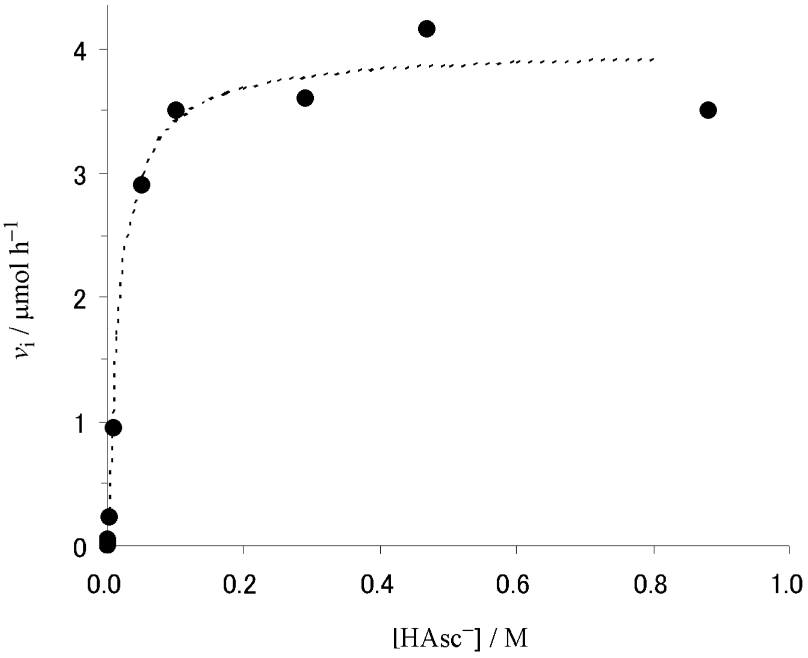


Fig. 3 Dependence of the initial rate of CO formation, v_i, on the initial concentration of HAsc$^-$ added to outer aqueous solution in the photocatalytic reduction of CO_2 in the vesicle solution (Tris-HCl, pH 6.5, C_s(Ru) = 34 ~ 40 µM, C_s(Re) = ~ 40 µM, > 390 nm).

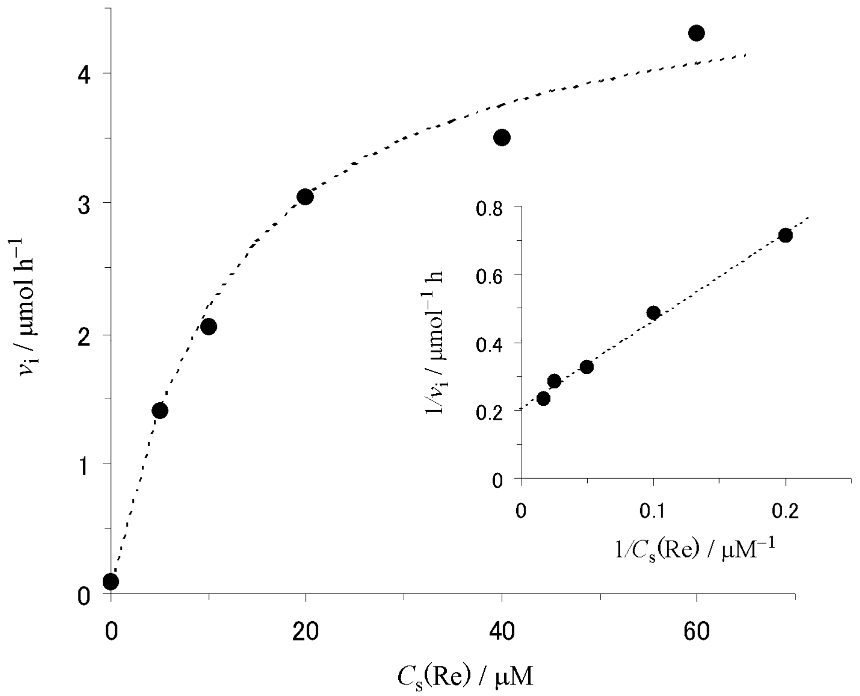


Fig. 4 Dependence of the initial rate of CO formation, v_i, on the concentration of the Re complex, Re(dtb)(CO)$_3$Cl, C_s(Re), in the photocatalytic reduction of CO$_2$ in the vesicle solution (Tris-HCl, pH 6.5, C_s(Ru) = 33 ~ 40 μM, [HAsc$^-$] = 0.10 M, > 390 nm). The inset figure shows the plot of a reciprocal of v_i *vs*. a reciprocal of C_s(Re). The linear relationship implies that an increase in v_i with C_s(Re) is attributed to an increase in the efficiency of the electron transfer to the Re complex, η_{el}.

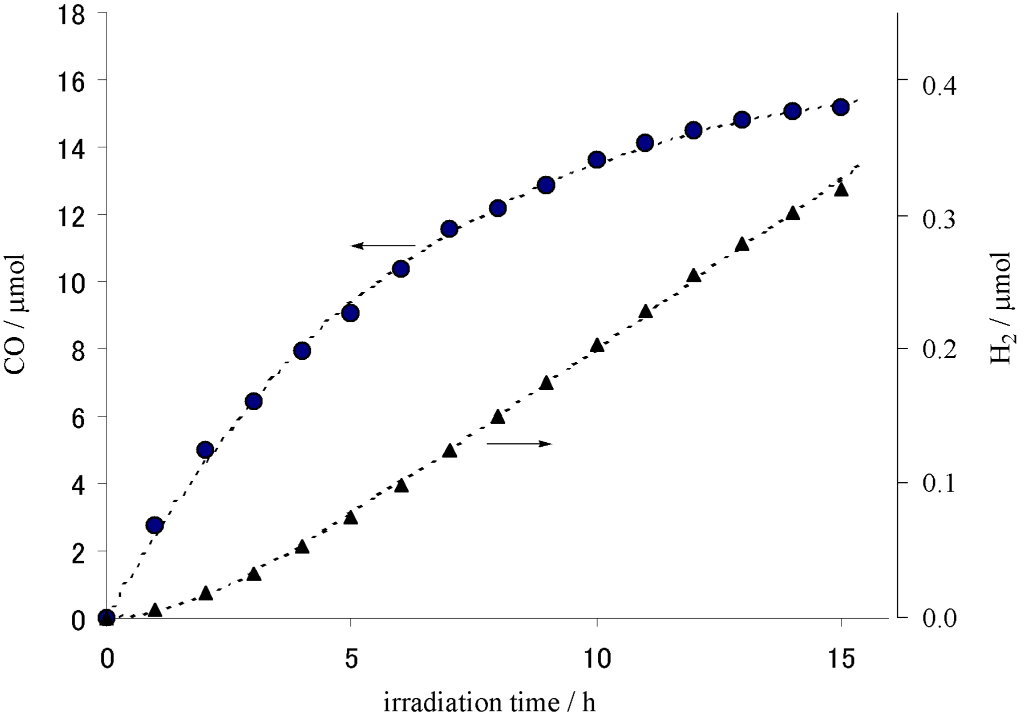
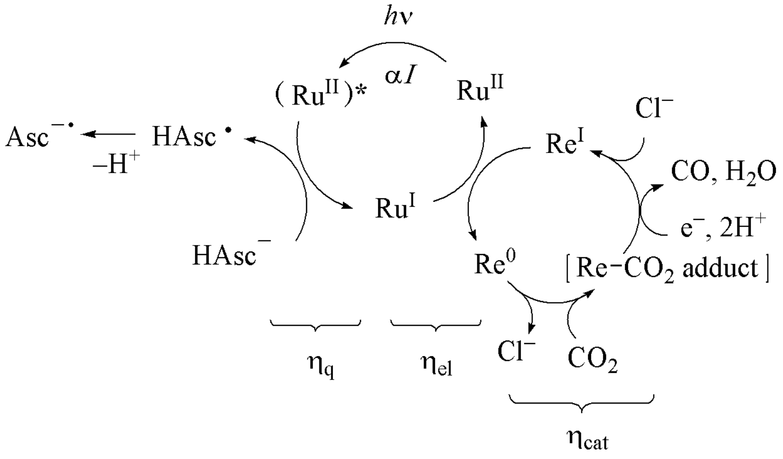


Fig. 5 The amounts of CO and H_2 produced in the photocatalytic reduction of CO_2 in the vesicle solution as a function of irradiation time (Tris-HCl, pH 6.5, C_s(Ru) = 41 µM, C_s(Re) = 40 µM, [HAsc$^-$] = 0.10 M, > 390 nm).



Scheme. 1 Proposed mechanism for the photocatalytic reduction of CO_2 in the vesicle solution. The Ru complex (Ru^{II} = $[Ru(dtb)(bpy)_2]^{2+}$) and the Re complex (Re^{I} = $Re(dtb)(CO)_3Cl$) are incorporated into the vesicle membrane, and an ascorbate anion ($HAsc^{-}$) is located in an outer aqueous phase. In the scheme, αI is the number of photons absorbed by the sensitizer located in the vesicle membranes close to the outer aqueous solution in unit time, and η's denote the efficiencies of the corresponding processes, see text.