Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting Information

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

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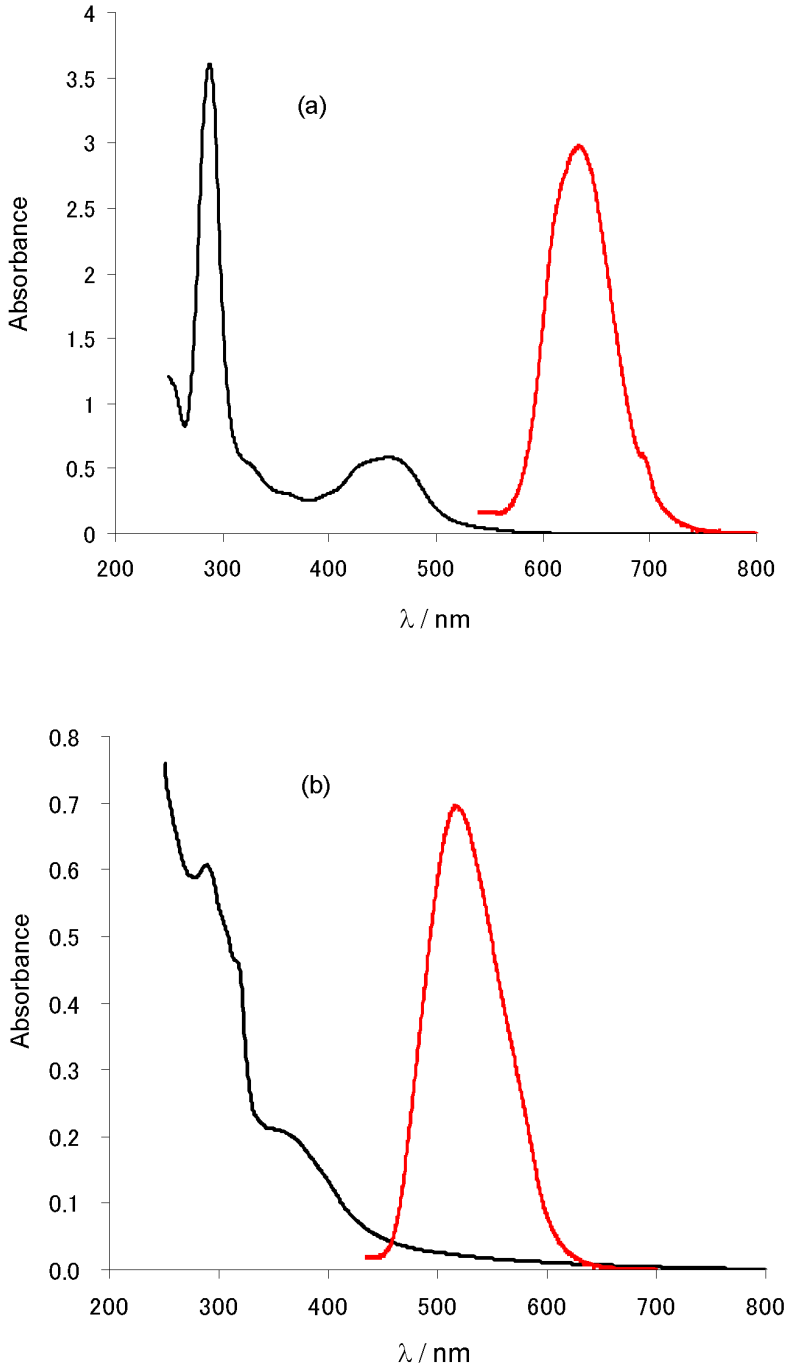

Fig. S1 Absorption (black) and emission (red) spectra of the metal complexes recorded in DPPC vesicle solution: (a) $[Ru(dtb)(bpy)_2]^{2+}$ (C_s(Ru) = 41.8 μM, λ_{ex} = 450 nm), (b) $Re(dtb)(CO)_3Cl$ (C_s(Re) = 42.4 μM, λ_{ex} = 380 nm). The intensity of emission is shown in an arbitrary unit.

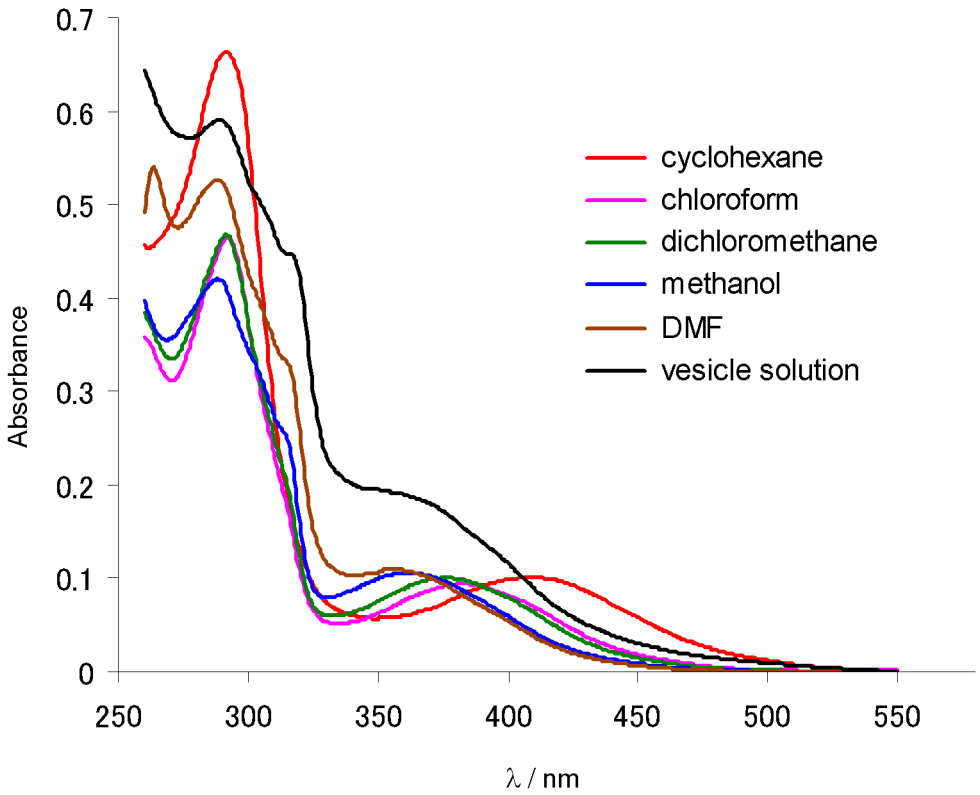

Fig. S2 Absorption spectra of $Re(dtb)(CO)_3Cl$ recorded in cyclohexane (red), chloroform (pink), dichloromethane (green), methanol (blue) and DMF (browm), together with in DPPC vesicle solution (Tris-HCl, pH 7.5, black). The concentration of $Re(dtb)(CO)_3Cl$ is 25 ~ 30 μM. The spectrum recorded in DPPC vesicle solution is shown in an arbitrary unit.

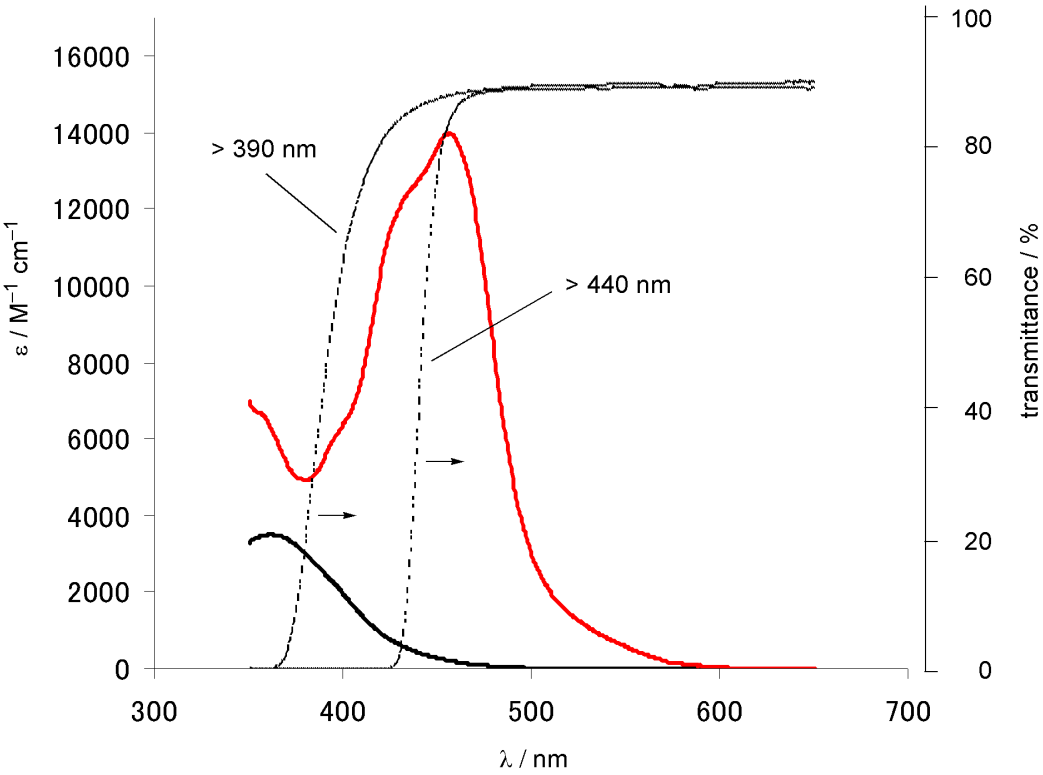

Fig. S3 Absorption spectra of $[Ru(dtb)(bpy)_2](PF_6)_2$ (red) and $Re(dtb)(CO)_3Cl$ (black) recorded in chloroform in the wavelength range of >350 nm. The dotted lines show the wavelength dependence of the transmittance of the optical filters employed in the irradiation.

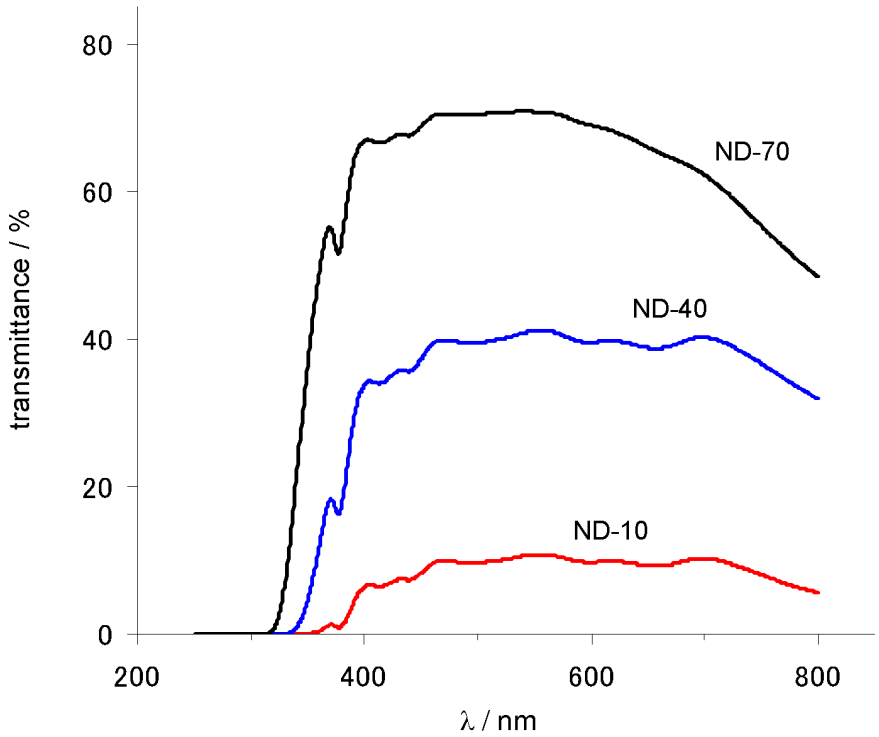

Fig. S4 Wavelength dependence of the transmittance of the neutral density filters, ND-70 (black), ND-40 (blue), and ND-10 (red), employed in the experiments of dependence of the initial rate of CO formation on the incident light intensity.

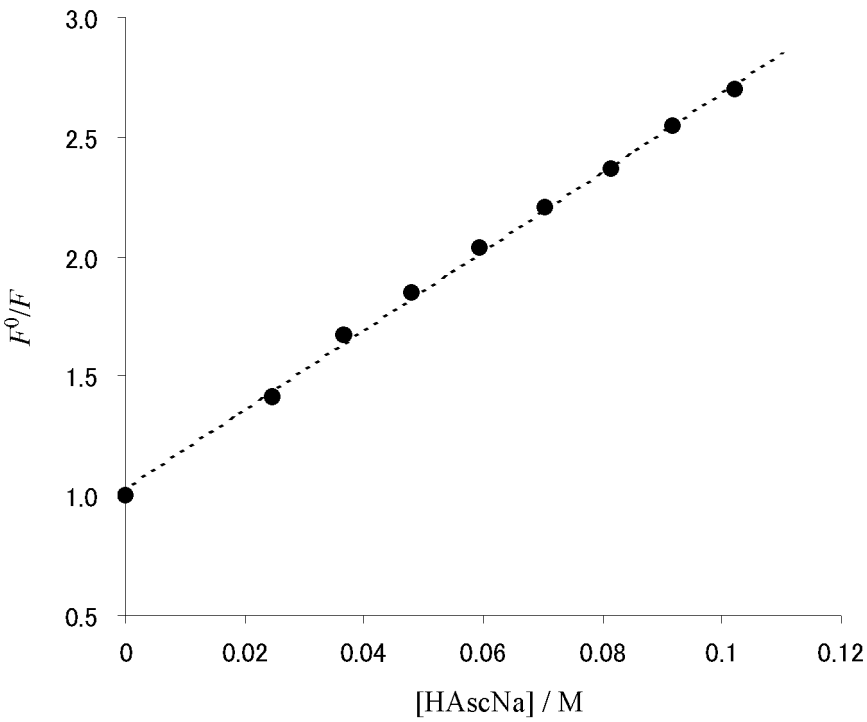

Fig. S5 Stern-Volmer plot for quenching of emission from $[Ru(bpy)_3]^{2+}$ (λ_{ex} = 450 nm) with sodium ascorbate (HAscNa) in water. The least-square analysis of the plot yields a quenching constant, $k_q\tau$, of 16.6 M^{-1}.

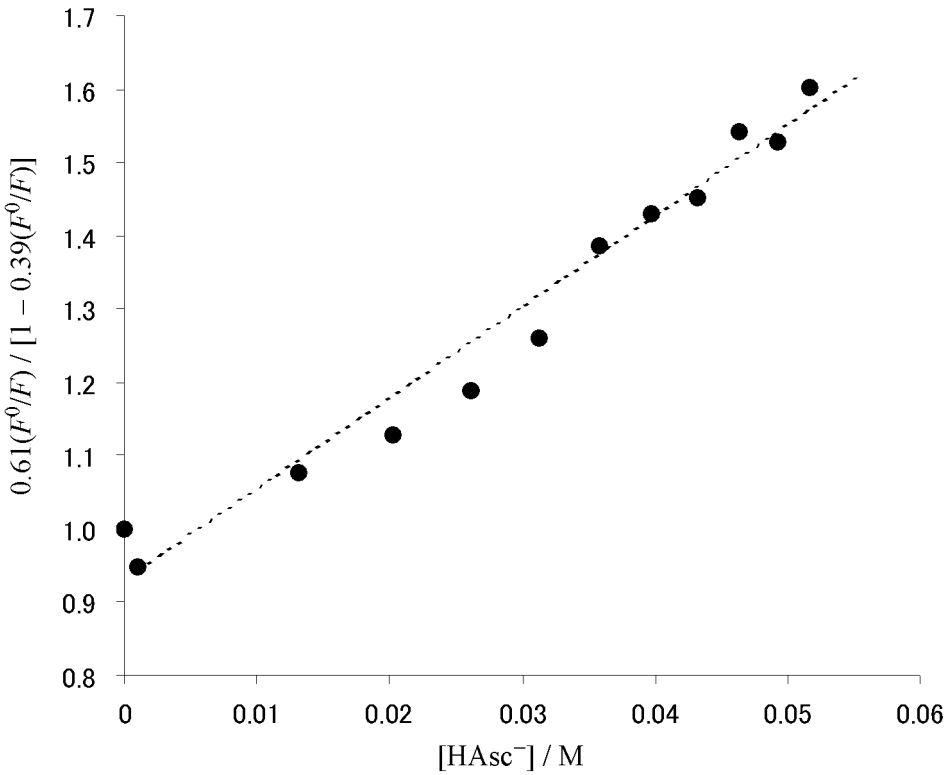

Fig. S6 Modified Stern-Volmer plot for quenching of emission from $[Ru(dtb)(bpy)_2]^{2+}$ (λ_{ex} = 450 nm) with sodium ascorbate (HAscNa) in vesicle solution (Tris-HCl, pH 7.5, C_s(Ru) = 46 μM). The quenching data are analyzed by assuming that $HAsc^-$ can quench the emission only from the Ru complexes located in the vesicle membranes close to the outer aqueous solution, the fraction of which is estimated to be 0.61. The least-square analysis of the plot yields a quenching constant, $k_q\tau$, of 12.3 M^{-1}.

Derivation of Modified Stern-Volmer equation. Assuming that $HAsc^-$ added to the outer the aqueous solution can quench the emission only from the sensitizers located in the vesicle membranes close to the outer aqueous solution (S_o), but not from the sensitizers close to the inner waterpool (S_i), the rate laws for the sensitizers in their excited state are described by the following equations,

$$-\frac{d}{dt}[S_o{}^*] = \alpha I - (\tau_0{}^{-1} + k_q[HAsc^-])[S_o{}^*]$$

$$-\frac{d}{dt}[S_i{}^*] = (1 - \alpha)I - \tau_0{}^{-1}[S_i{}^*]$$

where α and I are the fraction of sensitizers located in the vesicle membranes close to the outer aqueous solution and the number of photons absorbed by the sensitizers in unit time, respectively, and τ_0 is the lifetime of the excited state of the sensitizer in the absence of $HAsc^-$. Applying a steady-state approximation to $S_o{}^*$ and $S_i{}^*$, we can write the intensity of fluorescence, F, which is proportional to a total concentration of the sensitizers in the excited state, as

$$F = C\left[\frac{\alpha I}{\tau_0{}^{-1} + k_q[HAsc^-]} + \frac{(1 - \alpha)I}{\tau_0{}^{-1}}\right]$$

where C is a proportionality constant. If we write the intensity of fluorescence in the absence of $HAsc^-$ as F^0, we can obtain Eq. (S1).

$$\frac{F^0}{F} = \frac{1 + k_q\tau_0[HAsc^-]}{1 + (1 - \alpha)k_q\tau_0[HAsc^-]} \qquad \text{(S1)}$$

Modification of Eq. (S1) gives a modified Stern-Volmer equation Eq. (S2).

$$\frac{(F^0/F)\alpha}{1 - (F^0/F)(1 - \alpha)} = 1 + k_q\tau_0[HAsc^-] \qquad \text{(S2)}$$

Assuming that the $[S_o]/[S_i]$ ratio is equal to a ratio of the surface area of outer sphere to that of inner sphere of the vesicle, the diameter and the membrane thickness of which are roughly estimated to be 50 and 5 nm,[S1] respectively, we used $\alpha = [S_o]/([S_o] + [S_i]) = 0.61$ in the modified Stern-Volmer plot shown in Fig. S6.

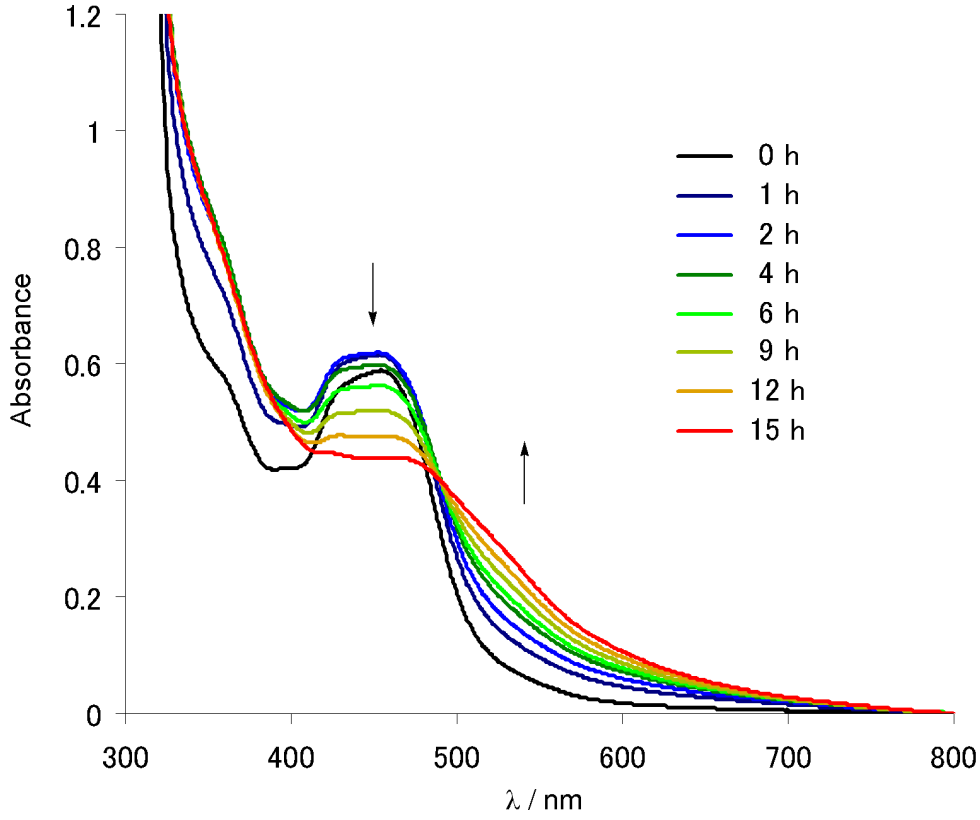

Fig. S7 Changes in the absorption spectra during the photocatalytic reduction of CO_2 in the vesicle solution (Tris-HCl, pH 6.5, C_s(Ru) = 41 μM, C_s(Re) = 40 μM, [HAsc$^-$] = 0.10 M, > 390 nm).

Table S1 Dependence of the initial rate of CO formation on the concentration of the sensitizer $[Ru(dtb)(bpy)_2]^{2+}$ in the photocatalytic reduction of CO_2 in the vesicle solution [a]

n[b] / μmol	C_s(Ru)[c] / μM	C_s(Re)[d] / μM	I(rel)[e]	Reduction products		v_i[f] / μmol h^{-1}	TON(Re)[g]
				CO / μmol	H_2 / nmol		
0	0	40	0.000	< 0.01	< 1	0.0	0.0
0.065	5.70	40	0.137	0.77	1.9	0.39	6.4
0.13	11.4	40	0.256	1.8	2.4	0.90	15
0.26	21.3	40	0.432	4.4	6.2	2.2	37
0.52	38.3	40	0.659	6.2	6.9	3.1	52
1.0	81.0	40	1.0	5.6	16	2.8	47

[a] Irradiation was carried out in the solution (3.0 mL) of DPPC vesicle containing both of the Ru and Re complexes in a Tris-HCl buffer (pH 6.5) in the presence of $HAsc^-$ (0.10 M) with the light of > 440 nm for 2 h. [b] Amounts of $[Ru(dtb)(bpy)_2]^{2+}$ employed in the vesicle preparation. [c] Concentration of $[Ru(dtb)(bpy)_2]^{2+}$ determined by UV-vis spectrum. [d] Concentration of $Re(dtb)(CO)_3Cl$ estimated by using the vesicle solution prepared without the Ru complex. [e] Relative values of the number of photons absorbed by the sensitizer estimated by the integration of $I_f(\lambda)(1 - 10^{-\varepsilon(\lambda)Cs l})$. ($I$(rel) = 1.00 for C_s(Ru) = 81.0 μM). [f] Initial rate of CO formation. [g] Turnover number for the Re complex used.

Table S2 Dependence of the initial rate of CO formation on the concentration of the Re complex $Re(dtb)(CO)_3Cl$ in the photocatalytic reduction of CO_2 in the vesicle solution [a]

n[b] / μmol	C_s(Ru)[c] / μM	C_s(Re)[d] / μM	Reduction products		v_i[e] / μmol h^{-1}	TOF(Re)[f] / h^{-1}	η_{el}[g]
			CO / μmol	H_2 / nmol			
0	32.7	0	0.18	23	0.09	–	0
0.065	36.8	5.0	2.8	72	1.4	93	0.29
0.13	36.0	10	4.1	26	2.1	68	0.45
0.26	36.8	20	6.1	17	3.1	51	0.62
0.52	39.3	40	7.0	15	3.5	29	0.76
0.78	39.8	60	8.6	53	4.3	24	0.83

[a] Irradiation was carried out in the solution (3.0 mL) of DPPC vesicle containing both of the Ru and Re complexes in a Tris-HCl buffer (pH 6.5) in the presence of $HAsc^-$ (0.10 M) with the light of > 390 nm for 2 h. [b] Amounts of $Re(dtb)(CO)_3Cl$ employed in the vesicle preparation. [c] Concentration of $[Ru(dtb)(bpy)_2]^{2+}$ determined by UV-vis spectrum. [d] Concentration of $Re(dtb)(CO)_3Cl$ estimated by assuming that the concentration in the vesicle solution is proportional to the amounts employed in the vesicle preparation. [e] Initial rate of CO formation. [f] Turnover frequency for the Re complex used. [g] The efficiency of the electron transfer from $[Ru(dtb)(bpy)_2]^+$ to the Re complex calculated on the basis of the analysis of Fig. 4, in which $k_{el}\tau_s m$ is estimated to be 0.080 μM^{-1}.

References

S1 J. N. Robinson and D. J. Cole-Hamilton, Electron transfer across vesicle bilayers, *Chem. Soc. Rev.,* 1991, **20**, 49-94.