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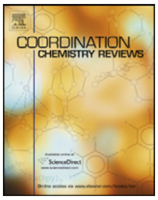

Review

# Development of efficient photocatalytic systems for $CO_2$ reduction using mononuclear and multinuclear metal complexes based on mechanistic studies

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ABSTRACT

Photocatalytic systems for $CO_2$ reduction using metal complexes, especially rhenium(I) complexes as a main component, are reviewed: mononuclear Re(I) complexes, mixed systems with two different Re(I) complexes, and supramolecule systems with a Re(I) complex connected to a ruthenium(II) complex. We focus on the mechanistic studies and the architecture for constructing the photocatalytic systems based on the mechanism.

## 1. Introduction

Global warming caused by increasing atmospheric $CO_2$ concentration and the depletion of fossil fuels are two problems that must be addressed in the near future. If we could convert $CO_2$ efficiently to useful compounds with solar light as an energy source, both these serious problems could be solved at once.

Reduction of $CO_2$ is a difficult task because of its stability as the most oxidized carbon compound. High reduction potential is required for electrochemical activation of $CO_2$, i.e. $-1.9$ V vs. NHE for one-electron reduction of $CO_2$ [1], giving unstable $CO_2^{\bullet-}$, which is difficult to handle. However, these difficulties can be solved by introducing multi-electron transfer into the reduction of $CO_2$. Scheme 1 shows the redox reactions affording the stable reduction products of $CO_2$ and also the potentials for the reactions. For example, the reduction potentials for converting $CO_2$ to CO and formic acid (Eqs. (1) and (2)), are about 1.3 eV lower than that of the one-electron reduction of $CO_2$. This consideration strongly suggests that a multi-electron redox system is necessary for constructing a practical photocatalytic system for $CO_2$ reduction.

Both the excited state and one-electron reduced (OER) species of metal complexes, which are respectively produced by light-absorption and photochemical electron transfer with a reductant, have strong reduction abilities. In the case of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), as a typical example of redox photosen-

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$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E° = -0.61\ V \quad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E° = -0.53\ V \quad (2)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E° = -0.48\ V \quad (3)$$

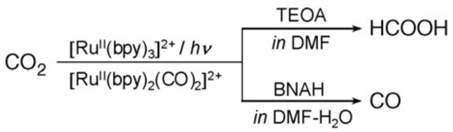
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E° = -0.38\ V \quad (4)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E° = -0.24\ V \quad (5)$$

**Scheme 1.** Redox potentials vs. NHE for multi-electrons reduction of $CO_2$ in an aqueous solution at pH 7 [1].

sitizer, its reducing power increases to $E_{ox} = -0.59$ V vs. NHE by absorbing the excitation energy while that of the ground state is +1.53 V vs. NHE. Because, however, photochemical electron transfer can be generally caused only by one-electron transfer, a catalyst which can convert photochemical one-electron transfer to multi-electron reduction of $CO_2$ is required in addition to the redox photosensitizer for photocatalytic fixation of $CO_2$.

As a typical example, the mixed system of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ is briefly introduced [2–4]. Photochemical reduction of $CO_2$ proceeds efficiently using $[Ru(bpy)_3]^{2+}$ as a photosensitizer and $[Ru(bpy)_2(CO)_2]^{2+}$ as a catalyst in the presence of reductant such as an NAD(P)H model compound. In this photocatalytic system, the OER species $[Ru^{II}(bpy^{\bullet-})(bpy)_2]^+$ is generated by sequential processes of excitation of $[Ru(bpy)_3]^{2+}$ and quenching of its lowest excited state ($^3$MLCT) by the reductant. Reduction of $CO_2$ proceeds via electron capture by the catalyst $[Ru(bpy)_2(CO)_2]^{2+}$ from the OER species. A $CO_2$ molecule coordinates to an open site on the ruthenium center, which is produced by dissociation of one of the CO ligands after the reduction of $[Ru(bpy)_2(CO)_2]^{2+}$. The pH of the reaction solution determines the reaction product(s) of $CO_2$. Protonation gives the carboxylato complex $[Ru(bpy)_2(CO)(COOH)]^{2+}$, and the carboxylato complex then dissociates the carboxylate ligand to formic acid by further two-electron reduction at pH > 9.5 or enters the CO production cycle by protonation and dehydration of the carboxylate ligand, which reproduce $[Ru(bpy)_2(CO)_2]^{2+}$ (Eq. (6)). Although in both cases, capture of another electron by the intermediate is required for production of HCOOH and CO; however, the origin of this electron has not been discovered.



(6)

Table 1 summarizes some reported photocatalytic systems for $CO_2$ reduction, which do not include semiconductor photocatalysts. In any cases, $[Ru(bpy)_3]^{2+}$ and its derivatives have also been used as a photosensitizer. When $[Co(bpy)_n]^{2+}$ [5,6], $[Co(macrocycle)]^{2+}$ [7], and $[Ni(cyclam)]^{2+}$ [8,9] have been used as catalysts, the photocatalytic reactions also proceed via photochemical reduction of $[Ru(bpy)_3]^{2+}$ by the reductant, and CO is formed as a dominant reduction product of $CO_2$. However, such photocatalytic systems have problems on both the selectivity of products and the efficiency of the $CO_2$ reduction because competition with the hydrogen evolution from hydride complexes produced as a key intermediate in the photocatalytic reactions [10].

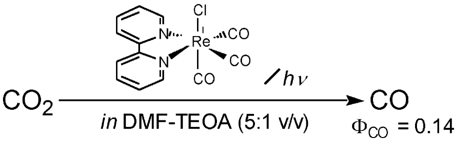
In the presence of viologen dications ($V^{2+}$), the excited state of $[Ru(bpy)_3]^{2+}$ is oxidatively quenched to give the viologen cation radical ($V^{\bullet+}$) and $[Ru(bpy)_3]^{3+}$, which is reduced by the reductant to recover $[Ru(bpy)_3]^{2+}$ (Nos. 5 and 6 in Table 1). The produced $V^{\bullet+}$ affords one-electron to the catalyst which reduces $CO_2$ (the role of $V^{2+}$ is called redox mediator). For example, the use of formate dehydrogenase as a catalyst gives HCOOH selectively in the photocatalytic system [11]. On the other hand, Ru or Os colloid used as a catalyst gives $CH_4$ as a $CO_2$ reduction product with $H_2$ evolution [12]. Use of $[Ru(bpz)_3]^{2+}$ (bpz = bipyrazine) instead of the combination system of $[Ru(bpy)_3]^{2+}$ and $V^{2+}$ induces selective production of $CH_4$ in the presence of the Ru colloid and TEOA. Although $H_2$ evolution is suppressed, the efficiency of $CO_2$ reduction is still low ($\Phi = 4.0 \times 10^{-4}$) [12,13].

The photocatalytic activities of rhenium(I) diimine complexes *fac*-$[Re^I(LL)(CO)_3(L')]^{n+}$ [5,14–20] and *cis,trans*-$[Re^I(LL)(CO)_2(L')_2]^{n+}$ [21–23] (LL = bidentate diimine ligand, L′ = monodentate ligand) have been extensively investigated for last two decades because of their high and unique photocatalytic abilities. This type of rhenium(I) complex is a unique photocatalyst, which can work without another complex as photosensitizer or catalyst.

In this review, we summarize mechanistic studies aiming at the development of highly efficient photocatalytic systems for $CO_2$ reduction using rhenium(I) complex(es) as key player(s), and we will also review supramolecular photocatalytic systems for efficient $CO_2$ reduction with visible light.

## 2. Photocatalytic $CO_2$ reduction using a mononuclear rhenium(I) complex

Lehn and his co-workers [15] have reported that *fac*-$Re(bpy)(CO)_3X$ (X = Cl, Br) works as photocatalyst for $CO_2$ reduction to selectively produce CO [5,15]. Quantum yield of the CO formation was 0.14 (X = Cl), which was the most efficient photocatalyst for $CO_2$ reduction at that time (Eq. (7)). Another advantage of this photocatalytic system is the relatively small, or completely absent formation of by-product(s) such as hydrogen and formic acid.



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The reaction mechanism of the photocatalytic $CO_2$ reduction using these rhenium(I) complexes has attracted much attention because of their unique and excellent properties as described above. The starting process of the photocatalytic reaction, which has been clarified with laser spectroscopy [24–26], is the reductive quenching of the triplet metal-to-ligand charge transfer ($^3$MLCT) excited state of the rhenium complex by triethanolamine (TEOA), generating one-electron reduced (OER) species of the rhenium

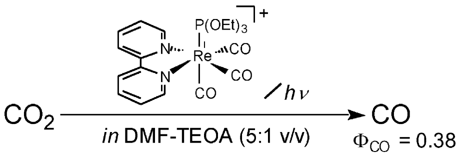
**Table 1**
Photocatalytic $CO_2$ reduction systems using photosensitizer and catalyst.

| | Photosensitizer | Catalyst | Reductant | Product | Ref. |
|---|---|---|---|---|---|
| 1 | $[Ru(bpy)_3]^{2+}$ | $[Co(bpy)_n]^{2+}$ | $R_3N$ | CO, $H_2$ | [5,6] |
| 2 | $[Ru(bpy)_3]^{2+}$ | $[Co(macrocycle)]^{2+}$ | Ascorbic acid | CO, $H_2$ | [7] |
| 3 | $[Ru(bpy)_3]^{2+}$ | $[Ni(cyclam)]^{2+}$ | Ascorbic acid | CO, $H_2$ | [8,9] |
| 4 | $[Ru(bpy)_3]^{2+}$ | $[Ru(bpy)_2(CO)_2]^{2+}$ | $R_3N$ or BNAH | CO, HCOOH | [2–4] |
| 5 | $[Ru(bpy)_3]^{2+}$ | Viologen derivatives/formate dehydrogenase | Cysteine | HCOOH | [11] |
| 6 | $[Ru(bpy)_3]^{2+}$ | Viologen derivatives/Ru, Os colloids | $R_3N$ | $CH_4$, $H_2$ | [12] |
| 7 | $[Ru(bpz)_3]^{2+}$ | Ru colloid | $R_3N$ | $CH_4$ | [12,13] |

complex $[Re^{I}(bpy^{\bullet -})(CO)_3X]^-$. The following processes should not be simple. There are still many important questions about the reaction mechanism of the photocatalytic $CO_2$ reduction using the rhenium complexes, which are as follows: (1) which ligand dissociates before coordination of $CO_2$ to the rhenium center in the photocatalytic cycle, (2) what structure does the $CO_2$ adduct have, and (3) which species donates another electron to the OER species or the $CO_2$ adduct, and so on.

Lehn and his co-workers [15] have reported the following clues: (1) substitution of the $Br^-$ ligand from *fac*-$Re(bpy)(CO)_3Br$ with $Cl^-$, which was added into the reaction solution during the photocatalytic reaction, (2) increasing the durability of the photocatalyst in the presence of excess $X^-$ in contrast to addition of excess bpy, which did not cause any effects on the photocatalytic reaction, (3) gradual formation of *fac*-$Re(bpy)(CO)_3(OCHO)$, which has a much lower photocatalytic ability for $CO_2$ reduction, and (4) formation of isotope labeled products with $^{13}CO$, i.e. *fac*-$Re^{I}(bpy)(^{13}CO)_3X$ and *fac*-$Re^{I}(bpy)(^{13}CO)_3(O^{13}CHO)$ when the photocatalytic reaction proceeded under a $^{13}CO_2$ atmosphere. From these experimental results they supposed that the elimination of the CO ligand and/or one of the pyridine units in the bpy ligand might be an important process but $Cl^-$ loss might not be. On the other hand, electrochemical studies [27] have suggested dissociation of the $Cl^-$ ligand is an important process for $CO_2$ reduction. One of the reasons which induces such a mechanistic confrontation should be the instability of the OER species of *fac*-$Re(bpy)(CO)_3X$.

The chloro ligand on *fac*-$Re(bpy)(CO)_3Cl$ can be easily substituted with various phosphorus ligands $PR_3$ (R = alkyl, alkoxy, or allyl group) giving *fac*-$[Re(bpy)(CO)_3(PR_3)]^+$ [28], of which the photocatalytic abilities for $CO_2$ reduction are highly affected by the phosphorus ligand [17]. For example, *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ is an efficient photocatalyst with the quantum yield of 0.38 for producing CO by irradiation with 365-nm light [14], which is twice as large compared with that with *fac*-$Re(bpy)(CO)_3Cl$ (Eq. (8)). Incomparably longer excited-state lifetime (920 ns) of *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ than *fac*-$Re(bpy)(CO)_3Cl$ ($\tau$ = 25 ns) and stronger oxidation power ($^*E_{red}$ = +0.82 V vs. Ag/AgNO$_3$) cause efficient reductive quenching of the excited state by TEOA, giving the OER species $[Re^{I}(bpy^{\bullet -})(CO)_3\{P(OEt)_3\}]$. This OER species is a fairly stable in solution under anaerobic conditions even at room temperature.



(8)

On the contrary, *fac*-$[Re(bpy)(CO)_3(PPh_3)]^+$ has very low photocatalytic ability, even though its excited state is also reductively quenched by TEOA efficiently giving the corresponding OER species $[Re(bpy^{\bullet -})(CO)_3(PPh_3)]$ [16]. Dissociation of the $PPh_3$ ligand from the OER species efficiently occurs giving the OER species of the solvento complexes $[Re(bpy^{\bullet -})(CO)_3(S)]$ (S = DMF, TEOA). These OER species have strong reducing power ($E_{1/2}$ = −1.57 and −1.64 V vs. Ag/AgNO$_3$, respectively) and donate an electron to another *fac*-$[Re(bpy)(CO)_3(PPh_3)]^+$ ($E_{1/2}$ = −1.56 V vs. Ag/AgNO$_3$). This electron transfer triggers a chain reaction, which converts the $PPh_3$ complex to the solvento complexes. In consequence, *fac*-$[Re(bpy)(CO)_3(PPh_3)]^+$ is rapidly converted to the solvento complexes, which have low photocatalytic abilities, in the first stage of the photocatalytic reaction. The species *fac*-$[Re(bpy)(CO)_3(py)]^+$ (py = pyridine) has a low photocatalytic ability because it decomposes by a similar chain reaction [18].

The thiocyanato complex *fac*-$Re(bpy)(CO)_3(NCS)$ is an efficient photocatalyst for $CO_2$ reduction producing CO with quantum yield of 0.30 while *fac*-$Re(bpy)(CO)_3(CN)$ has no photocatalytic ability [19,20].

As described, the photocatalytic abilities of the *fac*-$[Re(bpy)(CO)_3L]^{n+}$ type complexes for $CO_2$ reduction are strongly affected by the monodentate ligand L.

## 3. Reaction mechanism of the photocatalytic $CO_2$ reduction

### 3.1. Properties of the OER species

The OER species of *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$, which can work as efficient photocatalyst for $CO_2$ reduction, is fairy stable in solution at room temperature as described above because of the strong electron-withdrawing property of the $P(OEt)_3$ ligand. The lifetime of the OER species, which was generated by the photo-induced electron transfer from TEOA, is 514 s under an Ar atmosphere [17]. Fig. 1(a) shows the UV–vis absorption spectrum of the OER species generated by the continuous photoirradiation in the presence of TEOA. The spectrum shows the characteristic bands (at around 500 nm) with vibronic structure and a weak broad band at longer wavelength, which are attributed to the anionic radical of the bpy ligand. Flow-electrolysis of *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ gives quantitative production of this OER species [21], and the UV–vis and IR spectroscopic change are shown in Fig. 1(b) and (c). The molar extinction coefficient of the OER species obtained using this method was 5300 $M^{-1}$ $cm^{-1}$ at 504 nm. By using this coefficient, it is clear that the OER species is almost quantitatively produced by the photoirradiation in the presence of TEOA (Fig. 1(a)).

The IR spectrum of the OER species showed that three CO stretching bands are shifted 24–37 $cm^{-1}$ to lower wavenumber compared with the non-reduced complex, i.e. *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ Fig. 1(c). This suggests that the odd electron localizes mainly on the bpy ligand but not on the Re center [24,25,29].

Because the OER species $[Re^{I}(bpy^{\bullet -})(CO)_3\{P(OEt)_3\}]$ is accumulated in the reaction solution, its reactivity can be followed by the UV–vis absorption spectroscopic changes of the reaction solution as shown in Fig. 1(a) [17]. The quantitative formation of the OER species in the first stage of the photocatalytic reaction clearly indicates that formation of the OER species by irradiation is much more rapid than the following process(es). The quantum yield of formation of the OER species was 2, showing that an α-amino radical, which is a deprotonation product of $TEOA^{\bullet +}$ generated by the electron transfer to the excited state of the complex, can reduce another *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ [14]. The decay profile of the OER species in the dark, obeyed second-order kinetics for [OER] under an Ar atmosphere ($k_2$ = 25.4 $M^{-1}$ $s^{-1}$ for *fac*-$[Re(4,4'\text{-}Me_2bpy)(CO)_3\{P(OEt)_3\}]^+$). On the other hand, decay was accelerated under a $CO_2$ atmosphere and could be analyzed using linear combination of first-order kinetics for [OER] (Eq. (9); $k_1 = 3.5 \times 10^{-4}$ to $1.9 \times 10^{-2}$ $M^{-1}$ $s^{-1}$, see Table 2) with the second-order one ($k'_2$ = 23.3 $M^{-1}$ $s^{-1}$ for *fac*-$[Re(4,4'\text{-}Me_2bpy)(CO)_3\{P(OEt)_3\}]^+$). The first-order component is understandable as a pseudo first-order reaction of the OER species with excess $CO_2$, while the $k'_2$ well agreed with $k_2$.

Assuming that the reaction of the OER species with $CO_2$ quantitatively gives CO, the amount of CO formed during the photocatalytic reaction can be calculated using Eq. (10). On the other hand, if disproportionation of the OER species, which should obey second-order kinetics, mainly gave CO, formation of CO could be calculated using Eq. (11). Total amounts of CO formed during the photocatalytic reaction were always half of the value calculated using Eq. (10), but no relationship was observed with the value using Eq. (11). This strongly indicates that the photocatalytic CO formation proceeds via the reaction of the OER species or a deriva-

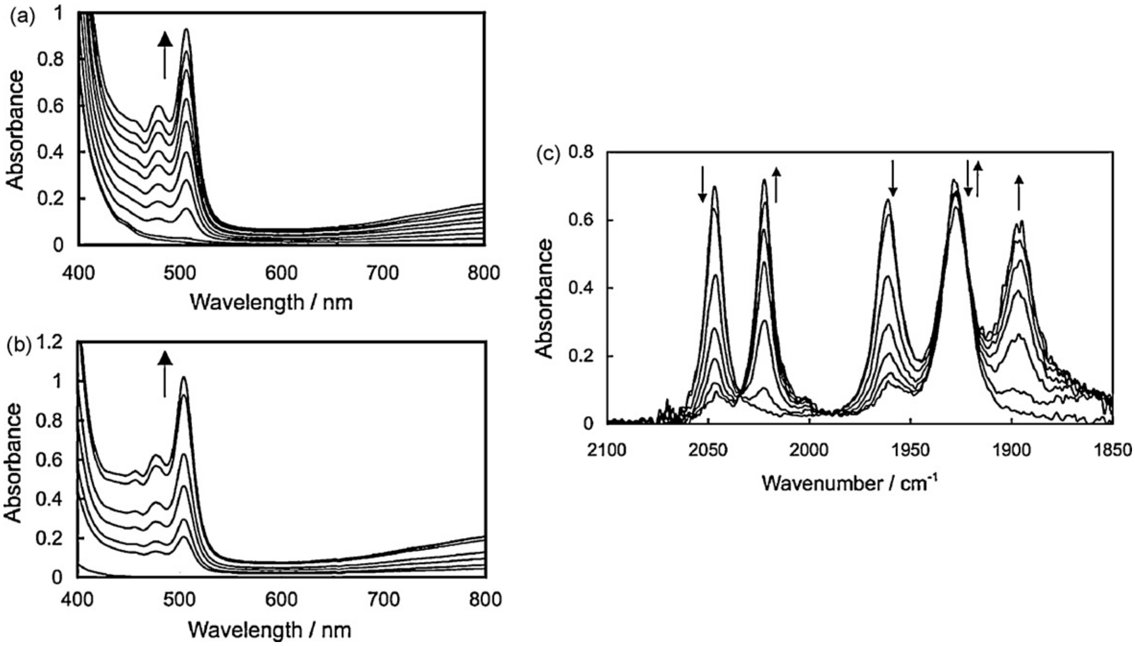


**Fig. 1.** UV–vis absorption spectroscopic changes of (a) a DMF-TEOA (5:1, v/v) solution containing *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (2.5 mM) during irradiation with 365-nm light (b) an MeCN solution of *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (1.5 mM) during flow-electrolysis under an Ar atmosphere ($E = -1.25$ to $-1.75$ vs. $Ag/AgNO_3$)[17]. IR spectroscopic change of the same solution as (b) is shown in (c).

tive which should be produced via an unimolecular reaction of the OER species with $CO_2$.

$$-\frac{d[OER]}{dt} = k_1[OER][CO_2] + k_2[OER]^2$$

$$([OER]) = \text{concentration of the OER species}) \quad (9)$$

$$[CO] = \int_0^t k_1[OER][CO_2]\,dt \quad (10)$$

$$[CO] = \int_0^t k_2[OER]^2\,dt \quad (11)$$

### 3.2. Photocatalysis vs. redox potential

The photocatalytic abilities of a series of *fac*-$[Re(4,4'\text{-}Y_2bpy)(CO)_3(PR_3)]^+$ with various substitution groups Y at the 4,4′ position of the bpy ligand and/or various phosphorus ligand were compared to each other. The results are summarized in Table 2. The complexes with H and Me as Y showed high photocatalytic abilities while introduction of electron withdrawing $CF_3$ groups made the photocatalysis of the complex much lower. The reaction rate of the OER species with $CO_2$ was also strongly affected; that of the complexes with Y = Me and H were one-order larger than that with Y = $CF_3$. Furthermore, the electron-withdrawing ability of the phosphorus ligand, which can be quantified by Tolman's $\chi$ value shown in Table 2, also strongly affected photocatalyses of the rhenium(I) complexes and the reactivities of the corresponding OER species. A rhenium complex with a more electron-withdrawing ligand, such as trialkylphosphite, has a higher photocatalytic ability with larger $k_1$. These results are consistently understandable by comparing the first reversible reduction potentials ($E_{1/2}$) for the complexes: the OER species with $E_{1/2} > -1.4$ V vs. $Ag/AgNO_3$ have poor photocatalytic abilities for $CO_2$ reduction (Table 2).

Because the OER species cannot reduce $CO_2$ via an outer-sphere one-electron reduction process, the good correlation among $E_{1/2}$, the $CO_2$ reduction ability, and $k_1$ is attributable to increasing reactivity of the 17-electron species, which is produced by dissociation of a ligand with $CO_2$. The fact that the values estimated with Eq. (10) for CO formation were about half of the experimental amount indicates that both two electrons used for reduction of $CO_2$ to form CO are donated by the OER species.

**Table 2**
Photocatalytic $CO_2$ reduction using *fac*-$[Re(2,2'\text{-}Y_2bpy)(CO)_3(PR_3)]^+$,[a] reaction of the corresponding OER species with $CO_2$, and their reduction potentials [17]. Adapted with permission from [17]. Copyright 1997 American Chemical Society.

| $[Re(Y_2bpy)(CO)_3(PR_3)]^+$ | | $\Phi_{CO}$[b] | $k_1$[c]/$10^{-5}$ $M^{-1}$ $s^{-1}$ | $\chi$[d] | $-E_{1/2}$[e]/V |
|---|---|---|---|---|---|
| Y | $PR_3$ | | | | |
| H | $P(n\text{-}Bu)_3$ | 0.013 | 10.7 | 5.25 | 1.39 |
| H | $PEt_3$ | 0.024 | 3.5 | 6.30 | 1.39 |
| H | $P(O\text{-}i\text{-}Pr)_3$ | 0.20 | 94.2 | 19.05 | 1.44 |
| H | $P(OEt)_3$ | 0.16 | 56.0 | 21.6 | 1.43 |
| H | $P(OMe)_3$ | 0.17 | 60.0 | 24.1 | 1.41 |
| Me | $P(OEt)_3$ | 0.18 | 186 | | 1.55 |
| $CF_3$ | $P(OEt)_3$ | 0.005 | 5.2 | | 1.03 |

[a] A DMF-TEOA (5:1, v/v) solution containing the complex (2.6 mM) was irradiated at 365 nm (light intensity, $1.27 \times 10^{-8}$ Einstein $s^{-1}$).
[b] Quantum yield of CO formation.
[c] Second-order reaction rate constants of the OER species and $CO_2$ (0.139 M).
[d] Tolman's $\chi$ [30].
[e] Reduction potentials of the complexes vs. $Ag/AgNO_3$.

### *3.3. Ligand dissociation from the OER species*

The information on ligand loss from the OER species during the photocatalytic $CO_2$ reduction was obtained by careful comparison among the photocatalytic reactions using three complexes each with a different anionic ligand, i.e. *fac*-Re(bpy)$(CO)_3$X (X = $NCS^-$ (**Re-NCS**), $Cl^-$ (**Re-Cl**), $CN^-$ (**Re-CN**)) [20]. Both **Re-NCS** and **Re-Cl** work as photocatalyst for $CO_2$ reduction while **Re-CN** cannot. The photocatalytic ability of **Re-NCS** is about twice higher than that of **Re-Cl**. Although both the lifetime of the excited state of all these complexes ($\tau$ = 25–87 ns in solution at room temperature) and the quenching rate constant of emission by TEOA ($k_q = 10^7$ to $10^8\,M^{-1}\,s^{-1}$) were similar, the behaviors of the OER species formed by the reductive quenching were very different. In the case of **Re-NCS** and **Re-CN**, 6% and 15% of the OER species were accumulated in the first stage of the photocatalytic reaction (light intensity = $7.5 \times 10^{-9}$ Einstein $s^{-1}$), respectively, while only a small amount of the OER species of **Re-Cl** was detected (maximum yield <1%). The OER species of **Re-NCS** more rapidly decayed in the dark in the presence of $CO_2$ than under an Ar atmosphere ($\tau_{1/2}$ = 98 s under an Ar atmosphere; 49 s under a $CO_2$–Ar (1:1) mixed gas atmosphere; and 39 s under a $CO_2$ atmosphere). In the case of **Re-Cl**, $\tau_{1/2}$ under a $CO_2$ atmosphere was less than 1 s while 39 s under an Ar atmosphere. These results clearly indicate that both the OER species of **Re-NCS** and **Re-Cl** react with $CO_2$. On the other hand, the OER species of **Re-CN** has no reactivity to $CO_2$, i.e. the decay profile of the OER species of **Re-CN** did not change between under an Ar atmosphere and a $CO_2$ atmosphere ($\tau_{1/2}$ = 33–44 s) though a similar amount of the corresponding OER species to the case of **Re-NCS** was accumulated under a photo-irradiation.

Fig. 2 shows the accumulated amounts of the OER species of the three complexes during the photocatalytic reaction. In the cases of **Re-NCS** and **Re-Cl** which show photocatalytic abilities, the concentration of the corresponding OER species decreased quickly within 30-min irradiation and then reached a photostationary state. The drastic increase of the concentration of the OER species of **Re-NCS** at the photostationary state was observed in the presence of excess $SCN^-$ (Fig. 2a). This clearly indicates that the decrease of the OER species of **Re-NCS** in the initial stage of the photocatalytic reaction is attributed to loss of the $SCN^-$ ligand, and re-coordination of $SCN^-$ on the Re center causes the photostationary state.

The dissociation of the ligand $X^-$ from the OER species of **Re-NCS** and **Re-Cl** was also confirmed by analysis using HPLC of the reaction solution and capillary electrophoresis, i.e. $[Re(bpy)(CO)_3(O_2CH)]$, $[Re(bpy)(CO)_3(S)]^+$ (S = solvent), and $X^-$ ($SCN^-$ or $Cl^-$) were detected according to decrease of the starting complex. The amount of detected $X^-$ was almost same as the decreased amount of the starting complexes. The ligand dissociation should not be the simple deactivation process but an important process for the photocatalytic reaction. Although, as described above, addition of excess $SCN^-$ salt in the reaction solution of **Re-NCS** caused an increase of the steady-state concentration of the OER species, the photocatalytic ability did not increase at all, and the reaction rate of the OER species with $CO_2$ in the dark decreased ($\tau_{1/2}$ = 64 and 83 s in the presence of 50 and 100 mM $SCN^-$, respectively).

On the other hand, the OER species of **Re-CN** slowly decreased during irradiation, but a rapid decrease of the OER species, characteristic of dissociation of the anionic ligand, was not observed as shown in Fig. 2b. The complexes $[Re(bpy)(CO)_3(O_2CH)]$ and $[Re(bpy)(CO)_3(S)]^+$, and $CN^-$ were not detected in the irradiation solution at all. Loss of the $CN^-$ ligand from the OER species of **Re-CN**, which has no photocatalytic ability, should be too slow to proceed during the photochemical reaction in the presence of TEOA even under a $CO_2$ atmosphere.

These results strongly indicate that dissociation of the anionic ligand $X^-$ from the OER species is one of the important processes in

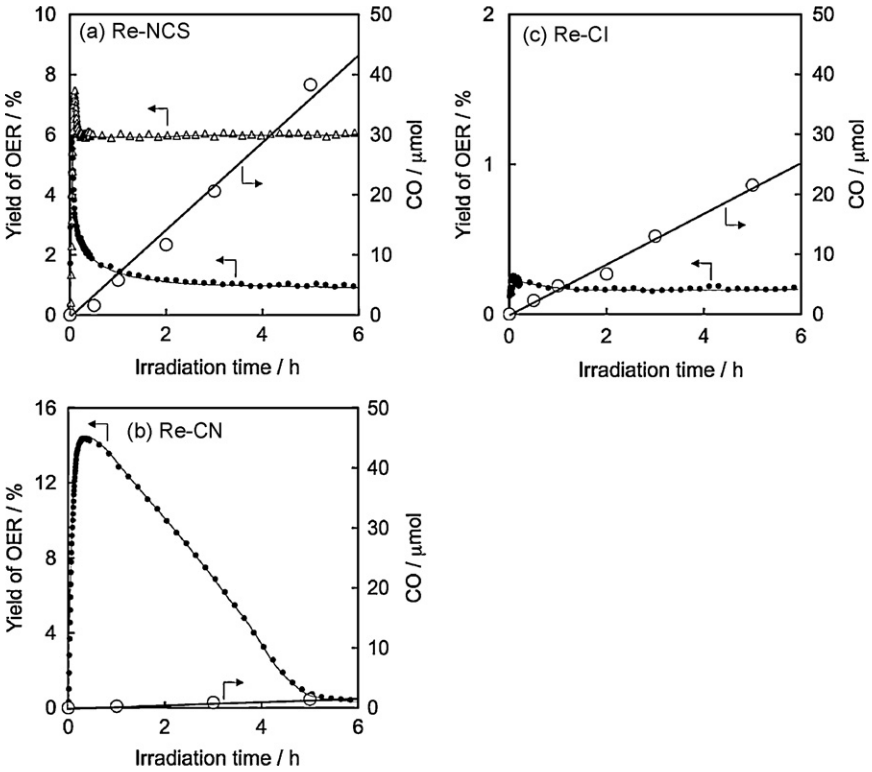


**Fig. 2.** CO generation (○) and concentration of the OER species (●) during photocatalytic reaction using 365-nm light with an intensity of $7.5 \times 10^{-9}$ Einstein/s: (a) *fac*-$[Re(bpy)(CO)_3(NCS)]$; (b) *fac*-$[Re(bpy)(CO)_3(CN)]$; (c) *fac*-$[Re(bpy)(CO)_3Cl]$ [20]. In (a), concentration of the OER species of **Re-NCS** in the presence of $SCN^-$ (50 mM) is also plotted using △.

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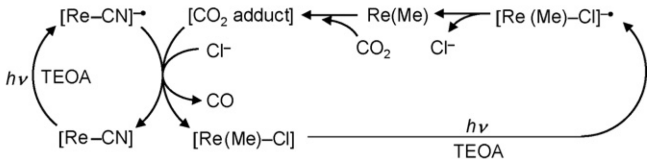
the photocatalytic reduction of $CO_2$ and that the "17e$^-$ species" formed via the ligand dissociation reacts with $CO_2$ but the OER species itself does not. The three CO ligands were equally substituted with $^{13}CO$ in the photocatalytic reactions using either **Re-NCS** or **Re-Cl** under a $^{13}CO_2$ atmosphere (22% of the CO ligands was substituted using **Re-NCS** at $TN_{CO} = 2.2$). This suggests that CO formed by the reduction of $CO_2$ is exchanged for the CO ligand, which slowly dissociates from the Re center.

The formation of $[Re(bpy)(CO)_3(O_2CH)]$ during the photocatalytic reaction is a deactivation process because of its low photocatalytic ability ($\Phi_{CO} = 0.05$) [15,16]. The other products $[Re(bpy)(CO)_3(S)]^{n+}$ (S = solvent, TEOA ($n = 1$) and $OCOC_2H_4N(C_2H_4OH)_2^-$ ($n = 0$)) also showed low photocatalytic ability ($\Phi_{CO} = 0.04$) because of the short lifetimes of the excited state. Accordingly, re-coordination of the dissociated $X^-$ into the Re center after CO formation to recover the starting complex should be another crucial process for maintaining the efficient photocatalytic ability and durability of the system.

The complex **Re-NCS** shows not only higher efficiency for $CO_2$ reduction but also higher durability ($TN_{CO} = 30$) compared with **Re-Cl**. When the photocatalytic reaction using **Re-NCS** (0.5 mM) proceeded in the presence of $Cl^-$, a photostationary state with a 1:3 mixture of **Re-NCS** and **Re-Cl** was reached after 5 h of irradiation. It is noteworthy that during the photostationary state, CO was continuously produced even in the presence of 20 times more $Cl^-$ than $SCN^-$, which should be produced from the OER species of **Re-NCS**; however, only a three times larger amount of **Re-Cl** than **Re-NCS** was produced during the photocatalytic reaction. This strongly suggests much more rapid reproduction of **Re-NCS** than production of **Re-Cl** by re-coordination of the $SCN^-$ to the Re center. As described above, both loss of the anionic ligand from the OER species and its re-coordination to the Re center after CO generation are important for the photocatalytic reduction of $CO_2$ using *fac*-$Re(bpy)(CO)_3X$ type of complexes. Although dissociation of the $Cl^-$ ligand is more rapid than the $SCN^-$ ligand, the re-coordination of $SCN^-$ is more efficient than $Cl^-$. The fact that **Re-NCS** has higher photocatalytic ability than **Re-Cl** offers the following guides for constructing efficient photocatalysts: the complex must have balanced properties for efficient elimination of the anionic ligand from the OER species and effective addition of the anion to the metal center after CO formation, but such properties seem to conflict with each other. Accordingly, design for a new photocatalytic system is necessary for developing more efficient photocatalysts for $CO_2$ reduction using rhenium(I) complexes.

Electrochemical investigations into the properties of the OER species of some rhenium(I) complexes and intermediates have also been reported regarding electrochemical $CO_2$ reduction. The studies using cyclic voltammetry, controlled potential electrolysis [27], and spectroelectrochemical techniques with UV–vis, FT-IR, and EPR spectroscopies of *fac*-$Re(bpy)(CO)_3Cl$ [29,31–34] have indicated the importance of the loss of the $Cl^-$ ligand from the OER species on the electrocatalytic reduction of $CO_2$. It has been suggested that dissociation of the $Cl^-$ ligand from the OER species is caused by destabilization of the **Re-Cl** bond induced by partial inflow of the odd electron in the $\pi^*$ orbital of the bpy ligand into the $d\sigma^*$ orbital of the **Re-Cl** bond [29]. Dissociation of the ligand L from the OER species of *fac*-$[Re(bpy)(CO)_3L]^{n+}$ occurs more rapidly in order of the following L = $Cl^-$, $Br^- >> PPh_3$, $n$-PrCN > $P(OMe)_3$, which is also in order of $\pi$-acceptability of the ligand L [32]. Therefore, it is reasonable that the OER species of the rhenium complex with the $NCS^-$ ligand is much more stable than the complex with $Cl^-$. The stability of the **Re-CN** bond has also been shown by the CV study at low temperature [35].

Generation processes of CO including formation of $CO_2$ adduct(s), which might reflect an activation process of $CO_2$ on the rhenium center, have been reported [36–40]. Gibson et al. synthesized a carboxylic acid complex *fac*-$Re(dmb)(CO)_3(COOH)$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) using the reaction of $Re(dmb)(CO)_4^+$ with KOH and detected generation of CO in the thermal decomposition process of the reduction. On the other hand, Fujita et al. detected the rhenium dimer bridged with $CO_2$, i.e. $Re(bpy)(CO)_3$-$CO_2$-$Re(bpy)(CO)_3$ by tracing the reaction of $CO_2$ and 17e$^-$ species $[Re^0(bpy)(CO)_3]$, which is generated by photochemical homolysis of $Re(bpy)(CO)_3$-$Re(bpy)(CO)_3$ in THF. $[Re(bpy)(CO)_3]$ exists in an equilibrium to the OER species of the solvento complex, i.e. $[Re^I(bpy^{\bullet-})(CO)_3(THF)]$. They have found that free $CO_2$ abstracts an oxygen atom from the bridging $CO_2$ ligand giving CO.



**Scheme 2.** Photocatalytic reaction mechanism of the multicomponent system.

### 3.4. Another electron source for CO production

In the case of the photocatalytic system containing **Re-NCS**, CO formation proceeds with accumulation of the OER species as described above. Because formation of CO from $CO_2$ requires two-electron reduction of $CO_2$, another electron should be necessary, which is inputted into the 17−e$^-$ species generated by the loss of the $SCN^-$ ligand from the OER species or the $CO_2$ adduct. The OER species itself has strong reducing power ($E_{1/2} = -1.61$ V vs. $Ag/AgNO_3$), which is possibly the second electron source. In fact, *fac*-$[Re(bpy)(CO)_3(PR_3)]^+$ and **Re-NCS**, OER species which are accumulated in high yield during the photocatalytic reaction, have higher abilities for $CO_2$ reduction compared with **Re-Cl**, which can afford a reaction site for $CO_2$ more rapidly as described above. From this point of view, we examined the addition effect of **Re-CN** ($E_{1/2} = -1.67$ V vs. $Ag/AgNO_3$), OER species of which can not react with $CO_2$, to the photocatalytic $CO_2$ reduction using *fac*-$Re(dmb)(CO)_3Cl$ (**Re(Me)-Cl**, dmb = 4,4′-dimethyl-2,2′-bipyridine, $E_{1/2} = -1.77$ V vs. $Ag/AgNO_3$), which cannot be reduced by the OER species of **Re-CN** [20]. Using 1:1 mixed systems of **Re(Me)-Cl** and **Re-CN** (each complex concentration was 0.11 mM), the photocatalytic CO formation rate increased 1.2 times compared with using **Re(Me)-Cl** independently, but accumulation of the OER species of **Re-CN** during the photocatalytic reaction with the mixed system drastically decreased from that with only **Re-CN**. This strongly indicates that the increase of CO formation using the mixed system is caused by electron donation from the OER species of **Re-CN** to an intermediate, probably the $CO_2$ adduct(s), which is generated from the OER species of **Re(Me)-Cl**. This reaction mechanism is as follows (Scheme 2). Both excited **Re-CN** and **Re(Me)-Cl** are quenched by TEOA, producing the corresponding OER species. The OER species of **Re(Me)-Cl** is converted to the $CO_2$ adducts via rapid dissociation of the $Cl^-$ ligand while the OER species of **Re-CN** accumulates in the reaction solution because of lack of dissociation of the $CN^-$ ligand and donates an electron to the $CO_2$ adduct, giving CO.

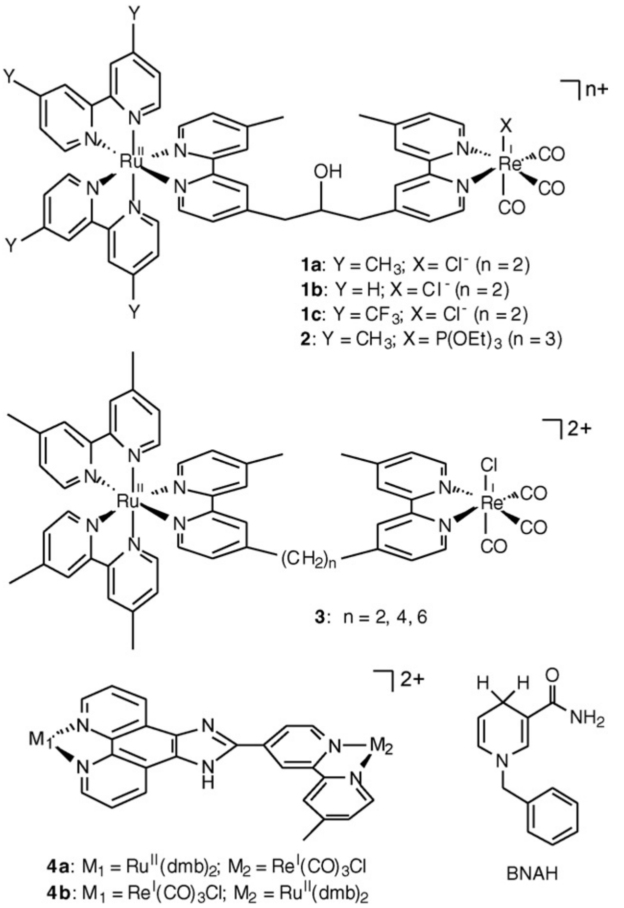
## 4. Multicomponent system constructed from different Re(I) mononuclear complexes

Based on the mechanistic study described above, important points for constructing efficient photocatalytic systems for $CO_2$ reduction using rhenium complexes can be drawn as follows: (1) efficient formation of the OER species of the complex via reductive quenching of the excited state by a sacrificial electron donor, (2) rapid loss of the monodentate ligand from the OER species and its rapid reaction with $CO_2$, (3) efficient reduction of the $CO_2$ adduct(s) with another OER species, and (4) efficient reproduction of the parent complex by re-coordination of the detached ligand to the rhenium center after CO formation. If only one rhenium complex is used as photocatalyst, factors (2) and (3) come into conflict each other because factor (2) requires that the OER species should be unstable for proceeding the ligand loss but the same OER species should be stable enough to pass an electron to the $CO_2$ adduct according to the factor (3).

Based on this consideration, a mixed system, which separates the two roles as photocatalyst (i.e. one is a redox photosensitizer and the other as a catalyst) was designed [32]. Results are summarized in Table 3. The best result was obtained using a mixed system with *fac*-$[Re\{4,4'\text{-}(MeO)_2bpy\}(CO)_3\{P(OEt)_3\}]^+$ (**Re(MeO)-P(OEt)$_3$**) as photosensitizer and *fac*-$[Re(bpy)(CO)_3(MeCN)]^+$ (**Re-MeCN**) as catalyst, and the optimized quantum yield for CO formation was 0.59 in the case of a 24:1 mixture of **Re(MeO)-P(OEt)$_3$** and **Re-MeCN**. This is the highest value among the reported homogeneous photocatalysts for $CO_2$ reduction [20]. This system can fulfill all the factors, especially (2) and (3) as follows. The formation quantum yield of the OER species of **Re(MeO)-P(OEt)$_3$** was almost 2 because $TEOA^{\bullet+}$, which is produced via efficient electron transfer from TEOA to the $^3$MLCT excited state, is deprotonated giving the corresponding α-amino radical which can also reduce another **Re(MeO)-P(OEt)$_3$** even in the dark, and therefore, factor (1) is completely fulfilled. The OER species of **Re(MeO)-P(OEt)$_3$** has enough strong reducing power ($E_{1/2} = -1.67$ V vs. Ag/$AgNO_3$) due to the electron-donating property of the MeO groups at 4,4′ positions of the bpy ligand to give one-electron to $[Re(bpy)(CO)_3(S)]^{n+}$ (**Re-S**: S = solvent ($n = 1$) and $OCOC_2H_4N(C_2H_4OH)_2^-$ ($n = 0$)), which formed via ligand substitution of **Re-MeCN** in the reaction solution, producing $[\mathbf{Re\text{-}S}]^{\bullet-}$. Rapid loss of ligand S from $[\mathbf{Re\text{-}S}]^{\bullet-}$ proceeds because of the weak bond between Re and S (the factor (2)). The OER species of **Re(MeO)-P(OEt)$_3$** can also work as electron donor to the $CO_2$ adduct(s) because of its stability and strong reducing power. Because **Re(MeO)-P(OEt)$_3$** is recovered via the electron transfer, the factors (3) and (4) are sufficiently fulfilled. As described here, the investigation into the reaction mechanism can provide useful information for constructing new photocatalytic systems with high activities.

## 5. Visible light driven $CO_2$ reduction with ruthenium(II)-rhenium(I) supramolecular photocatalysts

In view of the utilization of solar light it should be a problem that most of emissive rhenium complexes do not have strong absorption in the visible region. To overcome this problem, visible light driven efficient supramolecular photocatalytic systems for $CO_2$ reduction have been developed using a ruthenium(II) tris-diimine type complex as a redox photosensitizer, which has strong MLCT absorption in the visible region, covalently connected with rhenium(I) complex as a catalyst [41–43].



**Scheme 3.** Structures of the Ru-Re supramolecular photocatalysts and BNAH.

A DMF-TEOA (5:1, v/v) solution containing **1a** and 1-benzyl-1,4-dihydronicotinamide (BNAH, Scheme 3) as a reductant, which is a typical model compound of the coenzyme NAD(P)H, was irradiated with visible light giving CO selectively (Fig. 3) [32].

The photocatalytic ability of the supramolecule system was high, i.e. the quantum yield of CO formation ($\Phi_{CO}$) and its turnover number ($TN_{CO}$) reached to 0.12 and 170, respectively (irradiation at 480 nm). The predominance of the connection of the catalyst with the photosensitizer was clearly confirmed by comparison with a 1:1 mixture of the mononuclear complexes $[Ru(dmb)_3]^{2+}$ and *fac*-$Re(dmb)(CO)_3Cl$ ($\Phi_{CO} = 0.06$, $TN_{CO} = 101$).

**Table 3**
Quantum yields of CO formation in the mixed systems with rhenium(I) complexes[a].

| No. | Photocatalytic system | | $\Phi_{CO}$ |
|---|---|---|---|
| | Sensitizer (mM) | Catalyst (mM) | |
| 1 | $Re(bpy)(CO)_3(CN)$ | $[Re(bpy)(CO)_3(MeCN)]^+$ | |
| | 2.0 | 0.5 | 0.40 |
| 2 | $[Re\{(MeO)_2bpy\}(CO)_3\{P(OEt)_3\}]^+$ | $[Re(bpy)(CO)_3(MeCN)]^+$ | |
| | 2.5 | 0 | 0.33 |
| | 2.5 | 0.01 | 0.51 |
| | 2.4 | 0.1 | 0.59 |
| | 2.2 | 0.3 | 0.54 |
| | 2.0 | 0.5 | 0.47 |
| | 1.25 | 1.25 | 0.29 |

[a] DMF-TEOA (5:1, v/v) solution containing the complexes was irradiated at 365 nm. The light intensities were $1.4 \times 10^{-9}$ Einstein s$^{-1}$ for system 1, and $1.2 \times 10^{-9}$ Einstein s$^{-1}$ for system 2.

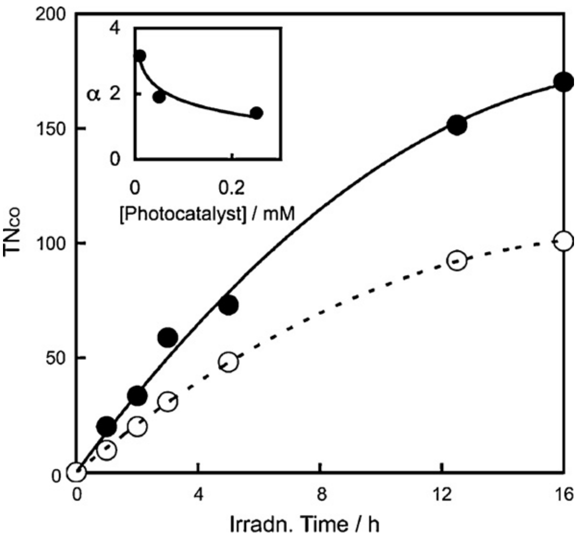


**Fig. 3.** Time-conversion curves for CO formation by photocatalytic $CO_2$ reduction ($\lambda > 500$ nm) using 0.05 mM of **1a** (●), and a mixture of $[Ru(dmb)_3]^{2+}$ (0.05 mM) and *fac*-$Re(dmb)(CO)_3Cl$ (0.05 mM) (○) [32]. Dependence of relative $TN_{CO}$ (α) using **1a** compared with that using a 1:1 mixture of $[Ru(dmb)_3]^{2+}$ and *fac*-$Re(dmb)(CO)_3Cl$ on the concentration of the complex(es) is shown in the inset.
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Because the rhenium unit does not absorb the irradiated light, the photocatalytic reaction should be initiated by light absorption with the ruthenium unit and reductive quenching of the excited state by BNAH. Since electron transfer from the OER species of the Ru unit to the Re unit is necessary, the photocatalytic ability of the supramolecule system is strongly affected by the electron acceptability of the two peripheral diimine ligands coordinating on the Ru unit. For example, the supramolecular complex with two 4,4′-dimethyl-2,2′-bipyridine as the peripheral ligands (**1a**) has high photocatalytic ability while the complexes with 2,2′-bipyridine (**1b**) or 4,4′-bis(trifluoromethyl)-2,2′-bipyridine (**1c**) have much lower or no photocatalytic abilities. These results indicate that captured electron should be mainly localized on the bridge ligand. In the cases that the electron is located on the peripheral ligands in the Ru unit, electron transfer from the Ru unit to the Re unit does not occur or is not fast enough for efficient $CO_2$ reduction.

Because the intramolecular electron transfer in the supramolecule systems does not require diffusion controlled collision between electron acceptor and donor in solution, the reaction rate is less dependent on the concentration of the substrates. On the other hand, the mixed photocatalytic system with two mononuclear complexes of lower concentrations has lower ability, and side reactions make the durability of the photocatalytic system lower. Accordingly, the supramolecular photocatalyst can especially establish higher superiority over the mixed system in the case of lower concentration of the complex(es) (inset in Fig. 3).

Another important factor for determining the photocatalytic ability of the supramolecular photocatalysts is whether there is a π-conjugation between the diimine parts in the bridge ligand. Although π-conjugation systems possibly have an advantage for rapid electron transfer between the Ru and Re units, their photocatalytic abilities were lower than those using non-conjugation system. For example, the conjugated systems **4a** and **4b** have lower photocatalytic abilities compared with the mixed system. On the other hand, the non-conjugated systems (**1a**, **3**) with a bridge ligand of which two diimine are connected with an alkyl chain have higher photocatalytic abilities as described above. This apparent contradiction can be explained by the fact that the energy level of $\pi^*$ orbital of diimine in the conjugation system is more positive than that in the corresponding non-conjugated system. The efficient reduction of $CO_2$ by the OER species of rhenium complexes requires high reduction power ($E_{1/2} < -1.40$ V vs. $Ag/AgNO_3$) as described in Sections 3 and 2, and introduction of π-conjugation into the bridge ligand lowered the reduction power. Actually, the supramolecular photocatalysts having the non-conjugated bridge ligand (**1a**, **3**) clarify this qualification, i.e. $E_{1/2}$ of the Re unit is −1.77 V. On the other hand, the complex having the π-conjugated bridge ligand (**4a**) has lower reduction power ($E_{1/2} = -1.10$ V) and much lower photocatalytic ability compared with those of **1a** and **3**.

Now we reach a guiding principle for constructing visible light driven supramolecular photocatalysts using a ruthenium(II) tris-diimine unit as a photosensitizer and a rhenium(I) unit as a catalyst for $CO_2$ reduction. (1) The $\pi^*$ orbital energy of the bridge ligand part coordinating the photosensitizer unit must be equal or lower than that of the peripheral ligands. (2) Although electron transfer must occur from the OER species of the photosensitizer unit to the catalyst unit, it is not necessary to be so fast because the rate limiting process is $CO_2$ reduction on the catalyst in most cases but not the electron transfer. (3) A bridging ligand with diimine units conjugated to each other is not suitable for the photocatalyst.

Moreover, recent studies have clarified that the peripheral ligands of rhenium unit also affect the photocatalytic abilities of the supramolecule systems [32]. For example, **2** with $P(OEt)_3$ as a peripheral ligand has higher ability as a photocatalyst for $CO_2$ reduction ($\Phi_{CO} = 0.21$, $TN_{CO} = 232$) than that of **1a**, while introduction of pyridine as a peripheral ligand into the Re unit lowers the photocatalytic ability. The dissociated pyridine from the OER species of the Re unit prevents the following process for $CO_2$ reduction.

## 6. Conclusion

In the present review, recent developments of efficient photocatalytic $CO_2$ reduction using metal complexes based on mechanistic studies have been summarized. Especially we focused on the rhenium(I) bipyridine complexes.

In the photocatalytic reactions the rhenium complexes play both roles of a photosensitizer and a catalyst. Efficient reduction of their excited state by TEOA and the following dissociation of the monodentate ligand from the OER species efficiently afford a reactive site for $CO_2$. The $CO_2$ adduct formed is reduced by another OER species of the Re complex.

According to these mechanistic investigations, the most efficient photocatalytic system for $CO_2$ reduction in homogeneous photocatalyst has been developed using a mixture of two rhenium complexes.

Supramolecule systems using a rhenium(I) complex connected with a ruthenium(II) tris-diimine as visible light driven photocatalyst for $CO_2$ reduction have been also summarized, and especially, their architectures have been discussed in detail based on the mechanistic studies.

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