Photocatalysis

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A Highly Efficient Mononuclear Iridium Complex Photocatalyst for CO_2 Reduction under Visible Light**

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Development of photocatalysts for the reduction of CO_2 by sunlight is increasingly becoming an important research area owing to fossil-fuel shortage and global warming. Developing a photosynthetic system that generates solar fuel from CO_2, H_2O, and sunlight is a promising approach.

Photocatalytic systems, including transition-metal complexes such as ruthenium(II) polypyridine carbonyl complexes,[1] cobalt(II) trisbipyridine,[2] and cobalt(II) macrocycles combined with a photosensitizer,[3] can reduce CO_2 with a relatively high quantum yield and high product selectivity. Among them, the rhenium(I) bipyridine (bpy) complex systems are the only mononuclear systems that exhibit definite photocatalytic activity for CO_2 reduction. A typical example is *fac*-[Re(bpy)$(CO)_3$Cl], developed by Lehn, which reduces CO_2 to CO under UV irradiation without any additional photosensitizers.[4] Cobalt porphyrins can also act as a CO_2 reduction catalyst without a photosensitizer.[3c]

A *fac*-[Re(bpy)$(CO)_3$\{P(OEt)$_3$\}]$^+$ complex is an efficient photocatalyst for CO_2 reduction in a homogeneous system that selectively produces CO with a quantum yield of 0.38 at the ultraviolet light irradiation of 365 nm.[4b] However, the compound must be modified to allow effective use of solar energy because its absorption in the visible region is limited to wavelengths less than 440 nm. Thus, activation of highly active Re complex photocatalysts toward the visible region is necessary. Furthermore, the photocatalytic activity for CO_2 reduction is very low in the presence of H_2O, even at a concentration of 10 %.[5a] Therefore, for CO_2 reduction, the development of metal complex photocatalysts that operate under visible light irradiation, even in the presence of H_2O, is desirable.

In Ir complexes, the stronger spin–orbit coupling coordinates with singlet and triplet excited states, leading to efficient luminescence and visible-light absorption from the singlet–triplet transition.[6] Therefore, Ir complexes have been used as an emitter for electroluminescence devices,[7] a photosensitizer for photocatalytic reactions,[8] and a light-absorber for Grätzel solar cells.[9] Recently, it was reported that an Ir complex acted as a water oxidation catalyst with a sacrificial electron accepter[10a] and a CO_2 reduction catalyst with an electronical bias[10b] or in the presence of hydrogen.[10c] Although Ir complexes are considered suitable for photocatalysis owing to visible-light absorption from S–T transitions and a longer lifetime of the excited state, no studies on Ir complex photocatalysts for CO_2 reduction have been reported.

This report describes the successful development of a novel photocatalyst, mononuclear iridium(III) terpyridine (tpy) 2-phenylpyridine (ppy) complex [Ir(tpy)(ppy)Cl]$^+$ ([Ir-ppy]), which selectively reduced CO_2 to CO under visible light at 480 nm without additional photosensitizers such as in the case for Re complexes. Furthermore, advantages of the Ir complexes over Re complexes include: 1) greater photocatalytic activity for CO_2 reduction; 2) CO_2 reduction under visible light, such as at a wavelength of 480 nm; and 3) the photocatalytic activity is maintained (including selectivity) even in a solution containing H_2O.

[Ir-ppy] catalyzed the reduction of CO_2 molecules to CO under visible-light irradiation. Figure 1 shows the photocatalytic formation of CO over [Ir-ppy] compared with conventional [Re(bpy)$(CO)_3$Cl] under visible light irradiation

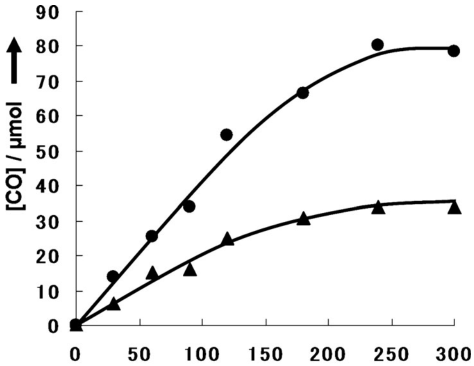

Figure 1. Amounts of CO formed from CO_2 as a function of irradiation time. Solutions were irradiated using a Xe lamp with filters producing light in the range of $410 \leq \lambda \leq 750$ nm. Concentrations of the photocatalysts were 0.5 mM (2 µmol) for [Ir-ppy] (●) in CO_2-saturated MeCN/TEOA (5:1) and [Re(bpy)$(CO)_3$Cl] (▲) in DMF/TEOA (5:1).

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(>410 nm). Small amounts of H_2 and HCOOH (total $<2\%$) were also produced over both photocatalysts (Supporting Information, Figure S1a). The initial CO formation rate over [Ir-ppy] was greater than that over [Re(bpy)(CO)$_3$Cl], and the turnover number of 38 (76 μmol) for CO generation (TN_{CO}) was also greater. The [Ir-ppy] reduced CO_2 even under irradiation at 480 nm with a quantum yield Φ_{CO} of 0.13 at 480 nm, which is the highest value among the reported homogeneous mononuclear photocatalytic systems active under visible light. For verification of CO derived through CO_2 reduction, isotope tracer analyses involving $^{13}CO_2$ were conducted (Supporting Information, Figure S2). Results confirmed that the CO detected in these photocatalytic reactions under visible light was produced from CO_2 dissolved in the solution.

These results indicated that the [Ir-ppy] functioned as a photocatalyst for CO_2 reduction with high efficiency and selectivity, and demonstrates that the [Ir-ppy] possesses two important and compatible functions within the mononuclear complex: catalytic ability for CO_2 reduction similar to Re, Ru, and Mn complexes,[11] and the ability to function as a photosensitizer in cooperation with CO_2 reduction, similar to Re complexes. Previous reports have indicated that catalytic activities over Re complexes were drastically degraded in aqueous solutions.[5a] In contrast, the [Ir-ppy] maintains its photocatalytic activity for CO_2 reduction even in an aqueous medium (Supporting Information, Figure S1b). This could be advantageous in the future for generating solar fuel from CO_2, H_2O, and sunlight.[12]

The UV/Vis absorption spectrum of [Ir-ppy] is shown in the Supporting Information, Figure S3, and the photophysical properties obtained from the emission spectra are summarized in Table S1. [Ir-ppy] showed a strong absorption band near 300 nm originating from π–π* absorption, and the two bands at 360 and 450–550 nm corresponded to MLCT singlet and triplet absorptions, respectively.[6] The emission from [Ir-ppy] is speculated to derive from ^{3}MLCT, judging from the observation of broad emission peaks. As the emission was quenched by the sacrificial electron donor, such as triethanolamine (TEOA), the quenching rate constant (k_q) was determined by the Stern–Volmer plot. The k_q was calculated to be 7.8×10^8. The quenching fraction (η_q) was approximately 100%, so that [Ir-ppy] in the photoexcited state was thoroughly quenched by TEOA during the photocatalytic CO_2 reduction reaction.

Cyclic voltammograms of [Ir-ppy] are shown in Figure 2, and the electrochemical properties are summarized in the Supporting Information, Table S2. Under an argon atmosphere, a primary reduction peak of the terpyridine (tpy) ligands appears near −1.05 V vs. SCE. The irreversible wave, attributable to the oxidation of the center metal of Ir complex, was observed at the potential of $E_{pOX}=1.76$ V vs. SCE (Supporting Information, Table S2). Under a CO_2 atmosphere, a catalytic current peak (ca. −1.05 V vs. SCE) was clearly observed when compared with data collected under an Ar atmosphere. This result indicates that [Ir-ppy] complexes have an electrocatalytic ability for CO_2 reduction. Furthermore, the catalytic current for CO_2 reduction was improved by addition of 5 vol% H_2O. The CO_2 reduction potential over [Ir-ppy] was close to that of ideal CO_2 reduction with electrons and protons (H^+) in H_2O (reduction of CO_2 to CO is about −0.76 V (vs. SCE) at pH 7)[13] when compared with those over conventional metal complex electrocatalysts, −1.40 V for [Re(bpy)(CO)$_3$Cl],[4] −1.44 V for [(POCOP)IrH(MeCN)$_2$]$^{2+}$(POCOP=C_6H_3-2,6-[CH_2P-(tBu)$_2$]$_2$),[10b] and −1.13–−1.88 V for other metal complex catalysts,[11] except for at −0.8–−1.3 V over a polymerized Ru electrocatalyst, [Ru(L-L)(CO)$_2$]$_n$, in which L-L is a diimine ligand.[14] These data indicate that [Ir-ppy] is not only an excellent photocatalyst for CO_2 reduction but also a good electrocatalyst that operates at a low electrical bias.

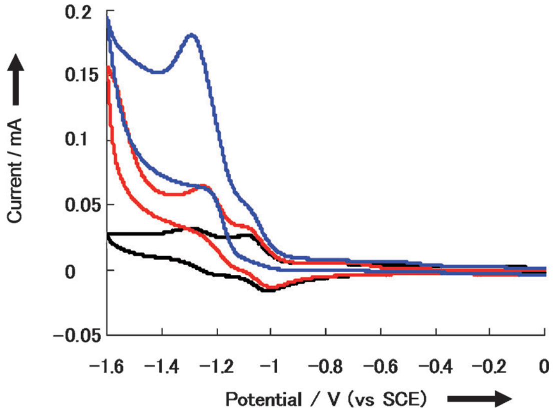


Figure 2. Cyclic voltammograms of [Ir-ppy] measured in acetonitrile solution containing 0.1 M $NEt_4^+BF_4^-$ under Ar (black), CO_2 (red), and CO_2 with 5% H_2O (blue). Measurements were carried out using a glassy carbon working electrode, a Pt counter electrode, and an I_2/I_3^- (0.1 M) reference electrode. Scan rate: 100 mV s^{-1}.

Steady-state measurements of changes in absorption spectra during irradiation under photocatalytic conditions with CO_2 are shown in the Supporting Information, Figure S4. Here, the light intensity for this steady-state measurement was greater than that for the photocatalytic reaction experiments, and the reaction was faster that shown in Figure 1. The absorption spectrum changed slightly within the first 2 min. Further photoirradiation induced a dramatic change in the spectra that accompanied two isosbestic points with increasing irradiation time. In contrast, this spectral change did not occur in the absence of TEOA (Supporting Information, Figure S5). Based on these results, the changes in absorption bands observed at 355, 510, and 720 nm can be interpreted as a structural change of [Ir-ppy] as CO_2 reduction progresses. Therefore, the change in [Ir-ppy] during photocatalytic reactions was monitored with ^{1}H NMR (Supporting Information, Figure S6) and ESI-MS (Figure 3). Before irradiation, only the starting complex [Ir-ppy] was detected by ^{1}H NMR. Results obtained after irradiation for 30 min, which resulted in the disappearance of almost all of the [Ir-ppy], suggest subsequent formation of a new Ir complex. A peak that is considered characteristic of protons in the new secondary complex was observed at −19.3 ppm. In general, a peak observed at such a high magnetic field is usually a hydride in a metal hydride complex.[15] Further irradiation for 300 min caused a disappearance of the hydrides, while the peaks assignable to ppy and tpy remained. These results led to

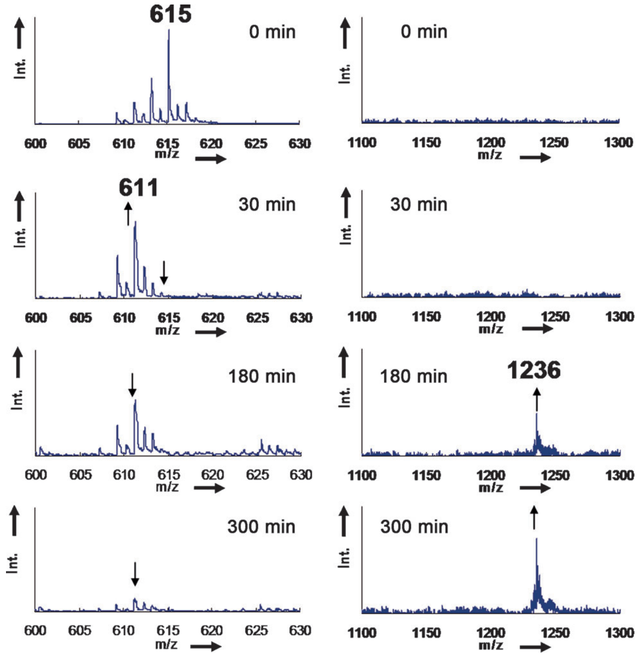
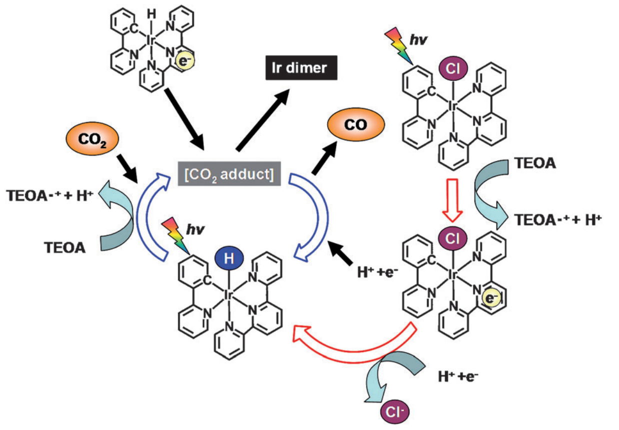


Figure 3. Steady-state measurements of changes in the ESI-MS spectra of a CO_2-saturated MeCN/TEOA (5:1) solution containing [Ir-ppy] during irradiation at wavelengths in the range of $410 \leq \lambda \leq 750$ nm.

speculation that the new second Ir complex detected after 30 min of irradiation was [Ir(tpy)(ppy)H] (see the Supporting Information). Interestingly, the ground state of [Ir(tpy)(ppy)H] was not reactive with CO_2 because [Ir(tpy)(ppy)H] was observed by ^1H NMR (Supporting Information, Figure S6b), even under a CO_2 atmosphere, which is different compared to other hydride complexes reported.[15] This result indicates that the structural change from [Ir-ppy] to [Ir(tpy)(ppy)H] occurs in the early stage of the photocatalytic reaction. After 300 min of irradiation, the [Ir(tpy)(ppy)H] species had nearly disappeared, and a peak attributable to a third Ir complex was generated (Supporting Information, Figure S6c). The CO formation leveled off at 300 min of irradiation (Figure 1). Thus, the third Ir complex is speculated to be inert for photocatalytic CO_2 reduction. Integration of the proton peak suggested that the structure of the deactivated product is [Ir(tpy)(ppy)L] (L = ligand other than H^-). The ESI-MS results (Figure 3) showed only the starting complex [Ir-ppy] peaking at $m/z = 615$ before irradiation. Irradiation for 30 min caused complete disappearance of [Ir-ppy], and a new Ir solvated complex subsequently formed with MeOH, giving rise to a peak at $m/z = 611$ ($[Ir(tpy)(ppy)(MeO)]^+$) in which the Cl ligand was replaced. This indicates that the loss of the Cl ligand occurred in the early stage of the photocatalytic reaction to give the solvated complex. However, a hydride complex [Ir(tpy)(ppy)H] was observed in the ^1H NMR spectra, while a solvated complex was not detected. This can be explained by the reaction of the hydride complex generated after 30 min irradiation with MeOH in the mobile phase to form the solvated complex during the ESI-MS measurement. Thus, the secondary complex generated at the early stage of photoreaction was [Ir(tpy)(ppy)H]. After 300 min irradiation, equivalent to the time for deactivation of CO_2 to CO conversion as shown in Figure 1, the solvated complexes (corresponding to [Ir(tpy)(ppy)H] in the actual photocatalytic reaction) almost disappeared and a new peak was generated at $m/z = 1236$ instead (Figure 3).

These results indicate that the active photocatalyst is not [Ir-ppy] but [Ir(tpy)(ppy)H], and that formation of [Ir(tpy)(ppy)H] from [Ir-ppy] occurs during the early stage of the photocatalytic reaction.[16] Owing to further photoirradiation, absorption of [Ir(tpy)(ppy)H] changed to other complex species, such as [Ir(tpy)(ppy)L], with a large mass number of $m/z = 1236$, which could be an Ir dimer complex, for example.

A mechanism of photocatalytic CO_2 reduction to CO over [Ir-ppy] postulated from these experiments is shown in Scheme 1. The lowest excited state ^{3}MLCT of [Ir-ppy] is reductively quenched by TEOA, giving the one-electron-reduced species. Elimination of Cl^- from the one-electron-reduced species and subsequent production of [Ir(tpy)(ppy)H] is a key step in the photocatalytic reaction, because [Ir(tpy)(ppy)H] is the active photocatalyst for CO_2 reduction in the present system. Photoexcited [Ir(tpy)(ppy)H] is also reductively quenched by TEOA, and the resulting one-electron-reduced species of [Ir(tpy)(ppy)H] can react with CO_2 to give the CO_2 adduct(s), because ground state of [Ir(tpy)(ppy)H] cannot react with CO_2. A deactivated complex, such as a Ir dimer, was generated during the photocatalytic CO_2 reduction reaction. An Ir radical complex, such as [Ir(tpy)(ppy)•], is indispensable for formation of the Ir dimer. However, a radical complex such as [Ir(tpy)(ppy)•] must be very unstable in MeCN, because MeCN possesses strong coordination ability.[17] Thus, to generate the Ir dimer, [Ir(tpy)(ppy)•] radicals must come close to one another to achieve frequent contact. These results indicate that another important key role of the one-electron-reduced species of [Ir(tpy)(ppy)H] is electron donation to the CO_2 adduct, which facilitates two-electron reduction as recently described in Re complexes.[5b,c] Here, most of the CO_2 adducts return to [Ir(tpy)(ppy)H] after releasing CO, while some of the CO_2 adducts form deactivated Ir dimers. A proton source is also required in this proposed photocatalytic reaction mechanism.



Scheme 1. Proposed mechanism for photocatalytic CO_2 reduction with [Ir-ppy] in MeCN/TEOA solution. TEOA = triethanolamine.

The ability of TEOA to act as a proton source in MeCN for a hybrid photocatalyst composed of a Ru complex linked with N-doped Ta_2O_5 has been confirmed.[18] Therefore, TEOA may also play a role as a proton source in the present photocatalytic reaction of Ir complexes. The improved catalytic current with addition of H_2O in the electrocatalytic reaction can be explained by this mechanism; that is, formation of [Ir(tpy)(ppy)H] from [Ir-ppy] was enhanced by the additional proton source (Figure 2). More detailed research on the reaction mechanisms (and especially the mechanism of [Ir(tpy)(ppy)H] production by a transient spectroscopy) is now underway.

Based on these results, a new photocatalyst with greater photocatalytic activity than [Ir-ppy] was constructed. As [Ir(tpy)(ppy)H] is the active photocatalyst in the present reaction, the properties of the hydride donor over [Ir(tpy)(ppy)H] play an important role for the overall CO_2 reduction. It is well-known that CO_2 reduction ability was changed by introduction of substituents for ligand of Re complexes.[4,5] Introduction of electron-donating methyl groups to the ppy ligands $[Ir(tpy)(Me\text{-}ppy)Cl]^+$ ([Ir-Meppy]) successfully achieved a negative shift of charge density of Ir (HOMO) by 0.07 V (Supporting Information, Table S1). In contrast, introduction of electron-withdrawing trifluoromethyl groups to the ppy ligands $[Ir(tpy)(CF_3\text{-}ppy)Cl]^+$ ([Ir-CF_3ppy]) caused a positive shift of charge density of Ir (HOMO) by 0.15 V (Supporting Information, Table S2). With the exception of the charge density of Ir (HOMO), properties such as CO_2 reduction potential, lifetime of the excited state, and quenching fractions (η_q) of TEOA of [Ir-ppy], [Ir-Meppy], and [Ir-CF_3ppy], were similar (Supporting Information, Table S1). Photocatalytic formation of CO, together with very small amounts of H_2 and HCOOH under >410 nm irradiation, was also observed for mononuclear [Ir-ppy], [Ir-Meppy], and [Ir-CF_3ppy], while the reaction rate and turnover number for CO formation (TN_{CO}) were different (Supporting Information, Figure S7). An initial CO formation rate and TN_{CO} (up to 50) over [Ir-Meppy] were greater than those over [Ir-ppy]. The quantum yield Φ_{CO} of [Ir-Meppy] was 0.21 at 480 nm, which is the greatest value reported for homogeneous mononuclear photocatalytic systems active under visible light. In contrast, [Ir-CF_3ppy] has a lower activity for CO_2 reduction than [Ir-ppy]. These results indicate that the hydride donor property of the Ir hydride complex, which is controlled by the electron-donating function of the ppy ligand, is very important for improving the CO_2 reduction activity.

In conclusion, a mononuclear Ir complex photocatalyst ([Ir(tpy)(R-ppy)Cl] was developed for efficient and selective CO_2 reduction, driven by visible light in a homogeneous solution, and even in solution containing H_2O. The most efficient photocatalyst was [Ir-Meppy], which had the best TN_{CO} value (up to 50), and the quantum yield Φ_{CO} of [Ir-Meppy] was 0.21, which is the best reported value in homogeneous photocatalytic systems using low-energy visible light at wavelengths such as 480 nm. The reaction mechanism of efficient photocatalytic CO_2 reduction using [Ir-ppy] was determined using ^1H NMR, ESI-MS, and absorption change spectra. The [Ir-ppy] was transformed into [Ir(tpy)(ppy)H] during the photocatalytic reaction; that is, [Ir(tpy)(ppy)H] is the active photocatalyst. The one-electron-reduced species of [Ir(tpy)(ppy)H] can react with CO_2 and [Ir(tpy)(ppy)H] can probably donate electrons to the CO_2 adduct. Finally, the [Ir(tpy)(ppy)H] gradually changed to a deactivated product, such as an Ir dimer.

A photoreduction system for CO_2 that utilizes H_2O as an electron donor and a proton source using a Z-scheme reaction of semiconductor/metal-complex hybrid photocatalysts was reported previously.[12] This system can be applied to many other inorganic semiconductors and metal-complex catalysts. Therefore, efficiency and reaction selectivity can be enhanced by optimizing the catalyst. The present Ir complexes are active photocatalysts for CO_2 reduction and also electrocatalysts that reduce CO_2 with a low overpotential, even in an aqueous medium. Therefore, advanced artificial photosynthetic system should be possible by constructing a semiconductor/Ir complex photocatalyst.

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