Article

Photocatalytic Systems for CO_2 Reduction: Metal-Complex Photocatalysts and Their Hybrids with Photofunctional Solid Materials

Published as part of the Accounts of Chemical Research special issue "CO2 Reductions via Photo and Electrochemical Processes".

Hiromu Kumagai,* Yusuke Tamaki,* and Osamu Ishitani*

Read Online

ACCESS | 📊 Metrics & More | 📰 Article Recommendations

CONSPECTUS: Photocatalytic CO_2 reduction is a critical objective in the field of artificial photosynthesis because it can potentially make a total solution for global warming and shortage of energy and carbon resources. We have successfully developed various highly efficient, stable, and selective photocatalytic systems for CO_2 reduction using transition metal complexes as both photosensitizers and catalysts. The molecular architectures for constructing selective and efficient photocatalytic systems for CO_2 reduction are discussed herein. As a typical example, a mixed system of a ring-shaped Re(I) trinuclear complex as a photosensitizer and fac-$[Re(bpy)(CO)_3\{OC_2H_4N(C_2H_4OH)_2\}]$ as a catalyst selectively photocatalyzed CO_2 reduction to CO with the highest quantum yield of 82% and a turnover number (TON) of over 600. Not only rare and noble metals but also earth abundant ones, such as Mn(I), Cu(I), and Fe(II) can be used as central metal cations. In the case using a Cu(I) dinuclear complex as a photosensitizer and fac-Mn(bpy)(CO)$_3$Br as a catalyst, the total formation quantum yield of CO and HCOOH from CO_2 was 57% and $TON_{CO+HCOOH}$ exceeded 1300.

Efficient supramolecular photocatalysts for CO_2 reduction, in which photosensitizer and catalyst units are connected through a bridging ligand, were developed for removing a diffusion control on collisions between a photosensitizer and a catalyst. Supramolecular photocatalysts, in which $[Ru(N^\wedge N)_3]^{2+}$-type photosensitizer and Re(I) or Ru(II) catalyst units are connected to each other with an alkyl chain, efficiently and selectively photocatalyzed CO_2 reduction in solutions. Mechanistic studies using time-resolved IR and electrochemical measurements provided molecular architecture for constructing efficient supramolecular photocatalysts. A Ru(II)−Re(I) supramolecular photocatalyst constructed according to this molecular architecture efficiently photocatalyzed CO_2 reduction even when it was fixed on solid materials. Harnessing this property of the supramolecular photocatalysts, two types of hybrid photocatalytic systems were developed, namely, photocatalysts with light-harvesting capabilities and photoelectrochemical systems for CO_2 reduction.

Introduction of light-harvesting capabilities into molecular photocatalytic systems should be important because the intensity of solar light shone on the earth's surface is relatively low. Periodic mesoporous organosilica, in which methyl acridone groups are embedded in the silica framework as light harvesters, was combined with a Ru(II)−Re(I) supramolecular photocatalyst with phosphonic acid anchoring groups. In this hybrid, the photons absorbed by approximately 40 methyl acridone groups were transferred to one Ru(II) photosensitizer unit, and then, the photocatalytic CO_2 reduction commenced.

To use water as an abundant electron donor, we developed hybrid photocatalytic systems combining metal-complex photocatalysts with semiconductor photocatalysts that display high photooxidation powers, in which two photons are sequentially absorbed by the metal-complex photosensitizer and the semiconductor, resulting in both high oxidation and reduction power. Various types of dye-

continued...
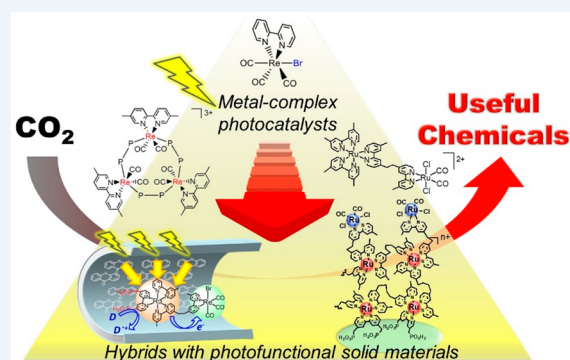
sensitized molecular photocathodes comprising the p-type semiconductor electrodes and the supramolecular photocatalysts were developed. Full photoelectrochemical cells combining these dye-sensitized molecular photocathodes and n-type semiconductor photoanodes achieved CO_2 reduction using only visible light as the energy source and water as the reductant. Drastic improvement of dye-sensitized molecular photocathodes is reported.

The results presented in this Account clearly indicate that we can construct very efficient, selective, and durable photocatalytic systems constructed with the metal-complex photosensitizers and catalysts. The supramolecular-photocatalyst architecture in which the photosensitizer and the catalyst are connected to each other is useful especially on the surface of solid owing to rapid electron transfer from the photosensitizer to the catalyst. On basis of these findings, we successfully constructed hybrid systems of the supramolecular photocatalysts with photoactive solid materials. These hybridizations can add new functions to the metal-complex photocatalytic systems, such as water oxidation and light harvesting.
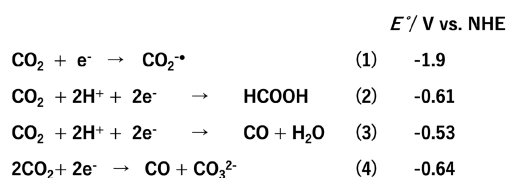
◼ KEY REFERENCES

- Takeda, H.; Kamiyama, H.; Okamoto, K.; Irimajiri, M.; Mizutani, T.; Koike, K.; Sekine, A.; Ishitani, O. Highly Efficient and Robust Photocatalytic Systems for CO_2 Reduction Consisting of a Cu(I) Photosensitizer and Mn(I) Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 17241−17254.[1] *A new binuclear Cu(I) complex with an excellent photosensitizing capability was developed. A mixed system with this Cu(I) photosensitizer and a Mn(I)-complex catalyst photocatalyzed CO_2 reduction with the total quantum yield of CO_2 reduction products was 57%, the turnover number was over 1300, and the selectivity of CO_2 reduction was 95%.*

- Saito, D.; Yamazaki, Y.; Tamaki, Y.; Ishitani, O. Photocatalysis of a Dinuclear Ru(II)−Re(I) Complex for CO_2 Reduction on a Solid Surface. *J. Am. Chem. Soc.* **2020**, *142*, 19249−19258.[2] *On the Al_2O_3 particles, superiority in photocatalysis of a supramolecular photo-catalyst consisting Ru(II) photosensitizer and Re(I) catalyst units was much reinforced compared to a mixed system of the corresponding mononuclear Ru(II) and Re(I) complexes.*

- Ueda, Y.; Takeda, H.; Yui, T.; Koike, K.; Goto, Y.; Inagaki, S.; Ishitani, O. A Visible-Light Harvesting System for CO_2 Reduction Using a $Ru^{II}−Re^{I}$ Photocatalyst Adsorbed in Mesoporous Organosilica. *ChemSusChem* **2015**, *8*, 439−442.[3] *In a hybrid system, that is, a Ru(II)−Re(I) supramolecular photocatalyst fixed on periodic mesoporous organosilica (PMO), acridone groups embedded in PMO worked as light harvester and transferred excitation energy to the Ru(II) photosensitizer unit, and CO_2 reduction efficiently proceeded on the supramolecular photocatalyst.*

- Kuttassery, F.; Kumagai, H.; Kamata, R.; Ebato, Y.; Higashi, M.; Suzuki, H.; Abe, R.; Ishitani, O. Supra-molecular photocatalysts fixed on the inside of the polypyrrole layer in dye sensitized molecular photo-cathodes: application to photocatalytic CO_2 reduction coupled with water oxidation. *Chem. Sci.* **2021**, *12*, 13216−13232.[4] *A dye-sensitized molecular photocathode with polypyrrole layer that involves Ru(II) photosensitizers and catalysts on NiO efficient photocatalyzed CO_2 reduction for 24 h. This photocathode was combined with semiconductor photoanodes to work as photocatalytic systems for CO_2 reduction with water oxidation.*

◼ INTRODUCTION

Photoelectron transfer has been extensively studied in various research fields. For example, the Marcus theory provides concrete kinetic and thermodynamic information,[5] and in redox photosensitized reactions (also known as photoredox catalytic reactions), photoelectron transfer is initiated by an

excited photosensitizer.[6,7] In these photochemical reactions, in principle, one-time excitation of a molecule causes a single one-electron transfer.

In CO_2 reduction, however, multielectron reduction, typically two-electron, is required because one-electron CO_2 reduction is a highly endothermic reaction (eq 1) and two-electron

$E°$/ V vs. NHE

$CO_2 + e^- \rightarrow CO_2^{-\bullet}$			(1)	-1.9
$CO_2 + 2H^+ + 2e^- \rightarrow$	HCOOH		(2)	-0.61
$CO_2 + 2H^+ + 2e^- \rightarrow$	$CO + H_2O$		(3)	-0.53
$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$			(4)	-0.64

reduction coupled with chemical reactions with protons (eqs 2 and 3 at pH 7) or another CO_2 molecule (eq 4) can drastically reduce the endothermicity of CO_2 reduction. For this reason, two-component systems are generally used, comprising a redox photosensitizer that initiates photochemical one-electron trans-fer from an electron donor to a catalyst, and the catalyst that obtains multiple electrons, reacts with CO_2, and releases reduction products.[7,8]

Transition metal complexes have various advantages, both as redox photosensitizers and catalysts for CO_2 reduction. For example, visible-colored and emissive metal complexes, such as $[Ru(N^\wedge N)_3]^{2+}$, $[Os(N^\wedge N)_3]^{2+}$, $[Re(N^\wedge N)(CO)_2(PR_3)_2]^+$, and $[Ir(ppy)_2(N^\wedge N)]^+$ ($N^\wedge N$ = diimine ligand; ppy = 2-phenyl-pyridinato-C^2,N ligand) have been reported as photosensitizers, and their colors can be systematically changed by changing the ligands.[7,9] Their excited states have sufficiently long lifetimes for photoelectron transfer with the electron donor owing to rapid intersystem crossing to the lowest triplet excited state. In terms of the catalyst, ligands, such as $N^\wedge N$, can function as a stable electron pool in the reduced metal complex, and the metal ion can fix CO_2 onto itself, which results in low overpotential and high selectivity for CO_2 reduction against hydrogen evolution. In typical photocatalytic CO_2 reduction systems, Tanaka and Ishida et al. employed $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), which is the frequently used photosensitizer, and $[Ru(bpy)_2(CO)_2]^{2+}$[10,11] or $Ru(bpy)(CO)_2Cl_2$[12] as the catalyst. Visible light irradiation of a mixed system of $[Ru(bpy)_3]^{2+}$ and one of these catalysts in the presence of an electron donor resulted in CO_2 reduction to HCOOH or CO.[12] Lehn and Ziessel et al. reported that *fac*-Re(bpy)(CO)$_3$X (X = Cl, Br) functions as a "single-handed" photocatalyst for CO_2 reduction selectively to CO when triethanolamine (TEOA) was used as an electron donor.[13] Recently, however, we established that the *fac*-Re(bpy)(CO)$_3$Br complex is largely transformed to a carbonic-acid-ester complex in the initial stage of the photocatalytic reaction (eq 5).[14] Therefore, a mixed system comprising the carbonic-acid−ester complex functioning as a catalyst and the

$$(5)$$
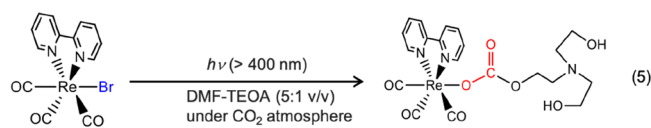
remaining fac-Re(bpy)$(CO)_3$Br operating as a photosensitizer is largely responsible for CO formation. In fact, a mixed system of $[Ru(bpy)_3]^{2+}$ and fac-Re(bpy)$(CO)_3$Cl exhibited superior photocatalytic activity than fac-Re(bpy)$(CO)_3$Cl alone.

Although photocatalytic systems based solely on metal complexes can attain high selectivities and low overpotentials for CO_2 reduction as described above, they lack several functionalities important for practical use, such as water oxidation capabilities for supplying electrons, and light-harvesting capacities. In this Account, we discuss our results on four interconnected research topics for photocatalytic CO_2 reduction: (1) efficient photocatalysis using mixed systems comprising photosensitizer and catalyst complexes; (2) constructing efficient supramolecular photocatalysts consisting of both the photosensitizer and catalyst complexes in one molecule; (3) imparting the photocatalyst with light-harvesting properties; and (4) photocatalytic reduction of CO_2 using water as a reductant and visible light as energy. Transition metal complexes play the central role in all of the above topics.

■ PHOTOSENSITIZER/CATALYST MIXED SYSTEMS

To improve CO_2-reduction photocatalysis by metal-complex systems in homogeneous solutions, three important objectives should be fulfilled: (1) the development of a photosensitizer that absorbs a wide range of visible light well, is highly oxidative in the excited state, highly reductive in the reduced state, and stable in both the excited and reduced states; (2) the development of a catalyst capable of rapid CO_2 reduction with a low overpotential, weak absorption of visible light, and is stable during the photocatalytic reaction; and (3) rapid electron transfer from the reduced photosensitizer to the catalyst. We have successfully developed highly efficient mixed photocatalytic systems by improving the photosensitizer and catalyst properties as described below.

Some ring-shaped Re(I) multinuclear complexes (**Re-rings**) display fascinating photosensitizing properties.[15−17] For example, **Re-ring-1** can absorb visible light to give a triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state having a long lifetime ($\tau = 5.4\ \mu$s) and high oxidation capacity (Figure 1).[15]
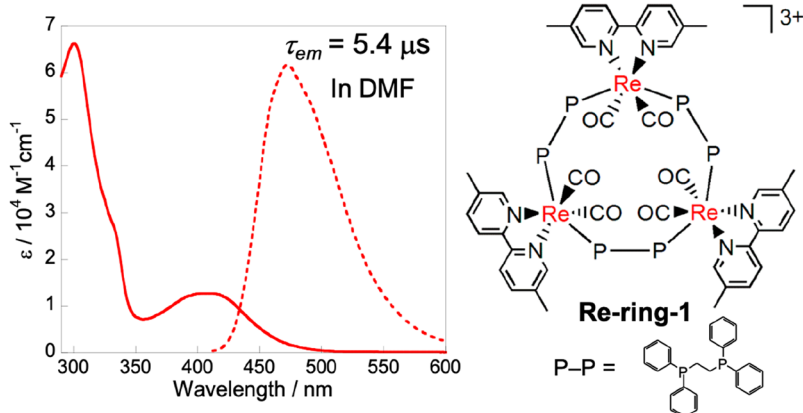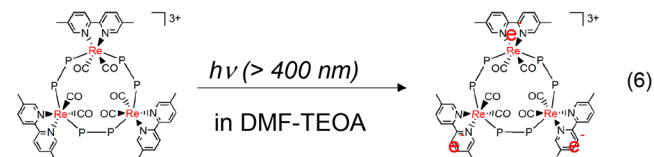
Re-ring-1 can accept three electrons in one molecule, and the reduced state is highly stable in solution, even at room temperature (eq 6). The one-electron reduced state (OERS) of **Re-ring-1** is highly reductive ($E_{1/2} = -1.87$ V vs Ag/AgNO$_3$).[18]

$$(6)$$

We found that fac-[Re(bpy)$(CO)_3$\{OC$_2$H$_4$N(C$_2$H$_4$OH)$_2$\}] can capture CO_2 to be converted into a carbonic-acid-ester complex (**Re-CO$_2$-TEOA** in eq 7).[14,19] Although this CO_2

$$(7)$$
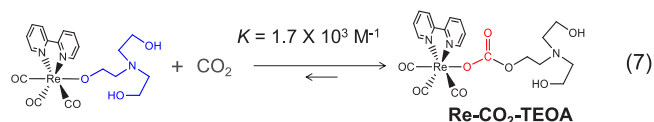
insertion into the Re−O bond is an equilibrium reaction, the equilibrium constant is very large ($K = 1.7 \times 10^3\ \text{M}^{-1}$); in other words, this reaction supplies CO_2 to the metal-complex catalyst before the photocatalytic reaction commences. This CO_2 capturing reaction enables direct reduction of low concentrations of CO_2, such as 1%, in electrocatalytic[19] and photocatalytic reactions.[20]

A mixed photocatalytic system of **Re-ring-1** and **Re-CO$_2$-TEOA** selectively reduced CO_2 to CO with the highest quantum yield ($\Phi_{CO} = 82\%$) among the reported systems (eq 8).[15]

$$(8)$$
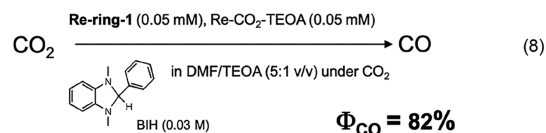
Herein, we used the formal definition of the quantum yield, that is, the product amount divided by the number of absorbed photons (eq 9). The turnover number (the product amount divided by the number of the photosensitizer or catalyst, TON) of produced CO was 526.

Figure 1. UV−vis absorption, emission, and structure of **Re-ring-1**.

$$\Phi_{product} = \frac{product\ amount}{absorbed\ photon\ number} \qquad (9)$$

Photocatalytic systems using only earth-abundant elements have recently been increasingly investigated for photocatalytic CO_2 reduction.[21] Because the lack of efficient rare- or noble-metal-free photosensitizers was a significant concern, we developed new binuclear Cu(I) complexes with excellent photosensitizing capabilities, in which two quadridentate ligands are complexed with two Cu(I) ions (**Cu2Xph** in Chart 1).[22−24]

Chart 1. Cu2Xph
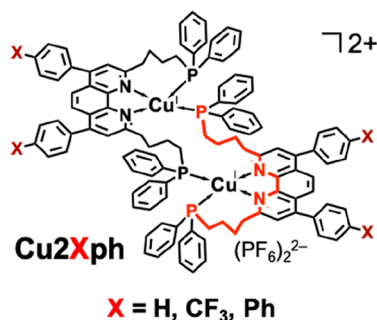
Although mononuclear Cu(I) complexes having both diimine and bisphosphine ligands have been reported as photosensitizers,[25] they are unstable in polar solvents even at room temperature owing to ligand detachment. However, **Cu2Xph** is highly stable under the same conditions, and the excited state and OERS of **Cu2Xph** are also stable with long lifetimes (several microseconds in acetonitrile at 25 °C). A mixed system comprising **Cu2Hph** with *fac*-Mn(MeO-bpy)(CO)$_3$Br[1] or Fe(phen)$_2$(SCN)$_2$[22] as catalysts efficiently photocatalyzed CO_2 reduction, as shown in Figure 2. The analogues bearing CF_3 or Ph groups as **X** in **Cu2Xph** (Chart 1) were more efficient photosensitizers than **Cu2Hph** because of stronger oxidation power in the excited state or stronger absorption in visible region.[24]

The heavy metal effect of Os increases the probability of direct excitation to the triplet excited state (S-T absorption), which is
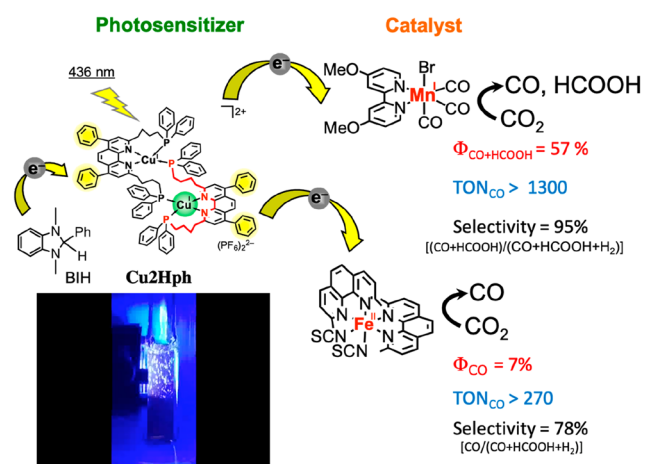
ordinarily a forbidden transition. We applied this phenomenon to create a panchromatic photosensitizer, **Os(L)(L′)** capable of utilizing the entire visible light range (Figure 3).[26] Irradiation of
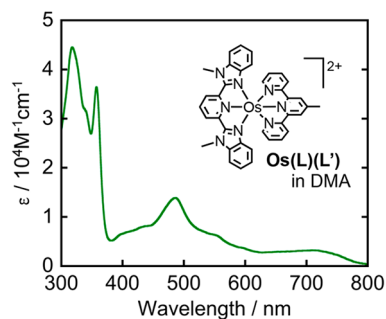

Figure 3. UV−vis absorption spectrum of **Os(L)(L′)** in DMA.

a *N,N*-dimethylacetamide (DMA) solution containing **Os(L)-(L′)**, Ru(bpy)(CO)$_2$Cl$_2$ as a catalyst, and 1,3-dimethyl-2-(*o*-hydroxyphenyl)-2,3-dihydro-1*H*-benzo[*d*]imidazole (BI(OH)-H) as a sacrificial electron donor, induced photocatalytic CO_2 reduction to HCOOH, even at $\lambda_{ex} > 770$ nm.

SUPRAMOLECULAR PHOTOCATALYSTS

In the mixed systems of a photosensitizer and catalyst, the electron transfer from the OERS of the photosensitizer to the catalyst is limited by diffusion collisions between them. To accelerate electron transfer and improve photocatalytic activity, multinuclear metal complexes consisting of photosensitizer and catalyst have been developed;[27] these are referred to as "supramolecular photocatalysts".[28] In 2005, we reported the successful supramolecular photocatalysts for CO_2 reduction for the first time.[29] The supramolecular photocatalysts comprising [Ru(N^N)$_3$]$^{2+}$-type photosensitizer and *fac*-Re(N^N)(CO)$_3$Cl-type catalyst units achieved both TONs ≫ 1 and better photocatalytic activities than a mixed system of the corresponding mononuclear complexes.

Chart 2 shows the structures and abbreviations of the Ru(II)−Re(I) multinuclear complexes, and Table 1 summarizes their
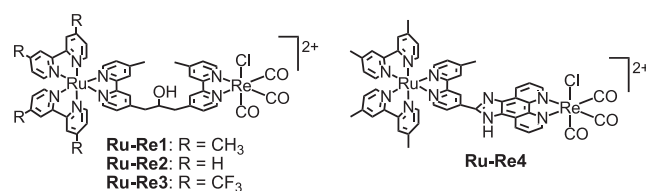
Chart 2. Ru(II)−Re(I) Complexes

Table 1. Photocatalytic Performances of Ru(II)−Re(I) Complexes[a]

entry	photocatalyst	Φ_{CO}	TON_{CO}
1	**Ru−Re1**	0.12	170
2	[Ru(dmb)$_3$]$^{2+}$ + *fac*-Re(dmb)(CO)$_3$Cl	0.062	101
3	**Ru−Re2**		50
4	**Ru−Re3**		3
5	**Ru−Re4**		28

[a]CO_2-saturated DMF−TEOA (5:1 v/v) solutions containing the complex and BNAH (0.1 M) were irradiated at $\lambda_{ex} > 500$ nm. dmb = 4,4′-dimethyl-2,2′-bipyridine.

Figure 2. Photocatalysis by **Cu2Hph** with *fac*-Mn(MeO-bpy)(CO)$_3$Br or Fe(phen)$_2$(SCN)$_2$ as catalysts. The photo shows active CO bubbles being produced during the photocatalytic reaction using *fac*-Mn(MeO-bpy)(CO)$_3$Br.

photocatalytic activities. **Ru−Re1**, in which the $[Ru(N^\wedge N)_3]^{2+}$ photosensitizer unit and the fac-Re$(N^\wedge N)(CO)_3$Cl catalyst unit are bridged by an alkyl chain between two $N^\wedge N$ moieties, photocatalytically reduced CO_2 selectively to CO in the presence of a sacrificial electron donor, 1-benzyl-1,4-dihydronicotinamide (BNAH), under visible-light irradiation ($\lambda_{ex} > 500$ nm).[29] CO produced with a high quantum yield (Φ) and the system was highly durable (entry 1 in Table 1: $\Phi_{CO} = 0.12$, $TON_{CO} = 170$), being superior to the mixed system of $[Ru(dmb)_3]^{2+}$ and fac-Re(dmb)$(CO)_3$Cl (entry 2: $\Phi_{CO} = 0.062$, $TON_{CO} = 101$). The reaction mechanism of photocatalytic CO_2 reduction using **Ru−Re1** was partially clarified as follows. [Process 1] Selective photon absorption by the Ru(II) photosensitizer unit forms the ^{1}MLCT excited state, which then relaxes to the ^{3}MLCT excited state via rapid intersystem crossing. [Process 2] The ^{3}MLCT excited Ru unit is reduced by BNAH, producing the OERS. [Process 3] The unpaired electron on the Ru unit transfers intramolecularly to the Re(I) unit. [Process 4] CO_2 is reduced to CO on the Re unit via a second one-electron reduction (Figure 4).
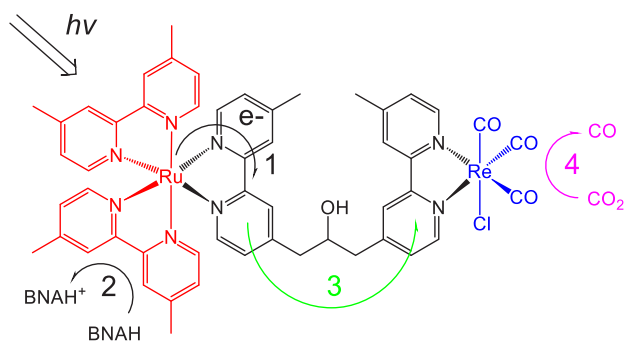

Figure 4. Reaction mechanism of photocatalytic reduction of CO_2 using **Ru−Re1**.

The peripheral ligands of the Ru(II) unit and the bridging ligand strongly affected the photocatalytic activity. **Ru−Re2** (entry 3: $TON_{CO} = 50$) and **Ru−Re3** (entry 4: $TON_{CO} = 3$) with 2,2′-bipyridine or 4,4′-bis(trifluoromethyl)-2,2′-bipyridine as peripheral ligands exhibited significantly lower photocatalytic activities than **Ru−Re1**. This was because of slow intramolecular electron transfer [process 3] in the cases of the OERS of **Ru−Re2** and **Ru−Re3**, whereby the unpaired electron localizes predominantly on the peripheral ligands of the Ru unit rather than the bridging ligands, and the intramolecular electron transfer becomes endergonic: in the case of **Ru−Re3**, for example, $E_{1/2}^{red}(Ru^{I/II}) = -1.23$ V while $E_{1/2}^{red}(Re^{0/I}) = -1.76$ V vs Ag/AgNO$_3$. On the other hand, both the Ru and Re units of **Ru−Re1** are reduced by one electron at an almost equal potential ($E_{1/2}^{red} = -1.77$ V), and intramolecular electron transfer proceeds readily. This intramolecular electron transfer process will be discussed in detail later.

Ru−Re4 exhibited a low photocatalytic activity (entry 5: $TON_{CO} = 28$), even though the intramolecular electron transfer from the one-electron reduced Ru unit to the Re unit should proceed rapidly as it is highly exothermic. The reason is that the conjugation of the bridging ligand lowers the reducing power of the OERS of the Re catalyst unit ($E_{1/2}^{red} = -1.10$ V), which inhibits CO_2 activation on the Re unit. We noted a strong relationship between the photocatalytic performances of mononuclear Re(I) complexes, namely, fac-[Re(4,4′-X$_2$-bpy)-(CO)$_3$(PR$_3$)]$^+$, and their first reduction potentials (Table 2):[30]

overall, the Re(I) complexes should have a more negative reduction potential than $E_{1/2}^{red} = -1.4$ V to function as effective catalysts for the reduction of CO_2.

Table 2. Photocatalytic Performances of fac-[Re(4,4′-X$_2$-bpy)(CO)$_3$(PR$_3$)]$^+$ Complexes and Their First Reduction Potentials

fac-[Re(4,4′-X$_2$-bpy)(CO)$_3$(PR$_3$)]$^+$				
X	R	$\Phi_{CO}{}^a$	$TON_{CO}{}^a$	$E_{1/2}^{red\,b}$/V
Me	OEt	0.18	4.1	−1.55
H	O^{i}Pr	0.20	6.2	−1.44
H	OEt	0.16	5.9	−1.43
H	OMe	0.17	5.5	−1.41
H	Et	0.024	0.83	−1.39
H	^{n}Bu	0.013	0.65	−1.39
CF$_3$	OEt	0.005	0.10	−1.03

^{a}A DMF-TEOA (5:1 v/v, 4 mL) solution of the complex (2.6 mM) was irradiated at 365 nm under CO_2 atmosphere. ^{b}Redox potentials measured in MeCN containing 0.1 M ^{n}Bu$_4$NClO$_4$ using Ag/AgNO$_3$ (10 mM) as a reference electrode.

To investigate the influence of the alkyl chain on the speed of intramolecular electron transfer from the OERS of the photosensitizer unit to the catalyst unit, we measured the rate constants of intramolecular electron transfers in the OERS of Ru(II)−Re(I) supramolecular photocatalysts bearing varying alkyl chain lengths conducting time-resolved IR (TR-IR) measurements of the stretching bands of the CO ligands (ν_{CO}), as shown in Figure 5.[31,32] Although there should be a
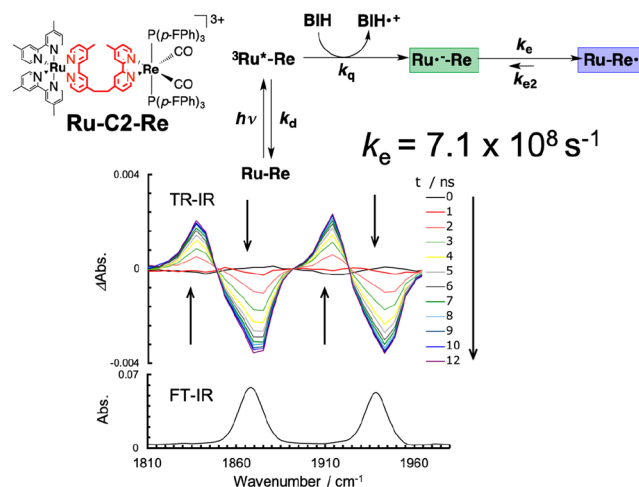

Figure 5. FT-IR and TR-IR spectra of **Ru−C2−Re** in DMF-TEOA (5:1 v/v) solution containing BIH (0.3 M): the excitation wavelength for TR-IR measurements was $\lambda_{ex} = 532$ nm.

ground state (**Ru−Re** in Figure 5) and two intermediates (^{3}**Ru*−Re** and **Ru$^{•-}$−Re**) in solution after irradiation in the presence of an electron donor before the intramolecular electron transfer proceeds, they should have similar ν_{CO} values owing to the alkyl chain separating the excited or reduced Ru unit from the Re unit. Only the product of intramolecular electron transfer (**Ru−Re$^{•-}$**) shows lower-energy shifts of its ν_{CO} bands owing to reinforcement by π-back-donation from the Re center. Figure 5 shows the FT-IR spectrum of **Ru−C2−Re**, which has an ethylene chain connecting the Ru and Re units, and the TR-IR
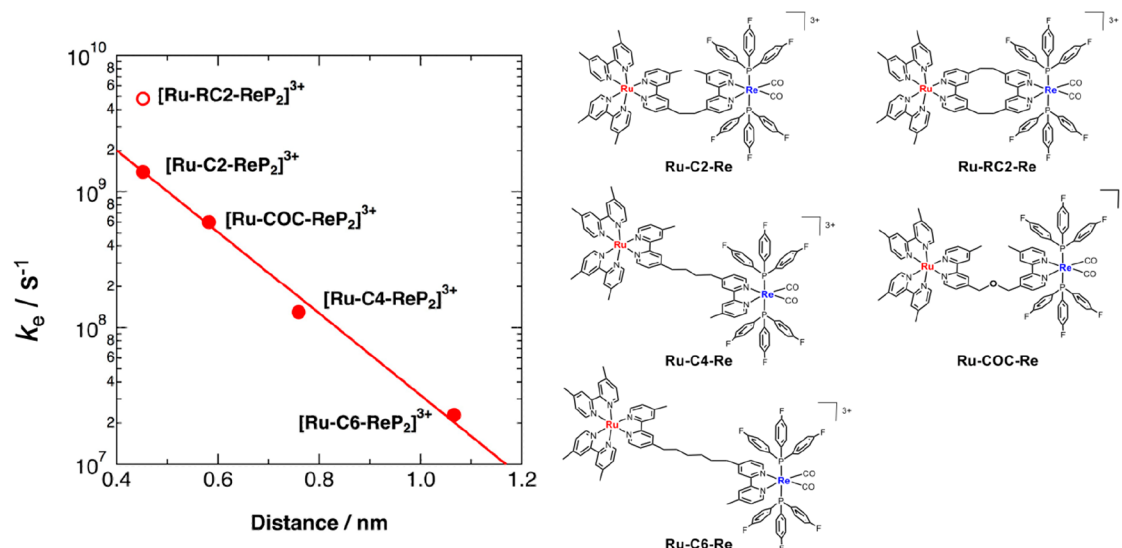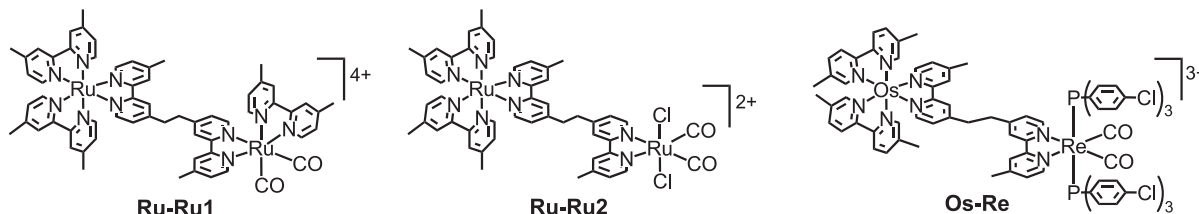
Figure 6. Relationship between the intramolecular electron transfer rate constant (k_e) and the distance between Ru and Re.

Chart 3. Ru(II)−Ru(II) and Os(II)−Re(I) Complexes

spectra obtained after selective excitation of the Ru photosensitizer unit in the presence of BIH as a sacrificial electron donor. We can calculate the rate constant of the intramolecular electron transfer at $k_e = 7.1 \times 10^8$ s^{-1} using increments in the ν_{CO} bands at 1872 and 1934 cm^{-1}. It is noteworthy that this electron transfer is sufficiently rapid not to be the rate-limiting process in the photocatalytic reaction.

When a longer alkyl chain was used in the bridging ligand (**Ru−Cn−Re**, n = 2, 4, 6 in Figure 6), the electron transfer rate k_e was lower, as shown in Figure 6, and a linear relationship was observed between the logarithm of k_e and the distance between Ru and Re with an apparent decay coefficient factor (β) of 0.74 Å^{-1}. In addition, **Ru−RC2−Re**, in which two ethylene chains connect the Ru and Re units, induced significantly faster intramolecular electron transfer than **Ru−C2−Re** bearing one ethylene chain. These results indicate that the intramolecular electron transfer from the OERS of the Ru unit to the Re unit proceeds via the through-bond mechanism.

From the results described above, the molecular architecture necessary to construct effective supramolecular photocatalysts can be obtained: [Rule 1] The photosensitizer unit must have equal to or more negative reduction potential than the catalyst unit to promote intramolecular electron transfer from the reduced photosensitizer unit to the catalyst unit. [Rule 2] The bridging ligand should not be conjugated to maintain the reducing power of the catalyst unit. On the basis of these rules, that is, employing dmb as peripheral ligands on the Ru photosensitizer unit and a bridging ligand with a −C$_2$H$_4$− chain, the supramolecular photocatalysts involving the Ru(II) carbonyl complexes as a catalyst unit instead of the Re(I) catalyst were developed (Chart 3).[33,34]

cis-[Ru(N^N)$_2$(CO)$_2$]$^{2+}$[35,36] and $cis,trans$-Ru(N^N)-(CO)$_2$Cl$_2$[36] are well-known electrochemical catalysts for the reduction of CO$_2$ to HCOOH with high selectivity under basic conditions. **Ru−Ru1** with a [Ru(N^N)(dmb)(CO)$_2$]$^{2+}$ unit photocatalyzed CO$_2$ reduction to HCOOH with high selectivity and durability in the presence of BNAH under visible-light irradiation (Φ_{HCOOH} = 0.038, TON$_{HCOOH}$ = 315, selectivity = 90%).[33,37] **Ru−Ru2** with a $cis,trans$-Ru(N^N)(CO)$_2$Cl$_2$ unit also functioned as a similarly active photocatalyst to reduce CO$_2$ to HCOOH.[34]

The photosensitizer unit was changed from the Ru complex to the corresponding [Os(N^N)$_2$(BL)]$^{2+}$-type complex. This complex (**Os−Re**, Chart 3) photocatalyzed CO$_2$ reduction under irradiation even at $\lambda_{ex} > 620$ nm, whereas the supramolecular photocatalysts containing the Ru photosensitizer unit do not absorb light at this wavelength and therefore did not induce CO$_2$ reduction under the same conditions.[38]

To impart additional functions to photocatalytic systems consisting of metal complexes, hybrid systems comprising photocatalysts and photofunctional solid materials such as semiconductor photocatalysts are good candidates. To fix the supramolecular photocatalysts on the solid, phosphonic acid anchoring groups were introduced at the peripheral ligands of the Ru(II) photosensitizing unit via −CH$_2$− to maintain the reduction power of the Ru(II) unit (Chart 4).

The advantage of supramolecular photocatalysts over the mixed systems consisting of mononuclear complexes is more pronounced when the metal complexes are fixed on a solid surface. When the mononuclear complexes of a photosensitizer and catalyst are fixed on a solid surface, the electron transfer from the photosensitizer to the catalyst should become

Chart 4. Supramolecular Photocatalysts Bearing Phosphonic Acid Anchoring Groups
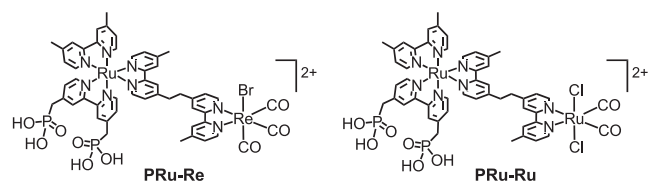
extremely slow or not occur at all depending on the distance between these complexes (Figure 7b). In the case of a supramolecular photocatalyst, on the other hand, this electron transfer occurs intramolecularly and should therefore be faster (Figure 7a).
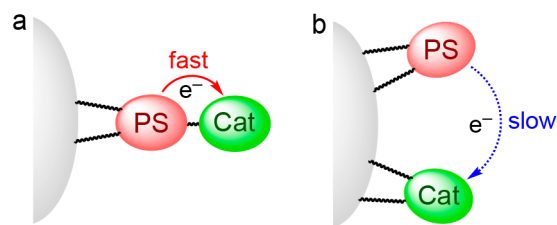
Figure 7. Conceptual images of a (a) supramolecular photocatalyst and (b) mixed system of mononuclear complexes on the surface of heterogeneous materials. PS and Cat represent photosensitizer and catalyst, respectively.

In fact, **PRu-Re** and the corresponding mononuclear complexes bearing anchoring groups were fixed on insulator Al_2O_3 particles, and their photocatalytic performances were compared using BNAH as a sacrificial electron donor.[25] The Al_2O_3/**PRu-Re** composite photocatalyzed CO_2 reduction to CO effectively even when the average distance between the supramolecular photocatalysts was considerably longer (6.3 nm) than the size of **PRu-Re** (maximum length = 2.4 nm). In contrast, in the case of Ru(II) and Re(I) mononuclear complexes, significantly less CO was produced at a comparable absorption density on Al_2O_3. Therefore, we decided to use a supramolecular photocatalyst for fabricating hybrid photocatalytic systems, as described below.

■ HYBRID PHOTOCATALYSTS WITH LIGHT-HARVESTING FUNCTIONALITY

Because the intensity of solar light is low and the absorption cross sections of molecular photosensitizers are small, introduction of light-harvesting capabilities is important for molecular photocatalytic systems.

We successfully combined a supramolecular photocatalyst with periodic mesoporous organosilica (**PMO**), in which abundant organic molecules (**R**) are embedded in the silica framework as light harvesters (Figure 8a).[3] Methyl acridone groups (**ACR**), which are capable of absorbing visible light, were used as the organic molecules in the PMO framework. The silica moiety interacts strongly with the phosphonic acid groups of **PRu-Re** (Chart 4, left) and confines **PRu-Re** mainly inside the mesopores, generating a hybrid (Figure 8b). The photons absorbed by approximately 40 **ACR** groups were transferred to a Ru(II) photosensitizer unit of one **PRu-Re** molecule in this hybrid, and then the photocatalytic reduction of CO_2 commenced. This light-harvesting function of the PMO hybrid enhanced the photocatalytic formation rate of CO by a factor of
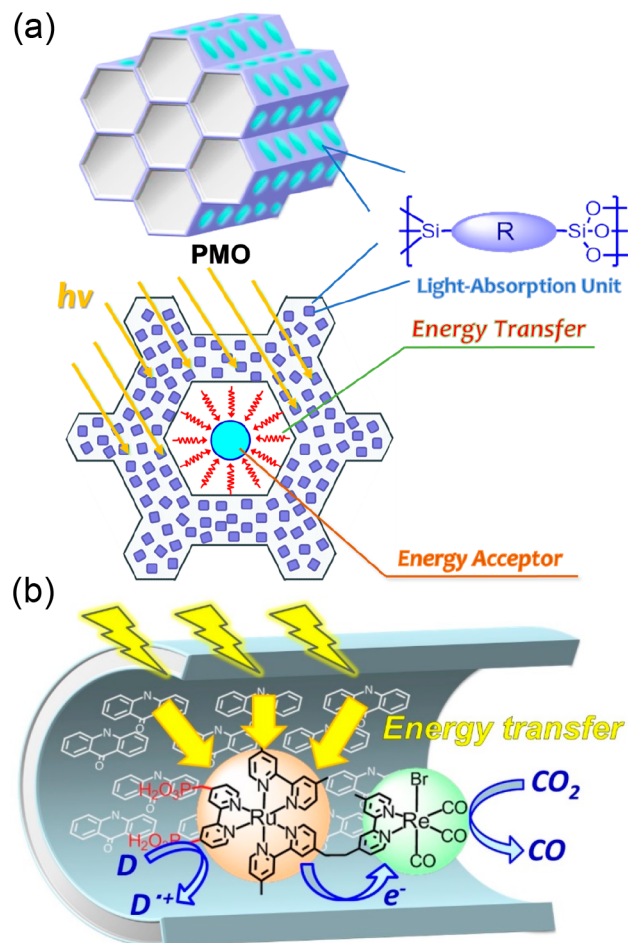
Figure 8. (a) Conceptual structure of **PMO**. (b) **PRu-Re** confined inside the mesopores of **PMO** with **ACR**, and photocatalytic CO_2 reduction by this hybrid capable of light harvesting.

10 compared to that of **PRu-Re**-adsorbed mesoporous silica without a light harvester. In the photocatalytic reaction using BIH as the electron donor, the TON_{CO} was >600.

■ HYBRID PHOTOCATALYTIC SYSTEMS USING WATER AS A REDUCTANT

In terms of practical photocatalytic CO_2 reduction, water is an ideal electron donor because of its abundance, low cost, and harmlessness. However, the low photooxidation power of metal-complex photosensitizers and the requirement of four-electron oxidation of two molecules of water lead difficulty in use of water in photocatalytic systems consisting of only metal complexes. To address these problems, we developed hybrid photocatalytic systems combining metal-complex photocatalysts with semiconductor photocatalysts that display high photooxidation powers, in which two photons are sequentially absorbed by the metal-complex photosensitizer and the semiconductor to obtain both high reduction and oxidation power.[39] The photocatalytic units for the CO_2 reduction and water oxidation were designed as photocathode and photoanode, respectively (Figure 9). The desired direction of photoelectron transfer from the semiconductor to the metal complex can be achieved by the appropriate coupling of these two photoelectrodes. In addition, the cell allows for separate product generation while avoiding reverse reactions.
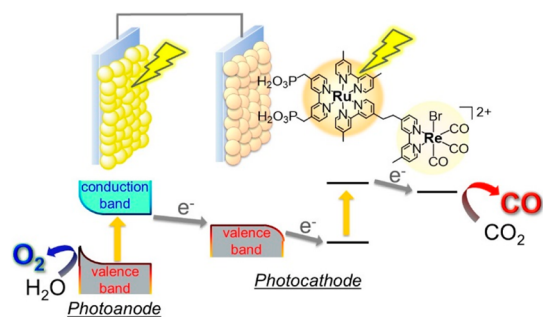
Figure 9. Hybrid photoelectrochemical cell constructed by combining a metal complex photocatalyst and a semiconductor photocatalyst for CO_2 reduction/water oxidation.

We developed a dye-sensitized molecular photocathode comprising **PRu-Re** (Chart 4, left) coupled with the p-type semiconductor NiO electrode.[40,41] The ^{3}MLCT excited state of the Ru photosensitizer unit of **PRu-Re** adsorbed on the electrode can obtain an electron from the valence band of NiO, instead of the ordinal sacrificial electron donor, to drive CO_2 reduction. The electron flow through this NiO/**PRu-Re** photocathode corresponds to the cathodic photocurrent, and **PRu-Re** produces CO as the photocatalytic reduction product of CO_2 under irradiation at $\lambda > 460$ nm and with appropriate external bias both in an organic solvent (DMF−TEOA (5:1, v/v)),[40] as well as in aqueous solution[41] with high selectivity (~100% and 91%, respectively). Here, the downward band bending at the solid−liquid interface of the p-type semiconductor is beneficial for the reductive quenching of the excited photosensitizer unit and subsequent charge separation. These results revealed that the **PRu-Re** photocatalyst can function as the CO_2 reduction side of the hybrid photoelectrochemical system.

We next combined the NiO/**PRu-Re** photocathode and an n-type semiconductor TaON photoanode for water oxidation to construct a full photoelectrochemical cell. TaON absorbs visible light ($\lambda < 500$ nm) and CoO_x cocatalyst was loaded onto it to improve the activity and stability for water oxidation.[42] Under irradiation at $\lambda > 400$ nm for both electrodes in an aqueous solution, the photoelectrochemical cell produced CO and O_2 from the photocathode and photoanode, respectively. The TON_{CO} based on the **PRu-Re** adsorbed on the electrode was 17. In this system, electrical and chemical biases (totally 0.4 V) were required to progress the photocatalytic reaction. The light-to-energy conversion efficiency of the reaction was 1.6×10^{-3}%.

The applicability of the hybrid cell was demonstrated by replacing the photoanode material with a Ta/N-codoped TiO_2.[43] This cell also required an external bias of 0.5 V between the two photoelectrodes and provided a conversion efficiency of 1.1×10^{-3}% with considering the bias applied.

These hybrid photoelectrochemical cells suffer several drawbacks. First, an external applied bias is necessary to drive the photocatalytic reaction, owing to the energy loss during electron transfer, even though potential of photoexcited electrons in the semiconductor photoanode is sufficiently negative to transfer an electron to the excited Ru photosensitizer unit in **PRu-Re**. Therefore, we replaced NiO with another p-type semiconductor, $CuGaO_2$ of which flat band potential is 0.16 V more positive than that of NiO.[44] The onset potential of the cathodic photocurrent of the photocathode comprising $CuGaO_2$ ($CuGaO_2$/**PRu-Re**) shifted 0.4 V more positive from that of NiO/**PRu-Re** (Figure 10). This large positive shift arises from reduced energy loss in the electron transfer process from the valence band of the p-type semiconductor electrode to the excited Ru photosensitizer unit. Owing to the improved photocathode, the hybrid photoelectrochemical cell consisting of the $CuGaO_2$/**PRu-Re** photocathode and the CoO_x/TaON photoanode achieved photocatalytic reduction of CO_2 and water oxidation without the application of an external bias (Figure 10c). The products were CO (232 nmol, TON_{CO} = 22) and H_2 (311 nmol) at the photocathode site and O_2 (232 nmol) at the photoanode site. This is the first self-driven photoelectrochemical cell constructed using a metal complex photocatalyst that achieves CO_2 reduction using only visible light as the energy source and water as the reductant.

Another problem with the dye-sensitized molecular photocathodes with metal complex photocatalyst described above is their low efficiency and stability. The external quantum efficiency (termed the incident-photon-to-current efficiency, IPCE) was very low. In addition, the photocurrent decayed rapidly within several hours of irradiation. One of the main reasons for this is inadequate adsorption of the metal complex photocatalyst onto the electrode surface; the **PRu-Re** molecules are adsorbed only via hydrogen bonding involving the phosphonic acid groups to form a unimolecular layer on the surface of the p-type semiconductors. Therefore, the amount of adsorbed **PRu-Re** was only ~4 nmol cm^{-2}, which limits light absorption and in turn the activity of the photocathodes. In addition, the phosphonate-acid anchor groups were weakly absorbed; thus, **PRu-Re** gradually detached and the photocathode activity decayed. We adopted electrochemical polymerization to reinforce the attachment of a larger amount of the
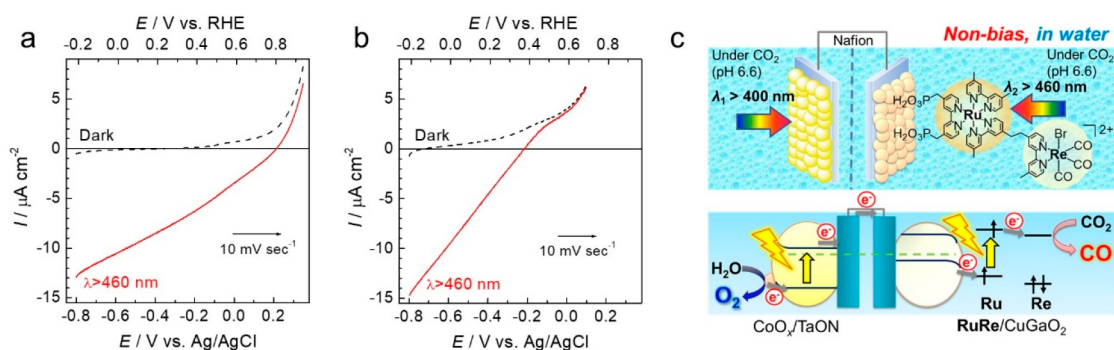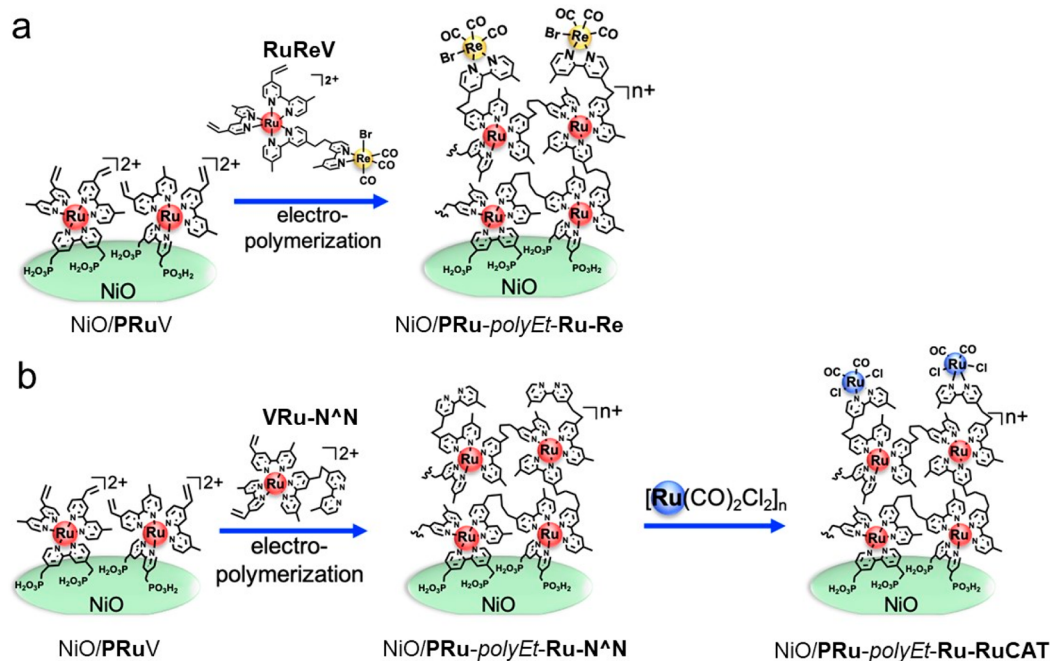

Figure 10. Current−potential curves of (a) $CuGaO_2$/**PRu-Re** and (b) NiO/**PRu-Re**. (c) The photoelectrochemical cell consisting of a $CuGaO_2$/**PRu-Re** photocathode and CoO_x/TaON photoanode. From ref 44 with permission. Copyright 2017 Royal Society of Chemistry.

Scheme 1. Preparation of (a) NiO/PRu-*polyEt*-Ru−Re and (b) NiO/PRu-*polyEt*-Ru-RuCAT

supramolecular photocatalyst onto the electrode surface.[45] We used two types of metal complexes bearing vinyl groups on the bipyridine ligands of the Ru(II) photosensitizer unit, that is, a mononuclear Ru(II) diimine-type photosensitizer (**PRuV**) and a Ru(II)−Re(I) supramolecular photocatalyst (**RuReV**, middle in Scheme 1a). **PRuV** has another bipyridine ligand bearing methyl phosphonic acid groups for its first attachment to the NiO electrode to form NiO/**PRuV** (the left side of Scheme 1a). NiO/**PRuV** was soaked in electrolyte containing **RuReV**, and then a negative potential was applied to the electrode to give the polyethylene-modified photocathode (NiO/**PRu**-*polyEt*-**Ru**−**Re**), which contained a larger amount of Ru photosensitizer units (∼10 nmol cm^{-2}) than **PRu-Re** adsorbed only via the methyl phosphonic acid anchor groups, and was more stable against detachment in the aqueous electrolyte. This molecular photocathode NiO/**PRu**-*polyEt*-**Ru**−**Re** produced approximately 2.5-fold more CO, and its total Faradaic efficiency of the reduction products also enhanced from 57% (NiO/**PRu-Re**) to 85%. The maximum IPCE was also improved to 0.93% at −0.5 V vs Ag/AgCl under 480 nm irradiation. However, the stability of the NiO/**PRu**-*polyEt*-**Ru**−**Re** was still unsatisfactory: the Re−C bonds were formed via the side reaction of the vinyl group with the Re center during reductive polymerization and cleaved during the photocatalytic reaction.

To address this issue, a three-step method for constructing dye-sensitized molecular photocathodes was developed (Scheme 1b).[46] In the first step, the NiO/**PRuV** electrode was synthesized as described above. In the second step, electrochemical polymerization was performed between the adsorbed **PRuV** and another Ru(II) mononuclear complex bearing diimine ligands with a vinyl group and a noncoordinated diimine moiety (**VRu-N^N**) to form NiO/**PRu**-*polyEt*-**Ru**−**N^N**. In the last step, a catalyst complex unit Ru(N^N)(CO)$_2$Cl$_2$ was formed via the reaction of the noncoordinated diimine moiety of NiO/**PRu**-*polyEt*-**Ru**−**N^N** with [Ru(CO)$_2$Cl$_2$]$_n$. The produced photocathode (NiO/**PRu**-*polyEt*-**Ru-RuCAT**) was highly stable: photoelectrochemical CO$_2$

reduction proceeded for over 100 h under visible light, affording CO and HCOOH without noticeable degradation (Figure 11,
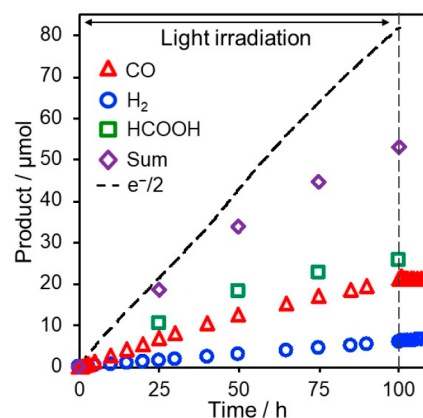

Figure 11. Time courses of the products from the NiO/**PRu**-*polyEt*-**Ru-RuCAT** photocathode during 100 h irradiation (460 nm < λ < 650 nm) at E = −0.7 V vs Ag/AgCl in a CO$_2$-purged NaHCO$_3$ aqueous solution. The dotted line shows a half number of the flowed electrons. Reproduced from ref 46 with permission. Copyright 2021 Royal Society of Chemistry.

the Faraday efficiency of the reduction product decreased due to slow air leakage). H$_2$ formation was very low even in aqueous media (selectivity toward CO$_2$ reduction was over 90%), and the TON$_{(CO+HCOOH)}$ reached 1200, which is the highest among the reported molecular photocathodes to date. The maximum incident photon to current conversion efficiency (IPCE) was 1.2% at −0.7 V vs Ag/AgCl under 480 nm irradiation in an aqueous solution (pH 6.6). The full cell consisting of the NiO/**PRu**-*polyEt*-**Ru-RuCAT** photocathode and a CoO$_x$-modified BiVO$_4$ semiconductor photoanode enabled both CO$_2$ reduction and water oxidation without any external bias under visible light irradiation with a light energy conversion efficiency of 0.017%.
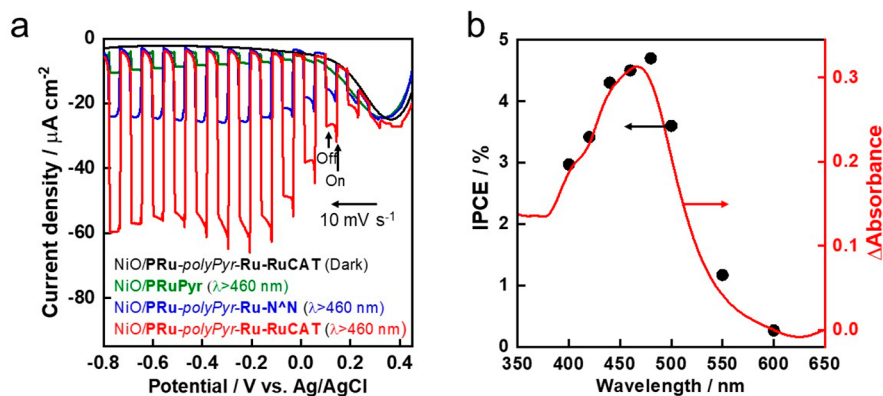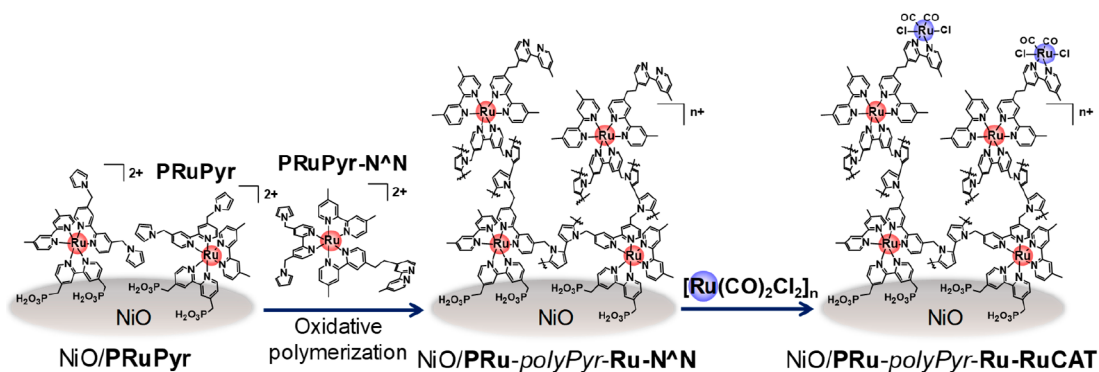
Scheme 2. Preparation of NiO/PRu-*polyPyr*-Ru-RuCAT

Figure 12. (a) Current–potential curves of NiO/**PRu**-*PolyPyr*-**Ru-RuCAT** under irradiation at λ_{ex} = 460–650 nm (28.2 mW cm^{-2}) in CO$_2$-purged 50 mM aqueous NaHCO$_3$. (b) Dependence of the IPCE of NiO/**PRu**-*PolyPyr*-**Ru-RuCAT** by the irradiated wavelength at −0.3 V vs Ag/AgCl with absorption spectrum of NiO/**PRu**-*PolyPyr*-**Ru-RuCAT** subtracted with the absorbance of the NiO electrode (red line).
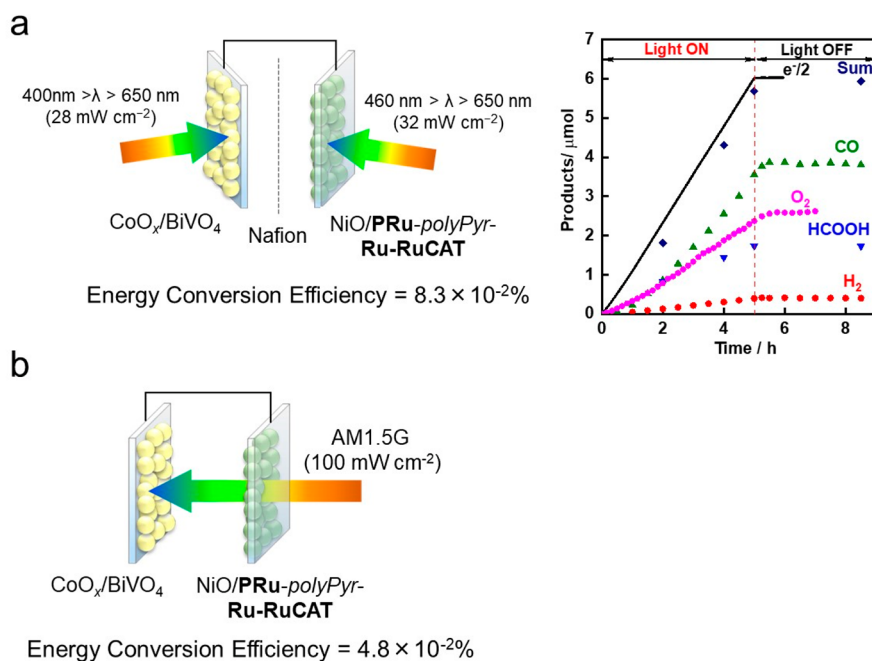
Figure 13. (a) Photoelectrochemical cell comprising the NiO/**PRu**-*polyPyr*-**Ru-RuCAT** photocathode and the CoO$_x$/BiVO$_4$ photoanode. (b) Tandem-type configuration in a single compartment cell irradiated by simulated sunlight (AM1.5G, 100 mW cm^{-2}).

Although the reductive polymerization approach using vinyl groups is highly effective for improving both the efficiency and stability of the dye-sensitized molecular photocathode, the saturated hydrocarbon chain formed by the vinyl polymerization possibly causes low conductivity in the polymer layer, which limits the improvement of its photocatalysis. Therefore, we

developed another dye-sensitized molecular photocathode produced by oxidative polymerization of pyrrole groups to afford a polypyrrole phase containing the metal complexes.[4] The synthesis method of this photoelectrode (NiO/**PRu**-*polyPyr*-**Ru-RuCAT**) is similar to that of NiO/**PRu**-*polyEt*-**Ru-RuCAT**, except for the use of Ru(II) complexes containing pyrrole groups (**PRuPyr** and **PyrRu-N^N** in Scheme 2) instead of **PRuV** and **VRu-N^N**, and the application of the potential scan in the positive instead of the negative direction. The produced NiO/**PRu**-*polyPyr*-**Ru-RuCAT** contained both the photosensitizer and catalyst units in a ratio of ∼3:1, and the photocurrent reached a maximum at E_{app} = −0.1 V vs Ag/AgCl (Figure 12a), whereas in the case of NiO/**PRu**-*polyEt*-**Ru-RuCAT**, an E_{app} of −0.5 V was required. This suggests an improvement in the conductivity of the polymer phase in the NiO/**PRu**-*polyPyr*-**Ru-RuCAT** photoelectrode. The maximum IPCE was 4.7% (Figure 12b), which is the highest value reported for dye-sensitized molecular photocathodes. Visible light irradiation of NiO/**PRu**-*polyPyr*-**Ru-RuCAT** at E_{app} = −0.7 V induced continuous photocatalytic CO_2 reduction for 24 h to produce CO and HCOOH with a small amount of H_2 (selectivity for CO_2 reduction was 92%) in CO_2-purged 50 mM aqueous $NaHCO_3$ solution. The TONs for CO and HCOOH were 566 and 185, respectively, after 24 h of irradiation. A full photoelectrochemical cell comprising this photocathode and the CoO_x/$BiVO_4$ photoanode induced simultaneous photocatalytic CO_2 reduction and water oxidation in the respective photoelectrodes (Figure 13a). For the same setup described in Figure 10c, the light energy conversion efficiency was 0.083% with Faraday efficiencies of 99% (photocathode) and 87% (photoanode). Another full cell in tandem configuration, wherein the photocathode was illuminated first and the photoanode absorbed the permeated light in the same compartment cell (Figure 13b), exhibited a solar-to-chemical conversion efficiency of 0.048% under simulated sunlight (AM1.5G). This state-of-the-art achievement suggests the possibility of solar energy conversion to useful chemicals with the use of a supramolecular photocatalyst as the photocatalytic center for CO_2 reduction. There are still many opportunities for improving the photocatalytic efficiency of full cells comprising dye-sensitized molecular photocathodes, such as strengthening the absorption of the photosensitizer units, especially at longer wavelengths, and enhancing the conductivities in p-type semiconductors and polymers, as well as between them.

CONCLUSIONS AND PERSPECTIVES

The results presented in this account clearly indicate that we can construct very efficient, selective, and durable photocatalytic systems consisting of metal-complex photosensitizers and catalysts according to the "rules". The supramolecular-photocatalyst architecture in which the photosensitizer and the catalyst are connected to each other is useful especially on the solid surface owing to rapid electron transfer between the photosensitizer and the catalyst. Based on these findings, we successfully constructed hybrid systems of the supramolecular photocatalysts with photoactive solid materials such as the mesoporous organosilica and the semiconductors. These hybridizations can add new functions, that is, light harvesting and water oxidation to the metal-complex photocatalytic systems.

For developing practical systems of photocatalytic CO_2 reduction, we have to add many functions to the systems as summarized in Figure 14. Although our approaches achieved to
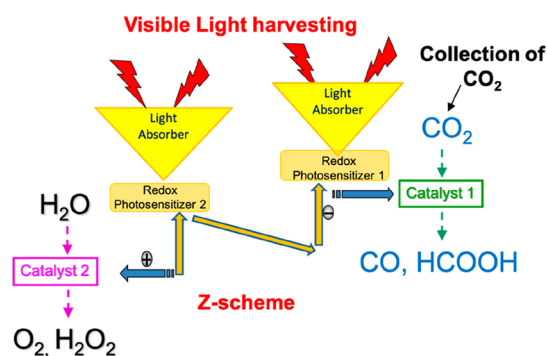

Figure 14. Required functions of artificial photosynthesis for CO_2 reduction.

combine some of these functions,[20] we have to add all of them in one system. Many additional efforts and new ideas should be directed to building "artificial photosynthesis" for CO_2 utilization.

AUTHOR INFORMATION

Corresponding Authors

Hiromu Kumagai — *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577, Japan;* ● orcid.org/0000-0003-2714-8577; Email: h.kumagai@tohoku.ac.jp

Yusuke Tamaki — *Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8550, Japan;* Email: tamaki@chem.titech.ac.jp

Osamu Ishitani — *Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8550, Japan;* ● orcid.org/0000-0001-9557-7854; Email: ishitani@chem.titech.ac.jp

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.accounts.1c00705

Notes

The authors declare no competing financial interest.

Biographies

Hiromu Kumagai is an assistant professor in the Institute of Multidisciplinary Research for Advanced Materials at Tohoku University. His current research interests include photoelectrochemistry, photocatalysis, and inorganic materials for energy conversion.

Yusuke Tamaki is an assistant professor at Tokyo Institute of Technology. His research interests involve photochemistry of transition metal complexes, photofunctional metal complexes and organic molecules, and photocatalytic CO_2 reduction.

Osamu Ishitani is a professor of Department of Chemistry at Tokyo Institute of Technology. His research interests are photochemistry and photofunctions of transition metal complexes, and artificial photosynthesis.

■ REFERENCES

(1) Takeda, H.; Kamiyama, H.; Okamoto, K.; Irimajiri, M.; Mizutani, T.; Koike, K.; Sekine, A.; Ishitani, O. Highly Efficient and Robust Photocatalytic Systems for CO_2 Reduction Consisting of a Cu(I) Photosensitizer and Mn(I) Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 17241−17254.

(2) Saito, D.; Yamazaki, Y.; Tamaki, Y.; Ishitani, O. Photocatalysis of a Dinuclear Ru(II)−Re(I) Complex for CO_2 Reduction on a Solid Surface. *J. Am. Chem. Soc.* **2020**, *142*, 19249−19258.

(3) Ueda, Y.; Takeda, H.; Yui, T.; Koike, K.; Goto, Y.; Inagaki, S.; Ishitani, O. A Visible-Light Harvesting System for CO_2 Reduction Using a Ru^{II}-Re^I Photocatalyst Adsorbed in Mesoporous Organosilica. *ChemSusChem* **2015**, *8*, 439−442.

(4) Kuttassery, F.; Kumagai, H.; Kamata, R.; Ebato, Y.; Higashi, M.; Suzuki, H.; Abe, R.; Ishitani, O. Supramolecular photocatalysts fixed on the inside of the polypyrrole layer in dye sensitized molecular photocathodes: application to photocatalytic CO_2 reduction coupled with water oxidation. *Chem. Sci.* **2021**, *12*, 13216−13232.

(5) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *J. Chem. Phys.* **1956**, *24*, 966−978.

(6) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322−5363.

(7) Yamazaki, Y.; Takeda, H.; Ishitani, O. Photocatalytic reduction of CO_2 using metal complexes. *J. Photochem. Photobiol. C* **2015**, *25*, 106−137.

(8) (a) Kojima, T. Photocatalytic CO_2 Reduction Using Nickel Complexes as Catalysts. *ChemPhotoChem.* **2021**, *5*, 512−520. (b) Boutin, E.; Merakeb, L.; Ma, B.; Boudy, B.; Wang, M.; Bonin, J.; Anxolabéhère-Mallart, E.; Robert, M. Molecular catalysis of CO_2 reduction: recent advances and perspectives in electrochemical and light-driven processes with selected Fe, Ni and Co aza macrocyclic and polypyridine complexes. *Chem. Soc. Rev.* **2020**, *49*, 5772−5809.

(9) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. Luminescent and redox-active polynuclear transition metal complexes. *Chem. Rev.* **1996**, *96*, 759−834.

(10) Ishida, H.; Tanaka, K.; Tanaka, T. Photoreduction of CO_2 in the $[Ru(bpy)_2(CO)_2]^{2+}$/$[Ru(bpy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$/Triethanolamine/N,N-Dimethylformamide System. *Chem. Lett.* **1987**, *16*, 1035−1038.

(11) Ishida, H.; Terada, T.; Tanaka, K.; Tanaka, T. Photochemical CO_2 Reduction Catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ Using Triethanolamine and 1-Benzyl-1,4-dihydronicotinamide as an Electron Donor. *Inorg. Chem.* **1990**, *29*, 905−911.

(12) Kuramochi, Y.; Fukaya, K.; Yoshida, M.; Ishida, H. trans-(Cl)-$[Ru(5,5$-diamide-2,2-bipyridine$)(CO)_2Cl_2]$: Synthesis, Structure, and Photochemical CO_2 Reduction Activity. *Chem.—Eur. J.* **2015**, *21*, 10049−10060.

(13) Hawecker, J.; Lehn, J. M.; Ziessel, R. Photochemical and Electrochemical Reduction of Carbon-Dioxide to Carbon-Monoxide Mediated by (2,2′-Bipyridine)Tricarbonylchlororhenium(I) and Related Complexes as Homogeneous Catalysts. *Helv. Chim. Acta* **1986**, *69*, 1990−2012.

(14) Morimoto, T.; Nakajima, T.; Sawa, S.; Nakanishi, R.; Imori, D.; Ishitani, O. CO_2 Capture by a Rhenium(I) Complex with the Aid of Triethanolamine. *J. Am. Chem. Soc.* **2013**, *135*, 16825−16828.

(15) Morimoto, T.; Nishiura, C.; Tanaka, M.; Rohacova, J.; Nakagawa, Y.; Funada, Y.; Koike, K.; Yamamoto, Y.; Shishido, S.; Kojima, T.; Saeki, T.; Ozeki, T.; Ishitani, O. Ring-Shaped Re(I) Multinuclear Complexes with Unique Photofunctional Properties. *J. Am. Chem. Soc.* **2013**, *135*, 13266−13269.

(16) Asatani, T.; Nakagawa, Y.; Funada, Y.; Sawa, S.; Takeda, H.; Morimoto, T.; Koike, K.; Ishitani, O. Ring-Shaped Rhenium(I) Multinuclear Complexes: Improved Synthesis and Photoinduced Multielectron Accumulation. *Inorg. Chem.* **2014**, *53*, 7170−7180.

(17) Rohacova, J.; Sekine, A.; Kawano, T.; Tamari, S.; Ishitani, O. Trinuclear and Tetranuclear Re(I) Rings Connected with Phenylene, Vinylene, and Ethynylene Chains: Synthesis, Photophysics, and Redox Properties. *Inorg. Chem.* **2015**, *54*, 8769−8777.

(18) It was reported that $Ag/AgNO_3$ (10 mM) in MeCN = +0.55 V versus NHE. Pavlishchuk, V. V.; Addison, A. W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25 °C. *Inorg. Chim. Acta* **2000**, *298*, 97−102. The readers should be careful that this relationship is changeable depending on the solvent used.

(19) Kumagai, H.; Nishikawa, T.; Koizumi, H.; Yatsu, T.; Sahara, G.; Yamazaki, Y.; Tamaki, Y.; Ishitani, O. Electrocatalytic reduction of low concentration CO_2. *Chem. Sci.* **2019**, *10*, 1597−1606.

(20) Nakajima, T.; Tamaki, Y.; Ueno, K.; Kato, E.; Nishikawa, T.; Ohkubo, K.; Yamazaki, Y.; Morimoto, T.; Ishitani, O. Photocatalytic Reduction of Low Concentration of CO_2. *J. Am. Chem. Soc.* **2016**, *138*, 13818−13821.

(21) (a) Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, Photons, Protons and Earth-Abundant Metal Complexes for Molecular Catalysis of CO_2 Reduction. *ACS Catal.* **2017**, *7*, 70−88. (b) Steinlechner, C.; Roesel, A. F.; Oberem, E.; Päpcke, A.; Rockstroh, N.; Gloaguen, F.; Lochbrunner, S.; Ludwig, R.; Spannenberg, A.; Junge, H.; Francke, R.; Beller, M. Selective Earth-Abundant System for CO_2 Reduction: Comparing Photo- and Electrocatalytic Processes. *ACS Catal.* **2019**, *9*, 2091−2100. (c) Zhang, X.; Cibian, M.; Call, A.; Yamauchi, K.; Sakai, K. Photochemical CO_2 Reduction Driven by Water-Soluble Copper(I) Photosensitizer with the Catalysis Accelerated by Multi-Electron Chargeable Cobalt Porphyrin. *ACS Catal.* **2019**, *9*, 11263−11273. (d) Wang, Y.; Gao, X.-W.; Li, J.; Chao, D. Merging an organic TADF photosensitizer and a simple terpyridine−Fe(III) complex for photocatalytic CO_2 reduction. *Chem. Commun.* **2020**, *56*, 12170−12173.

(22) Takeda, H.; Ohashi, K.; Sekine, A.; Ishitani, O. Photocatalytic CO_2 Reduction Using Cu(I) Photosensitizers with a Fe(II) Catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 4354−4357.

(23) Takeda, H.; Monma, Y.; Sugiyama, H.; Uekusa, H.; Ishitani, O. Development of Visible-Light Driven Cu(I) Complex Photosensitizers for Photocatalytic CO_2 Reduction. *Front. Chem.* **2019**, *7*, 418.

(24) Takeda, H.; Monma, Y.; Ishitani, O. Highly Functional Dinuclear CuI-Complex Photosensitizers for Photocatalytic CO_2 Reduction. *ACS Catal.* **2021**, *11*, 11973−11984.

(25) Rosas-Hernández, A.; Steinlechner, C.; Junge, H.; Beller, M. Earth-abundant photocatalytic systems for the visible-light-driven reduction of CO_2 to CO. *Green Chem.* **2017**, *19*, 2356−2360.

(26) Irikura, M.; Tamaki, Y.; Ishitani, O. Development of a panchromatic photosensitizer and its application to photocatalytic CO_2 reduction. *Chem. Sci.* **2021**, *12*, 13888−13896.

(27) (a) Kimura, E.; Bu, X.; Shionoya, M.; Wada, S.; Maruyama, S. A New Nickel(II) Cyclam (Cyclam = 1,4,8,11-Tetraazacyclotetradecane) Complex Covalently Attached to $Ru(phen)_3^{2+}$ (phen = 1,10-Phenanthroline). A New Candidate for the Catalytic Photoreduction of Carbon Dioxide. *Inorg. Chem.* **1992**, *31*, 4542−4546. (b) Komatsuzaki, N.; Himeda, Y.; Hirose, T.; Sugihara, H.; Kasuga, K. Synthesis and Photochemical Properties of Ruthenium-Cobalt and Ruthenium-Nickel Dinuclear Complexes. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 725−731. (c) Gabrielsson, A.; Lindsay Smith, J. R.; Perutz, R. N. Remote site photosubstitution in metalloporphyrin-rhenium tricarbonylbipyridine assemblies: photo-reactions of molecules with very short lived excited states. *Dalton Trans.* **2008**, 4259−4269. (d) Aukauloo, A.; Gotico, P.; Tran, T.-T.; Baron, A.; Vauzeilles, B.; Lefumeux, C.; Ha-Thi, M.-H.; Pino, T.; Halime, Z.; Quaranta, A.; Leibl, W. Tracking Charge Accumulation in a Functional Triazole-Linked Ru-Re Dyad Towards Photocatalytic CO_2 Reduction. *ChemPhotoChem.* **2021**, *5*, 654−664. (e) Brown, C. M.; Auvray, T.; DeLuca, E. E.; Ezhova, M. B.; Hanan, G. S.; Wolf, M. O. Controlling photocatalytic reduction of CO_2 in Ru(II)/Re(I) dyads via linker oxidation state. *Chem. Commun.* **2020**, *56*, 10750−10753. (f) Kiyosawa, K.; Shiraishi, N.; Shimada, T.; Masui, D.; Tachibana, H.; Takagi, S.; Ishitani, O.; Tryk, D. A.; Inoue, H. Electron Transfer from the Porphyrin S-2 State in a Zinc Porphyrin-Rhenium Bipyridyl Dyad having Carbon Dioxide Reduction Activity. *J. Phys. Chem. C* **2009**, *113*, 11667−11673. (g) Tamaki, Y.; Ishitani, O. Supramolecular Photocatalysts for the Reduction of CO_2. *ACS Catal.* **2017**, *7*, 3394−3409. (h) Pirzada, B. M.; Dar, A. H.; Shaikh, M. N.;

Qurashi, A. Reticular-Chemistry-Inspired Supramolecule Design as a Tool to Achieve Efficient Photocatalysts for CO_2 Reduction. *ACS Omega* **2021**, *6*, 29291–29324.

(28) Balzani, V.; Ceroni, P.; Juris, A.: *Photochemistry and Photophysics: Concepts, Research, Applications*; Wiley-VCH: Weinheim, 2014.

(29) Gholamkhass, B.; Mametsuka, H.; Koike, K.; Tanabe, T.; Furue, M.; Ishitani, O. Architecture of Supramolecular Metal Complexes for Photocatalytic CO_2 Reduction: Ruthenium-Rhenium Bi- and Tetra-nuclear Complexes. *Inorg. Chem.* **2005**, *44*, 2326–2336.

(30) Koike, K.; Hori, H.; Ishizuka, M.; Westwell, J. R.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Konno, H.; Sakamoto, K.; Ishitani, O. Key Process of the Photocatalytic Reduction of CO_2 Using $[Re(4,4'-X_2-\text{bipyridine})(CO)_3PR_3]^+$ (X = CH_3, H, CF_3; PR_3 = Phosphorus Ligands): Dark Reaction of the One-Electron-Reduced Complexes with CO_2. *Organometallics* **1997**, *16*, 5724–5729.

(31) Koike, K.; Grills, D. C.; Tamaki, Y.; Fujita, E.; Okubo, K.; Yamazaki, Y.; Saigo, M.; Mukuta, T.; Onda, K.; Ishitani, O. Investigation of excited state, reductive quenching, and intramolecular electron transfer of Ru(II)-Re(I) supramolecular photocatalysts for CO_2 reduction using time-resolved IR measurements. *Chem. Sci.* **2018**, *9*, 2961–2974.

(32) Yamazaki, Y.; Ohkubo, K.; Saito, D.; Yatsu, T.; Tamaki, Y.; Tanaka, S.; Koike, K.; Onda, K.; Ishitani, O. Kinetics and Mechanism of Intramolecular Electron Transfer in Ru(II)-Re(I) Supramolecular CO_2-Reduction Photocatalysts: Effects of Bridging Ligands. *Inorg. Chem.* **2019**, *58*, 11480–11492.

(33) Tamaki, Y.; Morimoto, T.; Koike, K.; Ishitani, O. Photocatalytic CO_2 reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15673–15678.

(34) Tamaki, Y.; Ishitani, O. Supramolecular Photocatalysts for the Reduction of CO_2. *ACS Catal.* **2017**, *7*, 3394–3409.

(35) Ishida, H.; Tanaka, K.; Tanaka, T. Electrochemical CO_2 Reduction Catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)-CI]^+$. The Effect of pH on the Formation of CO and $HCOO^-$. *Organometallics* **1987**, *6*, 181–186.

(36) Ishida, H.; Fujiki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. Ligand Effects of Ruthenium 2,2'-Bipyridine and 1,10-Phenanthroline Complexes on the Electrochemical Reduction of CO_2. *J. Chem. Soc., Dalton Trans.* **1990**, 2155–2160.

(37) Tamaki, Y.; Koike, K.; Ishitani, O. Highly efficient, selective, and durable photocatalytic system for CO_2 reduction to formic acid. *Chem. Sci.* **2015**, *6*, 7213–7221.

(38) Tamaki, Y.; Koike, K.; Morimoto, T.; Yamazaki, Y.; Ishitani, O. Red-Light-Driven Photocatalytic Reduction of CO_2 using Os(II)−Re(I) Supramolecular Complexes. *Inorg. Chem.* **2013**, *52*, 11902–11909.

(39) The other hybrid photocatalytic systems combining metal complex with semiconductor that display high photooxidation powers, have been also reported. As typical examples: (a) Suzuki, T. M.; Yoshino, S.; Takayama, T.; Iwase, A.; Kudo, A.; Morikawa, T. Z-Schematic and visible-light-driven CO_2 reduction using H_2O as an electron donor by a particulate mixture of a Ru-complex/$(CuGa)_{1-x}Zn_{2x}S_2$ hybrid catalyst, $BiVO_4$ and an electron mediator. *Chem. Commun.* **2018**, *54*, 10199–10202. (b) Sekizawa, K.; Sato, S.; Arai, T.; Morikawa, T. Solar-Driven Photocatalytic CO_2 Reduction in Water Utilizing a Ruthenium Complex Catalyst on p-Type Fe_2O_3 with a Multiheterojunction. *ACS Catal.* **2018**, *8*, 1405–1416. (c) Woo, S.-J.; Choi, S.; Kim, S.-Y.; Kim, P. S.; Jo, J. H.; Kim, C. H.; Son, H.-J.; Pac, C.; Kang, S. O. Highly Selective and Durable Photochemical CO_2 Reduction by Molecular Mn(I) Catalyst Fixed on a Particular Dye-Sensitized TiO_2 Platform. *ACS Catal.* **2019**, *9*, 2580–2593. (d) Sekizawa, K.; Maeda, K.; Domen, K.; Koike, K.; Ishitani, O. Artificial Z-Scheme Constructed with a Supramolecular Metal Complex and Semiconductor for the Photocatalytic Reduction of CO_2. *J. Am. Chem. Soc.* **2013**, *135*, 4596–4599. (e) Sato, S.; Morikawa, T.; Saeki, S.; Kajino, T.; Motohiro, T. Visible-Light-Induced Selective CO_2 Reduction Utilizing a Ruthenium Complex Electrocatalyst Linked

to a p-Type Nitrogen-Doped Ta_2O_5 Semiconductor. *Angew. Chem., Int. Ed.* **2010**, *49*, 5101–5105.

(40) Sahara, G.; Abe, R.; Higashi, M.; Morikawa, T.; Maeda, K.; Ueda, Y.; Ishitani, O. Photoelectrochemical CO_2 reduction using a Ru(II)−Re(I) multinuclear metal complex on a p-type semiconducting NiO electrode. *Chem. Commun.* **2015**, *51*, 10722–10725.

(41) Sahara, G.; Kumagai, H.; Maeda, K.; Kaeffer, N.; Artero, V.; Higashi, M.; Abe, R.; Ishitani, O. Photoelectrochemical Reduction of CO_2 Coupled to Water Oxidation Using a Photocathode With a Ru(II)-Re(I) Complex Photocatalyst and a CoO_x/TaON Photoanode. *J. Am. Chem. Soc.* **2016**, *138*, 14152–14158.

(42) Higashi, M.; Domen, K.; Abe, R. Highly stable water splitting on oxynitride TaON photoanode system under visible light irradiation. *J. Am. Chem. Soc.* **2012**, *134*, 6968–6971.

(43) Nakada, A.; Uchiyama, T.; Kawakami, N.; Sahara, G.; Nishioka, S.; Kamata, R.; Kumagai, H.; Ishitani, O.; Uchimoto, Y.; Maeda, K. Solar Water Oxidation by a Visible-Light-Responsive Tantalum/Nitrogen-Codoped Rutile Titania Anode for Photoelectrochemical Water Splitting and Carbon Dioxide Fixation. *ChemPhotoChem.* **2019**, *3*, 37–45.

(44) Kumagai, H.; Sahara, G.; Maeda, K.; Higashi, M.; Abe, R.; Ishitani, O. Hybrid photocathode consisting of a $CuGaO_2$ p-type semiconductor and a Ru(II)-Re(I) supramolecular photocatalyst: non-biased visible-light-driven CO_2 reduction with water oxidation. *Chem. Sci.* **2017**, *8*, 4242–4249.

(45) Kamata, R.; Kumagai, H.; Yamazaki, Y.; Sahara, G.; Ishitani, O. Photoelectrochemical CO_2 Reduction Using a Ru(II)-Re(I) Supramolecular Photocatalyst Connected to a Vinyl Polymer on a NiO Electrode. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5632–5641.

(46) Kamata, R.; Kumagai, H.; Yamazaki, Y.; Higashi, M.; Abe, R.; Ishitani, O. Durable photoelectrochemical CO_2 reduction with water oxidation using a visible-light driven molecular photocathode. *J. Mater. Chem. A* **2021**, *9*, 1517–1529.