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Red-Light-Driven Photocatalytic Reduction of CO_2 using Os(II)−Re(I) Supramolecular Complexes

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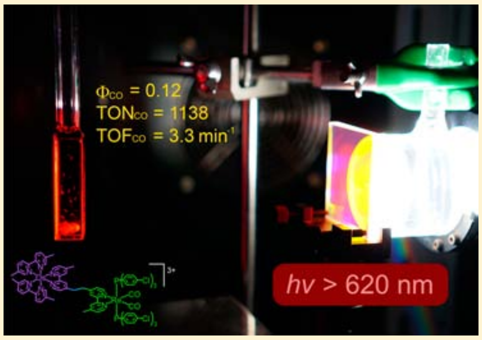
ABSTRACT: The novel supramolecular complexes, which are composed of an $[Os(5dmb)_2(BL)]^{2+}$-type complex (5dmb = 5,5′-dimethyl-2,2′-bipyridine; BL = 1,2-bis(4′-methyl-[2,2′-bipyridin]-4-yl)ethane) as a photosensitizer and *cis,trans*-$[Re(BL)(CO)_2\{P(p\text{-}X\text{-}C_6H_4)_3\}_2]^+$-type complexes (X = F, Cl) as a catalyst, have been synthesized. They photocatalyzed selective reduction of CO_2 to CO under red-light irradiation ($\lambda > 620$ nm). The photocatalytic abilities were affected by the phosphine ligands on the Re unit, and the supramolecule with $P(p\text{-}Cl\text{-}C_6H_4)_3$ ligands exhibited better photocatalysis ($\Phi_{CO} = 0.12$, $TON_{CO} = 1138$, $TOF_{CO} = 3.3\ min^{-1}$). The detailed studies clarified the electron balance and material balance; i.e., one molecule of the sacrificial electron donor (1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]-imidazole (BIH)) donated two electrons, one molecule of CO_2 accepted the two electrons, and another CO_2 molecule served as an "O^{2-}" acceptor to give each molecule of the two-electron oxidized compound of BIH, CO, and HCO_3^-.



■ INTRODUCTION

In recent years, an increase in the concentration of atmospheric CO_2 and shortages of energy and carbon resources have become serious problems. The development of systems that convert solar energy into chemical energy would serve as an ideal solution to these problems. Since solar light contains a small amount of UV light, the utilization of visible light is required for efficient solar energy conversion. Photocatalytic CO_2 reduction utilizing so-called sacrificial organic electron donors is one of the important processes in developing solar energy conversion systems, which should be combined with another process, i.e., photocatalytic water oxidation,[1] in the future.

Recently, visible-light-driven supramolecular photocatalysts for CO_2 reduction have been developed.[2−6] In these systems, ruthenium(II) tris-diimine complexes have been used as a photosensitizer unit most commonly because these complexes absorb visible light and because their excited and reduced forms are both relatively stable. However, the visible light of which the ruthenium(II) photosensitizer unit can absorb is relatively limited ($\lambda < 560$ nm).

In this study, to use a much wider wavelength range of the solar radiation, an osmium(II) complex was employed as a new photosensitizer unit. Although supramolecular photocatalysts for H_2 evolution using an osmium(II) tris-diimine[7] or bis-terpyridine[8] complex as a photosensitizer have been reported, one of the advantages of these units, i.e., the expansion of the utilizable wavelength range of visible light, has not been investigated. To the best of our knowledge, supramolecular photocatalysts for the reduction of CO_2 using an osmium complex as a photosensitizer have not been reported yet. In this study, two new supramolecular photocatalysts capable of reducing CO_2, composed of an $[Os(5dmb)_2(BL)]^{2+}$-type complex (5dmb = 5,5′-dimethyl-2,2′-bipyridine, BL = 1,2-bis(4′-methyl-[2,2′-bipyridin]-4-yl)ethane) as a photosensitizer unit and *cis,trans*-$[Re(BL)(CO)_2\{P(p\text{-}X\text{-}C_6H_4)_3\}_2]^+$-type complexes (X = F, Cl) as a catalyst unit, were developed. The structures and abbreviations of the synthesized complexes are shown in Chart 1. The abbreviation **X** in **Os−Re(X)** and **Re(X)** indicates the substituents of the phosphine ligands in the Re unit.

■ RESULTS AND DISCUSSION

The Os(II)−Re(I) supramolecular complexes were synthesized by a method similar to the synthesis of the reported Ru(II)−Re(I) supramolecules[3d] as shown in Scheme 1. $Os(5dmb)_2Cl_2$ was obtained by the reaction of $(NH_4)_2[OsCl_6]$ with two equivalents of 5dmb and reacted with an excess amount of BL, giving an Os(II) mononuclear complex with a noncoordinated diimine moiety, $[(5dmb)_2Os(BL)]^{2+}$. $[Re(CO)_3\{P(p\text{-}X\text{-}C_6H_4)_3\}_2(OTf)]$ was synthesized according to the method reported in the literature.[3d] The target molecules could be obtained by the reaction of $[Re(CO)_3\{P(p\text{-}X\text{-}C_6H_4)_3\}_2(OTf)]$ and $[(5dmb)_2Os(BL)]^{2+}$ and characterized by ^1H NMR, IR, and HR-MS.

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Chart 1. Structures and Abbreviations of the Os(II)−Re(I) Complexes and Their Mononuclear Model Complexes

Scheme 1. Synthesis of Os−Re(X)

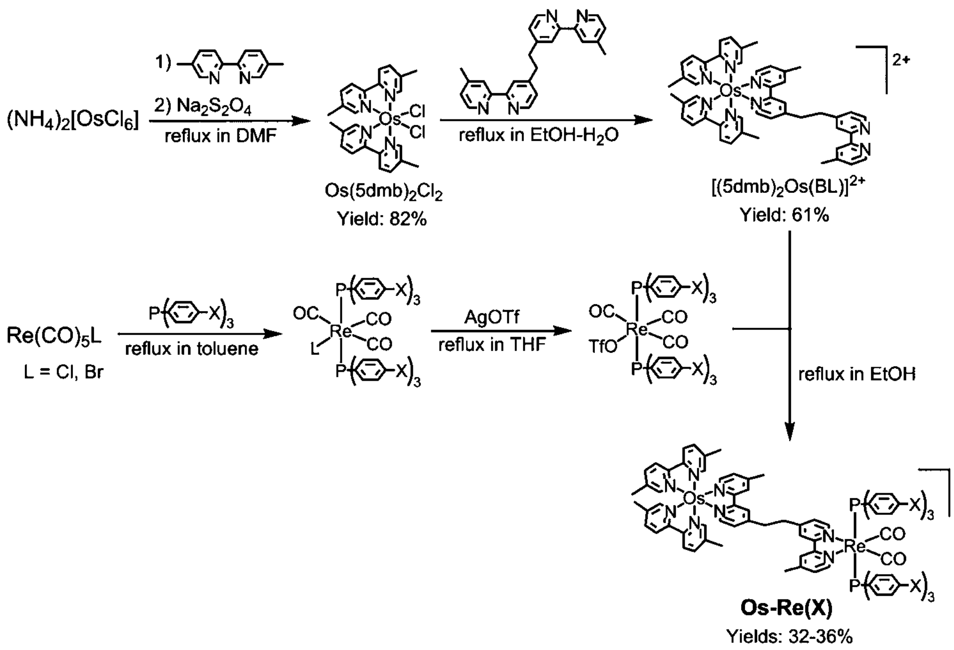


Table 1. Photophysical Properties of the Complexes[a]

complex	λ_{abs}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1}) $\pi-\pi^*$	^{1}MLCT	^{3}MLCT	$\lambda_{em}{}^{b}$/nm	$\Phi_{em}{}^{b}$	$\tau_{em}{}^{c}$/ns
Os−Re(F)	296 (111)	436 (16.0), 477 (14.6)	585 (4.26)	761	0.0044	25
Os−Re(Cl)	296 (114)	436 (15.9), 477 (14.5)	584 (4.29)	763	0.0039	30
Os	295 (88.8)	477 (14.3)	588 (3.99)	749	0.0071	41

[a] Measured in DMF at 25 °C. [b] Excitation wavelength: 520 nm. [c] Excitation wavelength: 559 nm.

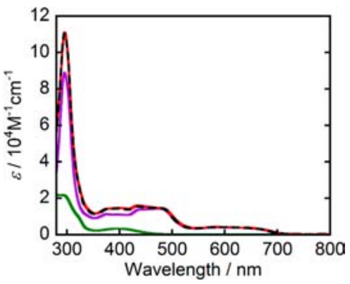


Figure 1. UV−vis absorption spectra of **Os−Re(F)** (red line), **Os** (purple line), and **Re(F)** (green line) in a DMF solution. The simple sum of the spectrum of **Os** and **Re(F)** is shown with a black broken line.

The photophysical properties of **Os−Re(X)** and **Os** are summarized in Table 1. As shown in Figure 1, the spectra of the Os complexes showed ^{3}MLCT absorption bands at 540−730 nm, which were not observed in those of Ru trisdiimine complexes, with absorption bands attributed to ^{1}MLCT (420−540 nm) and $\pi-\pi^*$ (295 nm) transitions of the diimine ligand. This difference should be due to the much stronger spin−orbit coupling of Os compared with that of Ru. Therefore, such osmium photosensitizers have the potential to utilize a much wider wavelength range of visible light (400−730 nm) compared with the ruthenium photosensitizers (<560 nm).

In Figure 1, the UV−vis absorption spectrum of **Os−Re(F)** is compared with those of both **Os** and **Re(F)**. The similarity of the spectrum of **Os−Re(F)** to the simple sum of those of **Os** and **Re(F)** strongly indicates that there is no strong interaction between the Os unit and Re unit of **Os−Re(F)** in its ground state.

In a typical run of photocatalytic reactions, a solution of DMF and triethanolamine (TEOA; 5:1 v/v) containing **Os−Re(F)** (0.05 mM) and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH, 0.1 M) as a reductant was irradiated under a CO_2 atmosphere using a halogen lamp equipped with a rhodamine B solution filter (0.2% w/v, 1-cm pass length: light of wavelengths at $\lambda > 620$ nm is transmitted) to selectively form CO (eq 1, Figure 2a). The turnover number for CO formation (TON_{CO}) reached 762 after 20 h of irradiation. The quantum yield for CO formation (Φ_{CO}) was determined as 0.10 with 650-nm monochromatic light for excitation (light intensity: 1.2×10^{-8} einstein s^{-1}), and the turnover frequency (TOF_{CO}) was 1.6 min^{-1}, which was measured using light at $\lambda > 420$ nm in order to get higher light intensity. In the absence of either **Os–Re(F)** or BIH, or without irradiation, CO was not produced. Also, the irradiation of the solution containing BIH and **Os** instead of **Os–Re(F)** did not produce CO.

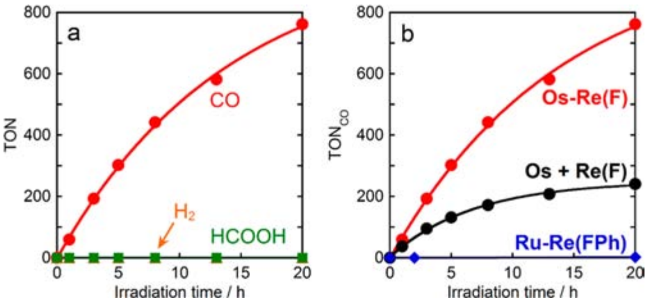
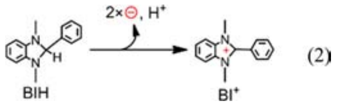


Figure 2. (a) Photocatalytic formation of CO, HCOOH, and H_2 as a function of irradiation time using **Os–Re(F)** and (b) photocatalytic formation of CO as a function of irradiation time using **Os–Re(F)** (red ●), **Os** + **Re(F)** (1:1, black ●), and **Ru–Re(FPh)** (blue ♦). CO_2-saturated DMF–TEOA (5:1 v/v, 2 mL) solutions containing the complex (0.05 mM) and BIH (0.1 M) were irradiated at λ >620 nm.

$$\mathrm{CO_2} \xrightarrow[\text{BIH (0.1 M) in DMF-TEOA (5:1 v/v)}]{\textbf{Os-Re(F)}\text{ (0.05 mM)}/h\nu\ (>620\text{ nm})} \mathrm{CO} \tag{1}$$

The photocatalytic abilities of **Os–Re(X)** and mixed systems of the corresponding mononuclear complexes together with those of the Ru(II)–Re(I) photocatalyst reported previously[3d,f] are shown in Table 2. The photocatalytic ability of **Os–Re(F)** was much greater than that of a mixed system of the corresponding mononuclear complexes (**Os** + **Re(F)**, 1:1); i.e., a higher TON and a faster formation of CO were achieved (Figure 2b, Table 2). The reported bimetallic photocatalyst composed of a ruthenium(II) photosensitizer unit and the same rhenium(I) catalyst unit (**Ru–Re(FPh)**), which served as a good photocatalyst for the reduction of CO_2 when irradiated with light at λ >500 nm,[3f] scarcely produced CO when only using longer wavelengths (Figure 2b, Table 2), because **Ru–Re(FPh)** cannot absorb light at $\lambda > 620$ nm.

The oxidized compound of BIH during the photocatalytic reaction was identified and quantified by HPLC. Only the two-electron oxidized and deprotonated compound (BI^+) was detected (eq 2).



(2)

Both the decrease of BIH and increase of BI^+ in the reaction solution are shown in Figure 3. The amount of BI^+ produced exactly agreed with that of BIH consumed. The amount of CO produced was also very similar to the amount of BI^+ produced. After 20 h of irradiation, for example, 76 μmol of CO and 78 μmol of BI^+ were produced, and 76 μmol of BIH was consumed. The formation of CO requires the injection of two electrons to one molecule of CO_2, and the formation of one BI^+ molecule from BIH leads to the donation of two electrons. These results clearly indicate that BIH acted as a two-electron donor in the photocatalytic reaction.

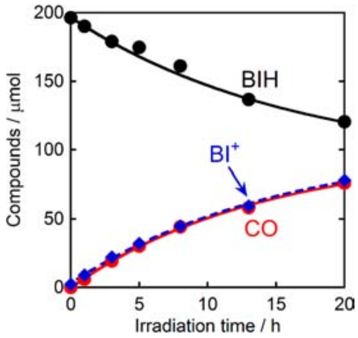


Figure 3. Photocatalytic production of CO (red ●) and BI^+ (blue ♦) and consumption of BIH (black ●): a CO_2-saturated DMF–TEOA (5:1 v/v, 2 mL) solution containing BIH (0.1 M) and an **Os–Re(F)** complex (0.05 mM) was irradiated at $\lambda > 620$ nm.

Table 2. Photocatalytic Reduction of CO_2 by the Os(II)–Re(I) Supramolecules and the Model System[a]

	TON[b]						
photocatalyst	CO	HCOOH	H_2	Φ_{CO}[c]	TOF_{CO}[d]/min^{-1}	k_q[e]/10^8 $M^{-1}s^{-1}$	η_q[f]/%
Os–Re(F)	762	<1	<1	0.10	1.6	2.1	34
Os–Re(Cl)	1138	4	<1	0.12	3.3	1.6	32
Os + **Re(F)**	240	3	<1			1.8[g]	43[g]
Os + **Re(Cl)**	363	3	<1			1.8[g]	43[g]
Ru–Re(FPh)[h]	3	<1	<1			97[i]	99[i]

[a] A CO_2-saturated DMF–TEOA (5:1 v/v) solution containing the complex (0.05 mM) and BIH (0.1 M) was irradiated. [b] Turnover number of the reaction products after 20 h of irradiation ($\lambda > 620$ nm) is calculated as [products (μmol)]/[added supramolecule or **Os** (μmol)]. [c] Quantum yield for CO formation calculated as [produced CO (μmol)]/[absorbed photon (μeinstein)] (irradiation wavelength, 650 nm; light intensity, 1.2×10^{-8} einstein s^{-1}). [d] Turnover frequency for CO formation calculated as [produced CO (μmol)]/[added supramolecule or **Os** (μmol) × irradiation time (min)], irradiation at $\lambda > 420$ nm. [e] Quenching rate constant for emission from the Os(II) units by BIH. [f] Quenching fractions for emission from the Os(II) units by 0.1 M of BIH calculated as $0.1k_q\tau_{em}/(1 + 0.1k_q\tau_{em})$. $k_q\tau_{em}$ are obtained from the slopes of Stern–Volmer plots (excitation wavelength, 650 nm). [g] Determined by emission from **Os** (excitation wavelength, 650 nm). [h] $[Ru(4dmb)_2(BL)]^{2+}$ (4dmb = 4,4′-dimethyl-2,2′-bipyridine) was used as a photosensitizer unit instead of $[Os(5dmb)_2(BL)]^{2+}$ (see refs 3d and 3f). [i] Determined by emission from the Ru(II) unit (excitation wavelength, 530 nm)

A labeling experiment using $^{13}CO_2$ was conducted to clarify the carbon source of CO and the "O^{2-}" acceptor in the photocatalytic reaction. Before irradiation, a strong signal attributed to $^{13}CO_2$ was observed at 125.6 ppm in the ^{13}C NMR spectrum of a DMF-d_7 solution containing TEOA (1.25 M), **Os−Re(F)** (1.0 mM), BIH (0.1 M), and $^{13}CO_2$ (625 Torr; Figure 4a). Irradiation at λ >620-nm light for 23 h resulted in a decrease of the $^{13}CO_2$ signal and an appearance of a new signal of relatively weak intensity, attributed to ^{13}CO at 185.2 ppm (Figure 4b). This relatively weak-intensity signal is attributed to the low solubility of CO in the solution. A strong signal attributed to $H^{13}CO_3^-$ was also observed at 158.3 ppm after irradiation, whereas a signal with a much weaker peak intensity of $H^{13}CO_3^-$ was observed before irradiation.[9]

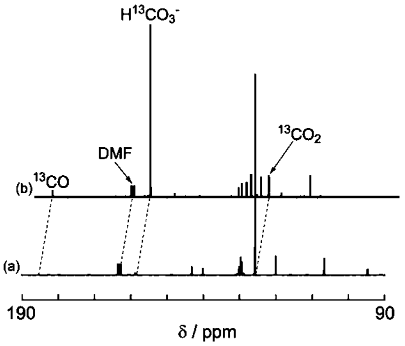


Figure 4. ^{13}C NMR spectra of the reaction solution (0.6 mL) before (a) and after (b) 23 h of irradiation. A DMF-d_7 solution containing TEOA (1.25 M), BIH (0.1 M), **Os−Re(F)** (1.0 mM), and $^{13}CO_2$ (625 Torr) was irradiated with a halogen lamp at λ > 620 nm.

A NOE complete ^1H-decoupling ^{13}C NMR[3f,10] result using the carbon of TEOA (1.25 M) as an internal standard for the area integration of the ^{13}C peaks showed that 0.092 M HCO_3^- was produced in the photocatalytic reaction. Simultaneously, the ^{13}C peaks attributed to BIH (0.1 M before irradiation) completely disappeared, while peaks representing BI^+ appeared (Figure 5). This means an amount of HCO_3^- almost equivalent to that of consumed BIH was produced in the reaction solution. These results clearly show that CO_2 worked both as a carbon source for the formation of CO and as an "O^{2-}" acceptor forming HCO_3^-.

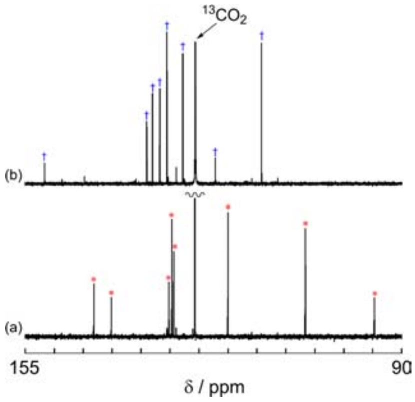


Figure 5. Enlarged ^{13}C NMR spectra of the reaction solution before (a) and after (b) 23 h of irradiation for the same sample shown in Figure 4. The symbols ∗ and † represent the ^{13}C peaks of BIH and BI^+, respectively.

From the product analyses, it can be concluded that BIH donated two electrons, one molecule of CO_2 accepted two electrons, and another molecule of CO_2 that served as an "O^{2-}" acceptor to give each molecule of BI^+, CO, and HCO_3^-, as shown in eq 3:

$$2CO_2 + BIH \xrightarrow[\text{DMF-TEOA(5:1v/v)}]{\textbf{Os-Re(F)}/h\nu(>620\text{nm})} CO + BI^+ + HCO_3^- \qquad (3)$$

Since, as shown in Figure 1, only the Os unit absorbed light at λ > 620 nm under the photocatalytic reaction conditions, the photochemical reactivity of **Os** in the presence of BIH was investigated. Emission from **Os** was quenched by BIH with a quenching rate constant k_q of 1.8×10^8 M^{-1} s^{-1} and a quenching efficiency η_q of 43% (Table 2: in the case of emission from the Os unit of **Os−Re(F)**, $k_q = 2.1 \times 10^8$ M^{-1} s^{-1} and η_q = 34%). UV−vis absorption spectral changes of a DMF−TEOA solution containing **Os** (0.05 mM) and BIH (0.1 M) during irradiation under a CO_2 atmosphere and differential spectra between post- and preirradiation spectra are shown in Figure 6a and b, respectively.

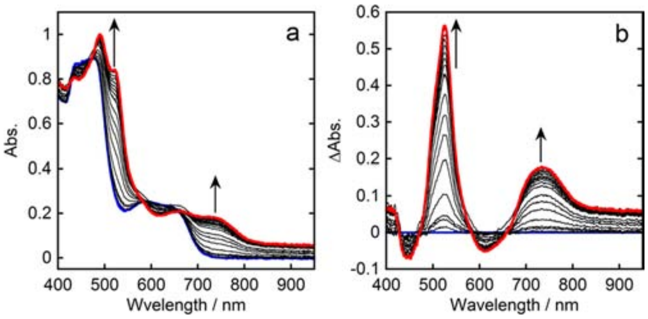


Figure 6. (a) UV−vis absorption spectral changes of a CO_2-saturated DMF−TEOA (5:1 v/v) solution containing **Os** (0.05 mM) and BIH (0.1 M) during irradiation at 650 nm (0−900 s at 50 s intervals) and (b) differential spectra between post- and preirradiation spectra. The blue and red lines represent the spectra before and after irradiation for 900 s, respectively.

New absorption bands at 525 and 730 nm appeared and increased during irradiation. The shape of the differential spectra was very similar to that of one-electron reduced (OER) species of **Os** (**Os**$^-$) obtained by electrochemical spectroscopy (Figure 7). These results strongly support that the ^{3}MLCT excited state of the Os unit of **Os−Re(F)** was reductively quenched by BIH to give **Os**$^-$**−Re(F)** (eq 4).

$$\textbf{Os-Re(F)} \xrightarrow{h\nu} {}^{*}\textbf{Os-Re(F)} \xrightarrow{\text{BIH}} \overset{\ominus}{\textbf{Os}}\textbf{-Re(F)} \qquad (4)$$

To investigate the reaction of photochemically produced **Os**$^-$**−Re(F)**, IR spectral changes of a solution containing **Os−Re(F)** and BIH were also measured during irradiation (Figure 8). Before irradiation, two peaks attributed to the symmetric and asymmetric stretching−vibration bands of two CO ligands of the Re unit of **Os−Re(F)** were observed at 1938 and 1867 cm^{-1}. During irradiation, these peaks decreased, and two new peaks appeared at about 1904 and 1835 cm^{-1}, which is attributed to the vibration bands of two CO ligands of the OER species of the Re unit.[11,12] This result clearly indicates that an intramolecular electron transfer occurred from the OER species of the Os unit to the Re unit during irradiation (eq 5). This is

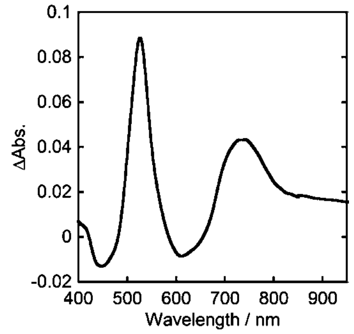


Figure 7. UV−vis differential spectrum between before and after electrolysis (one-electron reduction) of **Os**. **Os** (0.5 mM) dissolved in an Ar-saturated DMF solution containing Et_4NBF_4 (0.1 M) as an electrolyte was reduced at −1.85 V using a UV−vis OTTLE cell with a Pt-mesh working electrode and a $Ag/AgNO_3$ reference electrode.

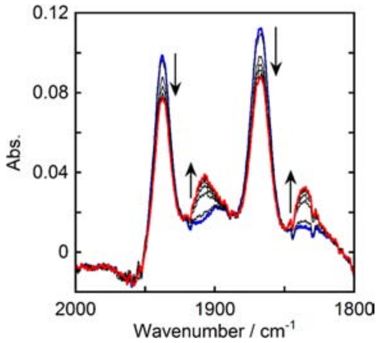


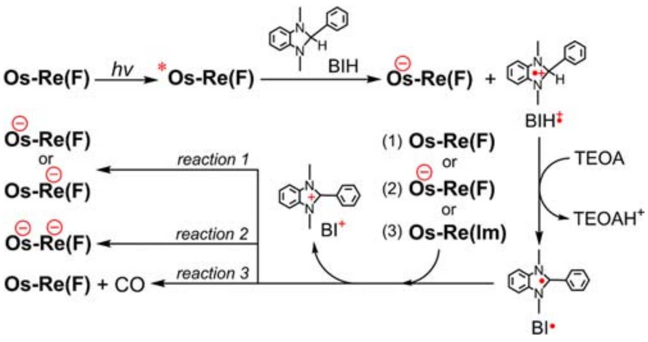
Figure 8. IR spectral changes of a CO_2-saturated DMF−TEOA (5:1 v/v) solution containing **Os−Re(F)** (0.8 mM) and BIH (0.1 M) during irradiation at 600 nm (0−300 s at 38 s intervals). The blue and red lines represent the spectra before and after irradiation for 300 s, respectively.

reasonable because this intramolecular electron transfer should be exergonic by 20 mV ($E_{1/2}{}^{red}$(**Os**) = −1.76 V, $E_{1/2}{}^{red}$(**Re(F)**) = −1.74 V vs $Ag/AgNO_3$: Table 3).

$$\overset{\ominus}{\text{Os}}\text{-Re(F)} \longrightarrow \text{Os-}\overset{\ominus}{\text{Re}}\text{(F)} \qquad (5)$$

The two-electron donation process of BIH has already been clarified in the photocatalytic reaction system using a Ru(II)−Re(I) supramolecular complex, which is composed of a $[Ru(4dmb)_2(BL)]^{2+}$-type (4dmb = 4,4′-dimethyl-2,2′-bipyridine) photosensitizer instead of the Os unit and the same catalyst unit (**Ru−Re(FPh)**), as a photocatalyst.[3f] In this case, the initial process of the photocatalytic CO_2 reduction is also a photoinduced electron transfer from BIH to the Ru(II) photosensitizer unit, forming the OER species of the photosensitizer unit and one-electron oxidized BIH ($BIH^{•+}$). $BIH^{•+}$ is rapidly deprotonated by TEOA to give $BI^•$. TEOA worked as a base, but it could not quench the excited state of the Os unit. Since $BI^•$ is a strong reducing agent ($E_{1/2}{}^{red}$ = −1.95 V vs $Ag/AgNO_3$),[13] it can donate one more electron to **Ru−Re(FPh)** and/or the OER species of **Ru−Re(FPh)** to be converted to BI^+. That is, BIH acts as a two-electron donor with one-photon excitation of the photocatalyst via the ECE mechanism.[3f] Similar processes should also proceed in the Os(II)−Re(I) photocatalytic system, because the same catalyst unit ($E_{1/2}{}^{red}$(**Re(F)**) = −1.74 V) is employed, and the reduction potentials of the Os and Ru photosensitizer units are similar to each other ($E_{1/2}{}^{red}([Ru(4dmb)_3]^{2+})$ = −1.81 V, $E_{1/2}{}^{red}$(**Os**) = −1.76 V: Table 3). On the basis of the above-described investigation, the electron-donation process of BIH is illustrated in Scheme 2. $BI^•$ should donate one electron to the photosensitizer unit or to the catalyst unit even in its ground state (reaction 1 in Scheme 2), and possibly to the intermediate(s), i.e., the OER species and/or **Os−Re(Im)**, which should be produced after the one-electron reduction of the catalyst unit and the subsequent chemical reaction(s), such as CO_2 addition (reactions 2 and 3 in Scheme 2).

Scheme 2. Electron-Donation Processes of BIH in the Photocatalytic Reaction[a]



[a]**Os−Re(Im)** is an intermediate produced via the one-electron reduction of the catalyst unit and the subsequent process(es).

The substituent group of the phosphine ligands in the Re unit influenced photocatalysis. **Os−Re(Cl)** with the P(*p*-Cl-$C_6H_4)_3$ ligands exhibited a higher photocatalytic ability (Φ_{CO} = 0.12, TON_{CO} = 1138 (20 h irradiation), TOF_{CO} = 3.3 min^{-1}) compared with **Os−Re(F)** (Φ_{CO} = 0.10, TON_{CO} = 762 (20 h irradiation), TOF_{CO} = 1.6 min^{-1}; Table 2, Figure 9).

Since efficiencies in the photochemical formation of the OER species of the photocatalysts (η_q) were very similar to each other (Table 2), the difference in photocatalytic abilities should

Table 3. Electrochemical Properties of Os(II)−Re(I) Complexes and Their Mononuclear Model Complexes

	$E_{1/2}$ (ΔE/mV)/V vs $Ag/AgNO_3$[a]					
complex	$Re^{I/II}$[b]	$Os^{II/III}$	M(N^N/N^N·⁻) (M = Os or Re)			$Re^{I/0}$[b]
Os−Re(F)	1.07	0.30 (69)	−1.73 (95)[c]	−1.95 (84)	−2.30 (82)	−2.18
Os−Re(Cl)	1.09	0.30 (69)	−1.72 (101)[c]	−1.95 (87)	−2.30 (89)	−2.17
Os		0.28 (69)	−1.76 (70)	−1.95 (73)	−2.30 (81)	
Re(F)	1.06		−1.74 (69)			−2.27
Re(Cl)	1.08		−1.72 (69)			−2.24

[a]Measured in a DMF solution containing the complex (0.5 mM) and Et_4NBF_4 (0.1 M) with a scan rate of 200 mV s^{-1} under an Ar atmosphere. [b]Peak potential of an irreversible wave. [c]Two-electron wave.

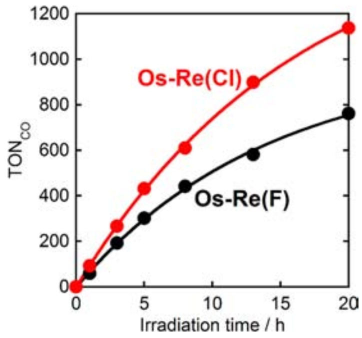


Figure 9. Photocatalytic formation of CO as a function of irradiation time using **Os−Re(Cl)** (red ●) and **Os−Re(F)** (black ●). CO_2-saturated DMF−TEOA (5:1 v/v, 2mL) solutions containing the complex (0.05 mM) and BIH (0.1 M) were irradiated with light at $\lambda > 620$ nm.

be caused by processes such as intramolecular electron transfer from the OER species of the Os unit to the Re unit. Figure 10 shows the cyclic voltammograms of both complexes and model complexes. These first reduction waves were attributed to the ligand-based redox, i.e., $N^\wedge N/N^\wedge N^{\bullet -}$ ($N^\wedge N$: diimine ligand). The waves of the supramolecules can be simulated by the summation of those of the models, i.e., **Os** and **Re(X)**. Both $E_{1/2}^{red}$ of **Re(Cl)** (−1.72 V) and **Re(F)** (−1.74 V) were more positive as compared with that of **Os** (−1.76 V);[14] therefore, the intramolecular electron-transfer process from the OER species of the Os unit to the Re unit is exergonic in both cases. $E_{1/2}^{red}$ of **Re(Cl)** was more positive than that of **Re(F)** by 20 mV, and this difference probably affected the localization of the inserted electron in the Os or Re unit of the OER species. In the case of **Os−Re(Cl)**, the electron localization on the Re unit should be larger than that in the case of **Os−Re(F)**, and this might be one of the reasons why **Os−Re(Cl)** worked as a more efficient photocatalyst.

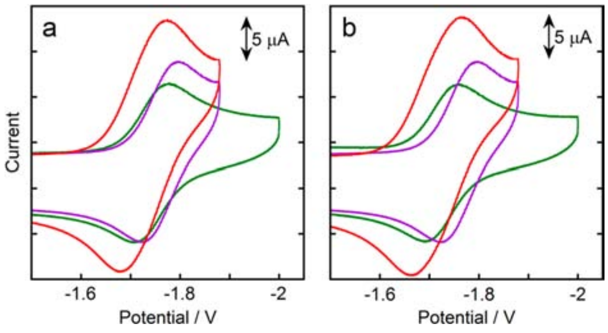


Figure 10. Cyclic voltammograms of **Os−Re(X)** (red line) and its mononuclear model complexes (**Os**, purple line; **Re(X)**, green line) measured in a DMF solution containing Et_4NBF_4 as a supporting electrolyte with a Ag/$AgNO_3$ reference electrode: (a) **Os−Re(F)**, (b) **Os−Re(Cl)**.

■ EXPERIMENTAL SECTION

General Procedures. UV−vis absorption spectra were measured with a JASCO V-670 or a Photal MCPD-9800 spectrophotometer. ^1H NMR spectra were measured in acetone-d_6 using a JEOL AL400 (400 MHz) or AL300 (300 MHz) system. Residual protons of acetone-d_6 were used as internal standards for the measurements. IR spectra were measured with a JASCO FT/IR-610 spectrometer in a dichloromethane or acetonitrile solution. Electrospray ionization mass spectroscopy (ESI-MS) was performed using a Shimadzu LCMS-2010A system with acetonitrile as a mobile phase. Electrospray ionization time-of-flight mass spectroscopy (ESI-TOFMS) was undertaken with a Waters LCT Premier, with acetonitrile as a mobile phase. Emission spectra were measured at 25 °C with a JASCO FP-8600 spectrofluorometer. The emission quantum yields were evaluated by emission from $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2′-bipyridine) in degassed acetonitrile (Φ_{em} = 0.095).[15] Emission lifetimes were obtained using a HORIBA TemPro fluorescence lifetime system with emission monochromator. The excitation light source was a NanoLED-560 (559 nm, 1.5 ns). The samples were degassed by the freeze−pump−thaw method before emission measurements. Emission quenching experiments were performed using Ar-saturated solutions containing a complex and five different concentrations of BIH. The redox potentials of the complexes were measured in a DMF solution containing Et_4NBF_4 (0.1 M) as a supporting electrolyte by cyclic voltammetric techniques using an ALS/CHI CHI-720Dx electrochemical analyzer with a glassy-carbon disk working electrode (3 mm diameter), a Ag/$AgNO_3$ (0.01 M) reference electrode, and a Pt counterelectrode. The supporting electrolyte was dried in a vacuum at 100 °C for 1 day prior to use. The scan rate was 200 mV s^{-1}.

Photocatalytic Reactions. Photocatalytic reactions were conducted using a DMF−TEOA (5:1 v/v) solution containing the photocatalyst, i.e., **Os−Re(X)** (X = F, Cl, 0.05 mM) or a mixture of **Os** (0.05 mM) and **Re(X)** (X = F, Cl, 0.05 mM), and BIH (0.1 M), which was purged with CO_2 for 20 min before irradiation.

For determining Φ, a 4 mL solution in an 11 mL quartz cubic cell (light pass length: 1 cm) was irradiated using 650 nm monochromatic light obtained using a 500-W Xenon short-arc lamp (Ushio UXL-500D-O) combined with a 5-cm-long water filter and a band-pass filter (fwhm = 10 nm). During irradiation, the temperature of the solutions was maintained at 25 °C using an IWAKI constant-temperature system CTS-134A. In situ measurements of UV−vis absorption spectra were conducted using a Photal MCPD-9800 spectrophotometer during irradiation to determine the absorbed photon number. The incident light intensity at 650 nm was determined using 480 nm light (4.3×10^{-8} einstein s^{-1}), which was determined using a $K_3Fe(C_2O_4)_3$ chemical actinometer,[16] as a standard because it does not absorb 650 nm light. The light intensity ratio between 650 and 480 nm was determined using a Photal MCPD-9800 photodiode array spectrometer calibrated for wavelength-dependent sensitivity.

For determining TON, a 2-mL solution in an 11 mL Pyrex glass tube (i.d. = 8 mm) was irradiated with light at $\lambda > 620$ nm using a merry-go-round irradiation apparatus with a halogen lamp and a Rhodamine B (0.2% w/v, d = 1 cm) solution filter.[17] During irradiation, the temperature of the solutions was maintained at 20 °C using a constant temperature system EYELA CTP-1000.

For determining TOF, a 4-mL solution in an 11 mL quartz cubic cell (light pass length: 1 cm) was irradiated with light at $\lambda > 420$ nm using a Xenon lamp with a 5-cm-long water filter and a cutoff filter ($\lambda > 420$ nm).

The gaseous reaction products (CO and H_2) were analyzed using GC−TCD (GL Science GC323). HCOOH was analyzed using a capillary electrophoresis system (Otsuka Electronics Co. CAPI-3300I). As pretreatment for HCOOH quantification, the photocatalytic reaction solution was diluted 10 times with H_2O. Since DMF is hydrolyzed to HCOOH in the presence of a base,[18] the photocatalytic reaction solution without irradiation and saturated with CO_2, which suppresses the hydrolysis of DMF by acting as an acid, was employed as a reference. Before and after the quantification of HCOOH, the reference solution was also measured, and its value was subtracted from the quantified HCOOH.

HPLC analyses for BIH and BI^+ were conducted using a JASCO 880-PU pump, a Develosil ODS-UG-5 column (250 × 4.6 mm), a JASCO 880−51 degasser, and a JASCO UV-2070 detector. The column temperature was maintained at 30 °C using a JASCO 860-CO oven. The mobile phase was a 6:4 (v/v) mixture of acetonitrile and a NaOH−KH_2PO_4 buffer solution (0.05 M, pH 7) with a flow rate of 0.5 mL min^{-1}. The retention times were 38.0 min (BIH) and 6.7 min (BI^+).

Labeling Experiments Using $^{13}CO_2$. The experiments with $^{13}CO_2$ were performed in a DMF-d_7 solution containing TEOA (1.25 M), **Os−Re(F)** (1.0 mM), and BIH (0.1 M). The tube was deaerated using the freeze−pump−thaw method, and then $^{13}CO_2$ (625 Torr) was introduced into it. The ^{13}C NMR spectra were measured with a JEOL AL300 (75 MHz) system before and after 23 h of irradiation with a halogen lamp at $\lambda > 620$ nm and the rhodamine B solution filter. The ^{13}C peaks from DMF-d_7 were used as an internal standard for these experiments. The integration of the peaks using the NOE complete ^1H-decoupling method (EXMOD, nne; pulse delay, 400 s) was used for determining the $H^{13}CO_3^-$ concentration, and the carbon of $N(CH_2CH_2OH)_3$ (TEOA) was used as an internal standard.

In Situ IR Spectral Measurements during Irradiation. A CO_2-saturated DMF−TEOA (5:1 v/v) solution containing the photocatalyst (0.8 mM) and BIH (0.1 M) was irradiated using a compact 300 W Xenon light source MAX-302 (Asahi Spectra Co.) with a 600 nm (fwhm =10 nm) band-pass filter (Asahi Spectra Co.). The IR spectra were measured with a JASCO FT/IR-610 spectrometer using an MCT detector. The solution temperature was controlled at 25 °C using a UNISOKU CoolSpeK IR USP-203IR-A during irradiation.

Electrochemical Spectroscopy. A UV−vis OTTLE cell (light pass length: 1.0 mm) equipped with a Pt-mesh working electrode, a $Ag/AgNO_3$ (0.01 M) reference electrode, and a Pt counterelectrode was employed for the UV−vis spectroelectrochemical experiments. UV−vis spectral changes were measured using a JASCO V-670 spectrometer. The controlled potential electrolysis experiments were conducted in a DMF solution containing Et_4NBF_4 (0.1 M) as a supporting electrolyte using an ALS/CHI CHI-720Dx electrochemical analyzer.

Materials. DMF was dried over 4A molecular sieves and distilled under reduced pressure (10−20 Torr). TEOA was distilled under reduced pressure (<1 Torr). They were kept under Ar prior to use. All other reagents were reagent-grade quality and were used without further purification.

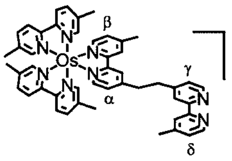
Synthesis. 1,2-Bis(4′-methyl-[2,2′-bipyridin]-4-yl)ethane ($bpyC_2bpy$),[19] *mer*-$[Re(CO)_3Cl\{P(p\text{-}F\text{-}C_6H_4)_3\}_2]$,[3d] **Re(F)**,[11a] **Re(Cl)**,[11a] BIH,[13,20] and $[BI^+](PF_6^-)$[3f] were prepared according to the methods reported in the literature.

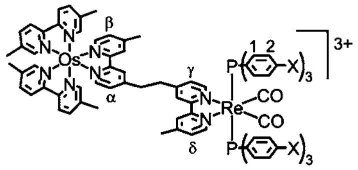
mer-$[Re(CO)_3Br\{P(p\text{-}Cl\text{-}C_6H_4)_3\}_2]$ was synthesized using a method similar to the synthesis of *mer*-$[Re(CO)_3Cl\{P(p\text{-}F\text{-}C_6H_4)_3\}_2]$ except for the use of $P(p\text{-}Cl\text{-}C_6H_4)_3$ instead of $P(p\text{-}F\text{-}C_6H_4)_3$. Yield: 98%. FT-IR (in dichloromethane), ν_{CO}/cm^{-1}: 2058, 1958, 1914.

$Os(5dmb)_2Cl_2$. A DMF solution (10 mL) of $(NH_4)_2[OsCl_6]$ (200 mg, 0.456 mmol) and 5,5′-dimethyl-2,2′-bipyridine (171 mg, 0.926 mmol) was refluxed under an Ar atmosphere for 3 h. After cooling to room temperature, the solution was added to an aqueous solution (30 mL) containing $Na_2S_2O_4$ (3.4 g) and then kept in a refrigerator for 15 h. The dark precipitate was collected by vacuum filtration, washed with water and diethyl ether, and used in the following reactions without further purification. Yield: 232 mg (81%).

$[Os(5dmb)_2(4dmb)](PF_6)_2$ ***(Os)***. A mixed solution of ethanol−H_2O (14 mL, 5:2 v/v) containing $Os(5dmb)_2Cl_2$ (50.2 mg, 0.0797 mmol) and 4,4′-dimethyl-2,2′-bipyridine (20.2 mg, 0.110 mmol) was refluxed for 3 h. The addition of an NH_4PF_6-saturated aqueous solution caused the precipitation of green-black solids. After being kept in a refrigerator for 15 h, the precipitate was collected by vacuum filtration. The product was isolated by column chromatography with basic alumina and dichloromethane−acetonitrile (0−20%). Yield: 29.8 mg (36%). ^1H NMR (400 MHz, acetone-d_6), δ/ppm: 8.58−8.62 (m, 6H, 4dmb-3,3′, 5dmb-3,3′), 7.80 (d, J = 8.4 Hz, 4H, 5dmb-4,4′), 7.69−7.71 (m, 6H, 4dmb-6,6′, 5dmb-6,6′), 7.30 (d, J = 6.8 Hz, 2H, 4dmb-5,5′), 2.63 (s, 6H, 4dmb-CH_3), 2.20−2.21 (m, 12H, 5dmb-CH_3). ESI-MS (in acetonitrile), m/z: 371 ($[M - 2PF_6^-]^{2+}$). Anal. Calcd for $C_{36}H_{36}F_{12}N_6OsP_2$: C, 41.86; H, 3.51; N, 8.14. Found: C, 41.78; H, 3.58; N, 8.02.

$[(5dmb)_2Os(bpyC_2bpy)](PF_6)_2$. $Os(5dmb)_2Cl_2$ (173 mg, 0.275 mmol) was added to an ethanol−H_2O (100 mL, 4:1 v/v) solution containing $bpyC_2bpy$ (400 mg, 1.09 mmol) and refluxed for 13.5 h. After ethanol was evaporated, residual $bpyC_2bpy$ was removed with filtration. The product was purified using ion-exchange column chromatography (absorbent, SP Sephadex C-25; eluent, acetonitrile−H_2O (1:1 v/v) containing NH_4PF_6), and a green-black powder was obtained. Yield: 203 mg (61%). ^1H NMR (400 MHz, acetone-d_6) δ/ppm: 8.73 (s, 1H, α-py-3), 8.56−8.59 (m, 5H, γ-py-6, 5dmb-3,3′), 8.49 (d, J = 4.8 Hz, 1H, δ-py-6), 8.41 (d, J = 5.2 Hz, 1H, α-py-6), 8.31 (s, 1H, β-py-3), 8.29 (s, 1H, γ-py-3), 7.77−7.79 (m, 4H, 5dmb-4,4′), 7.74 (d, J = 6.0 Hz, 1H, β-py-6), 7.68−7.70 (m, 4H, 5dmb-6,6′), 7.62 (s, 1H, δ-py-3), 7.38 (d, J = 6.0 Hz, 1H, α-py-5), 7.29 (d, J = 4.8 Hz, 1H, β-py-5), 7.22−7.24 (m, 2H, γ-py-5, δ-py-5), 3.16−3.35 (m, 4H, −CH_2CH_2−), 2.60 (s, 3H, β-py-CH_3), 2.43 (s, 3H, δ-py-CH_3), 2.15−2.19 (m, 12H, 5dmb-CH_3). ESI-MS (in acetonitrile) m/z: 309 ($[M - 2PF_6^- + H^+]^{3+}$), 463 ($[M - 2PF_6^-]^{2+}$).





$[(5dmb)_2Os(bpyC_2bpy)Re(CO)_2\{P(p\text{–}F\text{-}C_6H_4)_3\}_2](PF_6)_3$ ***(Os−Re(F))***. A THF solution (10 mL) of *mer*-$[Re(CO)_3Cl\{P(p\text{-}F\text{-}C_6H_4)_3\}_2]$ (39 mg, 0.041 mmol) and AgOTf (11 mg, 0.045 mmol) was refluxed for 3.5 h under an Ar atmosphere. After cooling to room temperature, the white precipitate (AgCl) was removed by filtration by passing through Celite, and the solvent was evaporated. An ethanol solution (50 mL) of the residue and $[(5dmb)_2Os(bpyC_2bpy)](PF_6)_2$ (43 mg, 0.035 mmol) was refluxed for 6 h. After the solvent was evaporated, the residue was reprecipitated from acetone/H_2O-containing NH_4PF_6. The product was isolated by column chromatography (basic alumina, eluent: dichloromethane−acetonitrile) and recrystallized from acetone/ether to produce a green-black powder. Yield: 28 mg (36%). ^1H NMR (400 MHz, acetone-d_6) δ/ppm: 8.65 (s, 1H, α-py-3), 8.47−8.51 (m, 5H, β-py-3, 5dmb-3,3′), 8.26 (s, 1H, γ-py-3), 8.16 (s, 1H, δ-py-3), 7.86−7.89 (m, 2H, γ-py-6, δ-py-6), 7.59−7.70 (m, 10H, α-py-6, β-py-6, 5dmb-4,4′, 5dmb-6,6′), 7.33 (d, J = 5.8 Hz, 1H, α-py-5), 7.19−7.25 (m, 13H, β-py-5, $P(p\text{-}F\text{-}C_6H_4)_3$-2), 6.97−7.01 (m, 13H, γ-py-5, $P(p\text{-}F\text{-}C_6H_4)_3$-1), 6.90 (d, J = 5.6 Hz, 1H, δ-py-5), 2.98−3.07 (m, 4H, −CH_2CH_2−), 2.54 (s, 3H, β-py-CH_3), 2.34 (s, 3H, δ-py-CH_3), 2.07−2.13 (m, 12H, 5dmb-CH_3). ESI-MS (in acetonitrile), m/z: 600 ($[M - 3PF_6^-]^{3+}$). FT-IR (in acetonitrile) ν_{CO}/cm^{-1}: 1940, 1870. HRMS (ESI-TOF) m/z: $[M - 3PF_6^-]^{3+}$ Calcd for $C_{86}H_{70}F_6N_8O_2OsP_2Re$: 599.8052. Found: 599.8043.

$[(5dmb)_2Os(bpyC_2bpy)Re(CO)_2\{P(p\text{-}Cl\text{-}C_6H_4)_3\}_2](PF_6)_3$ ***(Os−Re(Cl))***. A THF solution (10 mL) of *mer*-$[Re(CO)_3Br\{P(p\text{-}Cl\text{-}C_6H_4)_3\}_2]$ (44 mg, 0.041 mmol) and AgOTf (11 mg, 0.045 mmol) was refluxed for 3 h under an Ar atmosphere. After cooling to room temperature, the white precipitate (AgCl) was removed by filtration by passing through Celite, and the solvent was evaporated. An ethanol solution (50 mL) of the residue and $[(5dmb)_2Os(bpyC_2bpy)](PF_6)_2$ (43 mg, 0.035 mmol) was heated at 70 °C for 17 h. The product was purified by column chromatography (basic alumina, eluent: dichloromethane−acetonitrile) and recrystallized from acetone−methanol/H_2O-containing NH_4PF_6 and from dichloromethane/ether. The product obtained was a green-black powder. Yield: 26 mg (32%). ^1H NMR (400 MHz, acetone-d_6), δ/ppm: 8.76 (s, 1H, α-py-3), 8.58−8.61 (m, 5H, β-py-3, 5dmb-3,3′), 8.36 (s, 1H, γ-py-3), 8.26 (s, 1H, δ-py-3), 8.01 (d, J = 6.0 Hz, 1H, γ-py-6), 7.94 (d, J = 5.6 Hz, 1H, δ-py-6), 7.59−7.82 (m, 11H, α-py-5, α-py-6, β-py-6, 5dmb-4,4′, 5dmb-6,6′), 7.45 (d, J = 6.0 Hz, 1H, β-py-5), 7.28−7.38 (m, 24H, $P(p\text{-}Cl\text{-}C_6H_4)_3$), 7.09 (d, J = 5.6 Hz, 1H, γ-py-5), 6.98 (d, J = 6.4 Hz, 1H, δ-py-5), 3.08−3.25 (m, 4H, −CH_2CH_2−), 2.65 (s, 3H, β-py-CH_3), 2.50 (s, 3H, δ-py-CH_3), 2.18−2.25 (m, 12H, 5dmb-CH_3). ESI-MS (in acetonitrile), m/z: 633 ($[M - 3PF_6^-]^{3+}$). FT-IR (in acetonitrile) ν_{CO}/cm^{-1}: 1942, 1873. HRMS (ESI-TOF), m/z: $[M - 3PF_6^-]^{3+}$ Calcd for $C_{86}H_{70}Cl_6N_8O_2OsP_2Re$: 633.0786. Found: 633.0741.

■ CONCLUSION

We successfully developed red-light-driven supramolecular photocatalysts composed with an Os(II) tris-diimine complex as a photosensitizer and a Re(I) complex as a catalyst. Irradiation of the photocatalysts in the presence of BIH as a reductant using light at $\lambda > 620$ nm caused selective reduction of CO_2 to CO. The phosphine ligands on the Re catalyst unit affected its photocatalytic abilities, and the photocatalyst with $P(p\text{-Cl-}C_6H_4)_3$ ligands exhibited better photocatalytic activity ($\Phi_{CO} = 0.12$, $TON_{CO} = 1138$, $TOF_{CO} = 3.3\ min^{-1}$) than that with $P(p\text{-F-}C_6H_4)_3$ ligands. The photocatalytic reactions proceeded via (1) light-absorption by the Os unit, (2) electron transfer from BIH to the excited Os unit, (3) intramolecular electron transfer from OER species of the Os unit to the Re unit, and (4) CO_2 reduction on the Re unit giving CO and HCO_3^-.

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Notes

The authors declare no competing financial interest.

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