Highly efficient visible-light-driven CO2 reduction to CO using a Ru(II)–Re(I) supramolecular photocatalyst in an aqueous solution†

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a,b,c

In an aqueous solution, [Ru(dmb)2–(BL)–Re(CO)3Cl]2+ (BL = bridging ligand) most efficiently photocatalyzed the reduction of CO2 to CO under visible-light irradiation using 2-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)benzoic acid (Bl(CO2H)H) as a water-soluble sacrificial reductant (ΦCO = 13%, TON = 130). Since Bl(CO2H)H could efficiently produce one-electron-reduced species of [Ru(diimine)3]2+-type complexes under visible-light irradiation even in an aqueous solution, this is one of the main reasons why the photocatalytic system induced the highly efficient CO2 reduction. This result strongly indicates that Bl(CO2H)H should be a useful reductant for evaluating the real abilities of various photocatalytic systems in water as well.

The photocatalytic reduction of CO2 using water as a reductant and sunlight as an energy source is a promising technology for solving the serious problems of global warming, as well as energy and carbon-resource shortages. Although various photocatalytic systems involving transition-metal complexes as a photosensitizer and/or a catalyst have been reported, besides the semiconductor photocatalyst, most of the systems using metal complexes have been tested only in organic solvents with a sacrificial reductant. For future practical implementation of photocatalytic reduction technology, photocatalytic reactions must proceed using water as the reductant in aqueous solution. As the first step toward this objective, efficient photocatalysts for CO2 reduction that can function in an aqueous solution should be developed, even if they require a sacrificial reductant. Several photocatalytic systems based on a metal-complex catalyst with a [Ru(bpy)3]2+-type photosensitizer (bpy = 2,2′-bipyridine) in aqueous solutions have been tested for CO2 reduction and for hydrogen evolution from water in the presence of ascorbate ion (asc−) as a sacrificial reductant. Unfortunately, most of these systems exhibited very low efficiency, durability, and selectivity for CO2 reduction.

Ru(II)–Re(I) supramolecular photocatalysts constructed with both a Ru photosensitizer and Re catalyst units can efficiently and selectively reduce CO2 to CO in a dimethylformamide (DMF) and triethanolamine (TEOA) mixed solution; they also exhibit high durability. In particular, the use of 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzol[d]imidazole (BIH) as a sacrificial reductant achieved an extraordinarily high quantum yield of CO formation (ΦCO = 45%) by suppression of the back electron transfer from one-electron-reduced species (OERS) of the photocatalyst to the one-electron-oxidized species (OEOS) of the reductant because of the fast deprotonation of the OEOS.

We recently reported selective photocatalytic CO2 reduction to formic acid in an aqueous solution using a Ru(II)–Re(I) supramolecular photocatalyst and asc− as a reductant. In this system, however, the efficiency of the CO2 reduction was much lower than that using 1-benzyl-1,4-dihydropicolinate (BNHA) as a reductant in the DMF–TEOA mixed solution. Although asc− is, to the best of our knowledge, the only reported reductant that can be used in an aqueous solution for photocatalytic CO2 reduction using a [Ru(bpy)3]2+-type photosensitizer, back electron transfer from the reduced photosensitizer to the OEOS of asc− is efficient because of the stability of the OEOS, and the final product of the oxidized ascorbate (dehydroascorbic acid) accepts the electron from the reduced photosensitizer and/or reaction intermediates. Moreover, we observed that asc− accelerated a photochemical ligand-substitution reaction of the Ru(II) photosensitizer, which caused deactivation of the photocatalytic system. These properties of asc− as an inhibitor should make it difficult to evaluate the “real” photocatalytic activities of the systems constructed with such metal complexes in an aqueous solution.

†Electronic supplementary information (ESI) available: Experimental details, photophysical data, results of 13CO2 labeling experiments, 1H NMR observation of the reductant, and UV-vis absorption changes. See DOI: 10.1039/c5gc01720c
Herein, we report 2-(1,3-dimethyl-2,3-dihydro-1H-benimidazol-2-yl)benzoic acid (BI(CO$_2$)H, Chart 1) as a suitable water-soluble reductant for the photocatalytic CO$_2$ reduction; this reductant efficiently quenched the excited state of the Ru(II) photosensitizer unit, giving the OERS of the photosensitizer with a high yield. When this reductant was used, a Ru(II)–Re(I) supramolecular photocatalyst (RuRe, Chart 1) functioned as an efficient (Φ = 13%) and durable (TON = 130) photocatalyst for CO$_2$ reduction, selectively giving CO even in an aqueous solution.

As the first step in investigating the photocatalytic reaction, we evaluated the solubility of BI(CO$_2$)H in aqueous solutions: to dissolve BI(CO$_2$)H in an aqueous solution, more than an equal amount of NaOH should be added to the solution. This indicates that BI(CO$_2$)H dissolves as the carboxylate ion, BI(CO$_2$)$.\text{OH}$. The pH at the equivalence point was 8.9 for 10 mM BI(CO$_2$)H. Because bubbling of the solution containing BI(CO$_2$)H (10 mM) with CO$_2$ induced precipitation of BI(CO$_2$)H even in the presence of 0.1 M NaOH, the concentration of CO$_2$ in the solution should be controlled for the photocatalytic reaction. Suitable conditions were achieved using the following procedure: a CO$_2$-saturated NaOH (0.1 M) aqueous solution was mixed with the same amount of an aqueous solution containing BI(CO$_2$)H (20 mM) and NaOH (0.1 M), which was bubbled with Ar, giving a solution at pH = 9.8 in which all of the added BI(CO$_2$)H was completely dissolved.

In a typical run of the photocatalytic reaction, an aqueous solution containing RuRe (0.05 mM), BI(CO$_2$)H (10 mM), NaOH (0.1 M), and CO$_2$ was irradiated at $\lambda_{\text{ex}} > 500$ nm using a high-pressure Hg lamp combined with a K$_2$CrO$_4$ (30% w/w, d = 1 cm) filter. The Ru photosensitizer unit of RuRe was selectively excited because BI(CO$_2$)$_2$H and the Re catalyst unit could not absorb the $\lambda > 500$ nm light (Fig. S1, ESI†). The irradiation-time dependences of CO, formate, and H$_2$ production are shown in Fig. 1a. CO was the main product, and the turnover number of CO formation (TON$_{\text{CO}}$) based on the amount of photocatalyst used after 6 h of irradiation reached 130. The quantum yield of the photocatalytic CO formation was 13% under the optimized conditions using 480 nm monochromatic light (see ESI†). To the best of our knowledge, this value is 5.6 times greater than that of the best reported for photocatalytic CO$_2$ reduction in an aqueous solution under visible-light irradiation.$^{11}$ H$_2$ was also produced as a by-product during irradiation with long induction periods of up to 3 h. Fig. 1b shows the UV–vis absorption spectra of the reaction solution after irradiation, where the peak at approximately 460 nm is attributed to the MLCT absorption band of the Ru(II) unit. This result indicates that the Ru photosensitizer unit decomposed during the induction period. [Ru$^\text{II}$($\text{bpy}$)$_2$(X)(Y)]$^{n-}$ complexes have been reported to function as catalysts for the photocatalytic formation of H$_2$ in solutions containing water.$^{27}$ The decomposition product(s) of the Ru unit can therefore be reasonably assumed to catalyze H$_2$ evolution after 3 h of irradiation.

Table 1 summarizes the results of the photocatalytic reaction and its control experiments. As previously described, the irradiation to RuRe in the presence of BI(CO$_2$)$_2$H under a CO$_2$ atmosphere photocatalytically produced CO as the main product (entry 1, Table 1). On the other hand, in the control experiments without irradiation, RuRe, BI(CO$_2$)$_2$H, or CO$_2$$_2$, i.e., under an Ar atmosphere, did not give any CO$_2$ reduction products (entries 2–5). Notably, much less CO was produced with larger amounts of H$_2$ and formate when only a mononuclear model complex of the Ru photosensitizer unit, [Ru(dmb)$_2$(mmb)]$^{2+}$ (Ru, dmb = 4,4’-dimethyl-2,2’-bipyridine; mmb = 4-methyl-2,2’-bipyridine), was used instead of RuRe.

Table 1 Photocatalytic reaction and control experiments$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex$^b$</th>
<th>BI(CO$_2$)$_2$H$^c$</th>
<th>hv$^d$</th>
<th>CO$_2$</th>
<th>CO</th>
<th>HCOO$^-$$^e$</th>
<th>H$_2$</th>
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<tr>
<td>1</td>
<td>RuRe</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>13.5</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>RuRe</td>
<td>○</td>
<td>×</td>
<td>○</td>
<td>N.D.</td>
<td>N.D.</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>3</td>
<td>RuRe</td>
<td>×</td>
<td>○</td>
<td>○</td>
<td>N.D.</td>
<td>N.D.</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>RuRe</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>N.D.</td>
<td>N.D.</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>5</td>
<td>×</td>
<td>○</td>
<td>○</td>
<td>×</td>
<td>N.D.</td>
<td>N.D.</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>6</td>
<td>Ru$^f$</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>1.0</td>
<td>4.5</td>
<td>19.9</td>
</tr>
<tr>
<td>7</td>
<td>Re$^f$</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>N.D.</td>
<td>N.D.</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>8</td>
<td>Ru$^f$ + Re$^f$</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>1.5</td>
<td>0.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$^a$ Four milliliters of the reaction solutions were irradiated for 3 h. $^b$ The complex concentration was 0.05 mM. $^c$ The BI(CO$_2$)$_2$H concentration was 10 mM. $^d$ $\lambda_{\text{ex}} > 500$ nm. $^e$ [Ru(dmb)$_2$(mmb)]$^{2+}$ (dmb = 4,4’-dimethyl-2,2’-bipyridine; mmb = 4-methyl-2,2’-bipyridine), was used instead of RuRe. $^f$ [Ru(dmb)$_2$(mmb)]$^{2+}$ Cl.$^* = $ with, $\times =$ without.

Fig. 1 (a) Time-dependent production of CO (blue), HCOO$^-$ (green), and H$_2$ (orange) in the photocatalytic reaction using RuRe. A 4 mL of NaOH (0.1 M) aqueous solution containing RuRe (0.05 mM) and BI(CO$_2$)$_2$H (10 mM) was irradiated at $\lambda_{\text{ex}} > 500$ nm under a CO$_2$ atmosphere. (b) UV–vis absorption changes during the photocatalytic reaction. The inset shows time-dependent absorbance changes at 460 nm.
(entry 6). The formation of H₂ and formate is attributable to products obtained from the photocatalytic reaction system consisting of Ru as a redox photosensitizer and the decomposition product(s) of the Re as the catalyst. A mononuclear model complex of the Re catalyst unit, Re{4,A'-
(CHOPO₂H₂)₂bpy}{CO₂Cl (Re), did not drive CO₂ reduction (entry 7) because Re cannot absorb the irradiated light. A mixed system of two mononuclear model complexes Ru and Re did not work well (entry 8). This strongly suggests that the strategy of the supramolecular photocatalysts, i.e., connecting a photosensitizer and a catalyst with appropriate chemical bonding, is useful for constructing various efficient photocatalytic systems not only in organic solutions²⁰,²⁴ but also in aqueous solution.⁴

To clarify the carbon sources of the produced CO and formate, we conducted ¹³CO₂ labeling experiments. GC-mass spectra (Fig. S2, ESIF) show carbon monoxide and formic acid and/or formate produced by the photocatalytic reactions using RuRe under a ¹³CO₂ (99%, 609 mmHg) atmosphere and under an ordinary CO₂ atmosphere. These results clearly indicate that 93% of CO was obtained by CO₂ reduction. On the other hand, almost no formate was produced from CO₂. The formate might be produced by the partial decomposition of BI(CO₂⁻⁻)H; the oxidation products of BI(CO₂⁻⁻)H are described in greater detail below. The carbonyl ligands of Re(bpy)(CO₂Cl have been reported to be gradually substituted by ¹³CO during the photocatalytic reduction of ¹³CO₂,²⁸ and the amount of ¹²CO produced in the photocatalytic reduction was only 3.7 times the molar equivalents of RuRe added. Therefore, a similar ligand exchange between the carbonyl ligands and the produced CO on the Re center should proceed in the photocatalytic reduction of ¹³CO₂ in the presence of RuRe; this exchange should be the main carbon source of the produced ¹²CO. Another carbon source of ¹²CO might be the contaminant, i.e., ¹²CO₂ in the used ¹³CO₂ gas (the ¹³C content was 99%).

We evaluated the reducing power of BI(CO₂⁻⁻)H in the aqueous solution using cyclic voltammetry, where irreversible oxidation waves of BI(CO₂⁻⁻)H and asc⁻ were observed (Fig. S3, ESIF). The peak potential of BI(CO₂⁻⁻)H was negatively shifted by 340 mV compared to that of asc⁻; therefore, BI(CO₂⁻⁻)H has a much stronger reducing power compared with that of asc⁻, which is one of the properties that makes BI(CO₂⁻⁻)H a suitable sacrificial reductant for the photocatalytic CO₂ reaction in aqueous solution. Actually, BI(CO₂⁻⁻)H served as an efficient quencher of emission from the ¹¹MLCT excited state of the Ru photosensitizer unit of RuRe in an aqueous solution (eqn (1) and Fig. S4, ESIF). The emission quenching rate constant (k₈) was determined as 4.6 × 10⁸ M⁻¹ s⁻¹ from the slope of the linear Stern-Volmer plots (Fig. S4, inset, ESIF), eqn (2), and the emission lifetime of RuRe (τₑ = 366 ns, Fig. S5, ESIF). Notably, the k₈ value was similar to the diffusion-controlled rate constant in water (7.4 × 10⁸ M⁻¹ s⁻¹ at 25 °C), and the k₈ with ascobate instead of BI(CO₂⁻⁻)H was 2.4 × 10⁷ M⁻¹ s⁻¹.

RuIII(N⁺N⁻′) − ReI(N⁺N⁻) + hv → RuIII(N⁺N⁻′) − ReI(N⁺N⁻) (1a)

RuIII(N⁺N⁻′) − ReI(N⁺N⁻) + BI(CO₂⁻⁻)H → RuIII(N⁺N⁻′) − ReI(N⁺N⁻) + BI(CO₂⁻⁻)H⁻ (1b)

\[
\frac{I_0}{T} = 1 + k_q[BI(CO_2)^-H]
\]

The first reduction potentials (E¹/²) of Ru and Re(dbm)-
(CO₂Cl measured in MeCN were −1.73 V and −1.71 V vs. Ag/AgNO₃, respectively (Fig. S6, ESIF). Therefore, the intramolecular electron transfer from the OERS of the Ru unit to the Re unit (eqn (3)) should be thermodynamically favourable. Taking into account this fact and the results of the control experiments described previously, we can conclude that the CO₂ reduction proceeded on the Ru unit:

RuII(N⁺N⁻′) − ReI(N⁺N⁻) + BI(CO₂⁻⁻)H → RuIII(N⁺N⁻′) − ReI(N⁺N⁻) (3)

¹H NMR spectra of the reaction solution (Fig. S7, ESIF) show that BI(CO₂⁻⁻)H was converted into a two-electron-oxidized compound BI⁺(CO₂⁻⁻) in 79% yield after the photocatalytic reaction for 22.5 h (eqn (4)). Other smaller signals possibly associated with the formation of the hydrolysis product of BI(CO₂⁻⁻)H (eqn (5)) were also observed. Another possible product is the fragment(s) of BI(CO₂⁻⁻)H generated by the elimination of formate detected after the photocatalytic reaction:

RuII(N⁺N⁻′) + BI(CO₂⁻⁻)H → RuIII(N⁺N⁻′) + BI⁺(CO₂⁻⁻) + 2H⁺ + [O²⁻] (6)

As previously described, the photocatalysis of RuRe (ΦCO = 13%, TON = 130) when BI(CO₂⁻⁻)H was used as the reductant was substantially improved compared to the reported performance of a Ru(n)-Re(i) supramolecular system with asc⁻ (ΦHCOOH = 0.2%, TONHCOOH = 25). The reasons for the low photocatalytic activities in the case of asc⁻ were described previously; one of them is the efficient back electron transfer from the reduced Ru(n) photosensitizer unit to the oxidized asc⁻. To clarify the improvement of the photochemical
Conclusions

A Ru(II)-Re(I) binuclear complex exhibited high photocatalytic activity with 13% quantum yield for CO₂ reduction to CO even in aqueous solution. The new sacrificial reductant BI(CO₂)⁻H enabled the efficient production of the reduced photosensitizer unit, which allowed us to observe the real photocatalytic activities of the Ru(II)-Re(I) supramolecular photocatalyst in water. We believe that the water-suitable Ru(II)-Re(I) supramolecular photocatalyst can be used in a Z-scheme hybrid system³¹,³² with a semiconductor photocatalyst for CO₂ reduction, where water is used as an electron donor.

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References

29. The reduction potentials of the complexes could not be measured in an aqueous solution because of competing hydrogen evolution on the working electrode.