In an aqueous solution, [Ru(dmb)$_2$-(BL)-Re(CO)$_2$Cl]$_2^+$ (BL = bridging ligand) most efficiently photocatalyzed the reduction of CO$_2$ to CO under visible-light irradiation using 2-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)benzoic acid (Bl(CO$_2$)H) as a water-soluble sacrificial reductant ($\Phi_{\text{CO}}$ = 13%, TON = 130). Since Bl(CO$_2$)H could efficiently produce one-electron-reduced species of [Ru(diimine)$_2$]$_2^+$-type complexes under visible-light irradiation even in an aqueous solution, that is, one of the main reasons why the photocatalytic system induced the highly efficient CO$_2$ reduction. This result strongly indicates that Bl(CO$_2$)H should be a useful reductant for evaluating the real abilities of various photocatalytic systems in water as well.

The photocatalytic reduction of CO$_2$ 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 photosensitizers and/or catalysts have been reported, 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 CO$_2$ 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 CO$_2$ reduction and for hydrogen evolution from water$^{13-19}$ in the presence of ascorbate ion (asc$^-$) as a sacrificial reductant. Unfortunately, most of these systems exhibited very low efficiency, durability, and selectivity for CO$_2$ reduction.

Ru(n)-Re(i) supramolecular photocatalysts constructed with both a Ru photosensitizer and Re catalyst unit can efficiently and selectively reduce CO$_2$ to CO in a dimethylformamide (DMF) and triethanolamine (TEOA) mixed solution; they also exhibit high durability.$^{20-26}$ In particular, the use of 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) as a sacrificial reductant achieved an extraordinarily high quantum yield of CO formation ($\Phi_{\text{CO}}$ = 45%) by suppression of the back electron transfer from one-electron-reduced species of the photocatalyst to the one-electron-oxidized species of the photocatalyst. Therefore, the selective photocatalytic CO$_2$ reduction was much lower than that using 1-benzyl-1,4-dihyronicotinamide (BNAH) 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 CO$_2$ reduction using a [Ru(bpy)$_3$]$_2^+$-type photosensitizer, back electron transfer from the reduced photosensitizer to the OER$^2$ is efficient because of the stability of the OER, and the final product of the oxidized ascorbate (dehydroascorbic acid) accepts the electron from the reduced photosensitizer and/or reaction intermediates.$^{4,16,18,19}$ Moreover, we observed that asc$^-$ accelerated a photochemical ligand-substitution reaction of the Ru(n) photosensitizer, which caused deactivation of the photocatalytic system.$^4$ 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.

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Herein, we report 2-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)benzoic acid (Bl(CO₂H)H, Chart 1) as a suitable water-soluble reductant for the photocatalytic CO₂ 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 CO₂ reduction, selectively giving CO even in an aqueous solution.

As the first step in investigating the photocatalytic reaction, we evaluated the solubility of Bl(CO₂H)H in aqueous solutions: to dissolve Bl(CO₂H)H in an aqueous solution, more than an equal amount of NaOH should be added to the solution. This indicates that Bl(CO₂H)H dissolves as the carboxylate ion, Bl-(CO₂⁻). The pH at the equivalence point was 8.9 for 10 mM Bl(CO₂H)H. Because bubbling of the solution containing Bl-(CO₂⁻)H (10 mM) with CO₂ induced precipitation of Bl(CO₂H) H even in the presence of 0.1 M NaOH, the concentration of CO₂ in the solution should be controlled for the photocatalytic reaction. Suitable conditions were achieved using the following procedure: a CO₂-saturated NaOH (0.1 M) aqueous solution was mixed with the same amount of an aqueous solution containing Bl(CO₂H)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 Bl(CO₂H)H was completely dissolved.

In a typical run of the photocatalytic reaction, an aqueous solution containing RuRe (0.05 mM), Bl(CO₂H)H (10 mM), NaOH (0.1 M), and CO₂ was irradiated at λex > 500 nm using a high-pressure Hg lamp combined with a K₂CrO₄ (30% w/w, d = 1 cm) filter. The Ru photosensitizer unit of RuRe was selectively excited because Bl(CO₂⁻)H and the Re catalyst unit could not absorb the λ > 500 nm light (Fig. S1, ESI†). The irradiation-time dependences of CO, formate, and H₂ production are shown in Fig. 1a. CO was the main product, and the turnover number of CO formation (TON_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 CO₂ reduction in an aqueous solution under visible-light irradiation.¹¹ H₂ 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. [Ru⁵(.bpy)₂(X)(Y)⁺-type complexes have been reported to function as catalysts for the photocatalytic formation of H₂ in solutions containing water.²⁷ The decomposition product(s) of the Ru unit can therefore be reasonably assumed to catalyze H₂ 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 Bl(CO₂⁻)H under a CO₂ atmosphere photocatalytically produced CO as the main product (entry 1, Table 1). On the other hand, in the control experiments without irradiation, RuRe, Bl(CO₂⁻)H, or CO₂, i.e., under an Ar atmosphere, did not give any CO₂ reduction products (entries 2−5). Notably, much less CO was produced with larger amounts of H₂ 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**

| Entry | Complex | Bl(CO₂⁻)H⁻ | hv | CO₂ | CO | HCOO⁻ | H₂ |
|-------|---------|------------|----|-----|----|-------|----|
| 1     | RuRe   | ○         | ○  | ○  | 13.5 | 0.6   | 2.5 |
| 2     | RuRe   | ○         | ×  | ○  | N.D. | N.D.  | <0.1|
| 3     | RuRe   | ○         | ○  | ×  | N.D. | N.D.  | 0.5 |
| 4     | RuRe   | ×         | ○  | ○  | N.D. | N.D.  | N.D.|
| 5     | ×      | ○         | ○  | ○  | N.D. | N.D.  | <0.1|
| 6     | Ru⁺    | ○         | ○  | ○  | 1.0  | 4.5   | 19.9|
| 7     | Re⁺    | ○         | ○  | ○  | N.D. | N.D.  | <0.1|
| 8     | Ru⁺ + Re⁺ | ○   | ○  | ○  | 1.5  | 0.4   | 1.0 |

*Four milliliters of the reaction solutions were irradiated for 3 h. b The complex concentration was 0.05 mM. c The Bl(CO₂⁻)H concentration was 10 mM. d λex > 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(4,4'-(CH₂PO₃H₂)bpy)(CO)₂Cl. ○ = with, × = without.
RuRe \((N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) \(\stackrel{hv}{\longrightarrow}\) Ru\(^{III}(N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) (1a)

Ru\(^{III}(N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) \(\stackrel{hv}{\longrightarrow}\) Ru\(^{II}(N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) (1b)

\(I_0 = \frac{k_t}{T} [\text{Bl}(\text{CO}_2^-)\text{H}]\)

The first reduction potentials (\(E^{1/2}\)) of Ru and Re(dmb)\(-\) \((\text{CO}_2)\text{Cl}\) measured in MeCN were \(-1.73\) V and \(-1.71\) V vs. Ag/AgNO\(_3\), 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 \(\text{CO}_2\) reduction proceeded on the Re unit:

Ru\(^{II}(N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) \(\rightarrow\) Ru\(^{II}(N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) (3)

\(^1\)H NMR spectra of the reaction solution (Fig. S7, ESIF) show carbon monoxide and formic acid as the catalyst. A mononuclear molecular 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 \(\text{CO}_2\) reduction proceeded on the Re unit:

Ru\(^{II}(N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) \(\rightarrow\) Ru\(^{II}(N^\prime N^-)\) – Re\(^{I}(N^\prime N^-)\) (3)

On the basis of the quantitative analysis with the \(^1\)H NMR spectra, the amount of BI\(^{(-)}\text{(CO}_2^-)\) produced was very similar to the combined amounts of \(\text{CO}\) and \(\text{H}_2\) produced during the photocatalytic reaction (Fig. 2). This similarity clearly indicates that BI\(^{(-)}\text{(CO}_2^-)\) acted as a two-electron donor for the photocatalytic formation of \(\text{CO}\) and \(\text{H}_2\) because both require two-electron reduction. Given the results of both the \(^1\)CO\(_2\) labeling experiments and the \(^1\)H NMR analysis, we conclude that the material balance of the photocatalytic CO formation is as shown in eqn (6):

\(\text{CO}_2 + \text{BI}(\text{CO}_2^-)\text{H} \stackrel{\text{R}u\text{Re/}hv}{\longrightarrow} \text{CO} + \text{BI}^{(+)}(\text{CO}_2^-) + 2\text{H}^+ + [\text{O}^{2-}]\) (6)

As previously described, the photocatalysis of RuRe (\(\Phi_{\text{CO}} = 13\%\), TON = 130) when BI\(^{(-)}\text{(CO}_2^-)\) was used as the reductant was substantially improved compared to the reported performance of a Ru(u)-Re(i) supramolecular system with asc\(^-\) (\(\Phi_{\text{HCOOH}} = 0.2\%\), TON\(_{\text{HCOOH}}\) = 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(u) 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 system11,32 with a semiconductor photocatalyst for CO2 reduction, where water is used as an electron donor.

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References

1 A. J. Morris, G. J. Meyer and E. Fujita, Acc. Chem. Res., 2009, 42, 1983–1994.
2 G. Sahara and O. Ishitani, Inorg. Chem., 2015, 54, 5096–5104.
3 J. Mao, K. Li and T. Peng, Catal. Sci. Technol., 2013, 3, 2481–2498.
4 A. Nakada, K. Koike, T. Nakashima, T. Morimoto and O. Ishitani, Inorg. Chem., 2015, 54, 1800–1807.
5 A. H. A. Tinnemans, T. P. M. Koster, D. H. M. W. Thewissen and A. Mackor, Recl. Trav. Chim. Pays-Bas, 1984, 103, 288–295.
6 J. L. Grant, K. Goswami, L. O. Spreer, J. W. Otvos and M. Calvin, J. Chem. Soc., Dalton Trans., 1990, 7957–7960.
7 C. A. Craig, L. O. Spreer, J. W. Otvos and M. Calvin, J. Phys. Chem., 1990, 94, 7957–7960.
8 E. Kimura, X. Bu, M. Shionoya, S. Wada and S. Maruyama, Inorg. Chem., 1992, 31, 4542–4546.
9 E. Kimura, S. Wada, M. Shionoya and Y. Okazaki, Inorg. Chem., 1994, 33, 770–778.
10 K. Mochizuki, S. Manaka, I. Takeda and T. Kondo, Inorg. Chem., 1996, 35, 5132–5136.
11 D. J. Boston, C. Xu, D. W. Armstrong and F. M. MacDonnell, J. Am. Chem. Soc., 2013, 135, 16252–16255.
12 N. Ikuta, S. Y. Takizawa and S. Murata, Photochem. Photobiol. Sci., 2014, 13, 691–702.
13 G. M. Brown, B. S. Brunschwigg, C. Creutz, J. F. Endicott and N. Sutin, J. Am. Chem. Soc., 1979, 101, 1298–1300.
14 S. Fukuzumi, T. Kobayashi and T. Suenobu, Angew. Chem., Int. Ed., 2011, 50, 728–731.
15 Y. Sano, A. Onoda and T. Hayashi, Chem. Commun., 2011, 47, 8229–8231.
16 M. Guttentag, A. Rodenberg, R. Kopelent, B. Probst, C. Buchwalder, M. Brandstätter, P. Hamm and R. Alberto, *Eur. J. Inorg. Chem.*, 2012, **2012**, 59–64.

17 B. Shan, T. Baine, X. A. N. Ma, X. Zhao and R. H. Schmehl, *Inorg. Chem.*, 2013, **52**, 4853–4859.

18 M. Guttentag, A. Rodenberg, C. Bachmann, A. Senn, P. Hamm and R. Alberto, *Dalton Trans.*, 2013, **42**, 334–337.

19 C. Bachmann, B. Probst, M. Guttentag and R. Alberto, *Chem. Commun.*, 2014, **50**, 6737–6739.

20 B. Gholamkhass, H. Mametsuka, K. Koike, T. Tanabe, M. Furue and O. Ishitani, *Inorg. Chem.*, 2005, **44**, 2326–2336.

21 S. Sato, K. Koike, H. Inoue and O. Ishitani, *Photochem. Photobiol. Sci.*, 2007, **6**, 454–461.

22 K. Koike, S. Naito, S. Sato, Y. Tamaki and O. Ishitani, *J. Photochem. Photobiol., A*, 2009, **207**, 109–114.

23 H. Takeda and O. Ishitani, *Coord. Chem. Rev.*, 2010, **254**, 346–354.

24 Y. Tamaki, K. Watanabe, K. Koike, H. Inoue, T. Morimoto and O. Ishitani, *Faraday Discuss.*, 2012, **155**, 115–127.

25 Y. Tamaki, K. Koike, T. Morimoto and O. Ishitani, *J. Catal.*, 2013, **304**, 22–28.

26 E. Kato, H. Takeda, K. Koike, K. Ohkubo and O. Ishitani, *Chem. Sci.*, 2015, **6**, 3003–3012.

27 J.-M. Lehn and R. Ziessel, *J. Organomet. Chem.*, 1990, **382**, 157–173.

28 J. Hawecker, J.-M. Lehn and R. Ziessel, *Helv. Chim. Acta*, 1986, **69**, 1990–2012.

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

30 T. Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku and M. Kaneko, *J. Chem. Soc., Chem. Commun.*, 1993, 631–633.

31 K. Sekizawa, K. Maeda, K. Domen, K. Koike and O. Ishitani, *J. Am. Chem. Soc.*, 2013, **135**, 4596–4599.

32 F. Yoshitomi, K. Sekizawa, K. Maeda and O. Ishitani, *ACS Appl. Mater. Interfaces*, 2015, **7**, 13092–13097.