



Cite this: *Green Chem.*, 2016, **18**, 139

Received 26th July 2015,  
 Accepted 27th August 2015

DOI: 10.1039/c5gc01720c

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## Highly efficient visible-light-driven CO<sub>2</sub> reduction to CO using a Ru(II)–Re(I) supramolecular photocatalyst in an aqueous solution†

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

The photocatalytic reduction of CO<sub>2</sub> 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<sup>1,2</sup> besides the semiconductor photocatalyst,<sup>3</sup> 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<sub>2</sub> 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)<sub>3</sub>]<sup>2+</sup>-type photosensitizer (bpy = 2,2'-bipyridine) in aqueous solutions have been tested for CO<sub>2</sub> reduction<sup>4–12</sup> and for hydrogen evolution from water<sup>13–19</sup> in the presence of ascorbate ion (asc<sup>−</sup>) as a sacrificial reductant. Unfortunately, most of these systems exhibited very low efficiency, durability, and selectivity for CO<sub>2</sub> reduction.

Ru(II)–Re(I) supramolecular photocatalysts constructed with both a Ru photosensitizer and Re catalyst units can efficiently and selectively reduce CO<sub>2</sub> to CO in a dimethylformamide (DMF) and triethanolamine (TEOA) mixed solution; they also exhibit high durability.<sup>20–26</sup> 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 (OERS) of the photocatalyst to the one-electron-oxidized species (OEOS) of the reductant because of the fast deprotonation of the OEOS.<sup>25</sup>

We recently reported selective photocatalytic CO<sub>2</sub> reduction to formic acid in an aqueous solution using a Ru(II)–Re(I) supramolecular photocatalyst and asc<sup>−</sup> as a reductant.<sup>4</sup> In this system, however, the efficiency of the CO<sub>2</sub> reduction was much lower than that using 1-benzyl-1,4-dihydropyridinamide (BNAH) as a reductant in the DMF–TEOA mixed solution. Although asc<sup>−</sup> is, to the best of our knowledge, the only reported reductant that can be used in an aqueous solution for photocatalytic CO<sub>2</sub> reduction using a [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-type photosensitizer, back electron transfer from the reduced photosensitizer to the OEOS of asc<sup>−</sup> 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.<sup>4,16,18,19</sup> Moreover, we observed that asc<sup>−</sup> accelerated a photochemical ligand-substitution reaction of the Ru(II) photosensitizer, which caused deactivation of the photocatalytic system.<sup>4</sup> These properties of asc<sup>−</sup> 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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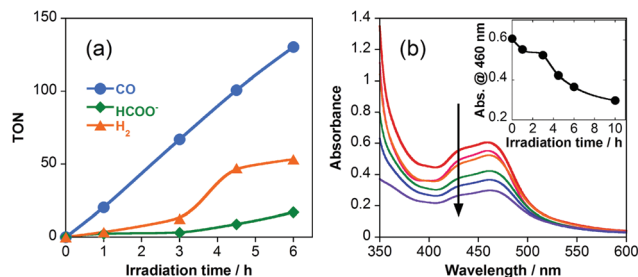
† Electronic supplementary information (ESI) available: Experimental details, photophysical data, results of <sup>13</sup>C<sub>2</sub> labeling experiments, <sup>1</sup>H NMR observation of the reductant, and UV-vis absorption changes. See DOI: 10.1039/c5gc01720c



Herein, we report 2-(1,3-dimethyl-2,3-dihydro-1*H*-benzimidazol-2-yl)benzoic acid (BI(CO<sub>2</sub>H)H, Chart 1) as a suitable water-soluble reductant for the photocatalytic CO<sub>2</sub> 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 ( $\Phi = 13\%$ ) and durable (TON = 130) photocatalyst for CO<sub>2</sub> 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<sub>2</sub>H)H in aqueous solutions: to dissolve BI(CO<sub>2</sub>H)H in an aqueous solution, more than an equal amount of NaOH should be added to the solution. This indicates that BI(CO<sub>2</sub>H)H dissolves as the carboxylate ion, BI(CO<sub>2</sub><sup>−</sup>)H. The pH at the equivalence point was 8.9 for 10 mM BI(CO<sub>2</sub>H)H. Because bubbling of the solution containing BI(CO<sub>2</sub>H)H (10 mM) with CO<sub>2</sub> induced precipitation of BI(CO<sub>2</sub>H)H even in the presence of 0.1 M NaOH, the concentration of CO<sub>2</sub> in the solution should be controlled for the photocatalytic reaction. Suitable conditions were achieved using the following procedure: a CO<sub>2</sub>-saturated NaOH (0.1 M) aqueous solution was mixed with the same amount of an aqueous solution containing BI(CO<sub>2</sub>H)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<sub>2</sub>H)H was completely dissolved.

In a typical run of the photocatalytic reaction, an aqueous solution containing **RuRe** (0.05 mM), BI(CO<sub>2</sub>H)H (10 mM), NaOH (0.1 M), and CO<sub>2</sub> was irradiated at  $\lambda_{\text{ex}} > 500$  nm using a high-pressure Hg lamp combined with a K<sub>2</sub>CrO<sub>4</sub> (30% w/w,  $d = 1$  cm) filter. The Ru photosensitizer unit of **RuRe** was selectively excited because BI(CO<sub>2</sub><sup>−</sup>)H and the Re catalyst unit could not absorb the  $\lambda > 500$  nm light (Fig. S1, ESI<sup>†</sup>). The irradiation-time dependences of CO, formate, and H<sub>2</sub> production are shown in Fig. 1a. CO was the main product, and the turnover number of CO formation (TON<sub>CO</sub>) 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<sup>†</sup>). To the best of our knowledge, this value is 5.6 times greater than that of the best reported for photocatalytic CO<sub>2</sub> reduction in an aqueous solution under visible-light irradiation.<sup>11</sup> H<sub>2</sub> 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



**Fig. 1** (a) Time-dependent production of CO (blue), HCOO<sup>−</sup> (green), and H<sub>2</sub> (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<sub>2</sub><sup>−</sup>)H (10 mM) was irradiated at  $\lambda_{\text{ex}} > 500$  nm under a CO<sub>2</sub> atmosphere. (b) UV–vis absorption changes during the photocatalytic reaction. The inset shows time-dependent absorbance changes at 460 nm.

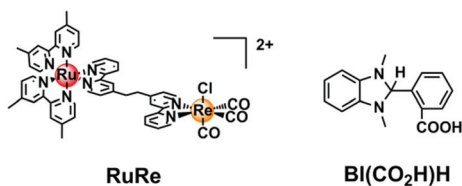
after irradiation, where the peak at approximately 460 nm is attributed to the MLCT absorption band of the Ru(II) unit. This result indicates that the Ru photosensitizer unit decomposed during the induction period. [Ru<sup>II</sup>(bpy)<sub>2</sub>(X)(Y)]<sup>n+</sup>-type complexes have been reported to function as catalysts for the photocatalytic formation of H<sub>2</sub> in solutions containing water.<sup>27</sup> The decomposition product(s) of the Ru unit can therefore be reasonably assumed to catalyze H<sub>2</sub> 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<sub>2</sub><sup>−</sup>)H under a CO<sub>2</sub> 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<sub>2</sub><sup>−</sup>)H, or CO<sub>2</sub>, *i.e.*, under an Ar atmosphere, did not give any CO<sub>2</sub> reduction products (entries 2–5). Notably, much less CO was produced with larger amounts of H<sub>2</sub> and formate when only a mononuclear model complex of the Ru photosensitizer unit, [Ru(dmb)<sub>2</sub>(mmb)]<sup>2+</sup> (**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<sup>a</sup>

Entry	Complex <sup>b</sup>	BI(CO <sub>2</sub> <sup>−</sup> )H <sup>c</sup>	$h\nu$ <sup>d</sup>	CO <sub>2</sub>	Product/ $\mu\text{mol}$		
					CO	HCOO <sup>−</sup>	H <sub>2</sub>
1	<b>RuRe</b>	○	○	○	13.5	0.6	2.5
2	<b>RuRe</b>	○	×	○	N.D.	N.D.	<0.1
3	<b>RuRe</b>	○	○	×	N.D.	N.D.	0.5
4	<b>RuRe</b>	×	○	○	N.D.	N.D.	N.D.
5	×	○	○	○	N.D.	N.D.	<0.1
6	<b>Ru</b> <sup>e</sup>	○	○	○	1.0	4.5	19.9
7	<b>Re</b> <sup>f</sup>	○	○	○	N.D.	N.D.	<0.1
8	<b>Ru</b> <sup>e</sup> + <b>Re</b> <sup>f</sup>	○	○	○	1.5	0.4	1.0

<sup>a</sup> Four milliliters of the reaction solutions were irradiated for 3 h. <sup>b</sup> The complex concentration was 0.05 mM. <sup>c</sup> The BI(CO<sub>2</sub><sup>−</sup>)H concentration was 10 mM. <sup>d</sup>  $\lambda_{\text{ex}} > 500$  nm. <sup>e</sup> [Ru(dmb)<sub>2</sub>(mmb)]<sup>2+</sup> (dmb = 4,4'-dimethyl-2,2'-bipyridine, mmb = 4-methyl-2,2'-bipyridine). <sup>f</sup> Re{4,4'-(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>bpy}(CO)<sub>3</sub>Cl. ○ = with, × = without.



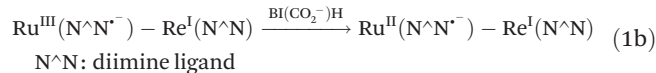
**Chart 1** The Ru(II)–Re(I) supramolecular photocatalyst **RuRe** and the reductant BI(CO<sub>2</sub>H)H used in this study.



(entry 6). The formation of H<sub>2</sub> 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 **Ru** as the catalyst. A mononuclear model complex of the Re catalyst unit, Re{4,4'-(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>bpy}(CO)<sub>3</sub>Cl (**Re**), did not drive CO<sub>2</sub> 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 solutions<sup>20,24</sup> but also in aqueous solution.<sup>4</sup>

To clarify the carbon sources of the produced CO and formate, we conducted <sup>13</sup>CO<sub>2</sub> labeling experiments. GC-mass spectra (Fig. S2, ESI†) show carbon monoxide and formic acid and/or formate produced by the photocatalytic reactions using **RuRe** under a <sup>13</sup>CO<sub>2</sub> (99%, 609 mmHg) atmosphere and under an ordinary CO<sub>2</sub> atmosphere. These results clearly indicate that 93% of CO was obtained by CO<sub>2</sub> reduction. On the other hand, almost no formate was produced from CO<sub>2</sub>. The formate might be produced by the partial decomposition of BI(CO<sub>2</sub><sup>-</sup>)H; the oxidation products of BI(CO<sub>2</sub><sup>-</sup>)H are described in greater detail below. The carbonyl ligands of Re(bpy)(CO)<sub>3</sub>Cl have been reported to be gradually substituted by <sup>13</sup>CO during the photocatalytic reduction of <sup>13</sup>CO<sub>2</sub>,<sup>28</sup> and the amount of <sup>12</sup>CO 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 <sup>13</sup>CO<sub>2</sub> in the presence of **RuRe**; this exchange should be the main carbon source of the produced <sup>12</sup>CO. Another carbon source of <sup>12</sup>CO might be the contaminant, *i.e.*, <sup>12</sup>CO<sub>2</sub> in the used <sup>13</sup>CO<sub>2</sub> gas (the <sup>13</sup>C content was 99%).

We evaluated the reducing power of BI(CO<sub>2</sub><sup>-</sup>)H in the aqueous solution using cyclic voltammetry, where irreversible oxidation waves of BI(CO<sub>2</sub><sup>-</sup>)H and asc<sup>-</sup> were observed (Fig. S3, ESI†). The peak potential of BI(CO<sub>2</sub><sup>-</sup>)H was negatively shifted by 340 mV compared to that of asc<sup>-</sup>; therefore, BI(CO<sub>2</sub><sup>-</sup>)H has a much stronger reducing power compared with that of asc<sup>-</sup>, which is one of the properties that makes BI(CO<sub>2</sub><sup>-</sup>)H a suitable sacrificial reductant for the photocatalytic CO<sub>2</sub> reaction in aqueous solution. Actually, BI(CO<sub>2</sub><sup>-</sup>)H served as an efficient quencher of emission from the <sup>3</sup>MLCT excited state of the Ru photosensitizer unit of **RuRe** in an aqueous solution (eqn (1) and Fig. S4, ESI†). The emission quenching rate constant (*k<sub>q</sub>*) was determined as 4.6 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> from the slope of the linear Stern–Volmer plots (Fig. S4, inset, ESI†), eqn (2), and the emission lifetime of **RuRe** (τ<sub>em</sub> = 366 ns, Fig. S5, ESI†). Notably, the *k<sub>q</sub>* value was similar to the diffusion-controlled rate constant in water (7.4 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> at 25 °C), and the *k<sub>q</sub>* with ascorbate instead of BI(CO<sub>2</sub><sup>-</sup>)H was 2.4 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>.

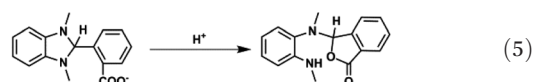
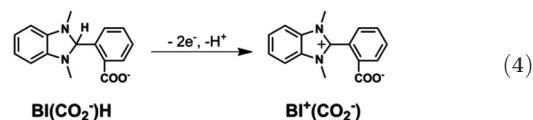


$$\frac{I_0}{I} = 1 + k_q \tau [\text{BI}(\text{CO}_2^-)\text{H}] \quad (2)$$

The first reduction potentials (*E*<sup>1/2</sup>) of **Ru** and Re(dmb)-(CO)<sub>3</sub>Cl measured in MeCN were -1.73 V and -1.71 V vs. Ag/AgNO<sub>3</sub>, respectively (Fig. S6, ESI†).<sup>29</sup> 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 CO<sub>2</sub> reduction proceeded on the Re unit:



<sup>1</sup>H NMR spectra of the reaction solution (Fig. S7, ESI†) show that BI(CO<sub>2</sub><sup>-</sup>)H was converted into a two-electron-oxidized compound BI<sup>+</sup>(CO<sub>2</sub><sup>-</sup>) 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(CO<sub>2</sub><sup>-</sup>)H (eqn (5)) were also observed. Another possible product is the fragment(s) of BI(CO<sub>2</sub><sup>-</sup>)H generated by the elimination of formate detected after the photocatalytic reaction:

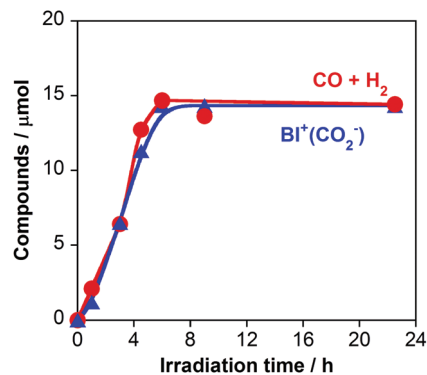


On the basis of the quantitative analysis with the <sup>1</sup>H NMR spectra, the amount of BI<sup>+</sup>(CO<sub>2</sub><sup>-</sup>) produced was very similar to the combined amounts of CO and H<sub>2</sub> produced during the photocatalytic reaction (Fig. 2). This similarity clearly indicates that BI(CO<sub>2</sub><sup>-</sup>)H acted as a two-electron donor for the photocatalytic formation of CO and H<sub>2</sub> because both require two-electron reduction. Given the results of both the <sup>13</sup>CO<sub>2</sub> labeling experiments and the <sup>1</sup>H NMR analysis, we conclude that the material balance of the photocatalytic CO formation is as shown in eqn (6):



As previously described, the photocatalysis of **RuRe** (Φ<sub>CO</sub> = 13%, TON = 130) when BI(CO<sub>2</sub><sup>-</sup>)H was used as the reductant was substantially improved compared to the reported performance of a Ru(II)–Re(I) supramolecular system with asc<sup>-</sup> (Φ<sub>HCOOH</sub> = 0.2%, TON<sub>HCOOH</sub> = 25). The reasons for the low photocatalytic activities in the case of asc<sup>-</sup> were described previously; one of them is the efficient back electron transfer from the reduced Ru(II) photosensitizer unit to the oxidized asc<sup>-</sup>. To clarify the improvement of the photochemical





**Fig. 2** Amounts of CO + H<sub>2</sub> (red) and BI<sup>+</sup>(CO<sub>2</sub><sup>-</sup>) (blue) produced during the photocatalytic reaction: a 2 mL of D<sub>2</sub>O solution containing RuRe (0.05 mM), BI(CO<sub>2</sub><sup>-</sup>)H (10 mM), and NaOD (0.1 M) was irradiated at λ<sub>ex</sub> > 500 nm under a CO<sub>2</sub> atmosphere.

reduction process of the Ru photosensitizer unit by BI(CO<sub>2</sub><sup>-</sup>)H, we monitored the UV-vis absorption spectral changes of an aqueous solution containing the mononuclear model complex **Ru** and BI(CO<sub>2</sub><sup>-</sup>)H during irradiation under an Ar atmosphere. A new absorption peak at λ<sub>max</sub> = 510 nm, which is attributed to the OERS of **Ru**, was observed during the irradiation (Fig. S8, ESI<sup>†</sup>). Notably, no such accumulation of the OERS was observed in the case where asc<sup>-</sup> (200 mM) was used instead of BI(CO<sub>2</sub><sup>-</sup>)H (10 mM).<sup>4</sup> Because the quenching efficiencies of emission from the excited Ru photosensitizer unit in the experiments were similar in both cases (94% by 10 mM of BI(CO<sub>2</sub><sup>-</sup>)H and 87%<sup>4</sup> by 200 mM of asc<sup>-</sup>), the efficiency of the back electron transfer from the OERS of **Ru** to the oxidized BI(CO<sub>2</sub><sup>-</sup>)H should be much lower compared to that in the case where asc<sup>-</sup> was used. This is one of the main reasons why BI(CO<sub>2</sub><sup>-</sup>)H remarkably improved the quantum yield for CO<sub>2</sub> reduction compared to that achieved with asc<sup>-</sup>.

Another significant difference between the cases where BI(CO<sub>2</sub><sup>-</sup>)H and asc<sup>-</sup> were used is the main product of CO<sub>2</sub> reduction: CO in the case of BI(CO<sub>2</sub><sup>-</sup>)H and formate in the case of asc<sup>-</sup>. Kaneko and co-workers reported that, in the electrocatalytic CO<sub>2</sub> reduction with Re(bpy)(CO)<sub>3</sub>Br as a catalyst in an aqueous solution, formic acid was the main product during the electrolysis at -1.3 V vs. SCE, whereas CO became the main product at more negative applied potentials.<sup>30</sup> This result might indicate that the electron-supply rate to the Re catalyst affects distribution of the reduction products, i.e., formate might become a main product under a slow electron-supply condition. If this is true, we can understand the difference of the main product between the photocatalytic systems in which BI(CO<sub>2</sub><sup>-</sup>)H and asc<sup>-</sup> are used as the reductants. The formation speed of the OERS of the Ru(II) photosensitizer unit was much lower in the case where asc<sup>-</sup> was used than in the BI(CO<sub>2</sub><sup>-</sup>)H system, which should cause slow electron supply to the Re catalytic unit.

## Conclusions

A Ru(II)-Re(I) binuclear complex exhibited high photocatalytic activity with 13% quantum yield for CO<sub>2</sub> reduction to CO even in aqueous solution. The new sacrificial reductant BI(CO<sub>2</sub><sup>-</sup>)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 system<sup>31,32</sup> with a semiconductor photocatalyst for CO<sub>2</sub> reduction, where water is used as an electron donor.

## Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Artificial photosynthesis (AnApple)” (no. 24107005) from the Japan Society for the Promotion of Science (JSPS).

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