

Article

# Highly Efficient and Selective Photocatalytic CO Reduction to CO in Water by a Cobalt Porphyrin Molecular Catalyst

Arnau Call, Mihaela Cibian, Keiya Yamamoto, Takashi Nakazono, Kosei Yamauchi, and Ken Sakai ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.8b04975 • Publication Date (Web): 17 Apr 2019 Downloaded from http://pubs.acs.org on April 17, 2019

# **Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

# Highly Efficient and Selective Photocatalytic CO<sub>2</sub> Reduction to CO in Water by a Cobalt Porphyrin Molecular Catalyst

Arnau Call,\*<sup>†§</sup> Mihaela Cibian,\*<sup>†‡§</sup> Keiya Yamamoto,<sup>†‡</sup> Takashi Nakazono,<sup>†‡</sup> Kosei Yamauchi,<sup>†‡</sup> Ken Sakai\*<sup>†‡#</sup>

<sup>‡</sup>Department of Chemistry, Faculty of Science, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan. <sup>†</sup>International Institute for Carbon-Neutral Energy Research (WPI-I<sup>2</sup>CNER), Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan.

<sup>#</sup>Center of Molecular Systems (CMS), Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan. Supporting Information Placeholder

**ABSTRACT:** The performance of a water-soluble cobalt porphyrin (CoTPPS) as a catalyst for the photoreduction of  $CO_2$  in fully aqueous media has been investigated under visible light irradiation using  $[Ru(bpy)_3]^{2+}$  as a photosensitizer and ascorbate as a sacrificial electron donor. CO is selectively produced (> 82%) with high efficiency (926 TON<sub>CO</sub>). Upon optimization, selectivities of at least 91% are achieved. Efficiencies up to 4000 TON<sub>CO</sub> and 2400 h<sup>-1</sup> TOF<sub>CO</sub> are reached at low catalyst loadings, albeit with loss in selectivity. This work successfully demonstrates the ability of CoTPPS to perform highly efficient photoreduction of  $CO_2$  in water while retaining its high selectivity for CO formation.

KEYWORDS: CO2 reduction, cobalt porphyrin, photocatalysis, selectivity, molecular catalysis

### INTRODUCTION

Photocatalytic conversion of  $CO_2$  into chemical feedstocks is considered as a promising but challenging strategy to achieve an energy sustainable society.<sup>1</sup> One of the key goals is to develop systems capable of selectively and efficiently photocatalyzing  $CO_2$  reduction under visible light irradiation.<sup>2</sup> From a practical viewpoint, the  $CO_2$  reduction must be coupled with water oxidation in order to gain the electrons and protons required to drive the reduction processes.<sup>3</sup> Moreover, our intention has been to pursue a possibility of driving all reactions in fully aqueous media in hope to achieve the more practically useful photosynthetic systems. Nevertheless, the presence of water often promotes the photocatalytic proton reduction, thermodynamically and kinetically more favorable, resulting in decreased efficiency and selectivity for  $CO_2$  reduction.<sup>4</sup>

Up to now, a large number of homogeneous<sup>5</sup> and heterogeneous<sup>2</sup> photocatalytic systems for CO<sub>2</sub> reduction have been developed. Most of them exhibit reasonably high catalytic performances when the photochemical reactions are conducted in either non-aqueous solvents<sup>6</sup> or water-organic solvent mixtures.<sup>7</sup> However, photocatalytic systems showing *both high activity and high selectivity in fully aqueous media* are extremely rare and are predominantly noble metalbased.<sup>8</sup> Selected examples of first-row transition metal catalysts for photocatalytic CO<sub>2</sub>-to-CO conversion in water, of major interest in this study, are presented in Figure 1 (see also Table S1), highlighting the best performances in terms of selectivity and/or efficiency.<sup>9</sup> Co and Ni tetra-azamacrocycles were reported to promote photocatalytic CO<sub>2</sub>-to-CO conver-

sion when photo-driven by  $[Ru(bpy)_3]^{2+}$  in the presence of ascorbate (AscHNa) as a sacrificial electron donor (SED).9a,9b,10 For [Ni(cyclam)]<sup>2+</sup> derivatives, it was shown that the  $TON_{CO}$  value can be maximized to 38 but with loss in selectivity (Sel<sub>CO2</sub> < 10%). On the contrary, Sel<sub>CO2</sub> can be maximized up to 94% but by sacrificing the efficiency  $(TON_{CO} = 2.2)$ .<sup>10C,11</sup> The overall catalytic performances of [Ni(cyclam)]<sup>2+</sup> derivatives were significantly improved by using ZnSe quantum dots as visible light photosensitizer (PS) even though the selectivity still remained relatively low (TON<sub>CO</sub> =  $28_3$ ; Sel<sub>CO2</sub> = 34%).<sup>9e</sup> Similarly, the photocatalysis of CdS quantum dots anchored with nickel terpyridine catalysts under visible light resulted in high selectivity but low TON<sub>CO</sub> values (TON<sub>CO</sub> = 20; Sel<sub>CO2</sub> = 90%).<sup>9c</sup> Furthermore, Robert and co-workers reported that the trimethylaminefunctionalized iron tetraphenylporphyrin (FeTMA) can achieve high selectivity for CO formation ( $Sel_{CO_2} = 95\%$ ) when used in a photocatalytic system driven by an organic dye, in a H<sub>2</sub>O:CH<sub>3</sub>CN (9:1 v/v) solvent mixture.9d For this system the TON<sub>CO</sub> value was reported to be 120 after 4 days of visible light irradiation. More recently, Weiss and coworkers assembled the positively charged FeTMA catalyst with negatively charged colloidal CuInS<sub>2</sub>/ZnS quantum dots to reduce  $CO_2$  to CO with high selectivity (Sel<sub>CO2</sub> = 99%) in water (TON<sub>CO</sub> = 450 after 30 h of irradiation).<sup>12</sup> Importantly, the highly selective systems show rather low activity, and the overall efficiency is often raised only by sacrificing the selectivity, although one excellent example of a cobalt catalyst achieving both high efficiency and high selectivity (TON<sub>CO</sub>=1380, Sel<sub>CO2</sub> =95%) was very recently reported while this study was under the review process.13



**Figure 1.** Selected photocatalytic systems for CO<sub>2</sub>-to-CO reduction in *aqueous media* (PS: photosensitizer).

Herein we report on the performance of CoTPPS, [{*meso*-tetra(4-sulfonatophenyl)porphyrinato}cobalt(III)], as a catalyst for CO<sub>2</sub>-to-CO photoconversion when employed in the [Ru(bpy)<sub>3</sub>]<sup>2+</sup>/sodium ascorbate (AscHNa) system. We have found that CoTPPS is an outstanding catalyst not only due to its unprecedentedly high activity (TON<sub>CO</sub> = 4000, TOF<sub>CO</sub> = 2400 h<sup>-1</sup>, Sel<sub>CO2</sub> = 41 %) but also due to its ability to yield a high TON<sub>CO</sub> value (TON<sub>CO</sub> = 926) while also retaining a high selectivity for CO<sub>2</sub>-to-CO conversion (Sel<sub>CO2</sub> = 82%) under optimal conditions (Figure 1). Moreover, selectivities of at least 91% are achieved with high efficiency (TON<sub>CO</sub> = 400). We note that the previous studies of cobalt porphyrins in photocatalytic CO<sub>2</sub> reduction were only carried out under non-aqueous conditions.<sup>14,15</sup>

# **RESULTS AND DISCUSSION**

Photocatalytic CO<sub>2</sub> reduction assays were performed using CO<sub>2</sub>-saturated aqueous bicarbonate buffer (pH 6.7) in the presence of AscHNa (o.1 M) under visible light irradiation (Figures 2A and 2B). Photoirradiation of the solution containing CoTPPS (10  $\mu$ M) and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (500  $\mu$ M) affords CO as a major product (92.6  $\mu$ mol, 2.26 mL, TON<sub>CO</sub> = 926, TOF<sub>CO</sub> = 456 h<sup>-1</sup>) (Figure 2A). Dihydrogen (19.7  $\mu$ mol of H<sub>2</sub>) also evolves, together with a trace amount of formate (6.6  $\mu$ mol). The selectivity for CO<sub>2</sub> reduction *vs.* water reduction (Sel<sub>CO2</sub> = mol (CO)/(mol (H<sub>2</sub>) + mol (CO)) is estimated to be 82% (Table S2, entry 1), which is considerably high among those previously reported for the photocatalytic  $CO_2$ -to-CO conversion in *fully aqueous media* (Figure 1 and Table S1).

Control experiments were performed and are summarized in Table S2 (see also Figures S1 and S2). In the absence of CoTPPS in CO<sub>2</sub>-saturated solution (Table S2, entry 2), only a trace amount of CO forms (4.2 µmol), but a remarkably large amount of H<sub>2</sub> (36.8 µmol) evolves. Importantly, only a trace amount of formate is generated in both the presence and absence of CoTPPS (6.6 µmol and 5.0 µmol, respectively). In the absence of CO<sub>2</sub> (under N<sub>2</sub>-saturated condition), small amounts of CO and H<sub>2</sub> form only when CoTPPS is present (Figure 2B and Table S2, entries 3 and 4). Neither CO nor  $H_2$ evolves in the absence of CoTPPS under N<sub>2</sub>. As mentioned above, H<sub>2</sub> production significantly increases in the absence of CoTPPS under CO2 atmosphere, suggesting that the degradation of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> is greatly enhanced by the presence of CO<sub>2</sub> to yield the chemical species catalytically active for H<sub>2</sub> evolution (Figure 2B). This behavior is consistent with the reports by Grant *et al.* and others, in which the  $[Ru(bpy)_2]^{n+1}$ carbonyl-type photodegradation products, such as [Ru(bpy)<sub>2</sub>(CO)H]<sup>+</sup> and [Ru(bpy)<sub>2</sub>(CO)<sub>2</sub>]<sup>2+</sup>, were proposed to be the active catalysts for H<sub>2</sub> and formate production.<sup>8a,10b,16</sup> Furthermore, no reduced products form in the absence of either the photosensitizer or a suitable sacrificial electron donor (SED) (Table S2, entries 5 and 6). It was also confirmed that the pH remained unchanged after the photolysis experiments and that the substantial diminishment is seen in Sel<sub>CO2</sub> (45%) at pH 5.3 (CO<sub>2</sub>-purged phosphate buffer). All these results indicate that the cobalt porphyrin is necessary to catalyze the CO<sub>2</sub> reduction into CO. An isotopic labelling experiment conducted under a <sup>13</sup>CO<sub>2</sub> atmosphere led to the formation of <sup>13</sup>CO as a major product, thus confirming that CO is originated from CO<sub>2</sub> reduction (Figure S<sub>1</sub>).

Catalytic assays employing  $CoCl_2$  and/or the metal-free TPPS ligand in equimolar loadings yield a negligible amount of CO, while the amount of H<sub>2</sub> generated is higher than that formed using CoTPPS (Table S2, entries 7-9). Mercury poisoning experiments and assays performed with cobalt nanoparticles (Co NP, size 28 nm) demonstrate the homogeneous nature of the catalysis by CoTPPS (Table S2, entries 10 and 11, Figures S3 and S4). The effect of varying either the AscHNa concentration or the light intensity was also examined (Figures S6-S10).



**Figure 2.** A) Photocatalytic activity of CoTPPS. Amount (circles) and rate (triangles) profiles for CO (red) and H<sub>2</sub> (blue) production. B and C) Amounts of products at 4 h irradiation in the presence and the absence of CoTPPS measured for N<sub>2</sub>- or CO<sub>2</sub>- saturated solutions in a bicarbonate (B) (Table S<sub>2</sub>, entries 1-4) and phosphate (C) buffer.<sup>17</sup> Photolysis carried out in a 10 mL CO<sub>2</sub>- saturated solution containing CoTPPS (10  $\mu$ M), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (500  $\mu$ M), o.1 M buffer, and o.1 M AscHNa, at 25 °C, for 4 h using Xe lamp irradiation ( $\lambda > 400$  nm, 179 mW·cm<sup>-2</sup>). The experiments were performed at least in duplicate (error 1-15%).

1

2

3

4

5

6

7

8

9

10 11

12

13

14

15

16

17

18

19

20

21 22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60



**Figure 3.** Kinetic studies by varying A)  $[Ru(bpy)_3^{2+}]$  using 10 µM CoTPPS and B-D) [CoTPPS] using 500 µM  $[Ru(bpy)_3]^{2+}$ . E and F) Selectivities for the experiments shown in A and B, respectively. Photolysis carried out in a 10 mL CO<sub>2</sub>-saturated solution containing CoTPPS,  $[Ru(bpy)_3]Cl_2$ , 0.1 M NaHCO<sub>3</sub>, and 0.1 M AscHNa, at 25 °C, for 4 h using Xe lamp irradiation ( $\lambda > 400$  nm, 179 mW·cm<sup>-2</sup>).

The quantum yield ( $\Phi_{CO}$ ), estimated on the basis of the amount of photons absorbed (see Experimental Section), was determined as 0.81% using a 428-nm light, in agreement with the multistep nature of the photocatalytic CO<sub>2</sub> reduction. The corresponding value for the photocatalysis using an iron porphyrin catalyst and a tris(phenylpyridinato)iridium(III) photosensitizer in acetonitrile was reported as  $\Phi_{CO} = 0.0013\%$ .<sup>18</sup>

Employing a phosphate buffer (pH =6.9), the superior selectivity of CoTPPS for CO<sub>2</sub> reduction vs. water reduction at the same pH can be verified by observing the products in the presence and absence of CO<sub>2</sub> (Figure 2C and Figure S11). The H<sub>2</sub> evolution under N<sub>2</sub> is largely enhanced by the presence of CoTPPS, confirming that it is indeed an active H<sub>2</sub> evolution catalyst.<sup>19</sup> Remarkably, though, in the presence of CO<sub>2</sub>, CO is formed preferentially over H<sub>2</sub> (Sel<sub>CO2</sub> = 82%).

Although the CO formation ceases after 4 h (Figure 2A), a similar CO production profile and high selectivity (Sel<sub>CO2</sub> = 91%) can be restored by adding the initially added amount of  $[Ru(bpy)_3]Cl_2$  (50 µM) (Figure S12). In contrast, the readdition of CoTPPS and/or AscHNa did not restore the initial activity. The degradation of  $[Ru(bpy)_3]^{2+}$  is thus concluded to be the major cause for the cease of photocatalysis, as also demonstrated by photostability experiments (Figures S13 and S14). Upon increasing the  $[Ru(bpy)_3]^{2+}$  concentration, both the rate and the total amount of CO formation saturate at about 400 µM (Figures 3A, S15, and S16). Therefore, in the lower  $[Ru(bpy)_3]^{2+}$  concentration domain, the photosensitization limits the overall rate of photocatalysis.

The net performance is also dependent on the catalyst concentration, where two different regimes are identified (Figures 3, B-E, and S17). In agreement with the molecular nature of the catalysis, at low catalyst concentrations, the CO formation rate shows an enhancement with increasing [CoT-

PPS], reaching its maximum at around 30 µM. However, the rate gradually decreases at higher catalyst loadings. This behavior is attributable to the increased light absorption by Co<sup>II</sup>TPPS ( $\varepsilon_{412 \text{ nm}}$  = 1.6 x 10<sup>5</sup> M<sup>-1</sup>cm<sup>-1</sup>), interfering with the light absorption at the MLCT band of  $[Ru(bpy)_3]^{2+}$  ( $\varepsilon_{450 \text{ nm}} = 1.4 \text{ x}$ 104 M<sup>-1</sup>cm<sup>-1</sup>) (Figure S18).<sup>20</sup> The TON<sub>CO</sub> exponentially increases with decreasing [CoTPPS]. Under the optimal conditions which maximize the  $TON_{CO}$ , values of  $TON_{CO}$  = ca. 4000 and  $TOF_{CO} = 2400 \text{ h}^{-1}$  are attained at [CoTPPS] = 0.5  $\mu$ M, albeit with a lower apparent<sup>21</sup> selectivity for CO formation (Sel<sub>CO2</sub> = 41%) (Figure 3D). To the best of our knowledge, these values are among the highest values yet reported for the first-row transition metal molecular catalysts for the photocatalytic reduction of CO<sub>2</sub> to CO under visible light in fully aqueous media (Table S1). In sharp contrast, H<sub>2</sub> generation is markedly prevented by raising the catalyst concentration over the entire range studied, strongly supporting the conclusion that H<sub>2</sub> evolution is predominantly catalyzed by the degradation products of  $[Ru(bpy)_3]^{2+}$  (e.g., *cis*- $[Ru(bpy)_2(CO)H]^+$ ), as discussed above. Perhaps, the efficient catalytic cycle of CO<sub>2</sub> reduction by CoTPPS plays a role as an inhibitor for either the generation of the [Ru(bpy)<sub>2</sub>(CO)H]<sup>+</sup> species or the catalytic cycle of H<sub>2</sub> generation itself. This inhibition effect becomes more obvious at higher [CoTPPS]/[Ru(bpy)<sub>3</sub><sup>2+</sup>] ratios, resulting in the maximum  $Sel_{CO_2}$  value of 91% when the  $[Ru(bpy)_3]^{2+}$  concentration is minimized (50 µM) (Figures 3E and 3F). Under these conditions, the photocatalytic activity remains sufficiently high (TON<sub>CO</sub> = 400, TOF<sub>CO</sub> =  $31 h^{-1}$ ).

Interestingly, the present photocatalytic system preserves its activity even in the presence of a large amount of  $O_2$  in the headspace (p( $O_2$ )= 0.3, [ $O_2$ ]= 12.3 mM, even though inhibition in CO formation occurs due to the concomitant promotion of  $O_2$  reduction (Figures S19-S21).<sup>22</sup> On the basis of our experimental and theoretical results, together with those described in the literature,<sup>23,24</sup> a possible catalytic cycle is proposed in Scheme 1. The starting diaqua-cobalt(III) species  $[Co^{III}TPPS(H_2O)_2]^+$  (pK<sub>a1</sub>=7.02)<sup>25</sup> is readily reduced to the Co<sup>II</sup> species  $[Co^{II}TPPS(H_2O)]^{26}$  in the presence of a large excess of AscH<sup>-</sup> (Scheme 1 and Figures S22 and S23).<sup>27</sup> The photocatalytic cycle is initiated *via* light absorption by  $[Ru(bpy)_3]^{2+}$ , reductive quenching of  $[Ru(bpy)_3]^{2+*}$  by AscH<sup>-</sup> ( $k_q = 1.9 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$ ) (Figures S24 and S25), and electron transfer from  $[Ru^{II}(bpy)_2(bpy^{--})]^+$  ( $E_p = -1.49 \text{ V vs. SCE}$ ) to  $[Co^{II}TPPS(H_2O)]$  ( $E_{1/2} = -0.92 \text{ V}$ ) to afford  $[Co^{I}TPPS]^-$  (Figure 4A-C).

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

60

The electrochemistry results (Figure 4) reveal that this species is further reduced to give a porphyrin-reduced intermediate [Co<sup>I</sup>(TPPS<sup>-</sup>)]<sup>2-</sup> at -1.26 V vs. SCE (Figure 4C; both CV and SWV), which appears to be coupled with the rise of catalytic current. We note that upon introduction of CO2 there is no meaningful change at the first reduction wave  $(E_{1/2} = -0.92 \text{ V vs. SCE})$  (Figure 4A). Under the catalytic CO<sub>2</sub> reduction conditions, the reduction potential of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (-1.49 V vs. SCE, Figure 4B) is negative enough to reduce [Co<sup>I</sup>TPPS]<sup>-</sup> and generate the reactive [Co<sup>I</sup>(TPPS<sup>-</sup>)]<sup>2-</sup> species. Importantly, the above-mentioned second reduction peak potential is consistent with that computed by DFT in this work (-1.32 V vs. SCE; see Figure 5). Moreover, these values are also in line with the porphyrin-based reduction potentials reported for the free TPPS ligand as well as for some M(TPPS) derivatives (M = Zn, Pd) in aqueous media (-1.16 V to -1.23 V vs. SCE).<sup>28</sup> The CO<sub>2</sub>-binding with [Co<sup>I</sup>(TPPS<sup>-</sup>)]<sup>2-</sup> has exothermic path ( $\Delta G = -4.2 \text{ kcal} \cdot \text{mol}^{-1}$ ) with a lower activation barrier ( $\Delta G^{\ddagger} = 7.6 \text{ kcal} \cdot \text{mol}^{-1}$ ) to form CO<sub>2</sub>-bound species in comparison with the CO2-binding path with [Co<sup>I</sup>TPPS]<sup>-</sup> (see Figure 5). However, we do not completely rule out the latter path, since it can also result in the same porphyrin-reduced species [Co<sup>III</sup>(TPPS<sup>-</sup>)(CO<sub>2</sub><sup>2-</sup>)]<sup>2-</sup> and is only slightly uphill in energy ( $\Delta G = 1.2 \text{ kcal} \cdot \text{mol}^{-1}$ ,  $\Delta G^{\ddagger} = 9.9 \text{ kcal} \cdot$  $mol^{-1}$ ) (Table S23). We thus assume that the CO<sub>2</sub>-binding to [Co<sup>I</sup>(TPPS<sup>-</sup>)]<sup>2-</sup> is the major path under these experimental conditions. Although some reports describe the CO<sub>2</sub>-bound species as  $[Co^{I}(P^{-})(CO_{2})]^{2-}$  (P = porphyrin),<sup>24b</sup> based on our DFT results we adopt the formulation of [Co<sup>III</sup>(TPPS<sup>-</sup>)(CO<sub>2</sub><sup>2-</sup> )]<sup>2-</sup> (see SI for details), in accord with the results of XANES measurements carried out for the CO<sub>2</sub>-bound cobalt catalysts with tetra-azamacrocyclic ligands.<sup>29</sup> The spin density plots as well as the spin density values shown in Tables S4 and S7 provide strong support for the anion radical form of the porphyrin (e.g., TPPS<sup>-</sup>), indicating that the major radical character is delocalized over the porphyrin ring system.

Notably, under CO<sub>2</sub>, the formation of  $[Co^{III}(TPPS^{-})(CO_2^{2^-})]^{2^-}$  is significantly preferred over the formation of hydride species (e.g.,  $[Co^{III}(TPPS^{-})(H)]^-$ ) leading to H<sub>2</sub> evolution, as demonstrated by the high Sel<sub>CO2</sub> values (Figures 2 and 3). Our DFT results also indicate that further reduction of the porphyrin-reduced intermediate  $[Co^{III}(TPPS^{-})(CO_2^{2^-})]^{2^-}$  into  $[Co^{III}(TPPS^{2^-})(CO_2^{2^-})]^{3^-}$  (E<sub>calc</sub> = -1.71 V vs. SCE) by  $[Ru^{II}(bpy)_2(bpy^{-})]^+$  is rather uphill by 5.1 kcal· mol<sup>-1</sup>, not likely to compete well with the alternative protonation path shown in Scheme 1 and Figure 5.



**Figure 4.** A) Cyclic voltammograms (CV) of CoTPPS (1 mM) in a 0.1 M phosphate buffer under  $CO_2$  (red) and under Ar (blue) at pH 6.7. B) Square-wave voltammogram (SWV) of  $[Ru(bpy)_3]Cl_2$  (1 mM) in a 0.1 M NaHCO<sub>3</sub> buffer under CO<sub>2</sub> at pH 6.7. C) CV (red) SWV (green) of CoTPPS (1 mM) in a 0.1 M NaHCO<sub>3</sub> buffer under CO<sub>2</sub> at pH 6.7. Scan rate 0.1 V·s<sup>-1</sup>, T = 21 °C.



**Scheme 1.** Proposed reaction scheme for the CO<sub>2</sub>-to-CO photoconversion in the [Ru(bpy)<sub>3</sub>]<sup>2+</sup>/ascorbate/CoTPPS system in water. The peripheral charges of the sulfonated groups are neglected for simplicity and clarity.



**Reaction coordinate** 

**Figure 5.** Free energy diagram computed by DFT for the catalytic cycle by  $Co^{11}P(H_2O)$  (**P** = non-substituted porphyrin), promoted by the reductive equivalent of the  $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^+$  couple at pH = 6.7 (see Figure S27 for details)

The next step in the photocatalytic cycle is the protonation of  $[Co^{III}(TPPS^{-})(CO_2^{2^*})]^{2^*}$  into  $[Co^{III}(TPPS^{-})(CO_2H^{-})]^{-}$ , which is downhill by -3.1 kcal· mol<sup>-1</sup> (Figure 5). The subsequent C-O bond cleavage coupled with protonation and water elimination is more highly downhill (by -17.2 kcal· mol<sup>-1</sup>), affording  $[Co^{II}TPPS(CO)]$ , for which the low-spin  $Co^{II}$  d7 configuration is confirmed by DFT (Tables S6 and S9). Finally, simple dissociation of CO from  $[Co^{II}TPPS(CO)]$  ( $\Delta G = -0.6$ kcal· mol<sup>-1</sup>) may occur to give  $[Co^{II}TPPS]$ , but the aqualigated species  $[Co^{II}TPPS(H_2O)]$  is computed to be the major species in solution (Figure 5).

## CONCLUSIONS

In conclusion, while CoTPPS efficiently catalyzes the reduction of water to H<sub>2</sub> under N<sub>2</sub>, it selectively and efficiently catalyzes CO<sub>2</sub>-to-CO conversion under CO<sub>2</sub> even in fully aqueous media. Among the first-row transition metal molecular catalysts promoting CO<sub>2</sub>-to-CO photoconversion in water, CoTPPS exhibits high activity while retaining its high selectivity for CO<sub>2</sub> reduction vs. water reduction. Further studies focused on the detection and characterization of the key intermediates are still needed. We also note the importance of developing new photosensitizers robust enough to avoid *in situ* generation of any active water reduction catalysts. The extended studies are in progress in our group.

# EXPERIMENTAL SECTION

**Materials and reagents.** All solvents and reagents were of the highest quality available and were used as received. TPPS (meso-tetrakis(4-sulfophenyl)porphyrin) was purchased from Tokyo Chemical Industry Co., Ltd. and it was used as received. All other reagents were purchased from Kanto Chemicals Co., Inc. and used without further purification. Purification of water (0.055  $\mu$ S) was performed with a RFD250RB water distillation apparatus.

Instrumentation. UV-Visible absorption spectra were recorded on a Shimadzu UV2450SIM spectrophotometer. All

the sample solutions were maintained at 25 °C during the spectrophotometric measurements. ESI-TOF mass spectra were recorded on a JEOL JMS-T100LC mass spectrometer in positive or negative ion mode. <sup>1</sup>H NMR spectra were acquired on a JEOL JNM-ESA 600 MHz spectrometer. Luminescence spectra were recorded on a Shimadzu RF5300PC spectrofluorophotometer. Cyclic voltammetric experiments were recorded on a BAS ALS Model 602DKM electrochemical analyzer using a three electrode system consisting of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE) for the measurements in aqueous solutions. All reported potentials are given relative to SCE. The quantification of gases was done using a Shimadzu GC-14A gas chromatograph equipped with a molecular sieve 13X-S Å column of 2 m x 3 mm *i.d.*, at 30 °C. The injection of the sample gas (200 µL) was performed manually using a gas-tight syringe and the output signal from the thermal conductivity detector of the gas chromatograph was analyzed using a Shimadzu C-R8A integrator. The CO and H<sub>2</sub> peaks were determined using a calibration curve which had been previously obtained employing standard CO and H<sub>2</sub> gases. Photoirradiation experiments were carried out with an ILC Technology CERMAX LX-300 Xe lamp (179 mW·cm<sup>-2</sup>, 220 A) equipped with a CM-1 cold mirror which reflects lights in the range of  $400 < \lambda < 800$  nm. The photolysis vial (21 mL) was immersed in a 25 °C water bath to remove IR radiation and to eliminate the temperature effects.

Photocatalytic experiments and chromatographic detection of gases. In a typical photocatalytic run, a 10 mL aqueous solution containing CoTPPS (10  $\mu$ M), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (500  $\mu$ M), sodium ascorbate (0.1 M), and NaHCO<sub>3</sub> (0.1 M), was purged with CO<sub>2</sub> (purity  $\geq$  99.995 %) for 15 min prior to irradiation. The temperature was held constant at 25 °C throughout the experiment. The gases generated from the reaction during the photolysis were quantified by GC-TCD measurements of 200  $\mu$ L aliquots from the reaction vial headspace. The experiments were performed at least in duplicate (error 1-15%). It was found during this study that the purity of the compounds is very important for the reproducibility of the photocatalytic experiments.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38 39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

<sup>13</sup>CO<sub>2</sub> **labelling experiment.** A 2.5 mL aqueous solution containing CoTPPS (10 μM), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (500 μM), sodium ascorbate (0.1 M), and phosphate buffer (0.1 M), was purged with Ar for 15 min, followed by <sup>13</sup>CO<sub>2</sub> bubbling (pH<sub>final</sub>= 6.7). The <sup>13</sup>CO generated during irradiation was detected by GC-MS (HP 6890 Series GC SYSTEM, 5973 Mass Selective Detector). The <sup>13</sup>CO<sub>2</sub> gas was produced by adding water to a mixture of ascorbic acid with NaH<sup>13</sup>CO<sub>3</sub> (99 atom % <sup>13</sup>C, Cambridge Isotope Laboratories, Inc.).

**Quantification of formate.** The amount of formate in the liquid phase was determined by the following method. After 4 hours of irradiation, the reaction solvent was removed by freeze-drying. The resulting residue was dissolved in 0.8 mL D<sub>2</sub>O and 3-(trimethylsilyl)propionic-2,2,3,3- $d_4$  acid sodium salt (TSP- $d_4$ , 2 µmol) was added. After filtering the solution through Celite, the <sup>1</sup>H NMR spectrum was measured and the amount of formate was determined using the relative integrated intensity of its signal with respect to that of TSP- $d_4$  added as an internal standard.

Photocatalytic experiments in the presence of O<sub>2</sub>. Catalytic reactions varying the amount of O<sub>2</sub> in the reaction vessel were performed in a 10 mL aqueous solution containing CoTPPS (70  $\mu$ M), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (500  $\mu$ M), sodium ascorbate (0.1 M), NaHCO<sub>3</sub> (0.1 M), purged with CO<sub>2</sub> (purity  $\geq$  99.995 %) for 15 min. After the CO<sub>2</sub> purging, the corresponding amount of O<sub>2</sub> was introduced into the reaction vessel with a syringe through the septum. Before irradiation, the solution was vigorously shaken during 1 min and left under stirring for 30 min in order to dissolve the O<sub>2</sub> into the solution. The gases generated from the reaction during the photolysis were quantified by the analysis of an aliquot of gas (200  $\mu$ L) from the headspace of the reaction vial by GC-TCD measurements. The experiments were performed at least in duplicate (error 1-15%).

**Determination of the Quantum Yield.**<sup>18</sup> Considering the fact that the reduction of CO<sub>2</sub> to CO is a two-electron process, the overall quantum yield of the process ( $\Phi_{CO}$ ) was calculated using the following equation:

$$\Phi_{CO} = \frac{number of CO molecules x 2}{number of photons absorbed} x 100$$

The number of CO molecules can be determined from the moles of CO in the sample headspace (obtained by GC measurements as described above) and Avogadro's number (6.022×10<sup>23</sup>). The number of photons absorbed (1.81×10<sup>18</sup> photons·s<sup>-1</sup>) was estimated by measuring the incident light power inside the reaction vessel (140 mW·cm<sup>-2</sup>) (an Optical Power Meter TQ8210 with Optical Sensor Q82017A from Advantest was used), taking the photon wavelength equal to 428 nm (a set of interference filters L39 + SV490 (380 <  $\lambda$  < 490 nm) was used) and considering an illuminated area of 6 cm<sup>2</sup>. Under our conditions the complete absorption of photons is satisfied due to the high absorbance of the solution at the wavelength adopted. The obtained quantum yield is 0.81% at 1 hour of irradiation.

**Synthesis of CoTPPS.** CoTPPS [{*meso*-tetra(4-sulfonatophenyl)porphyrinato}cobalt(III)]·12H<sub>2</sub>O was prepared as previously described.<sup>30</sup>. CoCl<sub>2</sub>·6H<sub>2</sub>O (0.143 g, 6 mmol), and TPPS (0.090 g, 1 mmol) were dissolved in water (25 mL).

After adjusting the pH at 7.5 by adding 1 M NaOH, the solution was refluxed for 24 h and allowed to cool to room temperature. The solution was then filtered for the removal of insoluble materials. The filtrate was then reduced and passed through a column containing a Dowex 50W-X8 cation-exchange resin in the H<sup>+</sup> form (50-100-mesh) in order to remove residual cobalt ions present in the reaction mixture. The CoTPPS was precipitated as a purple solid from a water/acetone solvent mixture. The precipitate was collected by filtration, washed with acetone and diethyl ether, and dried in vacuo. Yield 65%. MS (ESI – MeOH, negative mode) (m/z): 328.98 [C<sub>44</sub>H<sub>24</sub>N<sub>4</sub>S<sub>4</sub>O<sub>12</sub>Co]<sup>3+</sup> (100%) (calcd: 328.99). Elemental analysis of CoTPPS calcd: (%) for C<sub>44</sub>H<sub>27</sub>N<sub>4</sub>S<sub>4</sub>O<sub>12</sub>Co·12H<sub>2</sub>O (1207.1): C 43.78, H 4.26, N 4.64; found: C 44.07, H 4.26, N 4.63.

DFT Calculations. Density functional theory (DFT) calculations were performed using the Gaussian og package of programs<sup>31</sup> to better understand the electronic structures of some possible intermediates and the energy diagram for the catalytic cycle of CO<sub>2</sub> reduction by the cobalt porphyrin. In our calculations, the simplest non-substituted cobalt porphyrin system (P) (e.g., without the four sulfonatophenyl moieties in CoTPPS) has been adopted. Therefore, for the computed model systems, descriptions such as [Co<sup>II</sup>P] and [Co<sup>I</sup>P]will be used to describe the species of interest. The structures were fully optimized at the B<sub>3</sub>LYP level of calculations with the effect of solvation in water taken into consideration by using the polarizable continuum model (PCM) method.32 Calculations were typically performed using the 6-31G\* basis set applied to all atoms. For some of the species, calculations were also performed using the SDD basis set adopted for the Co ion with the 6-31G\* basis set applied to the remaining HCNO atoms. Plots showing the spin density distribution were generated using GaussView 5.0.9.33 Detailed description is given in SI.

## **AUTHOR INFORMATION**

#### **Corresponding Authors**

\*E-mail: arnau\_call@chem.kyushu-univ.jp \*E-mail: cibian\_mihaela@chem.kyushu-univ.jp \*E-mail: ksakai@chem.kyushu-univ.jp

#### **Author Contributions**

§ AC and MC contributed equally to this work.

#### Notes

The authors declare no competing financial interests.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Additional data (control and optimization experiments, addition and photostability experiments, electrochemistry data, quenching experiments, and DFT results) (PDF).

1

2

3

4

5

6

7

8

9

16

58 59

60

# ACKNOWLEDGMENT

This work was supported by JSPS KAKENHI Grant Number JP18H01996 (Grant-in-Aid for Scientific Research (B)) and by JSPS KAKENHI Grant Number JP18H05171 in a Grant-in-Aid for Scientific Research on Innovative Areas "Innovations for Light-Energy Conversion (I4LEC)". This work was also supported by the International Institute for Carbon Neutral Energy Research (WPI-I<sup>2</sup>CNER), sponsored by the World Premier International Research Center Initiative (WPI), MEXT, Japan. MC thanks le Fonds du Québec pour la recher-10 ché sur la nature et les technologies (FRQNT) for a PD scholarship. The authors are also grateful to Kyushu University 11 Department of Chemistry and I<sup>2</sup>CNER services and person-12 nel. 13

#### 14 REFERENCES 15

(1) Gray, H. B. Powering the Planet with Solar Fuel. Nat. Chem. 2009, 1, 7.

17 (2) Li, K.; Peng, B.; Peng, T. Recent Advances in Heterogeneous 18 Photocatalytic CO2 Conversion to Solar Fuels. ACS Catal. 2016, 6, 19 7485-7527.

(3) Sato, S.; Arai, T.; Morikawa, T. Toward Solar-Driven 20 Photocatalytic CO<sub>2</sub> Reduction Using Water as an Electron Donor. 21 Inorg. Chem. 2015, 54, 5105-5113. 22

- (4) Elgrishi, N.; Chambers, M. B.; Fontecave, M. Turning it Off! 23 Disfavouring Hydrogen Evolution to Enhance Selectivity for CO 24 Production During Homogeneous CO2 Reduction by Cobalt-Terpyridine Complexes. Chem. Sci. 2015, 6, 2522-2531. 25
- (5) (a) Takeda, H.; Cometto, C.; Ishitani, O.; Robert, M. Electrons, 26 Photons, Protons and Earth-Abundant Metal Complexes for 27 Molecular Catalysis of CO<sub>2</sub> Reduction. ACS Catal. 2017, 7, 70-88; (b) 28 Elgrishi, N.; Chambers, M. B.; Wang, X.; Fontecave, M. Molecular Polypyridine-Based Metal Complexes as Catalysts for the Reduction 29 of CO2. Chem. Soc. Rev. 2017, 46, 761-796 30
- (6) (a) Wang, X.; Goudy, V.; Genesio, G.; Maynadié, J.; Meyer, D.; 31 Fontecave, M. Ruthenium-Cobalt Dinuclear Complexes as 32 Photocatalysts for CO<sub>2</sub> Reduction. Chem. Commun. 2017, 53, 5040-33 5043; (b) Takeda, H.; Ohashi, K.; Sekine, A.; Ishitani, O. Photocatalytic CO2 Reduction Using Cu(I) Photosensitizers with a 34 Fe(II) Catalyst. J. Am. Chem. Soc. 2016, 138, 4354-4357; (c) Guo, Z.; 35 Cheng, S.; Cometto, C.; Anxolabéhère-Mallart, E.; Ng, S. M.; Ko, C. 36 C.; Liu, G.; Chen, L.; Robert, M.; Lau, T. C. Highly Efficient and 37 Selective Photocatalytic CO2 Reduction by Iron and Cobalt Quaterpyridine Complexes. J. Am. Chem. Soc. 2016, 138, 9413-9416; 38 (d) Cometto, C.; Kuriki, R.; Chen, L.; Maeda, K.; Lau, T. C.; Ishitani, 39 O.; Robert, M. A Carbon Nitride/Fe Quaterpyridine Catalytic System 40 for Photostimulated CO2-to-CO Conversion with Visible Light. J. 41 Am. Chem. Soc. 2018, 140, 7437-7440.
- 42 (7) (a) Ouyang, T.; Huang, H. H.; Wang, J. W.; Zhong, D. C.; Lu, T. B. A Dinuclear Cobalt Cryptate as a Homogeneous Photocatalyst for 43 Highly Selective and Efficient Visible-Light Driven CO<sub>2</sub> Reduction to 44 CO in CH<sub>3</sub>CN/H<sub>2</sub>O Solution. Angew. Chem. Int. Ed. 2017, 56, 738-743; 45 (b) Hong, D.; Tsukakoshi, Y.; Kotani, H.; Ishizuka, T.; Kojima, T. 46 Visible-Light-Driven Photocatalytic CO2 Reduction by a Ni(II) Complex Bearing a Bioinspired Tetradentate Ligand for Selective CO 47 Production. J. Am. Chem. Soc. 2017, 139, 6538-6541. 48
- (8) (a) Nakada, A.; Koike, K.; Nakashima, T.; Morimoto, T.; Ishitani, 49 O. Photocatalytic CO<sub>2</sub> Reduction to Formic Acid Using a Ru(II)-Re(I) 50 Supramolecular Complex in an Aqueous Solution. Inorg. Chem. 2015, 54, 1800-1807; (b) Kuriki, R.; Matsunaga, H.; Nakashima, T.; Wada, 51 K.; Yamakata, A.; Ishitani, O.; Maeda, K. Nature-Inspired, Highly 52 Durable CO2 Reduction System Consisting of a Binuclear 53 Ruthenium(II) Complex and an Organic Semiconductor Using 54 Visible Light. J. Am. Chem. Soc. 2016, 138, 5159-5170; (c) Kuriki, R.; 55 Yamamoto, M.; Higuchi, K.; Yamamoto, Y.; Akatsuka, M.; Lu, D.; Yagi, S.; Yoshida, T.; Ishitani, O.; Maeda, K. Robust Binding between 56 Carbon Nitride Nanosheets and a Binuclear Ruthenium(II) Complex 57

Enabling Durable, Selective CO2 Reduction under Visible Light in Aqueous Solution. Angew. Chem. Int. Ed. 2017, 56, 4867-4871.

(9) (a) Méndez, M. A.; Voyame, P.; Girault, H. H. Interfacial Photoreduction of Supercritical CO<sub>2</sub> by an Aqueous Catalyst. Angew. Chem. Int. Ed. 2011, 50, 7391-7394; (b) Neri, G.; Forster, M.; Walsh, J. J.; Robertson, C. M.; Whittles, T. J.; Farràs, P.; Cowan, A. J. Photochemical CO2 Reduction in Water Using a Co-immobilized Nickel Catalyst and a Visible Light Sensitiser. Chem. Commun. 2016, 52, 14200-14203; (c) Kuehnel, M. F.; Orchard, K. L.; Dalle, K. E.; Reisner, E. Selective Photocatalytic CO<sub>2</sub> Reduction in Water through Anchoring of a Molecular Ni Catalyst on CdS Nanocrystals. J. Am. Chem. Soc. 2017, 139, 7217-7223; (d) Rao, H.; Bonin, J.; Robert, M. Visible-light Homogeneous Photocatalytic Conversion of CO2 into CO in Aqueous Solutions with an Iron Catalyst. *ChemSusChem* 2017, 10, 4447-4450; (e) Kuehnel, M. F.; Sahm, C. D.; Neri, G.; Lee, J. R.; Orchard, K. L.; Cowan, A. J.; Reisner, E. ZnSe Quantum Dots Modified with a Ni(cyclam) Catalyst for Efficient Visible-light Driven CO2 Reduction in Water. Chem. Sci. 2018, 9, 2501-2509.

(10) (a) Craig, C. A.; Spreer, L. O.; Otvos, J. W.; Calvin, M. Photochemical Reduction of Carbon Dioxide Using Nickel Tetraazamacrocycles. J. Phys. Chem. 1990, 94, 7957-7960; (b) Grant, J. L.; Goswami, K.; Spreer, L. O.; Otvos, J. W.; Calvin, M. Photochemical Reduction of Carbon Dioxide to Carbon Monoxide in Water Using a Nickel(II) Tetra-azamacrocycle Complex as Catalyst. J. Chem. Soc., Dalton Trans. 1987, 9, 2105-2109; (c) Mochizuki, K.; Manaka, S.; Takeda, I.; T. Kondo Synthesis and Structure of [6,6' Bi(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane)]dinickel(II)

Triflate and Its Catalytic Activity for Photochemical CO<sub>2</sub> Reduction. Inorg. Chem. 1996, 35, 5132-5136; (d) Herrero, C.; Quaranta, A.; El Ghachtouli, S.; Vauzeilles, B.; Leibl, W.; Aukauloo, A. Carbon Dioxide Reduction via Light Activation of a Ruthenium-Ni(cyclam) Complex. Phys. Chem. Chem. Phys. 2014, 16, 12067-12072.

(11) Schneider, C. R.; Manesis, A. C.; Stevenson, M. J.; Shafaat, H. S. A Photoactive Semisynthetic Metalloenzyme Exhibits Complete Selectivity for CO2 reduction in Water. Chem. Commun. 2018, 54, 4682-4684.

(12) Lian, S.; Kodaimati, M. S.; Weiss, E. A. Photocatalytically Active Superstructures of Quantum Dots and Iron Porphyrins for Reduction of CO<sub>2</sub> to CO in Water. ACS Nano 2018, 12, 568-575.

(13) Bi, Q.-Q.; Wang, J.-W.; Lv, J.-X.; Wang, J.; Zhang, W.; Lu, T.-B. Selective Photocatalytic CO<sub>2</sub> Reduction in Water by Electrostatic Assembly of CdS Nanocrystals with a Dinuclear Cobalt Catalyst. ACS Catal. 2018, 8, 11815-11821.

(14) Manbeck, G. F.; Fujita, E. A Review of Iron and Cobalt Porphyrins, Phthalocyanines and Related Complexes for Electrochemical and Photochemical Reduction of Carbon Dioxide. J. Porphyr. Phthalocyanines 2015, 19, 45-64.

(15) Zhao, G.; Pang, H.; Liu, G.; Li, P.; Liu, H.; Zhang, H.; Shi, L.; Ye, J. Co-Porphyrin/Carbon Nitride Hybrids for Improved Photocatalytic CO<sub>2</sub> Reduction Under Visible Light. Appl. Catal., B 2017, 200, 141-149. (16) (a) Kelly, J. M.; O'Connell, C. M.; Vos, J. G. Preparation, Spectroscopic Characterisation, Electrochemical and Photochemical Properties of *cis*-Bis(2,2'-bipyridyl)carbonylruthenium Complexes J. Chem. Soc. Dalton Trans. 1986, 253-258; (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. Photochemical Reduction of Carbon Dioxide to Formate Mediated by Ruthenium Bipyridine Complexes as Homogeneous Catalysts. J. Chem. Soc. Chem. Commun. 1985, 56-58.

(17) The pH was measured after bubbling with either  $N_2$  or  $CO_2$ . The phosphate buffer at pH 6.9 under CO2 (1 atm) was prepared by bubbling CO<sub>2</sub> through an aqueous solution containing Na<sub>3</sub>PO<sub>4</sub> (0.1 M) and AscHNa (0.1 M), which initially displayed pH 11.8 under air. The bicarbonate buffer at pH 6.7 was similarly prepared by bubbling CO<sub>2</sub> through an aqueous solution containing NaHCO<sub>3</sub> (0.1 M) and AscHNa (0.1 M), which initially displayed pH 9.1. The product yields for the  $CO_2$  reduction under the bicarbonate (pH = 6.7) (Figure 2B, left) and phosphate (pH = 6.9) (Figure 2C, left) conditions were similar in both the presence and absence of CoTPPS. Neither CO nor H<sub>2</sub> evolves under N<sub>2</sub>, in the absence of CoTPPS, under both bicarbonate (pH = 6.7) and phosphate (pH = 6.9) conditions.

(18) Bonin, J.; Robert, M.; Routier, M. Selective and Efficient Photocatalytic CO2 Reduction to CO Using Visible Light and an Iron-based Homogeneous Catalyst. J. Am. Chem. Soc. 2014, 136, 16768-16771.

(19) (a) Natali, M.; Luisa, A.; Iengo, E.; Scandola, F. Efficient Photocatalytic Hydrogen Generation from Water by a Cationic Cobalt(II) Porphyrin. *Chem. Commun.* 2014, 50, 1842-1844; (b) Beyene, B. B.; Hung, C.-H. Photocatalytic Hydrogen Evolution from Neutral Aqueous Solution by a Water-soluble Cobalt(II) Porphyrin. *Sustainable Energy Fuels* 2018, 2, 2036-2043

1

2

3

4

5

6

7

8

9

59

60

- (20) Aoi, S.; Mase, K.; Ohkubo, K.; Fukuzumi, S. Mechanism of a One-photon Two-electron Process in Photocatalytic Hydrogen Evolution from Ascorbic Acid with a Cobalt Chlorin Complex. *Chem. Commun.* 2015, 51, 15145-15148.
- 10(21) This Sel<sub>CO2</sub> value should be seen as an apparent selectivity11because it is calculated supposing that the H2 produced is only12yielded via the CoTPPS cycle. The role of the degradation products13of the photosensitizer (e.g., *cis*-[Ru(bpy)2(CO)H]\*) in H2 evolution is14catalysis by CoTPPS is expected to be even higher.
- (22) Olaya, A. J.; Schaming, D.; Brevet, P. F.; Nagatani, H.;
  Zimmermann, T.; Vanicek, J.; Xu, H. J.; Gros, C. P.; Barbe, J. M.;
  Girault, H. H. Self-Assembled Molecular Rafts at Liquid/Liquid
  Interfaces for Four-Electron Oxygen Reduction. *J. Am. Chem. Soc.*2012, 134, 498-506.
- (23) (a) Pander, J. E.; Fogg, A.; Bocarsly, A. B. Utilization of 19 Electropolymerized Films of Cobalt Porphyrin for the Reduction of 20 Carbon Dioxide in Aqueous Media. Chemcatchem 2016, 8, 3536-3545; 21 (b) Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y. Y.; Diaz-Morales, O.; 22 Kwon, Y.; Ledezma-Yanez, I.; Schouten, K. J.; Mul, G.; Koper, M. T. 23 Electrocatalytic Reduction of Carbon Dioxide to Carbon Monoxide and Methane at an Immobilized Cobalt Protoporphyrin. Nat. 24 Commun. 2015, 6, 8177; (c) Lin, S.; Diercks, C. S.; Zhang, Y.-B.; 25 Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, 26 P.; Yaghi, O. M.; Chang, C. J. Covalent Organic Frameworks 27 Comprising Cobalt Porphyrins for Catalytic CO<sub>2</sub> Reduction in Water. Science 2015, 349, 1208-1213; (d) Hu, X. M.; Ronne, M. H.; Pedersen, S. 28 U.; Skrydstrup, T.; Daasbjerg, K. Enhanced Catalytic Activity of 29 Cobalt Porphyrin in CO<sub>2</sub> Electroreduction upon Immobilization on 30 Carbon Materials. Angew. Chem. Int. Ed. 2017, 56, 6468-6472; (e) Mu, 31 X. H.; Kadish, K. M. Oxidative Electrochemistry of Cobalt Tetraphenylporphyrin under a CO Atmosphere. Interaction between 32 Carbon Monoxide and Electrogenerated [(TPP)Co]<sup>+</sup> in Nonbonding 33 Media Inorg. Chem. 1989, 28, 3743-3747.
- 34 (24) (a) Nielsen, I. M. B.; Leung, K. Cobalt-Porphyrin Catalyzed 35 Electrochemical Reduction of Carbon Dioxide in Water. 1. A Density Functional Study of Intermediates. J. Phys. Chem. A 2010, 114, 10166-36 10173; (b) Leung, K.; Nielsen, I. M. B.; Sai, N.; Medforth, C.; Shelnutt, 37 J. A. Cobalt-Porphyrin Catalyzed Electrochemical Reduction of 38 Carbon Dioxide in Water. 2. Mechanism from First Principles. J. 39 Phys. Chem. A 2010, 114, 10174-10184; (c) Shen, J.; Kolb, M. J.; Göttle, 40 A. J.; Koper, M. T. M. DFT Study on the Mechanism of the Electrochemical Reduction of CO2 Catalyzed by Cobalt Porphyrins. J. 41 Phys. Chem. C 2016, 120, 15714-15721; (d) Göttle, A. J.; Koper, M. T. M. 42 Proton-Coupled Electron Transfer in the Electrocatalysis of CO2 43 Reduction: Prediction of Sequential vs. Concerted Pathways Using DFT. Chem. Sci. 2017, 8, 458-465. 44
- (25) Ashley, K. R.; Leipoldt, J. G. Kinetic and Equilibrium Study of
  the Reaction of (meso-Tetrakis(p-sulfonatophenyl)porphyrinato)diaquocobaltate(III) with Pyridine in
  Aqueous Solution. Inorg. Chem. 1981, 20, 2326-2333.
- 48 (26) Based on our DFT results, three forms  $[Co^{II}(P)]$ ,  $[Co^{II}(P)(H_2O)]$ , 49 and  $[Co^{II}(P)(H_2O)_2]$  coexist in aqueous media for this oxidation state 50 with the relative abundances 11, 72, and 17%, respectively (see Table 51 S23).
- (28) Kalyanasundaram, K.; Neumann-Spallart, M. Photophysical and Redox Properties of Water-Soluble Porphyrins in Aqueous Media. *J. Phys. Chem.* 1982, *86*, 5163-5169.

(29) Fujita, E.; Furenlid, L. R.; Renner, M. W. Direct XANES Evidence for Charge Transfer in  $Co-CO_2$  Complexes. J. Am. Chem. Soc. **1997**, *119*, 4549-4550.

(30) (a) Nakazono, T.; Parent, A. R.; Sakai, K. Cobalt Porphyrins as Homogeneous Catalysts for Water Oxidation. *Chem. Commun.* **2013**, *49*, 6325-6327; (b) Fleischer, E. B.; Palmer, J. M.; Srivastava, T. S.; Chattrejee, A. Thermodynamic and Kinetic Properties of an Iron-Porphyrin System. *J. Am. Chem. Soc.* **2010**, *93*, 3162–3167.

(31) M. J. Frisch, et al., Gaussian 09 (Revision C.01), Gaussian Inc., Wallingford, CT, 2009.

(32) (a) Barone, V.; Cossi, M.; Tomasi, J. Geometry Optimization of Molecular Structures in Solution by the Polarizable Continuum Model. *J. Comput. Chem.* **1998**, *19*, 404-417; (b) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. New Developments in the Polarizable Continuum Model for Quantum Mechanical and Classical Calculations on Molecules in Solution. *J. Chem. Phys.* **2002**, *117*, 43-54; (c) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999-3094.

(33) R. Dennington and T. Keith and J. Millam, GaussView (Version 5), Semichem Inc., Shawnee Mission, KS, **2009**.

# ACS Catalysis

Water-soluble cobalt porphyrins are highly efficient catalysts for the CO<sub>2</sub>-to-CO photoreduction *in fully aqueous media* while retaining a high selectivity in CO formation *vs.* H<sub>2</sub> formation.

