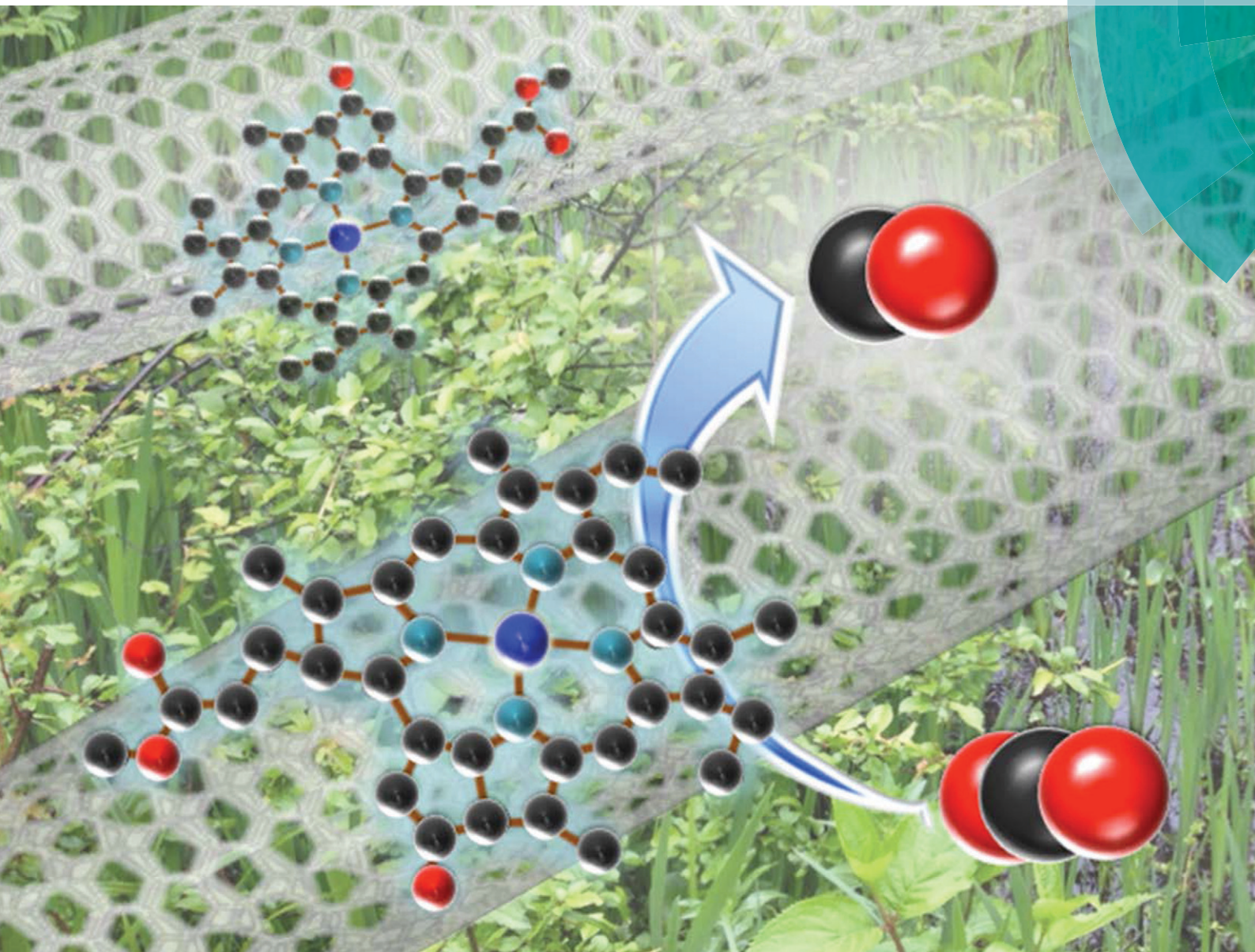


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## COMMUNICATION

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Photocatalytic reduction of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to  $\text{CO}$  and  $\text{H}_2$  with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes

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The photocatalytic reduction of CO<sub>2</sub> and H<sub>2</sub>O with triethylamine occurred efficiently using a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes as a CO<sub>2</sub> reduction catalyst and [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> (Me<sub>2</sub>phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst to yield CO and H<sub>2</sub> with a ratio of 2.4 : 1 and a high turnover number of 710.

Photocatalytic reduction of carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) to produce synthesis gas, which is a fuel gas mixture consisting primarily of hydrogen (H<sub>2</sub>) and carbon monoxide (CO), has merited significant interest, because synthetic gas can be converted to liquid hydrocarbon fuels by Fischer–Tropsch processes.<sup>1–6</sup> The 2nd and 3rd row transition metal complexes such as Re and Ir complexes have been used as effective photocatalysts for CO<sub>2</sub> reduction.<sup>7–13</sup> The much more earth abundant metal complexes such as Co complexes have also been used as catalysts for photocatalytic CO<sub>2</sub> reduction.<sup>14–21</sup> However, the turnover number has yet to be much improved for the photocatalytic reduction of CO<sub>2</sub> and H<sub>2</sub>O to produce synthetic gas with earth-abundant metal complexes.

We report herein the efficient photocatalytic reduction of CO<sub>2</sub> and H<sub>2</sub>O using triethylamine (TEA) as a reductant, a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes (MWCNTs) as a CO<sub>2</sub> reduction catalyst and [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> (Me<sub>2</sub>phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst in acetonitrile (MeCN) containing 5% (v/v) water to yield CO and H<sub>2</sub> with a 2.4 to 1.0 ratio and a high turnover

## Photocatalytic reduction of CO<sub>2</sub> and H<sub>2</sub>O to CO and H<sub>2</sub> with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes†

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number. The photocatalytic mechanism is clarified by examining each step of the catalytic cycle.

Visible light irradiation of a CO<sub>2</sub>-saturated MeCN solution of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup>, cobalt(II) chlorin complex Co<sup>II</sup>(Ch) (the chemical structure is shown in Scheme 1) and TEA containing 5% (v/v) H<sub>2</sub>O resulted in the formation of CO and H<sub>2</sub> as shown in Fig. 1. The optimised concentration of Co<sup>II</sup>(Ch) was 40 μM and the higher concentration of Co<sup>II</sup>(Ch) absorbed more light than [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> to retard the photocatalytic reaction (Fig. S1 in the ESI†). When Co<sup>II</sup>(Ch) was adsorbed on MWCNTs by adding MWCNTs to the reaction solution and then stirring it (Fig. S2 in the ESI†), the yield of CO was much improved as compared with that without MWCNTs (Fig. 2). The turnover number (TON) was determined to be 710 with Co<sup>II</sup>(Ch) (5.0 μM) and MWCNTs (1.0 mg) at 20 h.<sup>25</sup> The π–π interaction between MWCNTs and Co<sup>II</sup>(Ch) may provide a suitable hydrophobic environment for the binding of CO<sub>2</sub> instead of proton, because the binding of CO<sub>2</sub> to the Co(I) complex is required for the formation of CO.<sup>14</sup>

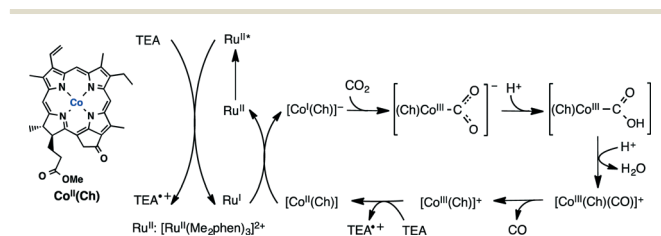
The emission of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> was hardly quenched by Co<sup>II</sup>(Ch) (Fig. S3 in the ESI†). The emission lifetime of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> remained the same in the presence of Co<sup>II</sup>(Ch) (100 μM) as that in the absence of Co<sup>II</sup>(Ch). The one-electron oxidation potential (*E*<sub>ox</sub><sup>\*</sup>) of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> was determined from the one-electron oxidation potential of the ground state (1.12 V vs. SCE) and the excitation energy

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† Electronic supplementary information (ESI) available: Experimental details and UV-vis absorption spectra (Fig. S1, S2 and S6), emission decay profiles (Fig. S3), cyclic voltammograms (Fig. S4 and S5), FTIR spectra (Fig. S7) and kinetic data (Fig. S8). See DOI: 10.1039/c6cy00376a



**Scheme 1** Mechanism of photocatalytic CO evolution from TEA with [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> and Co<sup>II</sup>(Ch).



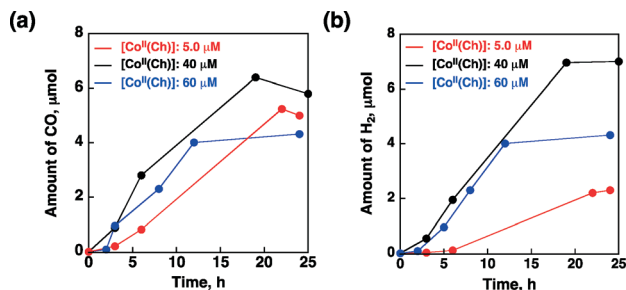


Fig. 1 Time courses of the production of (a) CO and (b) H<sub>2</sub> by photoirradiation of a CO<sub>2</sub>-saturated MeCN solution of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> (2.0 mM), Co<sup>II</sup>(Ch) (5.0, 40 and 60 μM) and TEA (0.50 M) containing 5% (v/v) H<sub>2</sub>O using a xenon lamp with a cut off filter (λ > 420 nm) at 298 K.

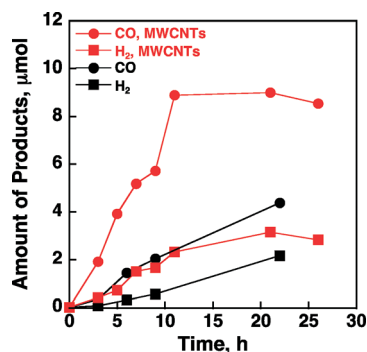


Fig. 2 Time courses of the production of CO and H<sub>2</sub> by photoirradiation of a CO<sub>2</sub>-saturated MeCN solution of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> (2.0 mM), TEA (0.50 M), Co<sup>II</sup>(Ch) (10 μM) adsorbed on MWCNTs (1.0 mg) (red) and Co<sup>II</sup>(Ch) (10 μM) without MWCNTs (black) containing 5% (v/v) H<sub>2</sub>O using a xenon lamp with a cut off filter (λ > 420 nm) at 298 K.

(2.1 eV) to be  $-0.98$  V vs. SCE.<sup>23</sup> The  $E_{\text{ox}}^*$  value is less negative than the one-electron reduction potential of Co<sup>II</sup>(Ch) ( $E_{\text{red}}$  vs. SCE =  $-0.89$  V), when the electron transfer from [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> to Co<sup>II</sup>(Ch) is exergonic (Fig. S4 in the ESI<sup>†</sup>).

On the other hand, the emission of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> was quenched by TEA by electron transfer from TEA to [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup>. The one-electron reduction potential ( $E_{\text{red}}^*$ ) of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> was determined from the one-electron reduction potential of the ground state ( $-1.47$  V vs. SCE) and the excitation energy (2.1 eV) to be  $0.67$  V vs. SCE. Because the  $E_{\text{ox}}$  value of TEA ( $0.74$  V vs. SCE), which was determined by second harmonic ac voltammetry (SHACV; Fig. S5 in the ESI<sup>†</sup>), is more positive than the  $E_{\text{red}}^*$  value, the electron transfer from TEA to [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> is slightly endergonic. The rate constant of electron transfer from TEA to [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> was determined from the Stern–Volmer plot (Fig. 3) to be  $1.7 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> in MeCN at 298 K. The quantum yield of the photocatalytic reduction of CO<sub>2</sub> to CO under photoirradiation of light at λ = 450 nm was determined to be 0.10% using a ferric oxalate actinometer (see the Experimental section in the ESI<sup>†</sup>).

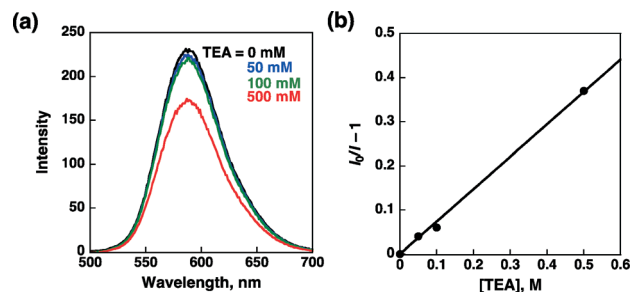


Fig. 3 (a) Emission spectra of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+</sup> (8.8 μM) with various concentrations of TEA (0–0.50 M) in deaerated MeCN containing 5% (v/v) H<sub>2</sub>O at 298 K. (b) Stern–Volmer plot.

The photocatalytic mechanism of the CO<sub>2</sub> reduction is shown in Scheme 1. Upon photoexcitation of [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup>, electron transfer from TEA to [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> occurs to produce a TEA radical cation and [Ru(Me<sub>2</sub>phen)<sub>3</sub>]<sup>+</sup>, the latter of which reduces Co<sup>II</sup>(Ch) to [Co<sup>I</sup>(Ch)]<sup>-</sup>. The TEA radical cation may be deprotonated to produce a neutral radical that may be further oxidized. Thus, the endergonic electron transfer from TEA to [Ru<sup>II</sup>(Me<sub>2</sub>phen)<sub>3</sub>]<sup>2+\*</sup> (*vide supra*) is irreversible. We have previously reported that CO<sub>2</sub> is reduced to CO when Co<sup>II</sup>(Ch) is electrochemically reduced to [Co<sup>I</sup>(Ch)]<sup>-</sup>.<sup>22</sup> At the same time [Co<sup>I</sup>(Ch)]<sup>-</sup> was reported to react with H<sup>+</sup> to produce the hydride complex ([Co<sup>III</sup>(H)(Ch)]), which reacts with H<sup>+</sup> to produce H<sub>2</sub>.<sup>24</sup> [Co<sup>III</sup>(H)(Ch)] is also an intermediate for H<sub>2</sub> evolution in the photocatalytic reduction of H<sub>2</sub>O to H<sub>2</sub>.<sup>26</sup>

In order to examine the reaction of [Co<sup>I</sup>(Ch)]<sup>-</sup> with CO<sub>2</sub>, [Co<sup>I</sup>(Ch)]<sup>-</sup> was prepared independently by the one-electron reduction of Co<sup>II</sup>(Ch) with decamethylcobaltocene [Co(Cp<sup>\*</sup>)<sub>2</sub>] in MeCN as reported previously.<sup>24</sup> The UV-vis absorption band of [Co<sup>I</sup>(Ch)]<sup>-</sup> (green line in Fig. 4a; λ<sub>max</sub> = 510 nm) decreased, accompanied by an increase in absorbance at 660 nm due to [Co<sup>III</sup>(Ch)(CO<sub>2</sub>)]<sup>-</sup> (blue line) at 65 ms upon introduction of CO<sub>2</sub> by mixing.<sup>27</sup> Then, this absorption band finally blue shifted to λ<sub>max</sub> = 652 nm, which is due to [Co<sup>III</sup>(Ch)(CO)]<sup>-</sup>.

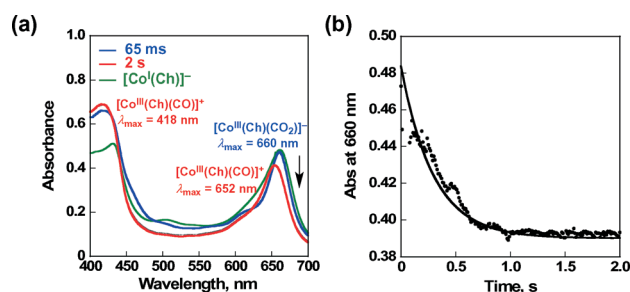


Fig. 4 (a) UV-vis absorption spectral changes of [Co<sup>I</sup>(Ch)]<sup>-</sup> (20 μM) upon introduction of CO<sub>2</sub>-saturated MeCN containing 5% (v/v) H<sub>2</sub>O at 298 K. The blue and red lines show the spectra taken at 65 ms and 2 s after mixing, respectively. The green line shows the UV-vis absorption spectrum of [Co<sup>I</sup>(Ch)]<sup>-</sup> (15 μM) formed by the electron-transfer reduction of Co<sup>II</sup>(Ch) (15 μM) with Co(Cp<sup>\*</sup>)<sub>2</sub> (300 μM) in deaerated MeCN at 298 K.<sup>24</sup> (b) Decay time profile of absorbance at 660 nm due to [Co<sup>III</sup>(Ch)(CO<sub>2</sub>)]<sup>-</sup>.



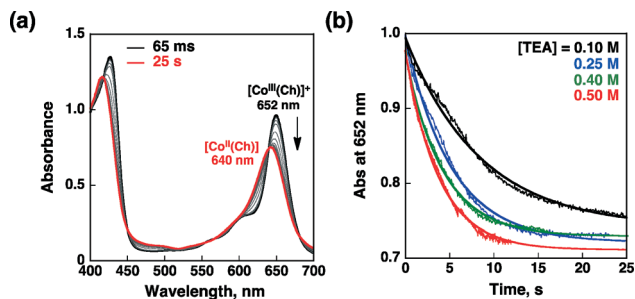


Fig. 5 (a) UV-vis absorption spectral changes in the electron-transfer reduction of  $[\text{Co}^{\text{III}}(\text{Ch})]^+$  (20  $\mu\text{M}$ ) with TEA (0.10 M) in deaerated MeCN containing 5% (v/v)  $\text{H}_2\text{O}$  at 298 K at 65 ms and 25 s after mixing. (b) Decay time profiles of absorbance at 652 nm due to  $[\text{Co}^{\text{III}}(\text{Ch})]^+$  in the presence of various concentrations of TEA in deaerated MeCN containing 5% (v/v)  $\text{H}_2\text{O}$  at 298 K.

(red line). This absorption band matched with that of  $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$  which was produced by introducing CO to  $[\text{Co}^{\text{III}}(\text{Ch})]^+$  in MeCN (Fig. S6 in the ESI<sup>†</sup>). When  $\text{N}_2$  was introduced to  $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$ , the spectrum returned to  $[\text{Co}^{\text{III}}(\text{Ch})]^+$ . This indicates that the binding of CO to  $[\text{Co}^{\text{III}}(\text{Ch})]^+$  is reversible. The CO stretching frequency of  $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$  was also measured in MeCN under an appropriate CO pressure (Fig. S7 in the ESI<sup>†</sup>).  $\nu\text{CO}$  is located at  $2158\text{ cm}^{-1}$ , which is nearly the same as the “free” CO molecule ( $\nu\text{CO} = 2155\text{ cm}^{-1}$ ),<sup>28</sup> suggesting a weak reversible coordination. Finally,  $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO}_2)]^-$  was converted to  $[\text{Co}^{\text{III}}(\text{Ch})]^+$  and CO by protonation with dehydration (Scheme 1). The rate constant of the formation of  $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$  was determined from the change in absorbance at 660 nm to be  $3.4\text{ s}^{-1}$  (Fig. 4b).

$[\text{Co}^{\text{III}}(\text{Ch})]^+$ , which was prepared by one-electron oxidation of  $\text{Co}^{\text{II}}(\text{Ch})$  with  $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ , was thermally reduced by TEA to produce  $\text{Co}^{\text{II}}(\text{Ch})$  (Scheme 1) as shown in Fig. 5a. The rate of reduction of  $[\text{Co}^{\text{III}}(\text{Ch})]^+$  by a large excess of TEA obeyed first-order kinetics and the pseudo-first-order rate constant was proportional to the concentration of TEA. From the slope of the linear plot of the pseudo-first-order rate constant vs. concentration of TEA, the second-order rate constant was determined to be  $0.64\text{ M}^{-1}\text{ s}^{-1}$  (Fig. S8 in the ESI<sup>†</sup>).

In conclusion,  $\text{Co}^{\text{II}}(\text{Ch})$  adsorbed on MWCNTs acts as an efficient catalyst for photocatalytic  $\text{CO}_2$  reduction to CO as well as  $\text{H}_2$  evolution from TEA in MeCN containing 5% (v/v) water. The present study paves a new way to produce synthetic gas from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  using an earth-abundant metal complex catalyst for  $\text{CO}_2$  reduction under visible light irradiation.

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- 24 S. Aoi, K. Mase, K. Ohkubo and S. Fukuzumi, *Chem. Commun.*, 2015, **51**, 15145.
- 25 The TON for CO formation was improved by the adsorption of the cobalt chlorin complex on MWCNTs, because two  $[\text{Co}^{\text{I}}(\text{Ch})]^-$  molecules are located close to each other where the two-electron reduction of  $\text{CO}_2$  to CO may occur. The optimized amount of MWCNTs was 1.0 mg under the present experimental conditions, because the amounts of CO and  $\text{H}_2$  produced in the present photocatalytic system became smaller when 0.5 mg and 1.5 mg of MWCNTs were employed instead of 1.0 mg of MWCNTs.
- 26 No  $\text{Co}(0)$  species was produced because a  $\text{Co}(\text{i})/\text{Co}(0)$  couple was not observed in CV measurements. Thus, the catalytically active species for proton reduction maybe  $\text{Co}(\text{iii})-\text{H}$ .<sup>24</sup>
- 27 An X-ray absorption near-edge spectroscopy (XANES) study of the  $\text{Co}(\text{iii})-\text{CO}_2$  adducts clearly indicated a significant charge-transfer from  $\text{Co}(\text{i})$  to the bound  $\text{CO}_2$  (see: E. Fujita, L. R. Furenlid and M. W. Renner, *J. Am. Chem. Soc.*, 1997, **119**, 4549).
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