# Functional Polypyridine Co Complex as an Efficient Catalyst for Photo-Induced Water Oxidation

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A novel mononuclear cobalt complex 1 was synthesized by treatment of  $CoCl_2 \cdot 6H_2O$  with a COOMe functionalized TPA ligand (TPA=tris(2-pyridylmethyl)amine). In a basic borate buffer, 1 acts as an efficient catalyst for water oxidation, which is confirmed by an extinct catalytic oxidant wave in electrochemistry. Visible light-driven water oxidation has been achieved by 1 with a TON of 127.7 and a TOF of 3.8 s<sup>-1</sup> respectively in a homogeneous system. In comparison to the reference **RC** with naked TPA, the higher efficiency of 1 evidences COOMe on ligand can improve the catalytic efficiency, leading to an effective pathway towards construction of a robust and stable artificial photosynthesis system.

Keywords cobalt complex, photo-induced, ligand-design, water oxidation

## Introduction

Artificial photosynthesis is considered as the potentially most controlled technology for the solar-tochemical energy conversion.<sup>[1,2]</sup> Frontline research in natural photosynthesis has served as inspiration and guidelines for the study in artificial photosynthesis for many years. In a global perspective, efforts have been made towards achieving stable and robust catalysts based on cheaper and earth-abundant element due to economical viability.<sup>[3]</sup> Recently, molecular design contributes to highly stable and efficient molecular catalysts since their redox and kinetic properties are, in principle, easily tunable by molecular modification.<sup>[4]</sup> The already demonstrated oxygen evolving activity can be further developed by using fundamental coordination chemistry to design a broader set of efficient catalysts. Cobalt becomes promising and strong candidate on account of high efficiency, low light competition with chromophore. In particular, paramagnetic cobalt species with typical EPR pronunciation fascinates an intensive investigation into intermediates generation, which further allows better exploration and understanding the O-O bond formation during water oxidation.<sup>[5]</sup>

Up to now, a few molecular cobalt complexes have been reported to promote visible light-driven water oxidation in homogeneous systems.<sup>[6]</sup> Some multi-coordinating ligands containing *N*-heterocycles are available to produce novel catalysts. In 2013, polar porphyrin ligands were developed to coordinate with cobalt salts to afford cobalt catalysts, which fascinated the active center to be attacked by water molecule during catalysis under a light-driven system.<sup>[6d]</sup> In 2015, a molecular cobalt(II) catalyst with a 2,6-bis(methoxydi(pyridine-2-yl)methyl)pyridine) was reported to enable water oxidation catalysis by means of visible light irradiation.<sup>[6e]</sup> Then, di(pyridin-2-yl)methanediol was developed to coordinate with cobalt salts to afford cobalt catalysts. which achieved the largest TON among metal-organic complexes for photocatalytic water oxidation up to now.<sup>[6f]</sup> Overall, ligand design and catalyst optimization are instrumental for stabilizing the catalytic system and sustained O<sub>2</sub> productivity. In 2014, we presented a mononuclear Co complex RC and dinuclear cobalt complex with the soft TPA ligand [TPA=tris(2-pyridylmethyl)amine], both serve as molecular catalysts to promote photo-induced water oxidation.<sup>[6g,6h]</sup> Since TPA provides a scaffold to introduce functional groups, tailoring of the catalytic activity is hopefully achieved by appropriate modification of the substituent. It is essential to find a robust ligand system that can hold the metal centre firmly and does not undergo self-oxidation in the oxidizing environment. Here we report a novel monometallic cobalt catalyst 1 [dichloride tris(2-pyridylmethyl)amine cobalt (II)] with electron-withdrawing COOMe functionalized TPA ligand for efficient light-

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Scheme 1 Synthesis of 1 and the structure of RC



driven water oxidation.

## Experimental

## General

The UV-Vis absorption spectra were measured on a U-3900H spectrophotometer. The emission spectra were measured on a F-7000 emission spectrometer from HITACHI. HPLC-MS data were obtained using an ekspert ultraLC 100-XL. Solvents used for HPLC: 0.05% formic acid in H<sub>2</sub>O and 0.05% formic acid in CH<sub>3</sub>OH. <sup>1</sup>H NMR spectra were recorded on a Bruker-400 MHz spectrometer at 293 K. Chemical shifts are referenced internally to the residual solvent signal.

### Materials

All reactions and operations were carried out under a dry argon atmosphere with standard Schlenk technique. All solvents were dried and distilled prior to use. Dimethyl pyridine-2,6-dicarboxylate, NaBH<sub>4</sub>, and CoCl<sub>2</sub>• 6H<sub>2</sub>O were purchased from HEOWNS and used as received.

### Synthesis

**Methyl 6-(hydroxymethyl) picolinate** NaBH<sub>4</sub> (104.4 mg, 2.76 mmol) was slowly added to a solution of dimethyl pyridine-2,6-dicarboxylate (500 mg, 2.56 mmol) in a 20 mL dry 7 : 3 (V: V) mixture of MeOH/ CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. The reaction mixture was stirred for 6 h at room temperature and then neutralized with an aqueous saturated NH<sub>4</sub>Cl solution. After extraction with CH<sub>2</sub>Cl<sub>2</sub> (2 mL×3), the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The resulting crude residue was purified by column chromatography (petroleum ether/ethyl acetate=1 : 6) giving the product (243.5 mg, 57.4%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.06 (br s, 1H; OH), 4.02 (s, 3H; OCH<sub>3</sub>), 4.89 (s, 2H; CH<sub>2</sub>O), 7.56

(d, J=8 Hz, 1H), 7.87 (t, J=8 Hz, 1H), 8.05 (d, J=8 Hz, 1H).

**Methyl 6-(bromomethyl) picolinate** PBr<sub>3</sub> (0.1 mL, 1.04 mmol) was added to methyl 6-(hydroxymethyl) picolinate (40 mg, 0.24 mmol) in 30 mL anhydrous CHCl<sub>3</sub> at 0 °C. The reaction mixture was stirred for 4 h at room temperature and then neutralized at 0 °C with an aqueous saturated K<sub>2</sub>CO<sub>3</sub> solution. After extraction with CH<sub>2</sub>Cl<sub>2</sub> (2 mL×3), the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure, leading to pure compound as a pale yellow solid (55.2 mg, 100%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.03 (s, 3H), 4.73 (s, 2H), 7.75 (d, *J*=8 Hz, 1H), 7.95 (t, *J*=8 Hz, 1H), 8.11 (d, *J*=8 Hz, 1H).

Tris[6-(methoxycarbonyl)-2-pyridylmethyl]amine (TPA<sup>COOMe</sup>) In a thick-walled Schlenk tube, 20 mL acetonitrile was added to methyl 6-(bromomethyl)picolinate (41.9 mg, 0.18 mmol) and ammonium carbonate (85.94 mg, 0.89 mmol). Then the tube was sealed with a Teflon stopper. The mixture was heated to 75 °C with vigorous stirring for 18 h. The mixture was allowed to cool to room temperature and carefully vented in a fume hood to release ammonia pressure. The solids were filtered, and washed with copious amounts of CH<sub>2</sub>Cl<sub>2</sub>. The combined filtrates were concentrated to the crude product as yellow oil, which was further purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH/ Et<sub>3</sub>N (V: V: V=10:1:0.2) as eluent. Evaporation of the solvent yielded 23 mg (34.4%) light yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.01 (t, J=6 Hz, 3H), 7.8 (m, 5H), 7.65 (d, J=8 Hz, 1H), 4.09 (s, 2H), 4.03 (s, 2H), 4.00 (s, 9H) (Figure S1). Elemental analysis of TPA<sup>COOMe</sup> calcd (%) for  $C_{24}H_{24}N_4O_6$  (464.4706): C 62.06, H 5.21, N 12.06; found C 61.91, H 5.12, N 11.94.

**Mononuclear cobalt complex 1** An oven-dried Schlenk flask equipped with a magnetic stir bar was evacuated and filled with nitrogen. In this flask  $CoCl_2 \cdot 6H_2O$  (16 mg, 0.06 mmol) was dissolved in  $CH_3CN$  (2 mL), degassed with Ar, and heated to reflux. To the above refluxing mixture, TPA<sup>COOMe</sup> (23 mg, 0.01 mmol) in 2 mL CH<sub>3</sub>CN was added dropwise to afford a green solution, which was kept refluxing overnight. When the solution was cooled down, the solvent was removed and ether was used to recrystallize product three times to give 18 mg **1** as green solids (50.7%). ESI-MS (*m*/*z*): 568.0985,  $[M-2Cl+HCOO]^+$  (calcd 568.4212); 261.5501,  $[M-2Cl]^{2+}/2$  (calcd 261.7019). Elemental analysis of cobalt complex **1** calcd (%) for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>O<sub>6</sub>Cl<sub>2</sub>Co•12H<sub>2</sub>O (810.3098): C 35.54, H 5.92, N 6.91; found C 35.19, H 6.01, N 7.16.

#### Electrochemistry

Electrochemical measurements were performed using a CHI660E B14514a. A three-electrode system with a 0.07 cm<sup>2</sup> glass carbon working electrode, platinum wire as auxiliary, and an Ag/AgCl (with saturated KCl aqueous solution) as reference electrode, was used to measure the cyclic voltammograms in borate buffer. The working electrode was polished with a 0.05  $\mu$ m alumina paste and sonicated for 15 min before use. The sample solution (10 mL) with 100 mmol•L<sup>-1</sup> borate buffer as supporting electrolyte was degassed with argon for 30 min before the measurement started. All cyclic voltammograms shown were recorded at a scan rate of 100 mV•s<sup>-1</sup>.

#### **Oxygen evolution measurements**

The oxygen evolution was measured using a standard Clark-type oxygraph electrode (Hansatech Instruments). The cell was thermostated at 25 °C for all experiments. The signal was recorded for the entire duration of the experiment at 0.1 s intervals using the Oxygraph+ software (Hansatech Instruments). The signal was calibrated using air saturated aqueous solutions  $([O_2]=276 \ \mu mol \cdot L^{-1}, T=25 \ ^{\circ}C)$ . For the oxygen evolution experiments, the each component was mixed in pH 8 borate buffer in the dark, flushed with argon to remove dissolved oxygen and then irradiated with visible light [LEDs,  $\lambda = (470 \pm 10) \ nm$ , 820  $\mu E/(m^2 \cdot s)$ ]. The maximum turnover frequency (TOF) was determined at the steepest slope of the oxygen evolution curve.

## **Results and Discussion**

As shown in Scheme 1, the synthesis of tri- $\alpha$ -COOMe substituted TPA ligand (TPA<sup>COOMe</sup>) was started with the preparation of methyl 6-(hydroxymethyl)picolinate through reduction of dimethyl pyridine-2,6-dicarboxylate in the mixture of dried MeOH and CH<sub>2</sub>Cl<sub>2</sub> with the addition of NaBH<sub>4</sub>.<sup>[7]</sup> Subsequently, methyl 6-(hydroxymethyl) picolinate was bromized by PBr<sub>3</sub> in CHCl<sub>3</sub> and resulted in the smooth conversion to the methyl 6-(bromomethyl)picolinate.<sup>[7]</sup> Then, the direct condensation of 6-(bromomethyl)picolinate with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN led to TPA<sup>COOMe</sup> as light yellow oil in a yield of 34.4%.<sup>[8]</sup> The mononuclear cobalt complex **1** was obtained as green solid by treatment of  $CoCl_2$ •6H<sub>2</sub>O with TPA<sup>COOMe</sup> in refluxed CH<sub>3</sub>CN overnight with a yield of 50.7%.

It is considered that UV-Vis spectroscopy can be employed to investigate the structure of the molecule catalyst. Particularly, upon dissolving the compound into CH<sub>3</sub>CN, the Cl<sup>-</sup> ligand can be replaced by the solvent CH<sub>3</sub>CN molecule resulting into a mono-acetronitrile species [(L)M(CH<sub>3</sub>CN)]<sup>2+</sup>, which is characterised by a long wavelength absorption band pattern between 600 and 700 nm in the UV-Vis spectra.<sup>[9]</sup> Like its parent compound RC, at room condition, the CH<sub>3</sub>CN solution of 1 exhibits two absorption bands centered at 590 and 680 nm respectively, accompanied by intense absorption before 300 nm from lignad  $\pi \rightarrow \pi^*$  transition, implying the mono-substituted Co center with Cl<sup>-</sup> ligand (Figure S2). Differently, in the aqueous solution, the electronic absorbance spectrum of 1 affords one intense ligand  $\pi \rightarrow \pi^*$  peak around 275 nm with a weak shoulder within visible-light absorption centered around 500 nm assigned to the  $\text{Co}^{2+}$  d-d transition, indicating the for-mation of  $[\text{Co}(\text{TPA}^{\text{COOMe}})(\text{H}_2\text{O})_2]$  in an octahedral complex.<sup>[10]</sup> The concentration dependence of absorbance satisfies Beer's law, which implies that 1 remains as a monomer under the condition (Figure S3). Monitoring the spectrum for 11 h with  $1 \times 10^{-4}$  mol·L<sup>-1</sup> 1 (Figure 1), almost identical line on each measurement confirms monomer as the single species to sustain in the presence of water.



**Figure 1** UV-Vis spectrum of  $1 \times 10^{-4}$  mol·L<sup>-1</sup> **1** in 75 mmol·L<sup>-1</sup> pH 8.4 borate buffer for 0–11 h. The inset is the enlarged absorption spectra of **1** ranging from 350–700 nm at 0 h.

The catalytic ability of **1** for water oxidation was firstly examined with electrochemistry in 0.1 mol·L<sup>-1</sup> borate buffer at pH 8.4. One irreversible oxidative wave was observed, followed by the appearance of catalytic current for water oxidation (Figure S4).<sup>[6d,6g]</sup> The onset potential is located at 1.10 V with an overpotential of 330 mV. This value is comparable to those recently reported for mononuclear molecular cobalt catalysts (300 -600 mV).<sup>[3c,6f,6c]</sup> Since the electrochemistry indicated that the appearance of **1** could promote water oxidation,

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a water oxidation in a light-driven system was considered to explore its catalytic behavior assisted by photosensitizer  $[Ru(bpy)_3]^{2+}$  and sacrificial electron acceptor. As shown in Figure S4,  $[Ru(bpy)_3]^{3+}$  exhibits oxidation potential at 1.41 V, more positive than the onset potential for water oxidation at 1.1 V in the presence of  $\mathbf{1}$ .<sup>[3i]</sup> Therefore, a system where  $[Ru(bpy)_3]^{3+}$  is formed through an electron transfer from a photo-excited  $[Ru(bpy)_3]^{2+}$  to an electron acceptor can be used in combination with **1** to give a thermodynamically favorable driving force for water oxidation. In comparison, the onset overpotential of **RC** is 490 mV (versus NHE), it is clear that in the combination of **1** and  $[Ru(bpy)_3]^{2+}$ , the driving force for water oxidation is much higher.

Visible-light induced water oxidation catalyzed by compound 1 was initiated in a borate buffer with [Ru(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as photosensitizer and electron acceptor, respectively, and evolution-oxygen measurement was monitored by a Clark electrode. It is found that the pH of the reaction mixture strongly influences the process. A pH of 8.4 was found optimal (see Table S1) as a lower pH renders photocatalysis much less efficient, while higher pH gives rise to increased initial oxygen evolution rates, but also fasters deactivation with overall lower TONs. Besides, it is noteworthy that the efficiency of oxygen evolution strongly depends on the concentration of buffer. Both the rate and yield of oxygen formed were enhanced when the concentration of buffer was increased by 75 mmol·L<sup>-1</sup>, implying O<sub>2</sub> formation proceeded a proton transfer with buffer base serving as the proton acceptor.<sup>[11]</sup> Besides, the ionic strength resuling from concentrated buffer could also influence the electron transfer rate.<sup>[11]</sup> Successive increase in buffer concentration led to a deactivation of the whole system, possibly due to the low solubility of the sensitizer, in accordance with the observation of red precipitate in the system.

Table 1  $O_2$  evolution, TON and TOF for different concentrations of 1

		$c(1)/(\mu \text{mol} \cdot L^{-1})$					
	0	1.25	2.50	3.75	5.00	7.50	
n(O <sub>2</sub> )/µmol	44.7	204.3	337.5	473.3	598.2	677.8	
TON	—	127.7	117.1	114.3	110.7	84.4	
$TOF/s^{-1}$	—	3.8	1.8	1.3	1.1	0.9	

Figure 2 and Table 1 shows the effect of varying the concentration of **1** in 75 mmol·L<sup>-1</sup> borate buffer at the optimal pH. The control experiment with a combination of  $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$  and  $\text{Na}_2\text{S}_2\text{O}_8$  in the absence of any **1** produces only a small amount of O<sub>2</sub>, and it is clear that **1** is required for efficient water oxidation (Figure 2). The maximum turnover frequency (TOF) and the turnover number (TON) for water oxidation depend on the catalyst concentration. At the lowest catalyst concentration, TOF of 3.8 s<sup>-1</sup> and TON of 127.7 respectively were given by **1**. Interestingly, varying the concentration of **1** 

up to 7.50  $\mu$ mol·L<sup>-1</sup> does not alter the initial rate of O<sub>2</sub> formation before the first 15 s, indicating that the rate is not dependent on the catalyst concentration under the conditions (Figure S5).<sup>[6f,12]</sup> In comparison with naked TPA chelated monomer compound **RC**, under the same controlled conditions with 5.00  $\mu$ mol·L<sup>-1</sup> catalyst, TON of 12.6 and TOF of 0.3 were obtained (Figure S6). Clearly, the COOMe groups on ligand can significantly enhance the catalytic ability, which is in consistence with the electrochemical analysis.



**Figure 2** Light-induced water oxidation in a mixture containing  $[\text{Ru}(\text{bpy})_3](\text{CIO}_4)_2 \ (0.4 \text{ mmol}\cdot\text{L}^{-1})$  and  $\text{Na}_2\text{S}_2\text{O}_8 \ (5 \text{ mmol}\cdot\text{L}^{-1})$  with **1** (0, 1.25, 2.50, 3.75, 5.00 and 7.50 µmol}\cdot\text{L}^{-1}) in borate buffer (75 mmol}\cdot\text{L}^{-1}, pH 8.4). The Clark cell was kept constant at 20 °C, and the system was irradiated using LEDs [ $\lambda$ =(470±10) nm, 820 µE/(m<sup>2</sup>\cdot\text{s})]. The arrow indicates the start of the irradiation.

Some reports showed that molecular cobalt systems serve as mere pre-catalysts yielding heterogeneous cobalt oxide active for water oxidation.<sup>[13]</sup> Therefore, care should be paid to ascertain whether such heterogeneous species are formed during the catalysis. Several evidences were collected to prove the stability of 1. As shown in Figure 1, there were no apparent changes in the UV-Vis spectrum even after 11 h. In contrast, the UV-Vis spectrum of the solution containing free  $Co^{2+}$  is totally different from its initial profile after 2 h.<sup>[13]</sup> Besides, in a sample that has been illuminated for  $\sim 200$  s, there is no evidence of any light scattering that would arise from particle formation, suggesting a homogeneous system remained during the illumination. In contrast, under the same condition, although  $Co(ClO_4)_2$  displayed much higher activity, white and floccus precipitate deposited from the solution, implying the creation of heterogeneity. This point is consistent with the analysis obtained from DLS (Figure S7),<sup>[6a,6b,6h]</sup> and further supported by Tyndall scattering analysis (Figure S8). Another evidence is related to an attempted recycling experiment where fresh  $[Ru(bpy)_3]^{2+}$  and  $Na_2S_2O_8$  were added to the illumination experiment when oxygen

evolution had ceased (after ~200 s). Unlike that in the presence of  $Co(ClO_4)_2$ , where the O<sub>2</sub> evolution was reinitiated, only an activity close to the background one was found in the case of 1, indicating the intact of 1 is required for  $O_2$  evolution (Figure S9).<sup>[6h]</sup> Attempt to separate the residues after O<sub>2</sub> evolution ceased for MS analysis was unsuccessful because there were not any precipitates obtained even if the pH of the mixture had been adjusted from 1-14. All together, the lack of particles formation implies 1 performs as a real catalyst for water oxidation. Usually, it is considered that the ligand plays a crucial role in determining the nature of the catalytic system. Electron-withdrawing COOMe on TPA is assumed to successfully resist self-oxidation, but also inhibits the dimerization of two cobalt centers in aqueous solution, leading to the enhanced stability of 1 for water oxidation.[6h]



**Figure 3** Light-induced water oxidation in a mixture containing  $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2 (0.4 \text{ mmol} \cdot \text{L}^{-1}), [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 (4 \text{ mmol} \cdot \text{L}^{-1})$  and **1** (30 µmol \cdot \text{L}^{-1}) in phosphate buffer (100 mmol \cdot \text{L}^{-1}, pH 7). The Clark cell was kept constant at 20 °C, and the system was irradiated using LEDs [ $\lambda$ =(470±10) nm, 820 µE/m<sup>2</sup> ·s]. The arrow indicates the start of the irradiation.

Unlike Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, where the generated strong oxidants  $SO_4^{-\square}$  is suspected of oxidizing water, [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> is regarded as a useful electron acceptor employed in the photo-induced water oxidation to suppress confusion resulting from Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.<sup>[14]</sup> Accordingly, the photo-induced water oxidation of 1 was carried out assisted by [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> as an electron acceptor and [Ru(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> as a photosensitizer in a neutral phosphate buffer. Typically, 46  $\mu$ mol·L<sup>-1</sup> O<sub>2</sub> were generated in the presence of 30  $\mu$ mol·L<sup>-1</sup> 1 (Figure 3). To prove that the oxygen evolution was indeed promoted by 1, several control experiments were conducted: (1) removing any one of the three components:  $[Ru(bpy)_3](ClO_4)_2$ ,  $[Co(NH_3)_5Cl]Cl_2$  and 1, no oxygen was generated in the presence of light, confirming that 1 is indeed involved in the catalytic processes; (2) although the cobalt ion was reported to serve as a moderate catalyst for water oxidation and the [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>

in the system can be reduced to form  $Co^{2+}$  when it acts like an electron acceptor, no obvious promotion of oxygen evolution was observed in the triad system, indicating under limited conditions, the O<sub>2</sub> evolution catalyzed by 1 is dominant; (3) a light control experiment shows that the catalytic water oxidation in the system is driven by light. Evidently, water oxidation in the system is initiated by 1, which serves as the dominant catalyst as well. However, in comparison, the initial rate and turnover numbers for oxygen evolution when [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> was chosen as an acceptor are significantly lower than that with Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, which might result from the fact that  $[Co(NH_3)_5Cl]Cl_2$  is usually active as an electron acceptor in acidic or neutral conditions.<sup>[14]</sup>

To acquire more insights into the photo-induced water oxidation, a steady-state emission spectroscopy was employed to shed light on electron transfer events between all the components. It has been found that the [Ru(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> in borate buffer solution is quenched by Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> with a rate constant  $k_q$  of 9.8×10<sup>9</sup> mol<sup>-1</sup>• L•s<sup>-1</sup>.<sup>[3i]</sup> However, a much smaller quenching rate con-stant ( $k_q$ ) of 3.5×10<sup>8</sup> mol<sup>-1</sup>•s<sup>-1</sup> is shown in the presence of compound 1 and  $[Ru(bpy)_3](ClO_4)_2$  (Figure S10). Therefore, it is concluded that the photocatalytic process is initiated by the reaction between  $[Ru(bpy)_3]^{2+}$  and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Then the generated Ru(III) species can oxidize 1 to produce highly active cobalt intermediate for the subsequent water oxidation. Research on the nature of the intermediate is on-going. This proposal was further evidenced by the water oxidation in a mixture of 1 and [Ru(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>. Although the self-degradation of Ru(III) led to water oxidation unavoidably, it is clear that 44  $\mu$ mol·L<sup>-1</sup> O<sub>2</sub> was caused by the Co catalyst in comparison to the background (Figure S11).

### Conclusions

In summary, a water-soluble cobalt complex was synthesized and displayed water oxidation activity as a molecular catalyst under a photo-irradiation condition. It is found that the modification of ligand scaffold with electron-withdrawing COOMe group fascinates to increase catalytic response. Although it is unclear whether the enhancement in catalytic efficiency results from the steric substitution on ligand or the electron-withdrawing effect, this study provides promising results for future designing robust and stable catalyst, to be readily incorporated into an efficient artificial photosynthesis system. Research on the nature of intermediate and mechanism is on-going.

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