

## Supplementary Information

### **High quantum yield photochemical water oxidation using a water-soluble cobalt phthalocyanine as a homogenous catalyst**

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## Materials

All solvents and reagents were of the highest quality available and were used as received. CoPcTS was synthesized according to literature.<sup>1</sup> It characterized by the elemental analysis and <sup>1</sup>H NMR, ESI-MS and elemental analysis. [Ru(bpy)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was prepared using literature method.<sup>2</sup>

## Photochemical Water Oxidation

Photolysis solutions (5.0 mL) contained in a gastight Pyrex vial (26.8 mL) were degassed with Ar for at least 30 min prior to photolysis. Photoirradiation was performed using an ILC Technology CERMAX LX-300 300 W Xe lamp equipped with a CM-1 cold mirror, sharp cut filter Y44 (HOYA) and blue filter B390 (HOYA). The photolysis vial is immersed in a 293 K water bath to remove IR radiation and to eliminate temperature effects. Oxygen concentration of the gas phase in reaction vial during photochemical reaction was monitored by FireSting Oxygen monitor (PyroScience GmbH). After oxygen evolution stopped, gas chromatography (Shimadzu Gas Chromatograph GC-2014 with Molecular Sieve 5A packed column) was performed to confirm that there was no inclusion of air. After then, Ar gas was passed through the reaction solution for 30 min to exclude oxygen evolved by photochemical reaction. Subsequently, 0.10 mL of oxygen gas was added to the reaction vial by gastight syringe and the oxygen concentration of the gas phase was measured by FireSting Oxygen monitor. By repeating adding oxygen gas and measuring oxygen concentration for five times, the standard curve (O<sub>2</sub> concentration [%] vs. volume of O<sub>2</sub> [μL]) was prepared. The prepared standard curve was used for evaluating volume of evolved oxygen.

## Procedure for Electrochemical Measurements

All electrochemical measurements were recorded on EC stat 301 (EC Frontier Ltd.). Electrochemical measurements in an aqueous solution were performed using a three electrodes system consisting of a FTO glass working electrode, a platinum wire counter electrode, and a SCE reference electrode. Electrochemical measurements in a *N,N*-dimethylformamide (DMF) solution were performed using a three electrodes system consisting of a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag(NO<sub>3</sub>) reference electrode. TBAP (tetra(*n*-butyl)ammonium perchlorate) was used as a supporting electrolyte of a DMF solution

## Procedure for Dynamic Light Scattering Analysis

Dynamic light scattering (DLS) experiments were carried out using an ELSZ-2000ZS (Otsuka Electronics Co. Ltd. Japan). A He laser operating at 660 nm was used. The DLS measurements were carried out for a 0.1 M borate buffer solution at pH = 9 containing 10 μM catalyst, 0.3 mM [Ru(bpy)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, and 10 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

## Procedure for UV–Vis Measurements

The UV–Vis absorption spectra were recorded using a Shimadzu UV1800 spectrophotometer. All the sample solutions were maintained at 293 K during the spectrophotometric measurements. Time cause UV-Vis spectra were recorded using a BAS ALS SEC 2020 spectrometer.

## Procedure for Determining the Quantum Yield of Photo Chemical Water Oxidation

Photolysis solution (2.5 mL) was placed in a long neck quartz cell and was degassed with Ar for at least 30 min prior to photolysis. Photoirradiation was performed using a 450 nm laser (Kikoh Giken Co., LTD). The

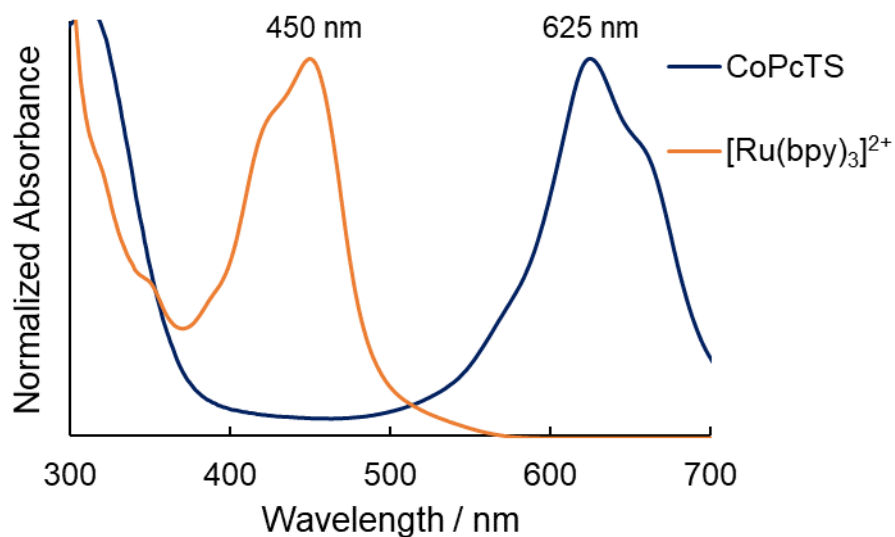
photon flux was monitored using a power meter (Newport Corporation, 919P-003-10), while the oxygen gas was monitored using a FireSting Oxygen monitor (PyroScience GmbH).

#### Procedure for Thermal Water oxidation

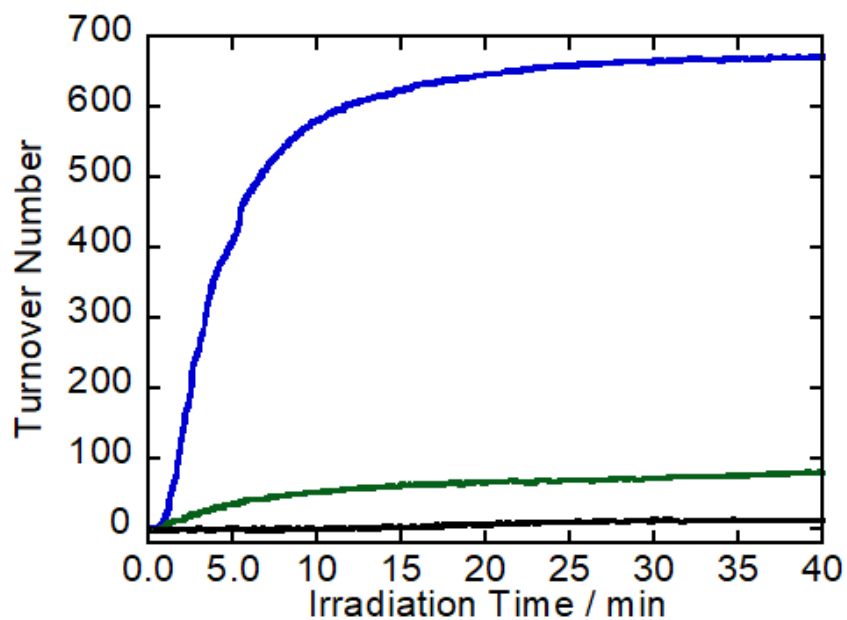
The  $2.5 \times 10^{-2}$   $\mu\text{mol}$  solution of CoPcTS containing a pH=9 0.10 M borate buffer (4.7 mL) was degassed with Ar. 0.30 mL of  $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$  (3.50  $\mu\text{mol}$ , 140 eq.) containing 0.05 M  $\text{H}_2\text{SO}_4$  solution, which was also degassed with Ar, was added to CoPcTS containing solution using a gas-tight syringe. The evolved oxygen gas was monitored using a FireSting Oxygen monitor (PyroScience GmbH).

#### Procedure for Stopped-flow experiment

A borate buffer solution (0.1 M, pH9) containing CoPcTS (20  $\mu\text{M}$ ) was mixed with a borate buffer solution (0.1 M, pH9) solution of  $\text{Na}_2\text{S}_2\text{O}_8$  (10 mM) at 298 K. The absorption spectral change of the solution was monitored using an RSP-1000 rapid scan-stopped-flow spectrometer (UNISOKU Co., Ltd).



**Figure S1.** Normalized UV-Vis spectra of  $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$  and CoPcTS.

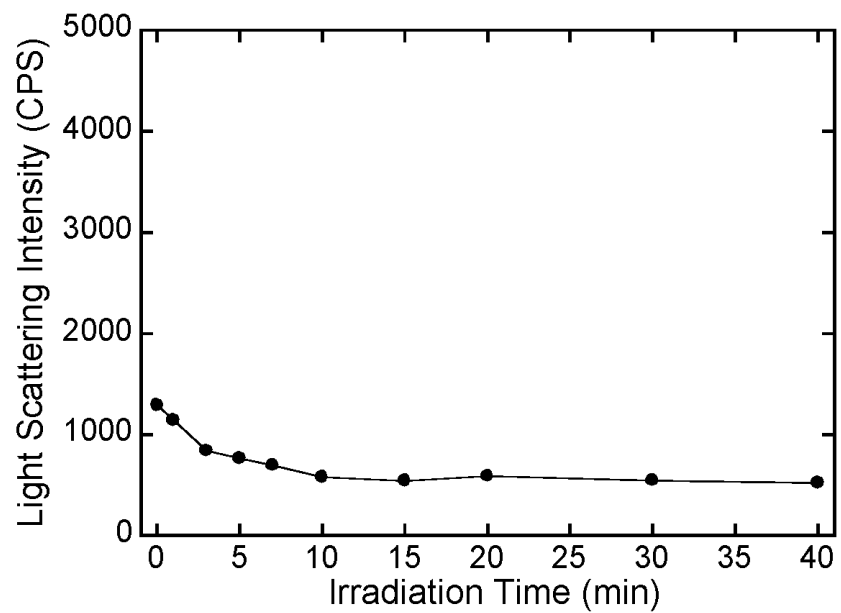


**Figure S2.** Photochemical oxygen evolution by photoirradiation (300 W Xe; 430-510 nm) of aqueous buffer solution (pH9.0) containing 3.0  $\mu\text{M}$  catalyst, 0.2 mM  $[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2$ , and 10.0 mM  $\text{Na}_2\text{S}_2\text{O}_8$  under Ar at 293 K. Catalyst: CoPcTS (blue line),  $\text{CoSO}_4$  (green line), no catalyst (black line). In the case without catalyst, TON was calculated assuming that 3.0  $\mu\text{M}$  catalyst was used.

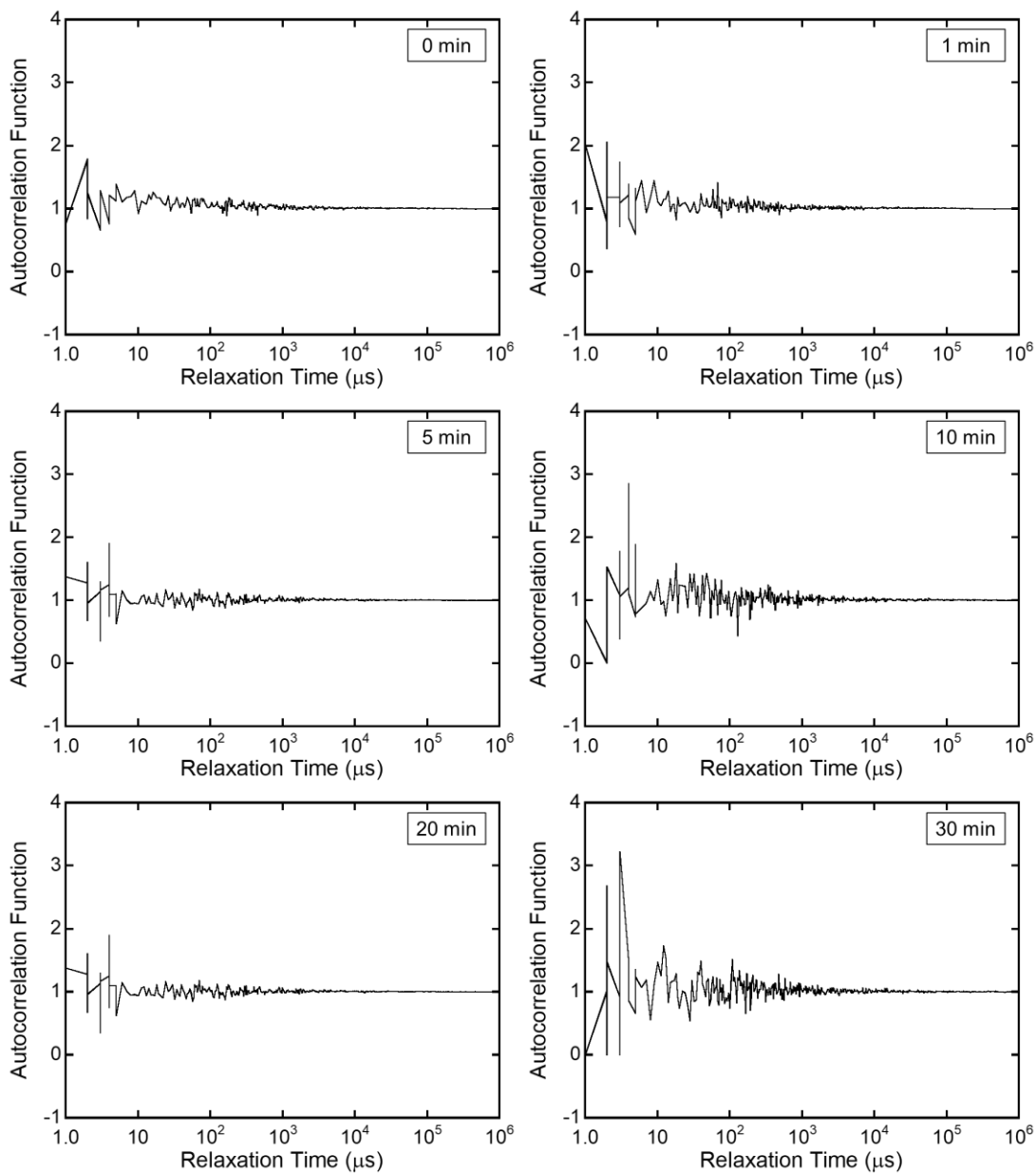
**Table S1** Summary of water oxidation catalysis of representative first-row transition-metal complexes having porphyrin or its analogue evaluated by the  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$  photosystem (PS = photosensitizer, SO = sacrificial oxidant, BB = borate buffer, PB = phosphate buffer).

Catalyst	TON	TOF ( $\text{s}^{-1}$ )	$\Phi$ (%)	PS/SO	Solvent	Light Source	Ref
CoPcTS	670	2.7	0.44 <sup>a,c</sup>	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	BB (0.1 M, pH 9.0)	300 W Xe (430-510 nm)	This work
Co <sub>2</sub> DNCH	1200	3.9	0.30 <sup>a,c</sup>	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	BB (0.1 M, pH 8.5)/acetone- <i>d</i> <sub>6</sub> (9/1)	300 W Xe (430-510 nm)	4
CoPF <sub>5</sub>	164	0.53	-	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	BB (0.1 M, pH 8.5)/acetone- <i>d</i> <sub>6</sub> (9/1)	300 W Xe (430-510 nm)	4
CoTMPyP	88.7	0.118	-	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	PB (0.1 M, pH 11)	300 W Xe (400-800 nm)	5
CoTCPP	103.4	0.138	-	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	PB (0.1 M, pH 11)	300 W Xe (400-800 nm)	5
CoTPPS	301	0.62	-	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	BB (0.1 M, pH 9.0)	300 W Xe (430-510 nm)	6
CoFPS	571	1.1	-	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	BB (0.1 M, pH 9.0)	300 W Xe (430-510 nm)	6
CoCIPS	836	1.7	0.27 <sup>a,c</sup>	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	BB (0.1 M, pH 9.0)	300 W Xe (430-510 nm)	6
CuPcTS	26	0.063	-	$[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2/\text{Na}_2\text{S}_2\text{O}_8$	BB (0.1 M, pH 9.5)	300 W Xe (400-800 nm)	7
NiTMPyP	36.5	0.01	0.15 <sup>e</sup> (0.29 <sup>b,d</sup> )	$[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2/\text{Na}_2\text{S}_2\text{O}_8$	PB (0.1 M, pH 7.0)	15.8 mW LED (450 nm)	8

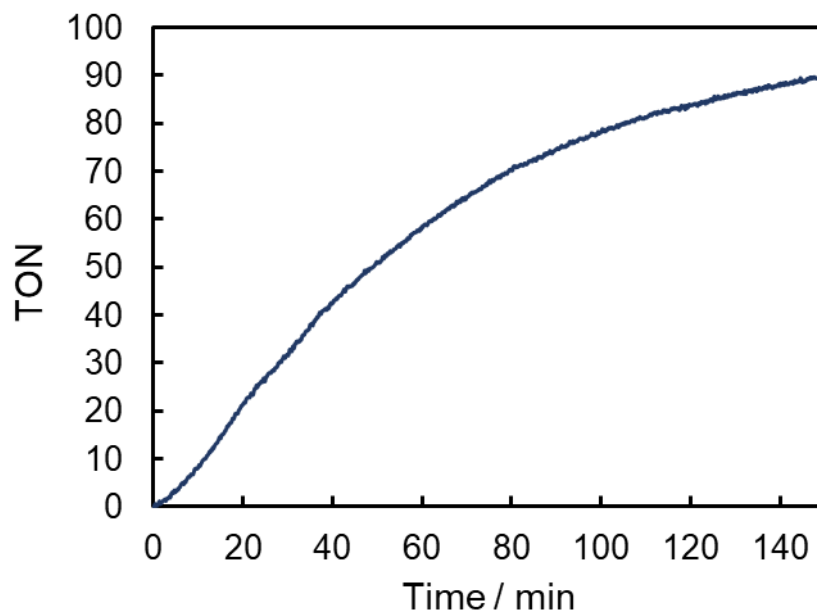
*a*: Quantum yields  $\Phi$  was determined using 0.12 mW LED (450 nm). *b*:  $\Phi$  was determined using 15.8 mW LED (450 nm). *c*:  $\Phi$  was calculated based on the molecular number of oxygen evolved during 20 min photoirradiation and defined by the equation  $\Phi = N_{\text{O}_2}/N_{\text{photon}}$ . The theoretical maximum  $\Phi$  is, therefore, 0.50. *d*: In ref.8,  $\Phi$  was calculated based on the maximum value of TOF and defined by the number of oxygen molecules evolved by two photons absorption. The theoretical maximum  $\Phi$  is, therefore, 1.00. *e*:  $\Phi$  was converted to the definition that  $\Phi = N_{\text{O}_2}/N_{\text{photon}}$ . DNCH: doubly N-confused hexaphyrin (1.1.1.1.1.1), PF<sub>5</sub>: 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, TMPyP: 5,10,15,20-tetrakis(4-N-methylpyridyl)porphyrinato, TCPP: 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, TPPS: 5,10,15,20-tetrakis(4-sulfophenyl)porphyrin, FPS: 5,10,15,20-tetrakis(2,6-difluoro-4-sulfophenyl)porphyrin, CIPS: 5,10,15,20-tetrakis(2,6-dichloro-4-sulfophenyl)porphyrin.



**Figure S3.** Light scattering intensity as a function of time during photo-irradiation in 0.10 M pH 9 borate buffer containing CoPcTS (10  $\mu$ M),  $\text{Na}_2\text{S}_2\text{O}_8$  (10.0 mM) and  $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$  (0.3 mM) under Ar.

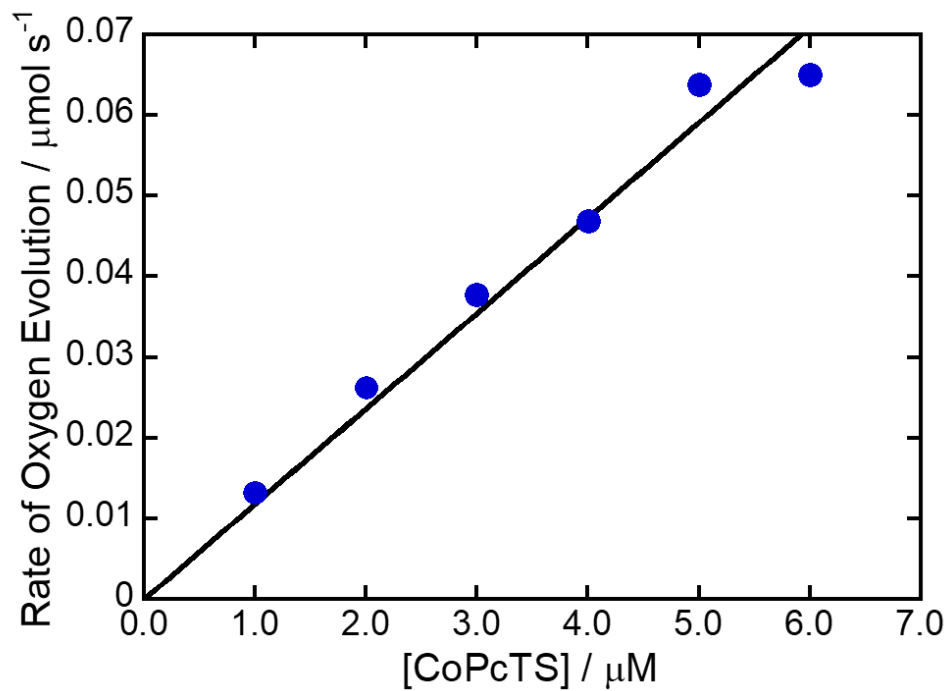


**Figure S4.** Autocorrelation function obtained by DLS measurements of CoPcTS (10  $\mu$ M) in a 0.10 M pH 9 borate buffer containing  $\text{Na}_2\text{S}_2\text{O}_8$  (10.0 mM) and  $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$  (0.3 mM). (Light source: 400-800 nm).

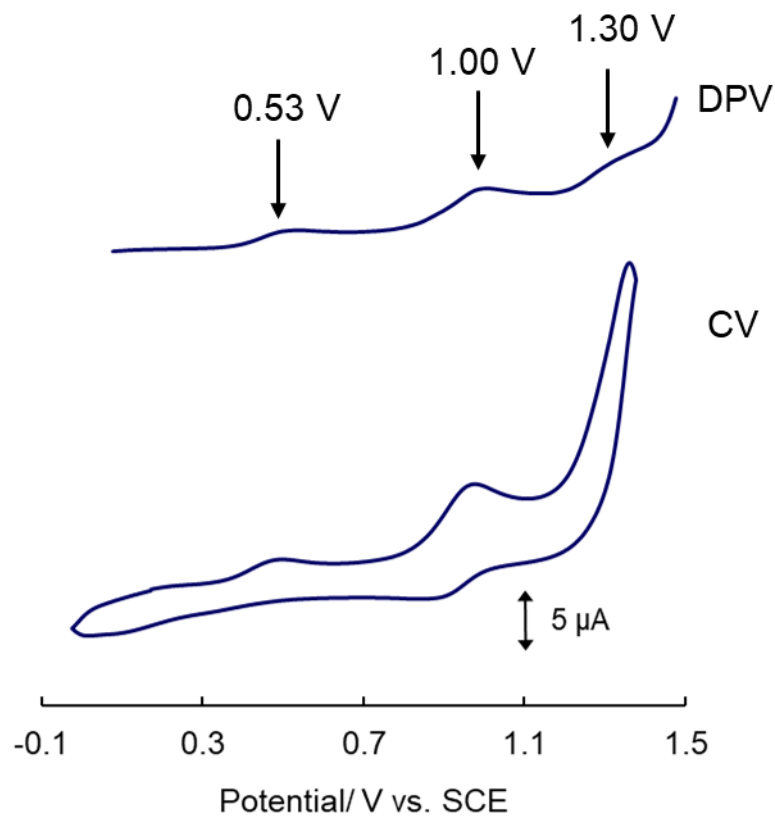


**Figure S5.** Photochemical water oxidation for calculating the quantum yield using 450 nm laser (0.12 mW) as the light source. The aqueous 0.10 M borate buffer solution (pH 9.0) contained 5.0  $\mu\text{M}$  CoPcTS, 50  $\mu\text{M}$   $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$ , and 5.0 mM  $\text{Na}_2\text{S}_2\text{O}_8$  under Ar atmosphere at 293 K (Light source: Xe lamp, 410-530 nm). The black vertical line indicates 20 minutes.

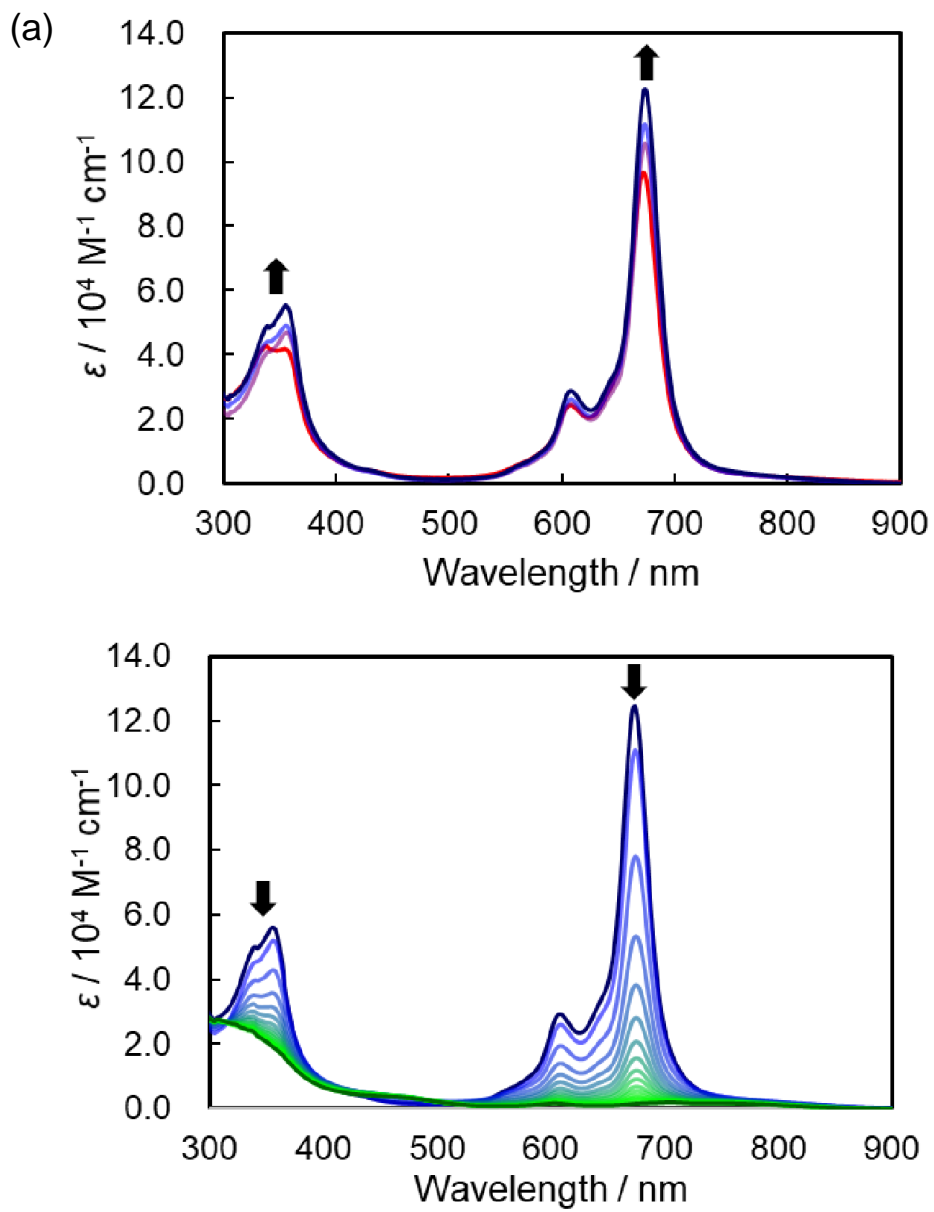




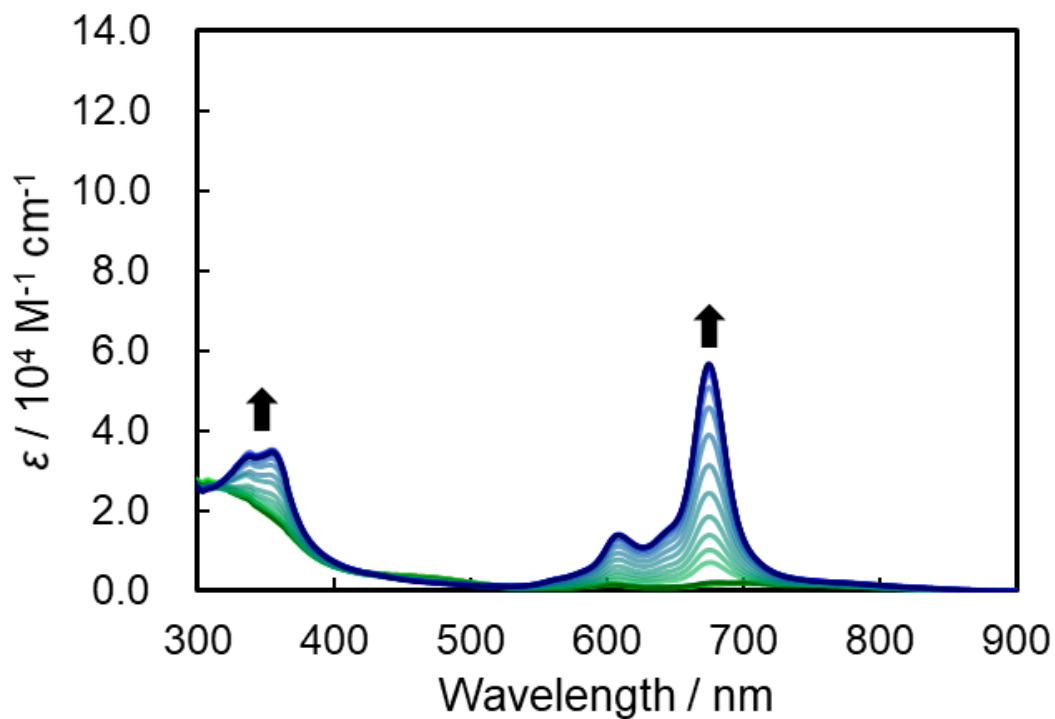
**Figure S6.** The initial rate of photochemical O<sub>2</sub> evolution as a function of the CoPcTS concentration. An aqueous pH 9.0 borate buffer solution (0.1 M) contains 0.30 mM [Ru(bpy)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> and 10.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Light source: Xe lamp, 410-530 nm).



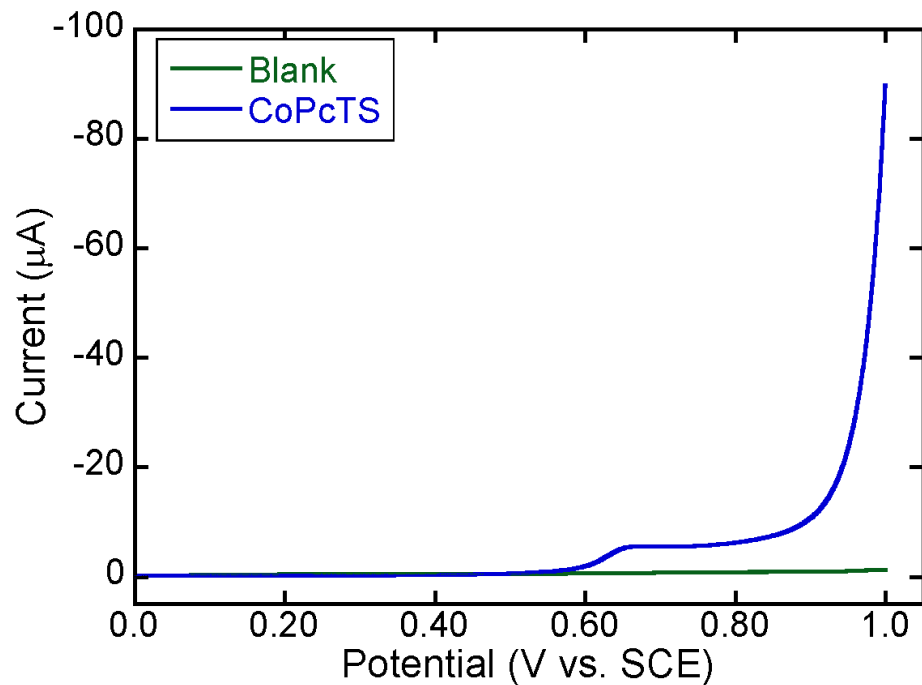
**Figure S7.** Differential pulse voltammogram (Top) and cyclic voltammogram (Bottom) of 1.00 mM of CoPcTS in *N,N*-dimethylformamide (DMF) containing 0.10 M of tetrabutylammonium perchlorate (TBAP) under Ar at 293 K. The working, counter, and reference electrodes were a glassy carbon disk, a Pt wire, and Ag/AgNO<sub>3</sub>, respectively. The cyclic voltammogram was recorded at the sweep rate of 50 mV s<sup>-1</sup>.



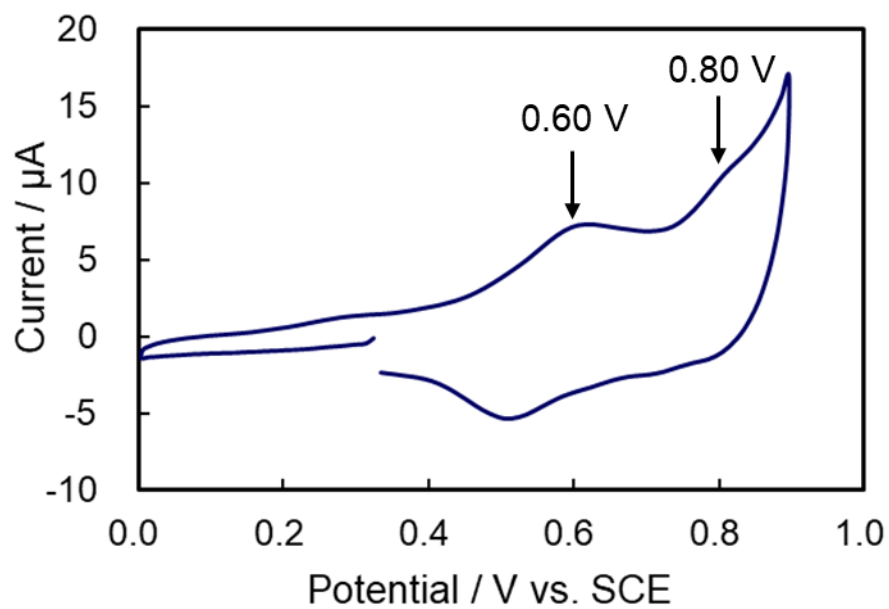
**Figure S8.** UV-vis spectral changes of a DMF solution of CoPcTS containing 0.10 M of TBAP by potentiostatic electrolysis at : 0.58 V (a); 0.90 V (b).



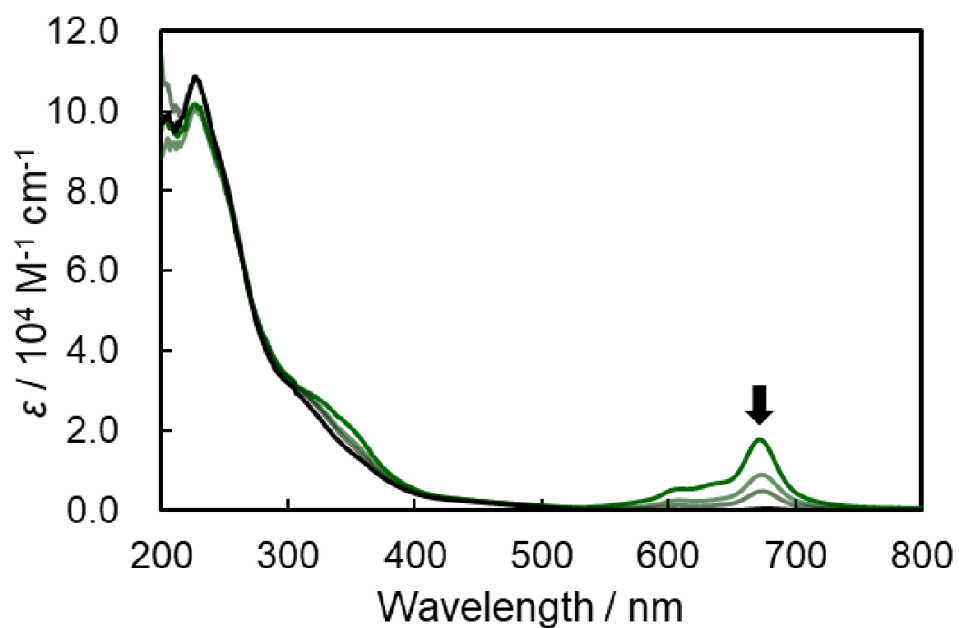
**Figure S9.** UV-vis spectral changes by re-reduction of the CoPcTS solution after two-electron oxidation. Controlled-potential electrolysis of the solution was carried out at 0.50 V after oxidation of the DMF solution contains CoPcTS, 0.10 M of TBAP at 0.90 V.



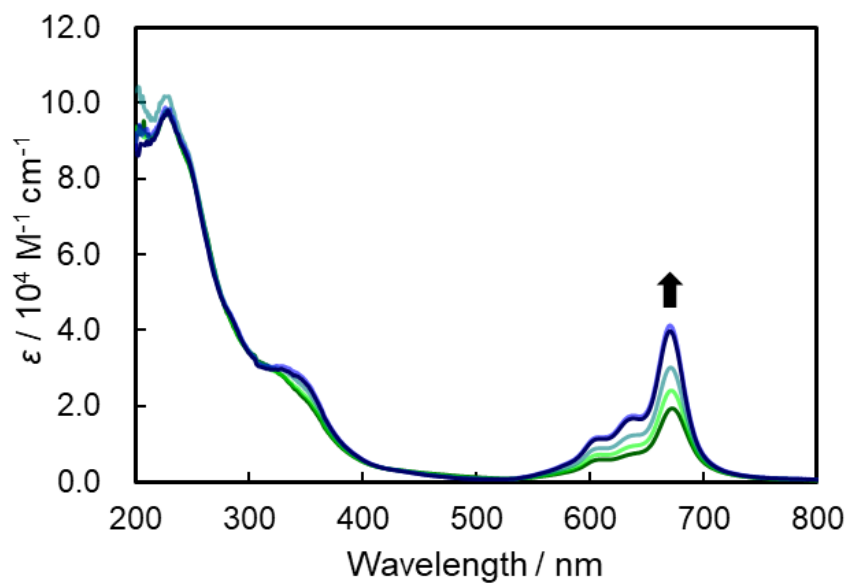
**Figure S10.** Linear sweep voltammograms of 500  $\mu\text{M}$  CoPcTS in pH 9 0.10 M borate buffer solution under Ar; the voltammograms were recorded at the sweep rate of  $50 \text{ mV s}^{-1}$  at 293 K. The working, counter, and reference electrodes were a glassy carbon disk, a Pt wire, and SCE, respectively.



**Figure S11.** Cyclic voltammogram of 1.0 mM CoPcTS in pH 9 0.10 M borate buffer solution under Ar; the voltammograms were recorded at the sweep rate of  $50 \text{ mV s}^{-1}$  at 293 K. The working, counter, and reference electrodes were a glassy carbon disk, a Pt wire, and SCE, respectively.

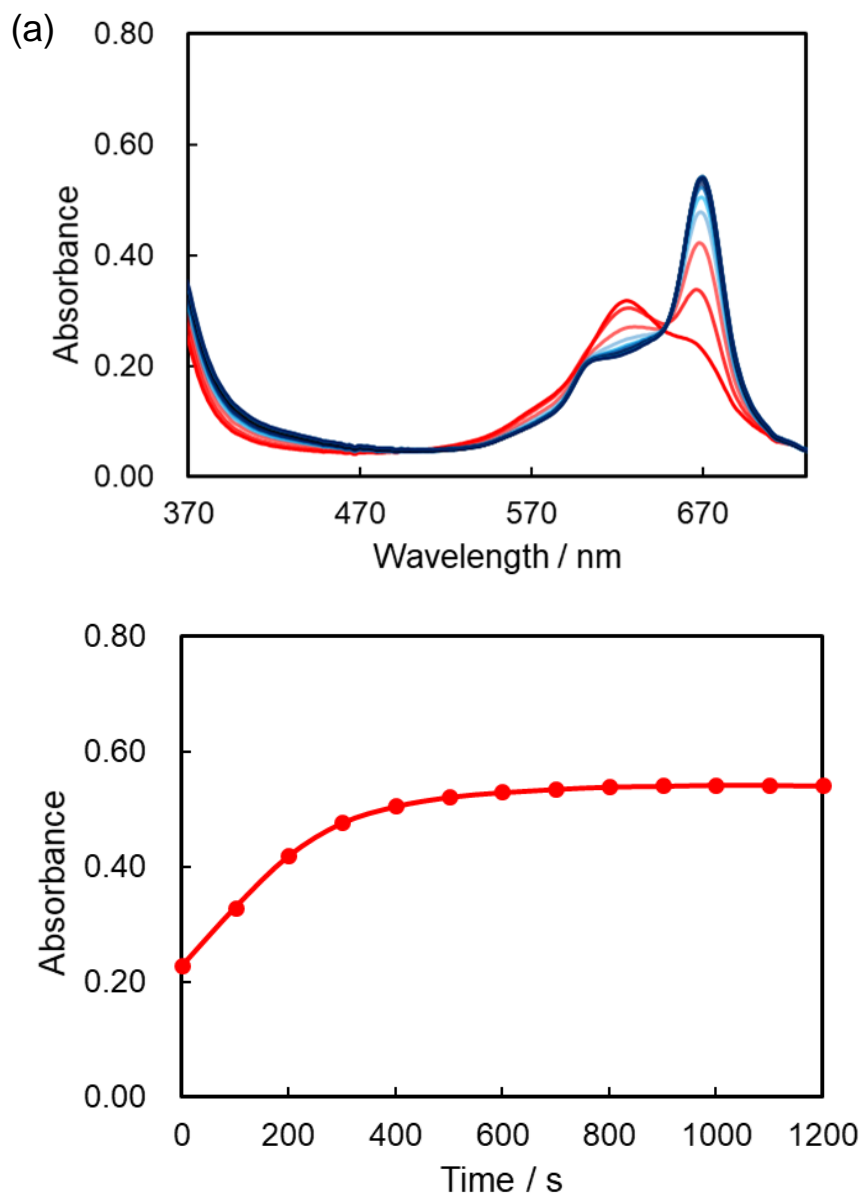


**Figure S12.** UV-vis spectral changes of further oxidation at after electrolysis at 0.75V. Controlled-potential electrolysis of the solution was carried out at 0.85 V after oxidation of a borate buffer solution (0.10 M, pH = 9.0) containing CoPcTS by potentiostatic electrolysis at 0.75 V.

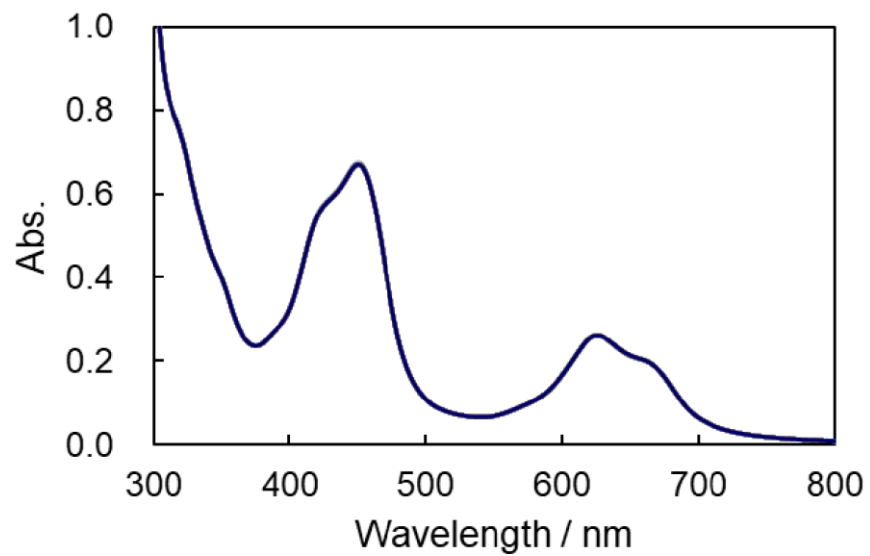


**Figure S13.** UV-vis spectral changes of re-reduction of the CoPcTS after electrolysis at 0.75V. Controlled-potential electrolysis of the solution was carried out at 0.67 V after oxidation of the DMF solution contains CoPcTS, 0.10 M of TBAP at 0.75 V.

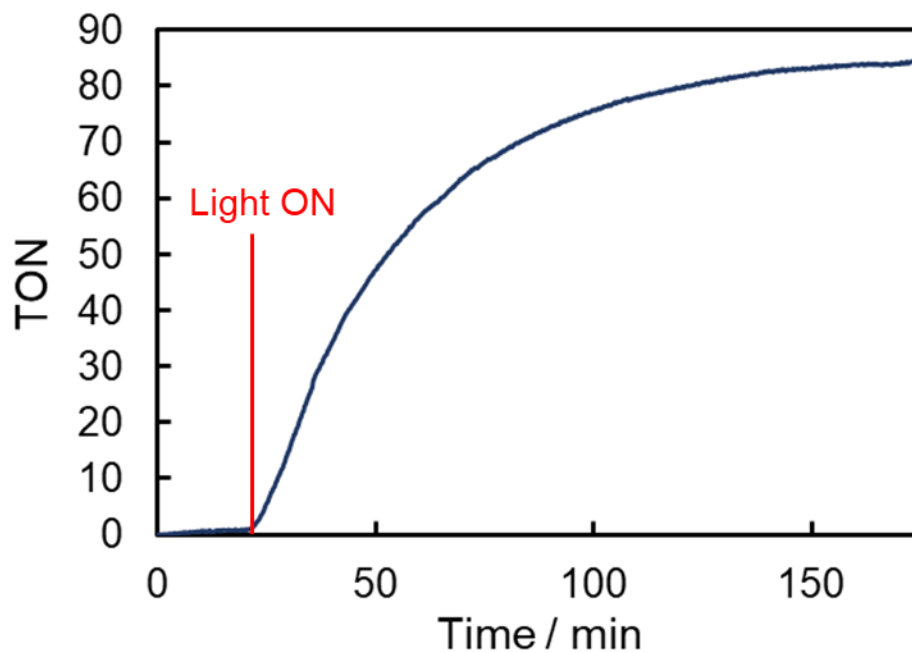




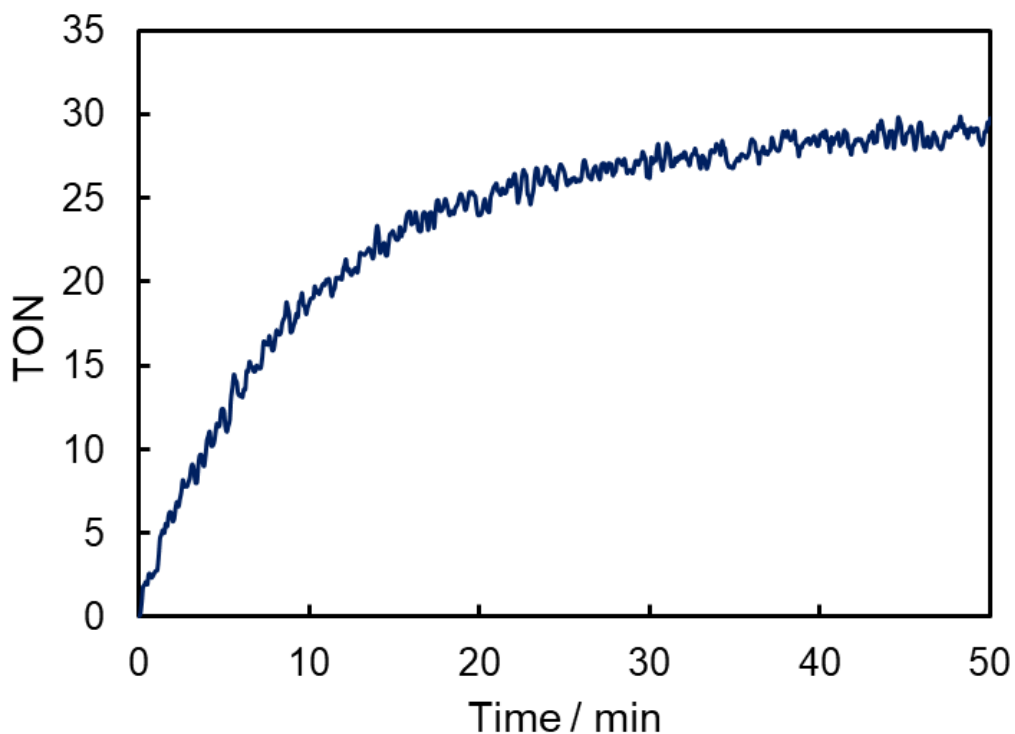
**Figure S14 (a)** Time-course UV-vis spectral changes of 10.0  $\mu\text{M}$  CoPcTS in an aqueous 0.10 M borate buffer solution containing 5.0 mM of  $\text{Na}_2\text{S}_2\text{O}_8$  in the dark. (b) Time profiles of the absorbance at 670 nm in (a). Cell path = 0.5 cm



**Figure S15.** Time-course UV-vis spectral changes of 5.0  $\mu\text{M}$  CoPcTS in an aqueous 0.10 M borate buffer solution containing 50  $\mu\text{M}$  of  $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$  in the dark (0 s –  $8.4 \times 10^3$  s).



**Figure S16.** Photochemical water oxidation after the time-course experiment of UV-Vis spectra (described at Figure 4 at main text). The aqueous 0.10 M borate buffer solution (pH 9.0) contained 5.0  $\mu\text{M}$  CoPcTS, 50  $\mu\text{M}$   $[\text{Ru}^{\text{II}}(\text{bpy})_3](\text{NO}_3)_2$ , and 5.0 mM  $\text{Na}_2\text{S}_2\text{O}_8$  under Ar atmosphere at 293 K. (Light source: 450 nm laser)



**Figure S17.** Water oxidation using  $2.5 \times 10^{-2}$   $\mu\text{mol}$  of CoPcTS and 3.5  $\mu\text{mol}$  of  $[\text{Ru}^{\text{III}}(\text{bpy})_3](\text{ClO}_4)_3$  in aqueous solution. The experimental details are provided in the experimental section.

#### References

1. J. H. Weber, and D. H. Busch, *Inorg. Chem.*, **1965**, 4, 469-471.
2. K. Sakai, Y. Kizaki, T. Tsubomura, K. Matsumoto, *J. Mol. Catal.*, **1993**, 79, 141-152.
3. C. J. P. Monteiro, M. M. Pereira, S. M. A. Pinto, A. V. C. Simões, G. F. F. Sá, L. G. Arnaut, S. J. Formosinho, S. Simões, M. F. Wyatt, *Tetrahedron*. **2008**, 64, 5132-5138.
4. T. Nakazono and T. Wada, *Inorg. Chem.* **2021**, 60, 1284-1288.
5. T. Nakazono, A. R. Parent and K. Sakai, *Chem. Commun.* **2013**, 49, 6325-6327.
6. T. Nakazono and K. Sakai, *Dalton Trans.*, **2016**, 45, 12649-12652.
7. R. Terao, T. Nakazono, A. R. Parent, K. Sakai, *ChemPlusChem*, **2016**, 81, 1064-1067.
8. C. Y. Liu, D. van den Bos, B. den Hartog, D. van der Meij, A. Ramakrishnan and S. Bonnet, *Angew. Chem., Int. Ed.*, **2021**, 60, 13463–13469