

Supplementary Information

**Improving the robustness of cobalt porphyrin
water oxidation catalysts by chlorination of aryl groups**

Takashi Nakazono^{*a,b} and Ken Sakai^{*a,b,c}

^a Department of Chemistry, Faculty of Science, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

^b International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

^c Center for Molecular Systems (CMS), Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

Materials

All solvents and reagents were of the highest quality available and were used as received. 2,6-dichloro benzaldehyde and pyrrole were purchased from TCI Fine Chemicals Co., were used as received. $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was prepared as previously described.¹

Synthesis of CoCIPS

CoCIPS was synthesized based on the preparation method of **CoFPS** previously described.² 5,10,15,20-tetra(2,6-dichloro-3-sulfophenyl)porphyrin (**CIPS**) was synthesized based on literature methods.³ $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.15 g, 6 mmol), **CIPS** (0.12 g, 1 mmol) were added to water (25 mL). The pH was adjusted to 7.5 by addition of 1 M NaOH. The solution was refluxed for 24 h, then passed through the H^+ form of the cation-exchange resin Dowex 50W-X8 (50-100-mesh) to remove excess Co^{2+} . The **CoCIPS** was then precipitated from solution via the addition of acetone (100 mL). The precipitate was collected by filtration, washed with acetone and diethyl ether, and dried in vacuum. Yield 0.12 g (0.82 mmol, 82 %).

ESI-TOF MS: m/z 421.01 [**CoCIPS**- 3H^+ - $2\text{H}_2\text{O}$] $^{3-}$ (Calcd. for $\text{C}_{44}\text{H}_{16}\text{Cl}_8\text{CoN}_4\text{O}_{12}\text{S}_4$: 420.88 m/z). m/z . Elemental analysis of **CoCIPS** calcd. (%) for $\text{C}_{44}\text{H}_{23}\text{Cl}_8\text{CoN}_4\text{O}_{14}\text{S}_4 \cdot 9\text{H}_2\text{O}$ (1464.59): C 36.08, H 2.82, N 3.83. Found: C 36.27, H 2.89, N 3.91. $^1\text{H-NMR}$ (600.13 MHz, D_2O): δ ppm 9.23-9.14 (m, 8H), 8.52-8.42 (m, 4H), 8.12-8.05 (m, 4H).

Oxygen Production

Photochemical oxygen production from water was analyzed by using an automatic $\text{GC H}_2/\text{O}_2$ monitoring system developed in our group. In this system, continuous flow of Ar (10.0 mL/min, controlled by a STEC SEC-E40/PAC-D2 digital mass flow controller) is bubbled through a photolysis solution (10 mL) contained in a Pyrex vial (*ca.* 20 mL). The vent gas from the vial is introduced into a valve which allows the automatic injection of the sample gas onto the GC (Shimadzu GC-8A equipped with a molecular sieve 5 Å column of 2 m \times 3 mm *i.d.*, at 30 °C). The injection of the sample gas is controlled by software developed by Prof. Ken Sakai, and the output signal from the thermal conductivity detector of the gas chromatograph is analyzed by the Shimadzu C-R8A integrator. Photolysis solutions 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 ($\lambda=400\text{-}800$ nm). Visible light cut-filter (HOYA Y44) and blue filter (HOYA B390) were used in some experiments (Figure 3 and 4). The photolysis vial is immersed in a 20 °C water bath to remove IR radiation and to eliminate temperature effects.

Procedure for Electrochemical Measurements

Square wave voltammograms were recorded on a BAS ALS Model 750C electrochemical analyzer, using a three electrode system consisting of a platinum working electrode, a platinum wire counter electrode, and a Ag/Ag⁺ reference electrode, where TBAP (tetra(n-butyl)ammonium perchlorate) was used as a supporting electrolyte. The potentials in DMF were corrected by employing the ferrocene/ferrocenium (Fc/Fc^+) couple as an internal standard.

Procedure for Dynamic Light Scattering Analysis

Dynamic light scattering (DLS) data were measured using an Otsuka Electronics ELSZ-2PS particle analyzer equipped with a diode laser (660 nm) (detection limit: 0.6 nm in particle diameter).

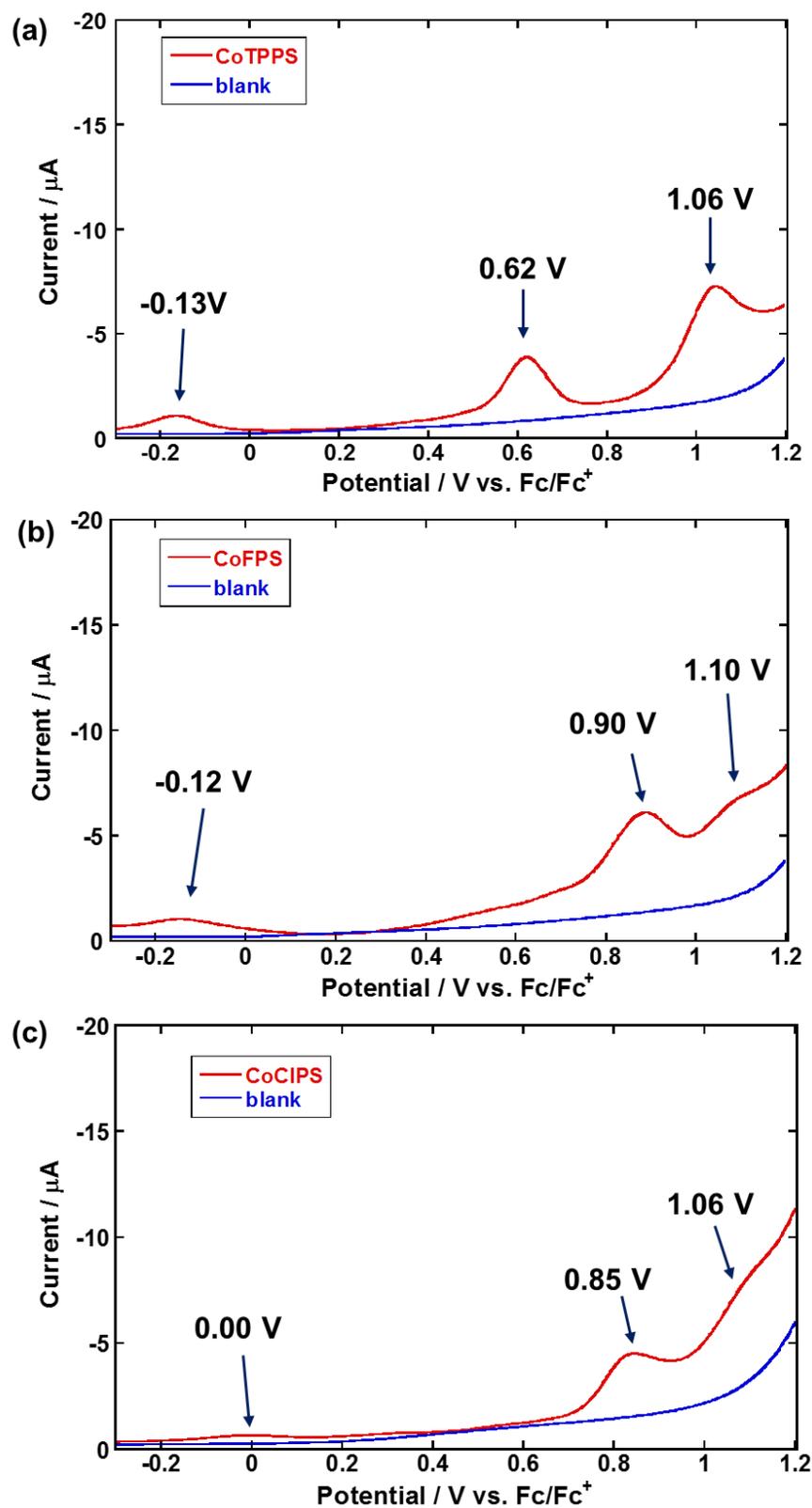


Figure S1. Square wave voltammograms of 1.0 mM (a)CoTPPS, (b)CoFPS and (c)CoCIPS in 100 mM TBAP DMF solution under Ar at 20 °C. The blue line indicates the blank electrode response.

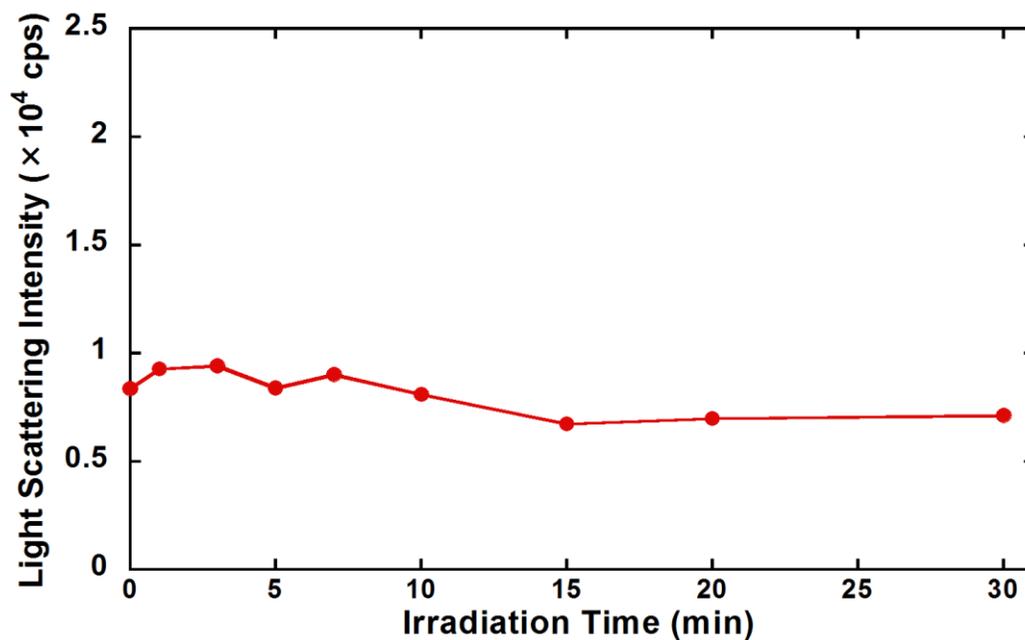


Figure S2. Light scattering intensity as a function of time during photo-irradiation of an aqueous 0.1 M pH 9.0 borate buffer solution containing 10 μ M CoCIPS, 0.2 mM [Ru(bpy)₃](NO₃)₂, and 7.0 mM Na₂S₂O₈ and under Ar.

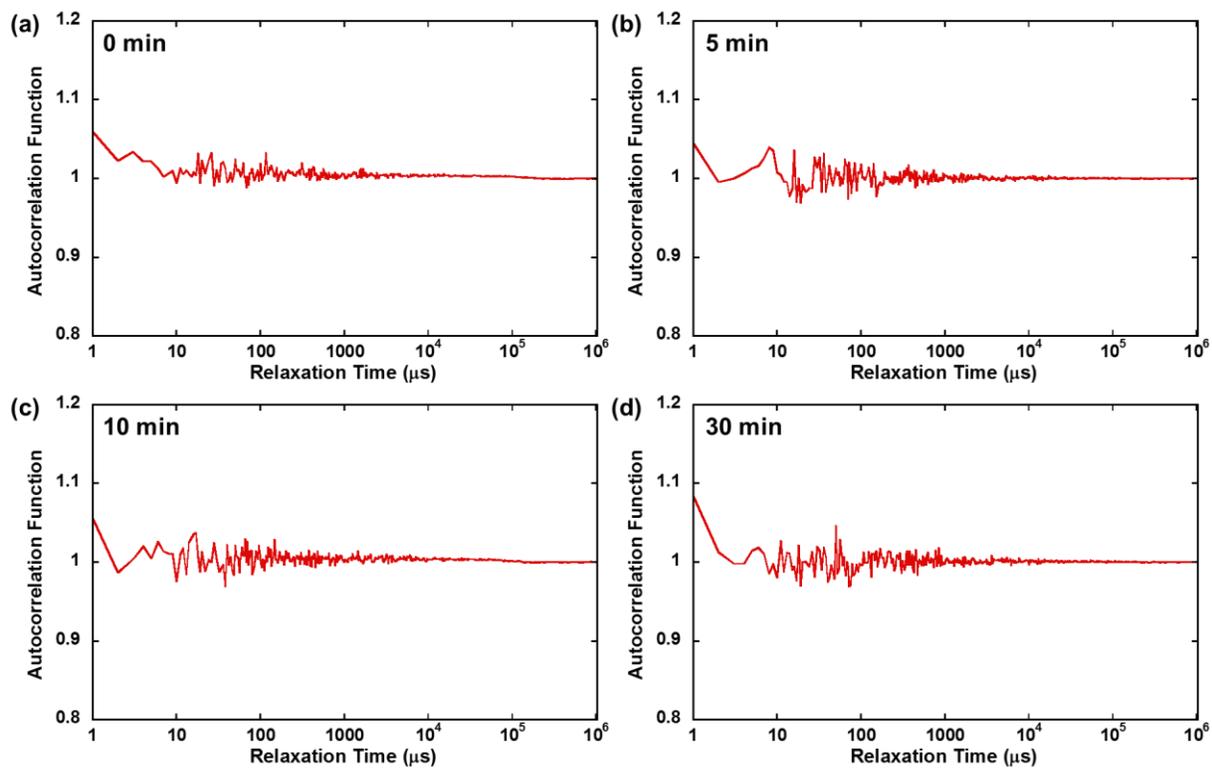


Figure S3. Autocorrelation function obtained by DLS measurements of an aqueous 0.1 M pH 9.0 borate buffer solution containing 10 μM CoCIPS, 0.2 mM $[\text{Ru}(\text{bpy})_3](\text{NO}_3)_2$, and 7.0 mM $\text{Na}_2\text{S}_2\text{O}_8$ and under Ar.

References

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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 and M. F. Wyatt, *Tetrahedron*. 2008, **64**, 5132-5138.