Supplementary Materials: Mechanism of Water Oxidation Catalyzed by a Dinuclear Ruthenium Complex Bridged by Anthraquinone

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1. Cystallographic Data for Btpyaq·C₆H₆

Table S1. Crystallographic data for btpyaq·C_6H_6.

Empirical Formula	$C_{50}H_{32}N_6O_2$
Formula weight	748.85
Temperature/K	90
Crystal system	triclinic
Space group	P-1
a (Å)	13.4638(5)
b (Å)	16.7498(7)
c (Å)	17.5439(8)
α (°)	78.481(2)
β (°)	79.345(2)
γ (°)	78.123(2)
Volume (Å³)	3750.8(3)
Z	4
Density (calculated) (g/cm³)	1.3260
Absorption Coefficient (mm⁻¹)	0.083
F(000)	1560.6
Crystal size (mm³)	1.12 × 0.55 × 0.48
Radiation	Mo $K\alpha$ (λ = 0.71073)
2Θ range for data collection (°)	4.34 to 54.96
Index ranges	$-17 \leq h \leq 16, -21 \leq k \leq 21, -22 \leq l \leq 22$
Reflections collected	34994
Independent reflections	16699 [R_{int} = 0.0490, R_{sigma} = 0.0677]
Data/restraints/parameters	16699/0/1300
Goodness-of-fit on F²	1.068
Final R indexes [$I \geq 2\sigma$ (I)]	R_1 [a] = 0.0509, wR_2 [b] = 0.1275
Final R indexes [all data]	R_1 [a] = 0.0711, wR_2 [b] = 0.1453
Largest diff. peak/hole/e (Å⁻³)	0.42/-0.42

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $\omega R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
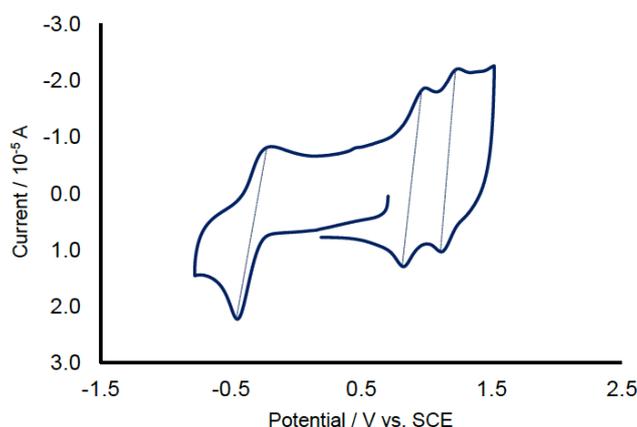
2. Cyclic Voltammetry

Figure S1. Cyclic voltammogram of [**3**](BF₄)₃ (1.0 mmol·L⁻¹) in CF₃CH₂OH solution of containing *n*-Bu₄NClO₄ (100 mmol·L⁻¹) using glassy carbon, Pt wire, and Ag/Ag(NO₃), as working, counter, and reference electrodes. The potential was converted to SCE.

3. Cyclic Voltammetry after Electrolysis

Controlled-potential electrolysis of the solution of [**3**](BF₄)₃ was conducted using a two-compartment cell separated by cation exchange membrane (Nafion 117, Sigma-Aldrich Chemical Co. (St. Louis, MO, USA)). The phosphate buffer solution (10 mmol·L⁻¹, 20 mL) at pH 2.6 of [**3**](BF₄)₃ (0.2 mmol·L⁻¹) containing NaNO₃ (100 mmol·L⁻¹) as the electrolyte was added to the one side of the cell with an ITO glass plate (2.0 cm²) and SCE as working and reference electrodes, respectively. The phosphate buffer solution (10 mmol·L⁻¹, 20 mL) containing NaNO₃ (100 mmol·L⁻¹) was added to the other side cell with a Pt plate (4.0 cm²). The controlled-potential electrolysis was conducted at +1.60 V (vs. SCE) under Ar. After 2.1 C passed in the electrolysis, 5 mL of the solution in a working cell was moved to a CV cell. CV of the solution at pH 1.3 (adjusted with HNO₃) was measured at a scan rate of 50 mV s⁻¹ at 298 K under Ar using plate material evaluating cell (ALS Co. Ltd. Tokyo, Japan) with an indium-tin-oxide (ITO) glass plate as the working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode (Figure S2). The diameter of ITO electrode surface in contact with liquid was 7.8 mm. The test solutions were deoxygenated by passing a stream of Ar through them.
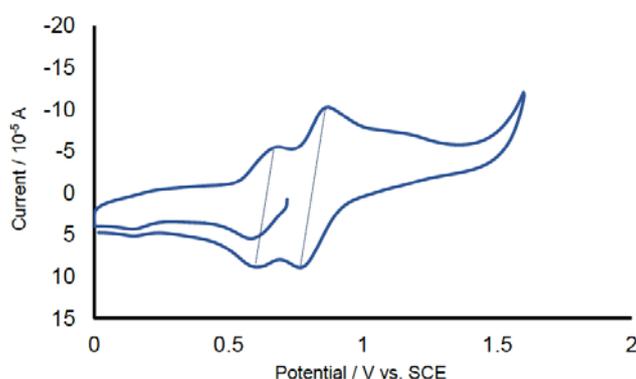

Figure S2. Cyclic voltammogram of the solution of [**3**](BF₄)₃ after electrolysis.