Supporting Materials for

Adaptive water oxidation catalysis on a carboxylate-sulfonate ligand

with low onset potential

Jing Yang^{1#*}, Shaoqi Zhan^{5#}, Linqin Wang³, Hao Yang⁴, Lele Duan³, Xiaolei Fan^{2,6}, Tianqi Liu^{2*},

Licheng Sun^{3,4*}

¹ College of Health Science and Environmental Engineering, Shenzhen Technology University, Shenzhen 518118, China

² Institute of Wenzhou, Zhejiang University, 325005, Wenzhou, China

³ Center of Artificial Photosynthesis for Solar Fuels, School of Science, Westlake University, 310024 Hangzhou, China

⁴ Department of Chemistry, School of Engineering Sciences in Chemistry Biotechnology and Health, KTH Royal Institute of Technology, 10044 Stockholm, Sweden

⁵ Department of Chemistry - Ångström, Uppsala University, Box 523, 751 20 Uppsala, Sweden

^{6.} Department of Chemical Engineering, School of Engineering, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

* Corresponding authors:

JY: yangjing2@sztu.edu.cn; TL: tianqil@kth.se; LS: sunlicheng@westlake.edu.cn;

[#] These authors contributed equally: JY and SZ.

General Procedures

Compounds and solvents are of reagent-grade quality and commercially available and used as received without further purification. Water used in all measurements was purified by Milli-Q technique. Nuclear magnetic resonance (NMR) spectra were obtained with 400 MHz of Bruker Advance spectrometer. Elemental analyses were performed with an Elementar Vario EL elemental analyzer. High-resolution mass spectrometry measurements were performed on a Thermo Scientific Q Exactive mass spectrometer. Electrochemistry measurements were performed with a CHI760 electrochemical workstation. For cyclic voltammetry and differential pulse voltammetry measurements, a glassy carbon disk (diameter 3 mm) was used as the working electrode and a platinum column as the counter electrode, and measured versus Ag/AgCl reference electrode (3 M KCl; 210 mV vs. NHE) in aqueous solutions (conditions: [cat] = 1.0 mM; pH 1.0 triflic acid or pH 7.0, 0.2 M phosphate buffer, I = 0.5 M (NaNO₃)). The Ce^{V-1} driven oxygen was detected by a pressure transducer (MIK-P300) driven at 10.00 V using a power supply (HY3005B) plus a data acquisition module (Omega OM-DAQ-USB-2401). The single crystal X-ray diffraction data were collected at 100.01 K on a Bruker APEX II CCD diffractometer with a graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS and refined by full-matrix least-squares on $|F^2|$ algorithm (SHELXL) using the Olex2 program.

Computational Details

Jaguar 8.3 program package by Schrödinger LLC was used to perform all DFT calculations for the estimation of Gibbs-free energies.¹ Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP)² with D3 correction of Grimme et al.^{3, 4} with the LACVP** core potential and basis set were used to optimize molecular geometries.⁵ Single-point energy corrections were performed with the B3LYP-D3 functional using the LACV3P**++ basis set augmented by two f-functions on the metal. Based on the gas-phase-optimized geometries, the implicit solvation energies were estimated by single-point calculations using the Poisson– Boltzmann reactive field (PBF) implemented in Jaguar in water. The Gibbs-free energy was defined by the following equation: G = E(B3LYP-D3/LACV3P**++ 2f on Ru) + G_{solv} + ZPE + H₂₉₈ – TS_{298} + 1.9 kcal mol⁻¹ (The value 1.9 kcal mol⁻¹ is a concentration correction to the free energy of solvation, which by default is calculated at 1 M (g) to 1 M (aq) in Jaguar).

Complex	Ru-bcs		
Empirical formula	$C_{21}H_{16}N_4O_5RuS$		
Formula weight	537.51		
Temperature/K	100.01		
Crystal system	orthorhombic		
Space group	Pbca		
a/Å	10.1221(6)		
b/Å	16.1027(10)		
c/Å	25.1176(16)		
α/°	90		
β/°	90		
γ/°	90		
Volume/ų	4094.0(4)		
Z	8		
$\rho_{calc}g/cm^3$	1.744		
µ/mm⁻¹	0.911		
F(000)	2160.0		
Crystal size/mm ³	$0.4 \times 0.16 \times 0.14$		
Radiation	ΜοΚα (λ = 0.71073)		
2θ range for data collection/°	on/° 5.022 to 55.042		
Index ranges	−13 ≤ h ≤13, −20 ≤ k ≤ 20, −32 ≤ l ≤ 32		
Reflections collected	55641		
Independent reflections	4706 [R _{int} = 0.0878, R _{sigma} = 0.0382]		
Data/restraints/parameters	4706/351/323		
Goodness-of-fit on F ²	1.128		
Final R indexes [I>=2σ (I)]	$R_1 = 0.0659, wR_2 = 0.1340$		
Final R indexes [all data]	R ₁ = 0.0770, <i>w</i> R ₂ = 0.1380		
Largest diff. peak/hole/e Å ⁻³	3.43/-1.71		

 Table S1. Crystallographic data for Ru-bcs.

Single crystals of **Ru-bcs** (CCDC no.: 2347388) was obtained by diffusing diethyl ether into CH_3OH/CH_2Cl_2 (1/4, v/v) solution of complex **Ru-bcs**. Crystallographic data are listed in Table S1.

Note S1: TOF values calculation from electrochemical experiments

Randles–Ševčík equation describes the effect of scan rate on the peak current (i_p) for reversible electrochemical couples.

$$i_p = 0.4463 \ n_p FA[cat] \sqrt{\frac{n_p FvD}{RT}}$$

where n_p is number of electrons transferred in the redox event, F is Faraday constant in C mol⁻¹, A is electrode area in cm², [*cat*] is the catalyst concentration in mol cm⁻³, v is scan rate in V s⁻¹, D is diffusion coefficient in cm² s⁻¹, R is gas constant in J K⁻¹ mol⁻¹ and T is temperature in K. At the steady-state experimental conditions, the scan-rate is independent on the catalytic current (i_{cat}). In this case, i_{cat} could be expressed by following equation

$$i_{cat} = n_{cat} FA[cat] \sqrt{Dk_{cat}}$$

where n_{cat} is 4 for water oxidation reaction.

Then the TOF value could be calculated according to equation (1):

$$\frac{i_{cat}}{i_p} = 0.359 \frac{n_{cat}}{n_p^{3/2}} \sqrt{\frac{k_{cat}}{v}}$$

TOF value is calculated based on three repeated runs and data is listed below.

	Slope	R ²	E _{cat} (<i>vs</i> NHE)	TOF (s ⁻¹)
1	47.5	0.999	1.8	1094
2	45.6	0.998	1.8	1007
3	51.9	0.998	1.8	1304
			TOF	1135±152

Note that this method applies when S-shaped catalytic response is observed, in which the plateau current is independent of the scan rate. While **equation 1** may not be strictly applicable in our scenario, its analysis can still offer valuable insights for an initial evaluation of catalyst performance. Even with non-ideal waves, any enhancements in current reflect catalytic activity. In such instances, it is important to note that **equation 1** typically underestimates the rate constant (TOF), especially when dealing with peak-shaped waves where the current never reaches a plateau. (Nature Reviews Chemistry, 2017, 1, 0039.).

Note S2: KIE values calculation from electrochemical experiments

$$pK_{D_20} = pOD + pD = 14.87$$

 $pK_{H_20} = pOH + pH = 14$

The CV curves were recorded with a scan rate of 20 mV s⁻¹ in 0.2 M phosphate buffer solution:

pH_{reading} = 7.43, *i.e.* PD = 7.83 in D₂O (J. Phys. Chem. B 2019, 123, 8195–8202)

$$pH_{reading} = 6.95 \text{ in } H_2O$$

The overpotential can be expressed by the following equations in H_2O and D_2O .

$$\eta^{H_2 0} = E_{RHE} - 1.229V_{RHE} = E_{Ag/AgCl}^{reading} + 0.059pH + E_{Ag/AgCl}^{H} - 1.229V_{RHE}$$
$$\eta^{D_2 0} = E_{RHE} - 1.262V_{RDE} = E_{Ag/AgCl}^{reading} + 0.059pD + E_{Ag/AgCl}^{D} - 1.262V_{RDE}$$

The difference between $E_{Ag/AgCl}^{H}$ and $E_{Ag/AgCl}^{D}$ is -0.013 V. (Bard, A. Standard potentials in aqueous solution, (Routledge, 2017).)

Therefore, in our case,

$$\eta^{H_2 0} - \eta^{D_2 0} = 0.059 x (6.95 - 7.83) + 0.033 = 0.01892 V$$

Based on equation (1), kinetic deuterium isotope effect was defined as equation (2):

$$KIE = \frac{k_{cat, H_20}}{k_{cat, D_20}} = \frac{\binom{i_{cat}}{i_p}_{H_20}^2}{\binom{i_{cat}}{i_p}_{D_20}^2}$$

Synthesis





Synthesis of 6'-methyl-[2,2'-bipyridine]-6-sulfonic acid (compound 4). Compounds of 1, 2 and 3 were synthesized according to references *J. Med. Chem.*, 2016, *59*, 10642–10660 and *CrystEngComm*, 2010, 12, 2928–2937. Compound 3 (101 mg, 0.50 mmol) was dissolved in 8 mL nitric acid (70%, purified by redistillation, \geq 99.999% trace metals basis), and the solution was heated at 100°C for 2 hours, then the acid was removed under vacuum. The product of 4 was obtained as pale yellow powder in a quantitative yield. ¹H NMR (400 MHz, CD₃OD) δ 8.69–8.51 (m, 2H), 8.44 (d, *J* = 7.9 Hz, 1H), 8.24 (t, *J* = 7.9 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 6.3 Hz, 1H), 2.95 (s, 3H). ¹³C NMR (101 MHz, CD₃OD) δ 161.74 (s), 155.75 (s), 147.43 (s), 146.73 (s), 146.05 (s), 140.24 (s), 128.26 (s), 123.53 (s), 123.35 (s), 121.90 (s), 18.40 (s). HRMS: m/z⁻ = 249.0330 (M–H⁺); calcd, 249.0339.



Scheme S2

Synthesis of 6'-sulfo-[2,2'-bipyridine]-6-carboxylic acid (compound 5). To a solution of compound 4 (125 mg, 0.50 mmol) in pyridine (5 mL), 2 equivalents of SeO₂ (112 mg, 1.0 mmol) was added. The reaction mixture was refluxed under 115°C for 4 days. The mixture was filtered through a pad of celite, rinsing with MeOH and DCM. The filtrate was evaporated under reduced pressure to afford the desired product (126 mg, 0.45 mmol) as a white solid. The obtained solid was used for the next step without purification. HRMS: $m/z^- = 279.0078 (M-H^+)$; calcd, 279.0081.



Scheme S3

Synthesis of [Ru(bcs)(pic)₂] (**Ru-bcs).** To a solution of **5** (112 mg, 0.40 mmol) in dry MeOH (5 mL), dichloro(*p*-cymene)ruthenium(II) dimer (122 mg, 0.20 mmol), 4 equivalents of pyridine was added. The resulting mixture was then heated under 125°C for 40 minutes using a microwave reactor. The solvent was removed by vacuum, and the crude product was purified by column chromatography. The target complex was afforded as a dark red powder (103 mg, 48% yield). ¹H NMR (400 MHz, CD₃OD) δ 8.60 (dd, J = 8.1, 1.4 Hz, 1H), 8.56 (dd, J = 8.2, 1.1 Hz, 1H), 8.49 (dd, J = 7.9, 1.4 Hz, 1H), 8.16 (t, J = 7.9 Hz, 1H), 8.01 – 7.94 (m, 5H), 7.86 – 7.81 (m, 1H), 7.70 (tt, J = 7.6, 1.5 Hz, 2H), 7.22 – 7.15 (m, 4H). ¹³C NMR (101 MHz, CD₃OD) δ 166.64, 161.36, 160.78, 155.99, 153.01, 136.99, 136.75, 131.49, 126.51, 125.77, 124.57, 124.46, 124.24, 122.46.HRMS: calcd for 538.9958 (M + H⁺); found m/z⁺ = 538.9949. Anal. Calcd for [Ru(bcs)(pic)₂]·2H₂O (C₂₁H₂₀N₄O₇RuS): C 43.98; H 3.51; N 9.77. Found: C 43.79; H 3.99; N 9.86.



Scheme S4. Proposed water activation pathway of Ru-bcs under acidic conditions.



Scheme S5. Possible species associated with the dynamic behavior of Ru^{II}-bcs. Axial ligands are omitted for clarity



Figure S1. The single-crystal X-ray structures of (a) Ru-bcs, (b) Ru-bda, and (c) Ru-bds ellipsoids at 20% probability, with selected bond distances and angles (axial ligands are omitted for clarity).

The X-ray crystal structure of Ru-bcs, depicted in **Figure 1b**, reveals a typical distorted octahedral geometry, being consistent with the expected configuration for low-spin d⁶ Ru^{II}. The Ru^{II} center is 6-coordinate with a N₄O₂ donor set. In detail, the equatorial positions are occupied by a bcs ligand, and the axial positions are occupied by two pyridine ligands. Notably, the O–Ru–O bite angle of Ru-bcs (117.91°) falls between its corresponding dicarboxylate and disulfonate counterparts, Ru-bds (114.72°), and Ru-bda (122.99°). A comparison of the bond distances and O–Ru–O angle is shown in **Figure S1**. The bond length of S1–O1 (1.418 Å) in the sulfonate group of Ru-bcs is shorter than the corresponding S–O bond distances (S5–O4: 1.487 Å and S4–O3: 1.485 Å) of Ru-bds, while the bond distance of C23–O5 (1.388 Å) is longer than those (C12–O3: 1.304 Å and C1–O2: 1.291 Å) of Ru-bda. Additionally, the C7–C6–C2 angle of 130.04° in Ru-bcs is close to the C8–C7–C6 angle of 129.57° in Ru-bda, whilst its C6–C2–C3 angle of 127.70° is close to the C18–C17–C16 angle of 127.02° in Ru-bds.



Figure S2. (a) The state-of-the-art single site water oxidation catalysts. tda = [2,2':6',2''-terpyridine]-6,6''-dicarboxylate, tpa = 2,2':6',2''-terpyridine-6,6''-diphosphonate, tds = [2,2':6',2''-terpyridine]-6,6''-disulfonate, t5a = 2,5-bis(6-carboxylatopyridin-2-yl)pyrrol-1-ide (b) Single crystal structure of Ru-bcs with thermal ellipsoids at 50% probability (Hydrogen atoms and solvent molecules are omitted for clarity) and structures of water oxidation catalysts discussed in the paper; L is pyridine-based ligand. bcs = 2,2'-bipyridine-6'-carboxylic-6-sulfonate, bpc = 2,2'-bipyridine-6-phosphonate-6'-carboxylate, bds = 2,2'-bipyridine-6,6'-disulfonate, bda = 2,2'-bipyridine-6,6'-dicarboxylate, bpa = 2,2'-bipyridine-6,6'-diphosphonate (c) Bond length for ruthenium-based catalysts, data extracted from their crystal structures of catalysts in Figure 1a and 1b; (d) Acid dissociation constant (pKa) at 25°C of commonly used proton relay groups.



Figure S3. Comparison of Ru-bcs with other state-of-the-art single-site water oxidation catalysts under neutral conditions.



Figure S4. Oxygen evolution curve. $[Ce^{V}] = 0.20$ M, $[Cat.] = 8.45 \mu$ M, and V = 3 mL, pH 1.0 triflic acid. TON = 1013.



Figure S5. (a) Initial phase of O_2 evolution versus time at various concentrations of **Ru-bcs**. [Ce^{IV}] = 0.08 M, [cat.] = 25–125 μ M (b) Initial rate of O_2 evolution versus [Cat.] based on the top oxygen evolution plots in the time interval of 13–23 s. The rate constant (O_2 rate = k[cat.]) is calculated by linear fitting of the O_2 evolution rate versus [cat.]. All experiments were carried out in pH 1.0 triflic acid aqueous solution at 298 K with a total volume of 3 mL.



Figure S6. CV curves of 1 mM **Ru-bcs** in pH 1.0 triflic acid aqueous solutions containing 10% TFE at a scanning rate of 100 mV/s. Inset: Enlargement of the 0.7–1.6 V zone in the CV.



Figure S7. Faradaic efficiencies of Ru-bcs for water oxidation in pH 6.95 phosphate buffer (0.2 M) containing 10% CF₃CH₂OH, working electrode: porous glassy carbon (0.35 cm², thickness = 0.4 cm); counter electrode: Pt mesh; applied potential: 1.8 V vs NHE.



Figure S8. (a) Controlled potential electrolysis (1.5 V vs NHE) in pH 6.95 phosphate buffer (0.2 M) containing 10% CF_3CH_2OH with Ru-bcs (1 mM, red) and only with the electrode (gray), working electrode: GC. (b) Controlled potential electrolysis of Ru-bcs with and without stirring.



Figure S9. CV scans of Ru-bcs before and after controlled potential electrolysis at pH 6.95 phosphate buffer (0.2 M) containing 10% CF₃CH₂OH, scan rate = 100 mV s⁻¹, working electrode: GC; inset: enlargement of the 0.4–1.2 V range.

To assess the catalytic stability of Ru-bcs, we conducted CPE under neutral conditions. Remarkably, the catalytic currents remained consistent before and after CPE, with the only noticeable change being the appearance of E_{ox2} after the process. Subsequent to CPE, the electrode was removed from the solution, rinsed with water, and placed into a fresh electrolyte solution without catalyst. The absence of redox and catalytic signals confirms that no active species were deposited on the electrode surface throughout the stability tests.

We also observed an abruptly decrease in current in the first 50 s of reaction, which might be due to tiny gas bubbles covering the electrode surface or a pH decrease caused by catalysis. To support this hypothesis, we repeated the CPE test under stirring (Figure S8b) to minimize bubble formation and pH changes near the electrode. The reduction of current in the first 50 seconds of the reaction was significantly improved.



Figure S10. CV scan rate dependence (0.5–0.9V) with 1 mM Ru-bcs in pH 6.95 phosphate buffer (0.2 M) containing 10% CF₃CH₂OH, and scan rate of 50 to 1000 mV/s.



Figure S11 Plot of the peak current (RullI/II couple) for Ru-bcs vs. the square root of scan rate.



Figure S12 CV scan rate dependence (0.4–1.8 V) with 1 mM Ru-bcs in pH 6.95 phosphate buffer (0.2 M) containing 10% CF₃CH₂OH, and scan rate of 50 to 1000 mV/s.



Figure S13 Enlargement of Figure S8: CV scan rate dependence (0.6–0.8 V) with 1 mM Ru-bcs in pH 6.95 phosphate buffer (0.2 M) containing 10% CF_3CH_2OH , and scan rate of 50 to 1000 mV/s.



Figure S14 Plot of the i_{cat}/i_{p} for Ru-bcs vs. v $^{\text{-1/2}}$, i_{cat} measured at 1.8 V.



Figure S15. Energy profile from density functional theory calculations with optimized geometries. Ru^{III} species (a), Ru^{III} species (b), six-coordinated Ru^{III}-aqua (c), seven-coordinated Ru^{III}-aqua (d), six-coordinated Ru^{III}-aqua (e), Ru^{III}-aqua (f), six-coordinated Ru^{III}-OH (g), seven-coordinated Ru^{III}-OH (h), seven-coordinated Ru^{IV}=O (i), six-coordinated Ru^{IV}=O (j).



Figure S16. DPV curves Ru-bcs under various pH conditions, working electrode: GC.



Figure S17. Potential versus pH diagram for **Ru-bcs** in 10% (vol/vol) TFE obtained from differential pulse voltammograms (DPVs). The asterisks indicate an unknown process related to an unkown species.



Figure S18. CV curves of 1 mM Ru-bcs in a 0.2 M phosphate buffer solution in H₂O and D₂O, (pH = 6.95 and pD = 7.83) containing 10% CF₃CH₂OH, scan rate = 20 mV s⁻¹, working electrode: GC.

Ref:

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