

## Supporting Information

for

# A Ruthenium Water Oxidation Catalyst Based on a Carboxamide Ligand

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**Materials and Methods.** Ru(dmsO)<sub>4</sub>Cl<sub>2</sub><sup>[S1]</sup> and Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>3</sub><sup>[S2]</sup> were prepared according to reported procedures. Ligand **3** (2,6-pyridine-dicarboxamide, Sigma-Aldrich) and methanol (VWR, HPLC grade) were used as received without further purification. <sup>1</sup>H NMR spectra were recorded on a 400 MHz Bruker UltraShield Spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm using residual solvent peak [CD<sub>3</sub>OD ( $\delta$ (H) = 3.31 ppm)] as standard. High-resolution mass spectrometry (HRMS) measurements were recorded on a Bruker Daltonics microTOF spectrometer with an electrospray ionizer. UV-vis absorption spectra were measured on a CARY 300 Bio UV-Visible spectrophotometer. Compounds were centrifuged on a Thermo centrifuge CR3i multifunction at 4000 rpm for 15 minutes. Elemental analyses were carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) at Medac Ltd, Analytical and Chemical Consultancy Services, United Kingdom.

**Single Crystal X-ray Diffraction.** Single crystal X-ray diffraction data were collected from a needle-like red crystal on a Rigaku Saturn 724+ diffractometer at 150(2) K using a synchrotron radiation ( $\lambda$  = 0.6889 Å) at beamline I19, Diamond Light Source, UK. Data reduction was performed using the CrysAlisPro program<sup>[S3]</sup> and multi-scan adsorption correction was applied. Structure was solved by direct method in the SHELXS program.<sup>[S4]</sup> Non-hydrogen atoms were located directly from difference Fourier maps. Final structure refinements were performed with the SHELXL program<sup>[S4]</sup> by minimizing the sum of the squared deviation of  $F^2$  using a full matrix technique. Crystal data: C<sub>25</sub>H<sub>26</sub>F<sub>6</sub>N<sub>6</sub>O<sub>2</sub>PRu, monoclinic,  $C2/c$  with  $a = 26.1423(2)$  Å,  $b = 13.5644(2)$  Å,  $c = 16.4508(3)$  Å and  $\alpha = 90$ ,  $\beta = 98.943$ ,  $\gamma = 90$ .

CCDC 1420348 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

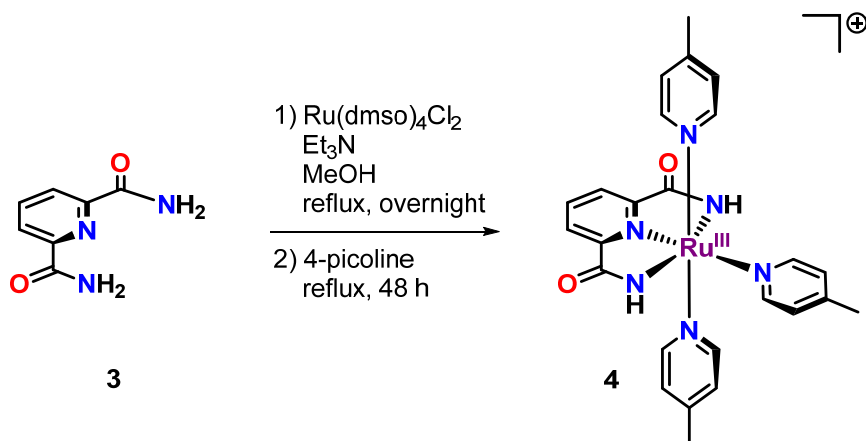
**Electrochemistry.** Electrochemical measurements were carried out with an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie), using a glassy carbon disk (diameter 3 mm) as the working electrode, and a platinum spiral as counter-electrode. The reference electrode was a saturated

calomel electrode (SCE; 3 M KCl aqueous solution) and the electrolyte used was an aqueous phosphate buffer (0.1 M, pH 7.2). All potentials are reported vs. NHE, using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple ( $E_{1/2} = 1.26$  V vs. NHE) as a reference.

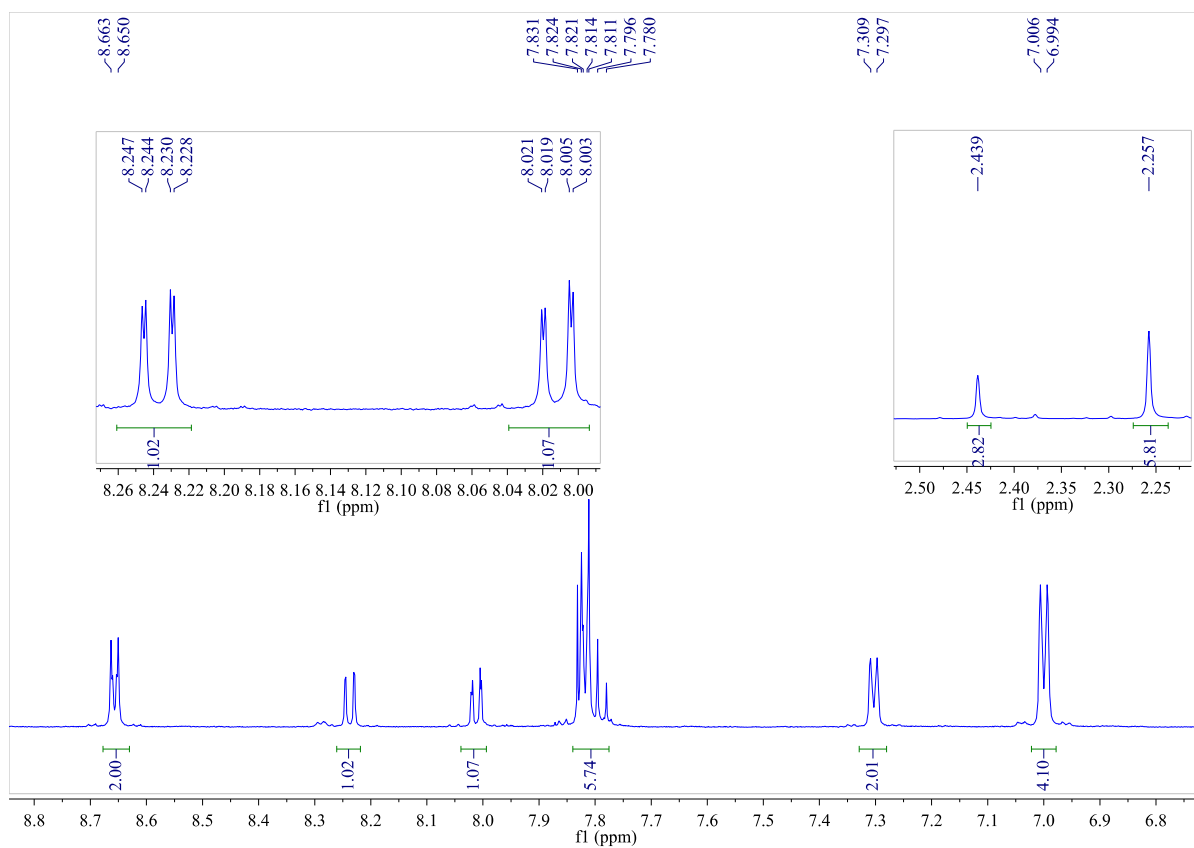
### **Oxygen Evolution Measurements**

**Oxygen Evolution Recorded by Mass Spectrometry.** Stock solutions were made of Ru complex **4** (350  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  1:9. The catalyst solutions used in the experiments were then prepared by diluting the stock solution with phosphate buffer (0.1 M, pH 7.2) to the desired concentrations. The resulting solutions were then deoxygenated by bubbling with  $\text{N}_2$  for at least 15 minutes. In a typical run, the chemical oxidant  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_3$  (3.6 mg, 3.6  $\mu\text{mol}$ ) was placed in the reaction chamber and the vessel was evacuated using a TRIVAC pump (model: D 2.5E) for 10 minutes. 42 mbar He was then introduced into the system. After a few minutes the catalyst solution (0.50 mL) was injected into the reaction chamber. The generated oxygen gas was then measured and recorded by MS.

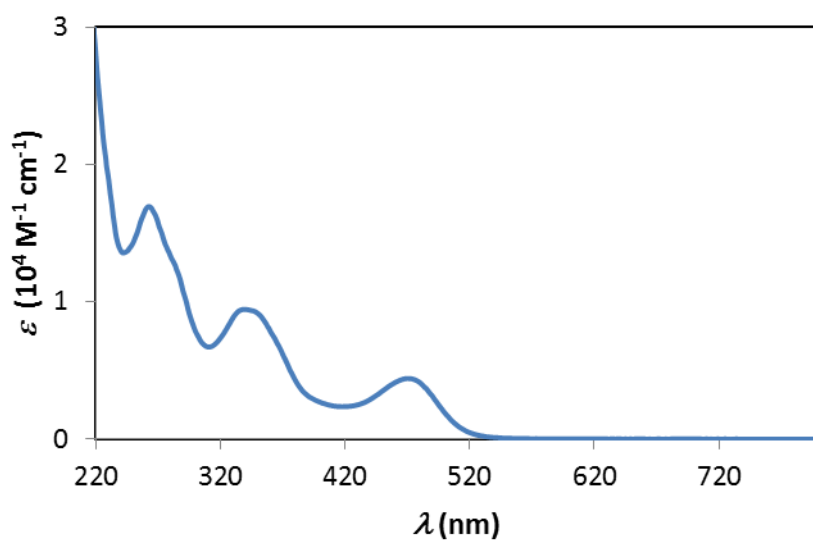
**Oxygen Evolution by Clark Electrode.** Oxygen evolution experiments were performed using a Clark electrode equipped with a Pt cathode and an Ag/AgCl anode (Oxygraph Plus by Hansatech Instruments Ltd.). A stock solution of Ru complex **4** (370  $\mu\text{M}$ ) was prepared in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:9). The desired catalyst solutions were prepared by dilution of the stock solution with 0.1 M phosphate buffer (pH 6.0, pH 7.2 or pH 8.0). The resulting solutions were then deoxygenated by bubbling  $\text{N}_2$  through the solution for at least 15 minutes. Prior to injection, the reaction chamber and chemical oxidant  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_3$  were deoxygenated with  $\text{N}_2$  until the  $\text{O}_2$  reading was zero.



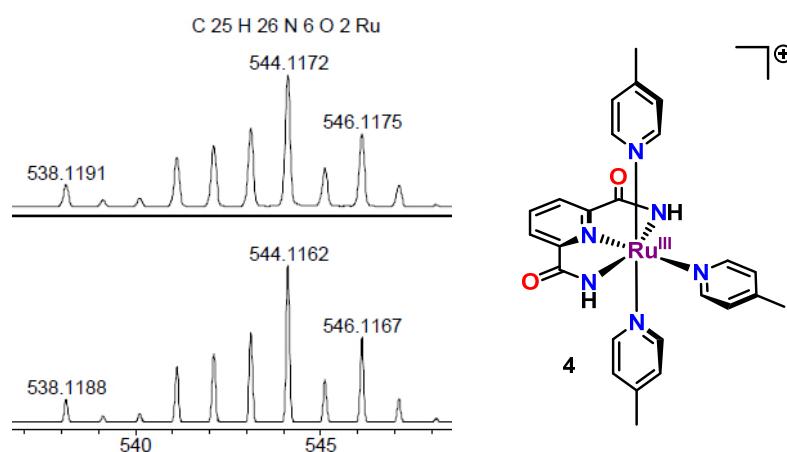
**Synthesis of Ru complex 4 ([Ru(H<sub>2</sub>pdca)(pic)<sub>3</sub>](PF<sub>6</sub>)).** To a mixture of 2,6-pyridine-dicarboxamide (**3**, H<sub>4</sub>pdca, 57.0 mg, 0.351 mmol), and Et<sub>3</sub>N (0.50 mL, 3.51 mmol) in methanol (10 mL) was added Ru(dmsO)<sub>4</sub>Cl<sub>2</sub> (170 mg, 0.351 mmol). The solution was degassed with N<sub>2</sub> and refluxed overnight. Excess of 4-picoline (1.00 mL, 10.5 mmol) was then added and the reaction mixture was subsequently refluxed for another 48 h. The reaction mixture was brought to room temperature and NH<sub>4</sub>PF<sub>6</sub> (171 mg, 1.053 mmol) was added and the resulting mixture was stirred for an additional 30 minutes at room temperature. To this mixture was added 15 mL of deionized H<sub>2</sub>O. The resulting suspension was centrifuged and the precipitate was discarded. The supernatant was stored at 4 °C in a refrigerator for three days producing an orange precipitate which was centrifuged to give Ru complex **4** as orange crystals (70 mg, 29%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD (0.40 mL) + CDCl<sub>3</sub> (0.10 mL), in the presence of ascorbic acid): δ = 8.65 (d, *J* = 6.50 Hz, 2H), 8.23 (dd, *J* = 8.50, 1.50 Hz, 1H), 8.01 (dd, *J* = 6.50, 1.00 Hz, 1H), 7.83–7.78 (m, 5H), 7.3 (d, *J* = 6.00 Hz, 2H), 7.00 (d, *J* = 6.00 Hz, 4H) 2.44 (s, 3H), 2.26 (s, 6H); HRMS-ESI: Calculated for C<sub>25</sub>H<sub>26</sub>N<sub>6</sub>O<sub>2</sub>Ru [M - PF<sub>6</sub>]<sup>+</sup>: 544.1162, found: 544.1172; Anal. Calcd. (%) for C<sub>25</sub>H<sub>28</sub>F<sub>6</sub>N<sub>6</sub>O<sub>3</sub>PRu ([Ru(H<sub>2</sub>pdca)(pic)<sub>3</sub>](PF<sub>6</sub>) · H<sub>2</sub>O): C 42.50, H 3.99, N 11.89 %; found: C 42.61, H 4.20, N 11.75 %.



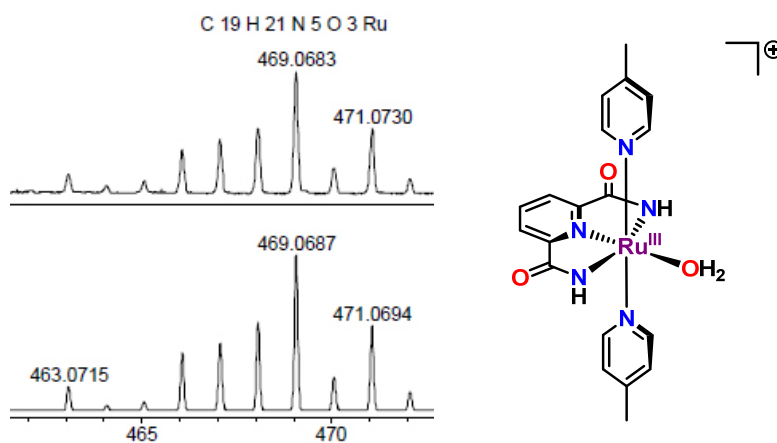
**Figure S1.**  $^1\text{H}$  NMR spectrum of Ru complex **4** in  $\text{CD}_3\text{OD}/\text{CDCl}_3$  (4:1) in the presence of ascorbic acid.



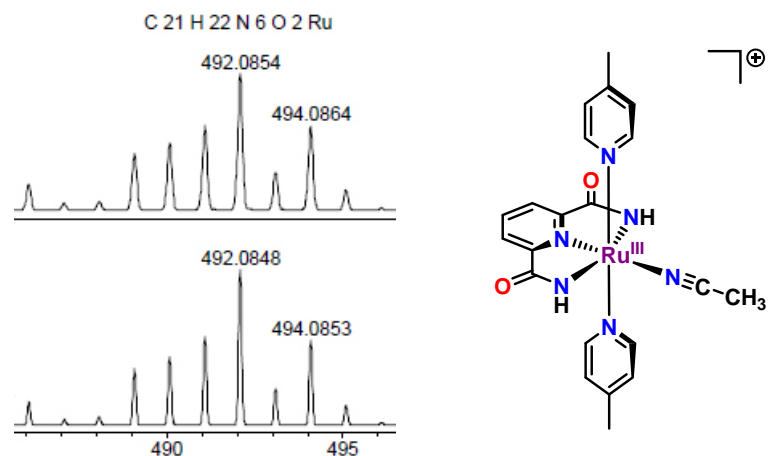
**Figure S2.** UV-vis spectrum of Ru complex **4** in an aqueous phosphate buffer solution (0.1 M, pH 7.2).



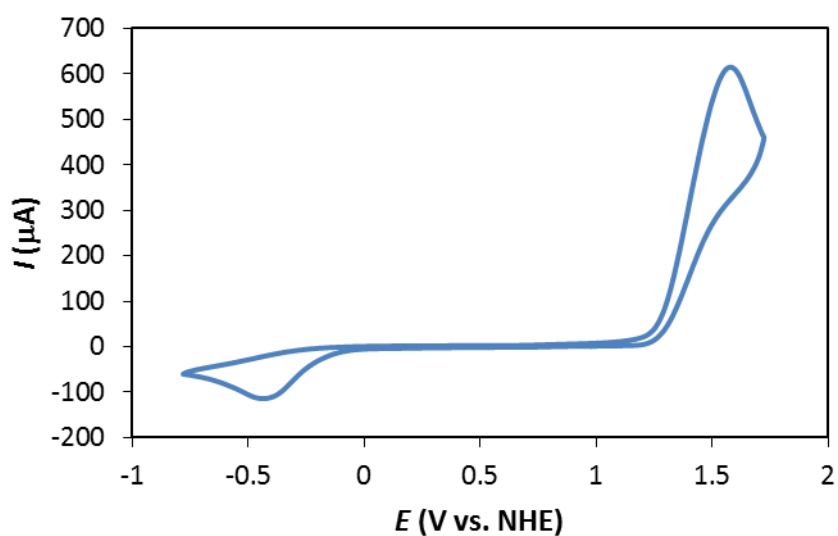
**Figure S3.** (Upper) Experimental high-resolution mass spectrum of Ru complex **4** ( $[\text{Ru}^{\text{III}}(\text{H}_2\text{pdca})(\text{pic})_3]^+$ ) in positive mode and (lower) simulated spectrum.



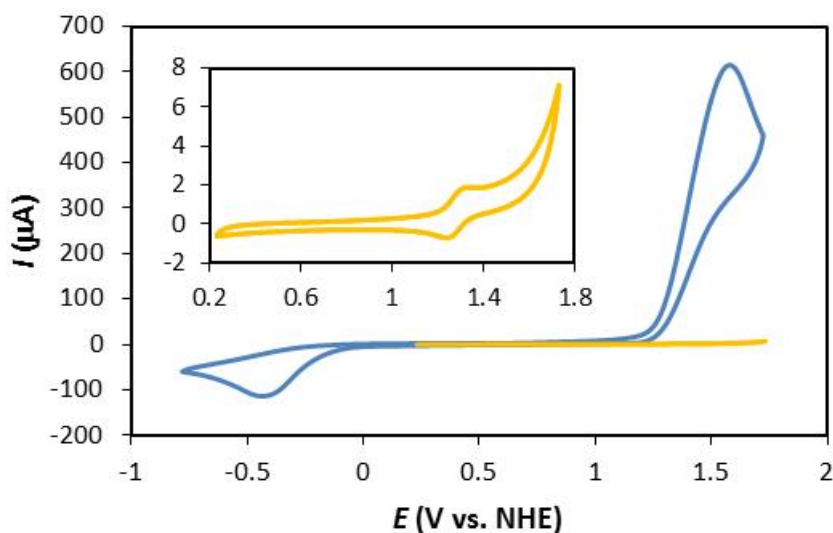
**Figure S4.** (Upper) Experimental high-resolution mass spectrum of the corresponding aqua complex of Ru complex **4** ( $[\text{Ru}^{\text{III}}(\text{H}_2\text{pdca})(\text{pic})_2(\text{OH}_2)]^+$ ) in positive mode and (lower) simulated spectrum.



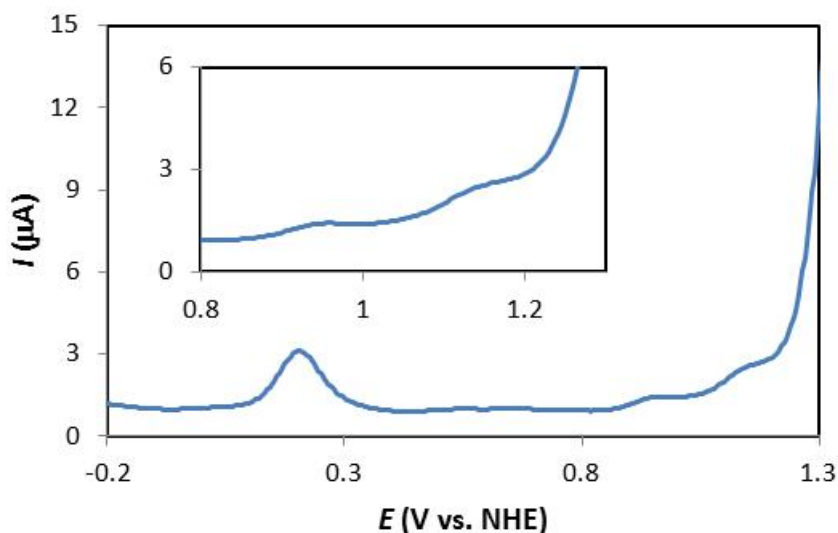
**Figure S5.** (Upper) Experimental high-resolution mass spectrum of the corresponding acetonitrile complex of Ru complex **4** ( $[\text{Ru}^{\text{III}}(\text{H}_2\text{pdca})(\text{pic})_2(\text{MeCN})]^+$ ) in positive mode and (lower) simulated spectrum.



**Figure S6.** Cyclic voltammogram of Ru complex **4** at pH 7.2. Conditions: Voltammogram was recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing complex **4** with a scan rate of  $0.1 \text{ V s}^{-1}$ , using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple as a standard ( $E_{1/2} = 1.26 \text{ V vs. NHE}$ ).

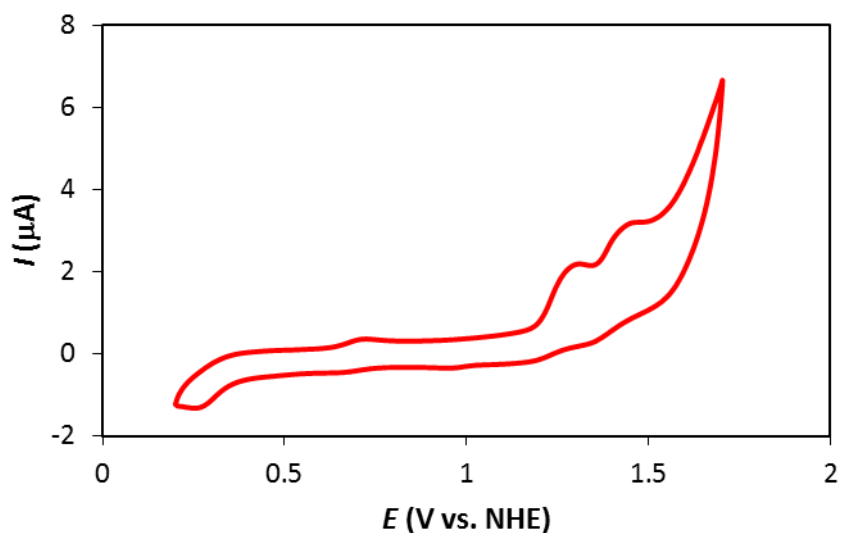


**Figure S7.** Cyclic voltammograms of Ru complex **4** (—) and  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  (—) at pH 7.2. Inset: Enlarged voltammogram of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  in the range  $0.20 < E < 1.80$  V. Conditions: Voltammograms were recorded in aqueous phosphate buffer solutions (0.1 M, pH 7.2) containing complex **4** or  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  with a scan rate of  $0.1 \text{ V s}^{-1}$ , using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple as a standard ( $E_{1/2} = 1.26 \text{ V vs. NHE}$ ).

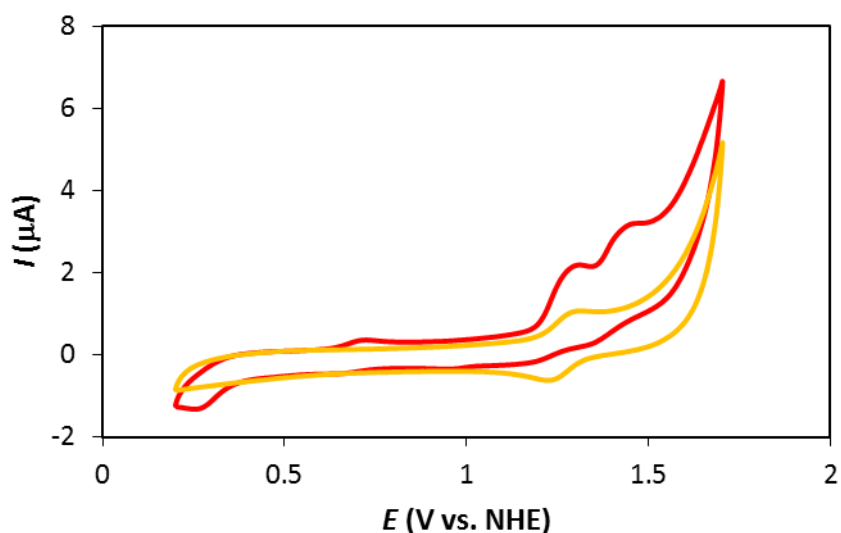


**Figure S8.** Differential pulse voltammogram of Ru complex **4** (—) at pH 7.2. Inset: Enlarged voltammogram in the range  $0.80 < E < 1.30$  V. Conditions: Voltammogram was recorded in an aqueous phosphate buffer solution (0.1 M, pH 7.2) containing Ru complex **4** with a scan rate of  $0.1 \text{ V s}^{-1}$ , using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple as a standard ( $E_{1/2} = 1.26 \text{ V vs. NHE}$ ).

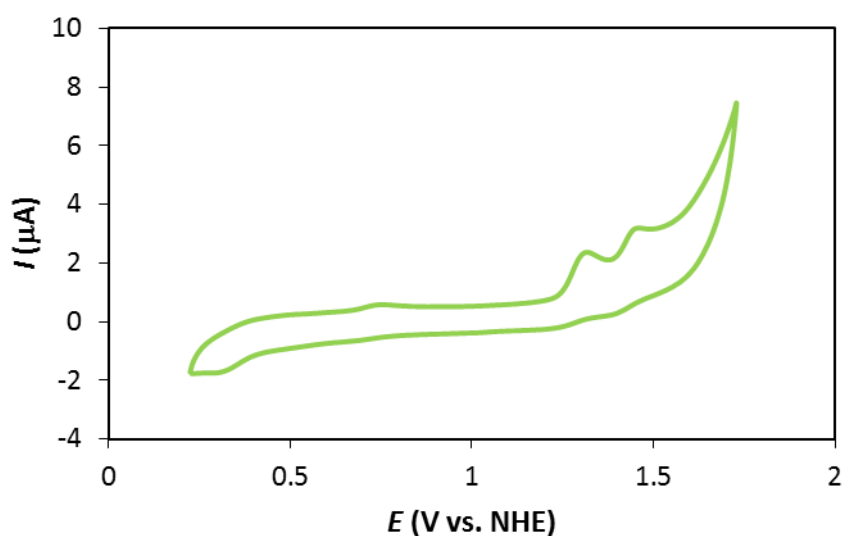




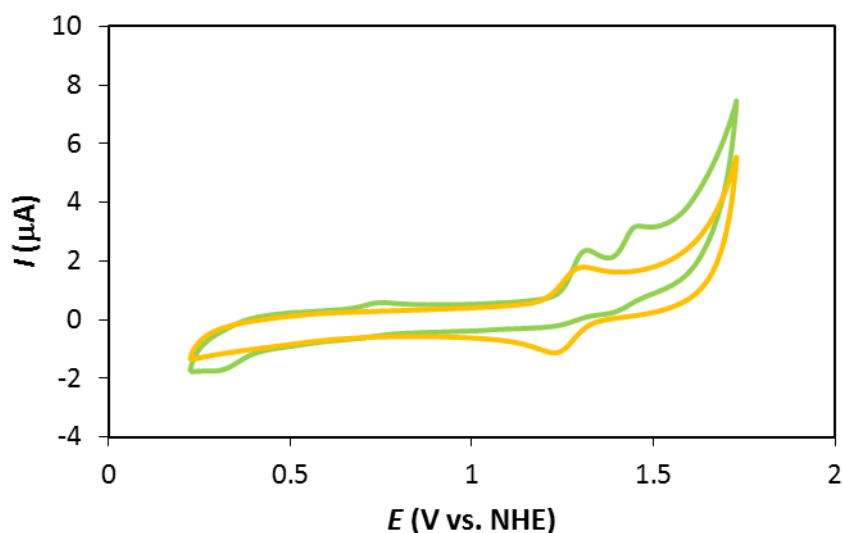
**Figure S9.** Cyclic voltammogram of Ru complex **4** (—) in an aqueous phosphoric acid solution at pH 1.0. Conditions: Voltammogram was recorded in an aqueous phosphoric acid solution (0.1 M, pH 1.0) containing complex **4** with a scan rate of  $0.1 \text{ V s}^{-1}$ , using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple as a standard ( $E_{1/2} = 1.26 \text{ V vs. NHE}$ ).



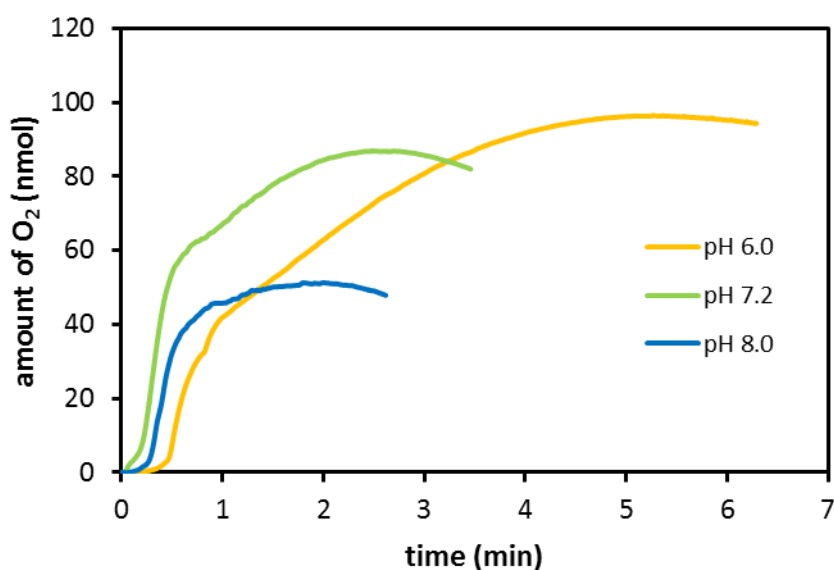
**Figure S10.** Cyclic voltammograms of Ru complex **4** (—) and  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  (—) in aqueous phosphoric acid solutions at pH 1.0. Conditions: Voltammograms were recorded in aqueous phosphoric acid solutions (0.1 M, pH 1.0) containing complex **4** or  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  with a scan rate of  $0.1 \text{ V s}^{-1}$ , using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple as a standard ( $E_{1/2} = 1.26 \text{ V vs. NHE}$ ).



**Figure S11.** Cyclic voltammogram of Ru complex **4** (—) in an aqueous triflic acid solution at pH 1.0. Conditions: Voltammogram was recorded in an aqueous triflic acid solution (0.1 M, pH 1.0) containing complex **4** with a scan rate of  $0.1 \text{ V s}^{-1}$ , using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple as a standard ( $E_{1/2} = 1.26 \text{ V vs. NHE}$ ).



**Figure S12.** Cyclic voltammograms of Ru complex **4** (—) and  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  (—) in aqueous triflic acid solutions at pH 1.0. Conditions: Voltammograms were recorded in aqueous triflic acid solutions (0.1 M, pH 1.0) containing complex **4** or  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  with a scan rate of  $0.1 \text{ V s}^{-1}$ , using the  $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$  couple as a standard ( $E_{1/2} = 1.26 \text{ V vs. NHE}$ ).



**Figure S13.** Oxygen evolution at different pH. Reaction conditions: An aqueous phosphate buffer solution (0.1 M, pH 6.0, 7.2, or 8.0, 0.50 mL) containing Ru complex **4** (1.94  $\mu\text{M}$ ) was added to the oxidant  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_3$  (3.6 mg, 3.6  $\mu\text{mol}$ ) and the generated  $\text{O}_2$  was measured by a Clark electrode.

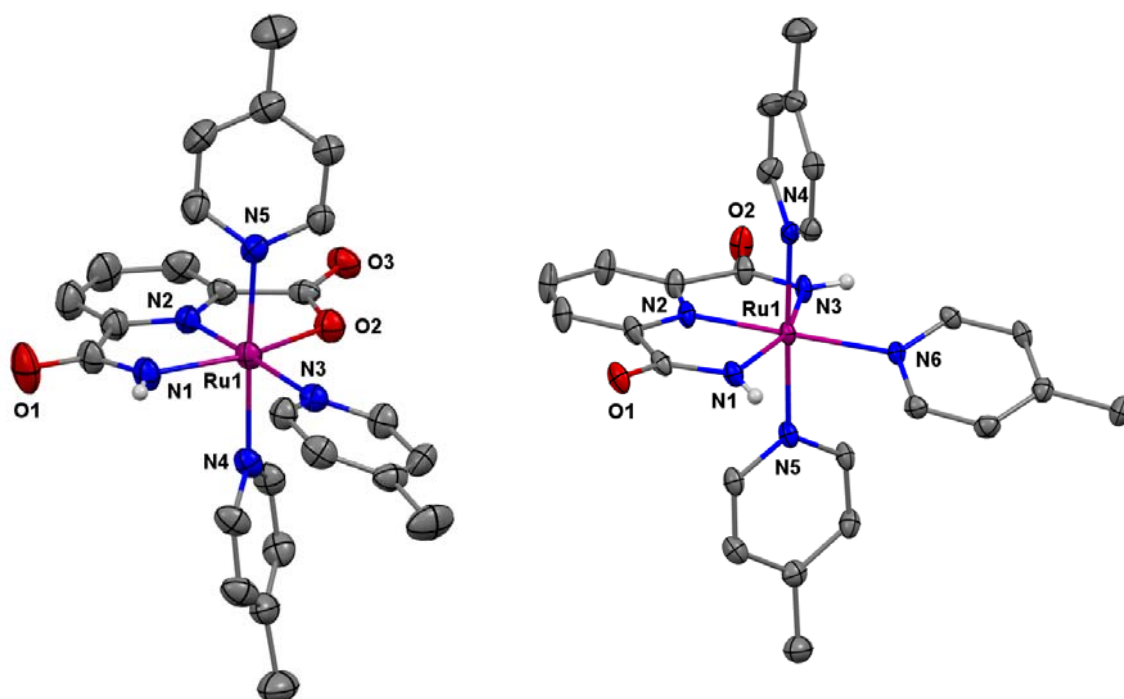
**Table S1.** Summary of the catalytic data for Ru complex **4** at different pH.<sup>a</sup>

pH	Evolved $\text{O}_2$ (nmol)	TON (nmol $\text{O}_2$ /nmol cat.)	TOF (nmol $\text{O}_2 \cdot \text{s}^{-1}$ /nmol cat.)
6.0	96.5	99.5	1.76
7.2	86.8	89.5	2.92
8.0	51.0	52.6	2.23

<sup>a</sup> An aqueous phosphate buffer solution (0.1 M, pH 6.0, 7.2, or 8.0, 0.50 mL) containing Ru complex **4** (1.94  $\mu\text{M}$ ) was added to the oxidant  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_3$  (3.6 mg, 3.6  $\mu\text{mol}$ ) and the generated  $\text{O}_2$  was measured by a Clark electrode.

**Table S2.** Crystal data and structure refinement for Ru complex **4** ([Ru(H<sub>2</sub>pdca)(pic)<sub>3</sub>](PF<sub>6</sub>)).

Compound	<b>4</b>
Empirical formula	C <sub>25</sub> H <sub>26</sub> F <sub>6</sub> N <sub>6</sub> O <sub>2</sub> PRu
Formula weight	688.56
Temperature	293(2) K
Wavelength	0.6889 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell parameters	$a = 26.1423(2)$ Å $b = 13.5644(2)$ Å $c = 16.4508(3)$ Å $\alpha = 90^\circ$ $\beta = 98.9430(10)^\circ$ $\gamma = 90^\circ$
Volume	5762.61(14) Å <sup>3</sup>
Z	8
Density (calculated)	1.587 Mg/m <sup>3</sup>
Absorption coefficient	0.611 mm <sup>-1</sup>
F(000)	2776
Crystal size	0.20 x 0.05 x 0.05 mm <sup>3</sup>
Theta range for data collection	1.58 to 26.37°
Index ranges	$-32 \leq h \leq 19$ , $-16 \leq k \leq 16$ , $-17 \leq l \leq 20$
Reflections collected	20082
Independent reflections	5746 [ $R_{\text{int}} = 0.0228$ ]
Completeness to theta = 26.37°	97.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.967 and 0.960
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	5746 / 0 / 370
Goodness-of-fit on $F^2$	0.960
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0304$ , $wR_2 = 0.1086$
$R$ indices (all data)	$R_1 = 0.0330$ , $wR_2 = 0.1127$
Largest diff. peak and hole	0.829 and $-0.626$ ( $e, \text{Å}^{-3}$ )



**Figure S14.** Comparison of the crystal structures of single-site Ru complexes **2** (left) and **4** (right). Hydrogen atoms (except the N-H) and PF<sub>6</sub> have been omitted for clarity.

**Table S3.** Comparison of selected bond lengths (Å) and angles (°) for Ru complexes **2** and **4**.

Bond Lengths			
Complex 2		Complex 4	
Ru(1)-N(1)	2.024(3)	Ru(1)-N(1)	2.032(2)
Ru(1)-N(2)	1.958(3)	Ru(1)-N(2)	1.973(2)
Ru(1)-O(2)	2.043(3)	Ru(1)-N(3)	2.033(2)
Ru(1)-N(5)	2.095(3)	Ru(1)-N(4)	2.110(2)
Ru(1)-N(4)	2.087(3)	Ru(1)-N(5)	2.098(2)
Ru(1)-N(3)	2.108(3)	Ru(1)-N(6)	2.117(2)
Bond Angles			
Complex 2		Complex 4	
N(1)-Ru(1)-N(2)	79.6(1)	N(1)-Ru(1)-N(2)	79.50(8)
N(1)-Ru(1)-O(2)	160.0(1)	N(1)-Ru(1)-N(3)	158.98(7)
N(1)-Ru(1)-N(5)	93.4(1)	N(1)-Ru(1)-N(4)	88.20(7)
N(1)-Ru(1)-N(4)	88.5(1)	N(1)-Ru(1)-N(5)	91.18(7)
N(1)-Ru(1)-N(3)	100.2(1)	N(1)-Ru(1)-N(6)	102.18(7)
N(2)-Ru(1)-O(2)	80.4(1)	N(2)-Ru(1)-N(3)	79.55(8)
N(2)-Ru(1)-N(5)	90.5(1)	N(2)-Ru(1)-N(4)	89.48(7)
N(2)-Ru(1)-N(4)	92.4(1)	N(2)-Ru(1)-N(5)	92.64(7)
N(2)-Ru(1)-N(3)	178.1(1)	N(2)-Ru(1)-N(6)	178.27(7)
O(2)-Ru(1)-N(5)	88.0(1)	N(3)-Ru(1)-N(4)	93.30(7)
O(2)-Ru(1)-N(4)	91.1(1)	N(3)-Ru(1)-N(5)	88.10(7)
O(2)-Ru(1)-N(3)	99.7(1)	N(3)-Ru(1)-N(6)	98.76(7)
N(4)-Ru(1)-N(5)	176.8(1)	N(4)-Ru(1)-N(5)	177.64(7)

N(3)-Ru(1)-N(5)	91.4(1)	N(4)-Ru(1)-N(6)	90.96(7)
N(3)-Ru(1)-N(4)	85.7(1)	N(5)-Ru(1)-N(6)	86.95(7)

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## Supporting References

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- [S2] R. E. DeSimone, R. S. Drago, *J. Am. Chem. Soc.* 1970, **92**, 2343–2352.
- [S3] CrysAlis Software System, Version 171.37.33, Agilent Technol. 2014.
- [S4] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112–122; b) G. M. Sheldrick, Program for Solution of Crystal structure, 1997.