Electronic Supplementary Information for Dalton Transactions

Highly active and tunable catalysts for O_2 evolution from water based on mononuclear ruthenium (II) monoaquo complexes

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Supporting Information

1. Synthesis and characterization of $[Ru(Rtpy)(bpy)OH_2]^{2+}$ complexes

(1) $[Ru(tpy)(bpy)OH_2](NO_3)_2$ (**1**$(NO_3)_2$)

1$(NO_3)_2$ was prepared in the procedure described in the literature,[S1] and characterized by UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (H_2O) : λ_{max} (ε) = 231 (23,900), 288 (34,200), 312 (33,100), 350 (4,400), and 477 nm (9,600 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, D_2O): δ 9.36 (d, J = 5.4 Hz, 1H), 8.49 (d, J = 8.1 Hz, 1H), 8.41 (d, J = 8.1 Hz, 2H), 8.26 (d, J = 8.0 Hz, 2H), 8.15 (t, J = 7.0 Hz, 2H), 8.04 (t, J = 8.1 Hz, 1H), 7.86 (d, J = 6.6 Hz, 1H), 7.79 (t, J = 8.3 Hz, 1H), 7.62 (d, J = 5.4 Hz, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.13 (m, 3H), and 6.74 ppm (t, J = 7.4 Hz, 1H).

(2) $[Ru(EtOtpy)(bpy)OH_2](NO_3)_2$ (**1a**$(NO_3)_2$)

4'-Ethoxy-2,2':6',2''-terpyridine (EtOtpy)

EtOtpy was prepared referring to the literatures.[S2,S3] 100 mg (0.37 mmol) of 4'-chloro-2,2';6',2''-terpyridine was added into a 25wt% sodium ethoxide solution (8.5 ml) in ethanol and refluxed under N_2 atmosphere for 24 h. The resulted suspension was allowed to be cooled to room temperature and insolubles were removed by suction filtration. The yellow-tan filtrate was added to water, giving the white precipitates of EtOtpy (94.6 mg, 91% yield). It was characterized by NMR spectroscopic measurement.

Ru(EtOtpy)Cl$_3$

Ru(EtOtpy)Cl$_3$ was prepared referring to the literature.[S4] An anhydrous ethanol solution containing 100 mg (0.36 mmol) of EtOtpy and 97 mg (0.47 mmol) of $RuCl_3$ was refluxed for 3 h. After cooling to room temperature, the precipitates were filtered and washed with anhydrous ethanol and ether, and then dried in vacuo at room temperature to give Ru(EtOtpy)Cl$_3$ (170 mg, 97% yield). It was characterized by UV-VIS spectroscopic measurement. UV-Visible spectrum (DMSO) : λ_{max} (ε) = 277 (25,600) and 400 nm (6,700 M^{-1} cm^{-1}).

[Ru(EtOtpy)(bpy)Cl]Cl

[Ru(EtOtpy)(bpy)Cl]Cl was prepared according to the literature.[S1] 90 mg (0.186 mmol) of Ru(EtOtpy)Cl_3 and 29 mg (0.186 mmol) of 2,2'-bipyridine (bpy) were refluxed for 4 h in 16.3 ml of 75 (v/v)% ethanol / water containing 8.1 mg (0.192 mmol) of LiCl and 41 μl (29.4 μmol) of triethylamine as a reductant. The hot contents in the vessel were filtered and then concentrated to ~ 4 ml with a rotary evaporator. The solution was then chilled in a refrigerator for 24 h. The solid was collected on a frit and washed with chilled 3 M HCl, acetone and anhydrous ether, and then dried in vacuo at room temperature to give [Ru(EtOtpy)(bpy)Cl]Cl (86.1 mg, 76% yield). It was characterized by UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (CH_3OH) : λ_{max} (ε) = 243 (28,400), 282 (30,000), 295 (33,400), 311 (24,800), 359 (7,000), and 501 nm (11,900 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, CD_3OD) : δ 10.1 (d, J = 5.6 Hz, 1H), 8.67 (d, J = 8.2 Hz, 1H), 8.46 (d, J = 8.0 Hz, 2H), 8.40 (d, J = 8.2 Hz, 1H), 8.21 (s, 2H), 8.18 (dd, J = 1.5 and 1.1 Hz, 1H), 7.86 (m, 3H), 7.66 (dd, J = 1.4 and 1.2 Hz, 1H), 7.61 (d, J = 5.4 Hz, 2H), 7.39 (d, J = 5.6 Hz, 1H), 7.22 (dtd, J = 3.2, 1.2 and 1.2 Hz, 2H), 6.99 (dtd, J = 3.1, 1.3 and 1.2 Hz, 1H), 4.46 (q, J = 7.0 Hz, 2H), and 1.54 ppm (t, J = 14 Hz, 3H). Anal. calcd. for $C_{27}H_{23}Cl_2N_5ORu\cdot0.5LiCl$: C, 51.75; H, 3.70; N, 11.18; Found: C, 51.41; H, 3.34; N, 11.35.

***1a**(NO$_3$)$_2$*

1a(NO_3)$_2$ was prepared referring to the literature.[S1] 50 mg (82.5 μmol) of [Ru(EtOtpy)(bpy)Cl]Cl and 28.1 mg (0.165 mmol) of $AgNO_3$ were refluxed for 1 h in 5.7 ml of 75 (v/v)% acetone / H_2O. AgCl precipitated in the contents was filtered off, and the mixture was chilled in a refrigerator after concentrating to ~1.5 ml with a rotary evaporator. Dark-red crystals of **1a**(NO_3)$_2$ were collected on a frit and washed with cold water, and then dried in vacuo at 60 ^{o}C to give **1a**(NO_3)$_2$ (38.6 mg, 69% yield). It was characterized by UV-VIS and NMR spectroscopic measurements and X-ray structure analysis. UV-Visible spectrum (H_2O) : λ_{max} (ε) = 242 (35,900), 274 (36,900), 290 (43,100), 307 (33,200), 353 (6,100), and 478 nm (12,000 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, D_2O) : δ 9.34 (d, J = 5.4 Hz, 1H), 8.47 (d, J = 8.2 Hz, 1H), 8.24 (d, J = 7.9 Hz, 2H), 8.12 (t, J = 8.4 Hz, 2H), 8.01 (s, 2H), 7.77 (td, J = 8.5 and 8.7Hz, 3H), 7.63 (d, J = 5.1 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.25 (d, *J* = 5.6 Hz, 1H), 7.12 (t, *J* = 6.5 Hz, 2H), 6.78 (t, *J* = 6.7 Hz, 1H), 4.39 (q, *J* = 6.9 Hz, 2H), and 1.43 ppm (t, *J* = 6.9 Hz, 3H). Anal. calcd. for $C_{27}H_{25}N_7O_8Ru$: C, 47.93; H, 3.72; N, 14.49; Found: C, 47.93; H, 3.65; N, 14.45.

(3) $[Ru(MeOtpy)(bpy)OH_2](NO_3)_2$ (**1b**$(NO_3)_2$)

4'-Methoxy-2,2':6',2''-terpyridine (MeOtpy)

MeOtpy was prepared and characterized by NMR spectroscopic measurement in the procedure described in the literature.[S3]

Ru(MeOtpy)Cl$_3$

Ru(MeOtpy)Cl$_3$ was prepared using MeOtpy (44 mg, 0.167 mmol) instead of EtOtpy in the same procedure as Ru(EtOtpy)Cl$_3$ (77.7 mg, 98% yield). Ru(MeOtpy)Cl$_3$ was characterized by UV-VIS spectroscopic measurement. UV-Visible spectrum (DMSO) : λ_{max} (ε) = 277 (22,800) and 401 nm (7,300 M^{-1} cm^{-1}).

[Ru(MeOtpy)(bpy)Cl]Cl

[Ru(MeOtpy)(bpy)Cl]Cl was prepared from Ru(MeOtpy)Cl$_3$ (70 mg, 0.149 mmol) in the same procedure as [Ru(EtOtpy)(bpy)Cl]Cl (57.4 mg, 65% yield). It was characterized by UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (CH_3OH) : λ_{max} (ε) = 243 (28,400), 282 (30,000), 295 (33,400), 312 (25,400), 366 (6,900), and 500 nm (12,400 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, CD_3OD) : δ 10.1 (d, *J* = 5.7 Hz, 1H), 8.66 (d, *J* = 8.1 Hz, 1H), 8.47 (d, *J* = 7.9 Hz, 2H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.25 (s, 2H), 8.19 (ddd, *J* = 1.54, 1.51 and 1.1 Hz, 1H), 7.84 (m, 3H), 7.66 (dd, *J* = 1.4 and 1.0 Hz, 1H), 7.61 (d, *J* = 4.7 Hz, 2H), 7.38 (d, *J* = 5.6 Hz, 1H), 7.22 (dtd, *J* = 3.3, 1.3 and 1.2 Hz, 2H), 6.98 (dtd, *J* = 3.0, 1.2 and 1.2 Hz, 1H), and 4.17 ppm (s, 3H). Anal. calcd. for $C_{26}H_{21}Cl_2N_5ORu \cdot CH_3OH$: C, 52.01; H, 4.04; N, 11.23; Found: C, 52.34; H, 4.01; N, 11.10.

***1b**$(NO_3)_2$*

1b$(NO_3)_2$ was prepared from [Ru(MeOtpy)(bpy)Cl]Cl (30 mg, 50.7 μmol) in the same procedure as **1a**$(NO_3)_2$ (24.3 mg, 72% yield). **1b**$(NO_3)_2$ was characterized by UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (H_2O) : λ_{max} (ε) = 218 (24,300), 240 (31,500), 289 (38,100), 306 (32,200), 350 (6,700), and 479 nm (12,700 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, D_2O) : δ 9.35 (d, J = 5.5 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.0 Hz, 2H), 8.13 (t, J = 8.3 Hz, 2H), 8.05 (s, 2H), 7.80 (dt, J = 7.1 and 8.2 Hz, 3H), 7.63 (d, J = 5.0 Hz, 2H), 7.50 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 5.7 Hz, 1H), 7.13 (t, J = 6.5 Hz, 2H), 6.78 (t, J = 6.2 Hz, 1H), and 4.08 ppm (s, 3H). Anal. calcd. for $C_{26}H_{23}N_7O_8Ru \cdot 0.25H_2O$: C, 46.81; H, 3.55; N, 14.70; Found: C, 46.95; H, 3.53; N, 14.58.

(4) $[Ru(Metpy)(bpy)OH_2](NO_3)_2$ (**1c**$(NO_3)_2$)

4'-Methyl-2,2':6',2''-terpyridine (Metpy)

Metpy was prepared and characterized by NMR spectroscopic measurement in the procedure described in the literatures.[S5, S6]

Ru(Metpy)Cl$_3$

Ru(Metpy)Cl_3 was prepared using Metpy (94.6 mg, 0.383 mmol) instead of EtOtpy in the same procedure as Ru(EtOtpy)Cl_3 (163 mg, 93% yield). Ru(Metpy)Cl_3 was characterized by UV-VIS spectroscopic measurement. UV-Visible spectrum (DMSO) : λ_{max} (ε) = 275 (17,300), 311 (15,700), and 404 nm (5,000 M^{-1} cm^{-1}).

[Ru(Metpy)(bpy)Cl]Cl

[Ru(Metpy)(bpy)Cl]Cl was prepared from Ru(Metpy)Cl_3 (100 mg, 0.22 mmol) in the same procedure as [Ru(EtOtpy)(bpy)Cl]Cl (78.7 mg, 62% yield). It was characterized by UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (CH_3OH) : λ_{max} (ε) = 241 (26,000), 289 (28,300), 294 (30,000), 316 (25,100), 367 (5,500), and 499 nm (10,100 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, CD_3OD) : δ 10.0 (d, J = 5.8 Hz, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.46 (s, 2H), 8.40 (m, 3H), 8.20 (ddd, J = 1.4, 1.4 and 1.1 Hz, 1H), 7.85 (m, 3H), 7.65 (dd, J = 1.3 and 0.8 Hz, 1H), 7.59 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 5.4 Hz, 1H), 7.21 (dtd, J

= 3.2, 1.2 and 1.2 Hz, 2H), 6.95 (dtd, *J* = 2.8, 1.2 and 1.1 Hz, 1H), and 2.77 ppm (s, 3H). Anal. calcd. for $C_{26}H_{21}Cl_2N_5Ru\cdot H_2O$: C, 52.62; H, 3.91; N, 11.80; Found: C, 52.78; H, 3.93; N, 11.66.

***1c**(NO$_3$)$_2$*

1c(NO_3)$_2$ was prepared from [Ru(Metpy)(bpy)Cl]Cl (50 mg, 0.087 mmol) in the same procedure as **1a**(NO_3)$_2$ (35.5 mg, 63% yield). **1c**(NO_3)$_2$ was characterized by UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (H_2O) : λ_{max} (ε) = 235 (24,700), 288 (34,200), 310 (29,400), 350 (4,800), and 477 nm (11,000 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, D_2O) : δ 9.36 (d, *J* = 5.3 Hz, 1H), 8.49 (d, *J* = 8.3 Hz, 1H), 8.32 (s, 2H), 8.24 (d, *J* = 8.2 Hz, 2H), 8.15 (t, *J* = 6.3 Hz, 2H), 7.82 (dt, *J* = 6.3 and 8.0 Hz, 3H), 7.62 (d, *J* = 5.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 5.5 Hz, 1H), 7.14 (t, *J* = 6.6 Hz, 2H), 6.76 (t, *J* = 6.4 Hz, 1H) and 2.68 ppm (s, 3H). Anal. calcd. for $C_{26}H_{23}N_7O_7Ru\cdot H_2O$: C, 46.99; H, 3.79; N, 14.75; Found: C, 46.94; H, 3.91; N, 14.66.

(5) [Ru(Cltpy)(bpy)OH_2](NO_3)$_2$ (**1d**(NO_3)$_2$)

4'-Chloro-2,2';6',2''-terpyridine (Cltpy)

Cltpy was prepared and characterized by NMR spectroscopic measurement in the procedure described in the literature.[S7]

Ru(Cltpy)Cl$_3$

Ru(Cltpy)Cl_3 was prepared using the Cltpy (100 mg, 0.373 mmol) instead of EtOtpy in the same procedure as Ru(EtOtpy)Cl_3 (163.2 mg, 92% yield). Ru(Cltpy)Cl_3 was characterized by UV-VIS spectroscopic measurement. UV-Visible spectrum (DMSO) : λ_{max} (ε) = 253 (22,200), 274 (20,500), 312 (16,500), and 408 nm (5,300 M^{-1} cm^{-1}).

[Ru(Cltpy)(bpy)Cl]Cl

[Ru(Cltpy)(bpy)Cl]Cl was prepared from Ru(Cltpy)Cl_3 (80 mg, 0.168 mmol) in the same procedure as [Ru(EtOtpy)(bpy)Cl]Cl (70.1 mg, 75% yield). It was characterized by

UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (CH_3OH) : λ_{max} (ε) = 242 (37,300), 285 (32,400), 293 (32,200), 317 (27,200), 366 (5,500), and 499 nm (9,400 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, CD_3OD) : δ 10.0 (d, *J* = 4.9 Hz, 1H), 8.75 (s, 2H), 8.70 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 2H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.25 (ddd, *J* = 1.5, 1.5 and 1.4 Hz, 1H), 7.90 (m, 3H), 7.69 (dd, *J* = 1.3 and 1.1 Hz, 1H), 7.64 (d, *J* = 5.1 Hz, 2H), 7.35 (d, *J* = 5.3 Hz, 1H), 7.28 (dtd, *J* = 3.2, 1.2 and 1.2 Hz, 2H), and 6.97 ppm (dtd, *J* = 3.1, 1.3 and 1.2 Hz, 1H).Anal. calcd. for $C_{25}H_{18}Cl_3N_5Ru\cdot 1.5H_2O$: C, 48.21; H, 3.40; N, 11.24; Found: C, 48.26; H, 3.32; N, 11.47.

1d(NO$_3$)$_2$

1d(NO_3)$_2$ was prepared from [Ru(Cltpy)(bpy)Cl]Cl (50 mg, 0.089 mmol) in the similar procedure to **1a**(NO_3)$_2$ (55.7 mg, 75% yield). **1d**(NO_3)$_2$ was characterized by UV-VIS and NMR spectroscopic measurements. UV-Visible spectrum (H_2O) : λ_{max} (ε) = 239 (34,100), 282 (39,800), 311 (35,100), 350 (5,000), and 477 nm (11,000 M^{-1} cm^{-1}). ^{1}H-NMR (270 MHz, D_2O) : δ 9.36 (d, *J* = 5.3 Hz, 1H), 8.54 (s, 2H), 8.51 (d, *J* = 8.3 Hz, 2H), 8.27 (d, *J* = 8.2 Hz, 2H), 8.18 (t, *J* = 7.2 Hz, 2H), 7.84 (dt, *J* = 6.5 and 8.1 Hz, 3H), 7.65 (d, *J* = 5.0 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.18 (dt, *J* = 5.8 and 4.9 Hz, 3H), and 6.78 ppm (t, *J* = 6.9 Hz, 1H). Anal. calcd. for $C_{25}H_{20}ClN_7O_7Ru\cdot H_2O$: C, 43.83; H, 3.24; N, 14.31; Found: C, 43.77; H, 3.33; N, 14.50.

References

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2. Experimental details

The cyclic voltammograms (CV) were measured in a 0.5 mM **1a** solutions (pH = 1.0) using a conventional single-compartment electrochemical cell equipped with a glassy carbon rod working electrode (effective area, 0.071 cm^2), a saturated calomel (SCE) reference electrode and a Pt wire counter electrode. The differential pulse voltammograms (DPVs) were taken under the conditions: pulse amplitude (E_{step}), 50 mV; pulse width, 10 ms; pulse period, 250 ms; scan rate, 5 mV s^{-1}. For Pourbaix diagram, the pHs of the solutions were buffered at an ionic strength of 0.1 M by HNO_3 (pH 0-2), Na_2HPO_4 and KH_2PO_4 (pH 3-10), and NaOH (pH 11-14). At pH = 0 and 14, the ionic strength was 1 M (1 M HNO_3 and 1 M NaOH, respectively). All the electrochemical experiments were implemented under argon atmosphere at 25°C using an electrochemical analyzer (Hokuto Denko, HZ-3000). For chemical water oxidation catalysis, an excess $Ce(NH_4)_2(NO_3)_6$ (0.5 mmol) as an oxidant was added quickly to a 20 μM $[Ru(Rtpy)(bpy)OH_2]^{2+}$ aqueous solution (5.0 ml) in a gas-tight vessel under argon atmosphere at 25°C and pH = 1.0 in typical conditions. The pH change during the reaction for several hours was less than 0.1. The O_2 gas in the head space of the vessel was analyzed on a gas chromatograph (Shimadzu, GC-8A) equipped with a molecular sieve 5Å column using argon carrier gas (flow rate = 40 cm^3 min^{-1}) at 50°C.

3. Data of X-ray analysis of [Ru(EtOtpy)(bpy)OH$_2$] (NO$_3$)$_2$ (1a(NO$_3$)$_2$)

Table S1 Data of X-ray structure analysis for **1a**(NO$_3$)$_2$

compound	**1a**(NO$_3$)$_2$·2.5H$_2$O
empirical formula	RuO$_{10.50}$N$_7$C$_{27}$H$_{30}$
fw	721.64
cryst syst	triclinic
space group	$P\bar{1}$(#2)
a, Å	11.0976(7)
b, Å	11.4129(7)
c, Å	13.8155(8)
α, deg	91.808(5)
β, deg	102.944(5)
γ, deg	115.411(2)
V, Å^3	1524.1(2)
Z	2
T, ℃	23.0
λ, Å	0.71069
d_{cal}, g/cm^3	1.572
F_{000}	738.00
no. of reflns toal/unique	12187/6474
no. observations (I > 2.00σ(I))	5787
refln/param ratio	14.35
R; R_{w}	0.082^{a} ; 0.137^{b}
GOF indicator	1.26

$$^{a}R = \Sigma\left\|F_o\right|\Sigma\left|F_c\right\| / \Sigma\left|F_o\right|$$

$$^{b}R_w = \left[\Sigma w\left(\left|F_o\right|\Sigma\left|F_c\right|\right)^2 / \Sigma w F_o{}^2\right]^{1/2}$$

Crystal data for **1a**: RuO$_{10.50}$N$_7$C$_{27}$H$_{30}$, M = 721.64, deep-red platelet, triclinic, $P\bar{1}$(#2), a = 11.0976(7), b = 11.4129(7), c = 13.8155(8) Å, α = 91.808(5), β = 102.944(5),γ = 115.411(2), V = 1524.1(2) Å^3, Z = 2, T = 296 K, 12187 reflections of which 6474 were unique (R_{int} = 0.038), 451 variable parameters, R = 0.082 [based on all F_2], R_{w} = 0.137. Three nitrate anions were found in an asymmetric unit: one of them has occupancy 1 and the others are located on different two sites with occupancy 0.5. Four oxygen atoms of H$_2$O were found in an asymmetric unit: one of them has occupancy 1 and the others are located on different three sites with occupancy 0.5. Data were collected over the $2\theta < 55.0°$ on a Rigaku RAXIS-IV Imaging Plate diffractometer with graphite monochromated MoKα radiation.

4. Electrochemical data

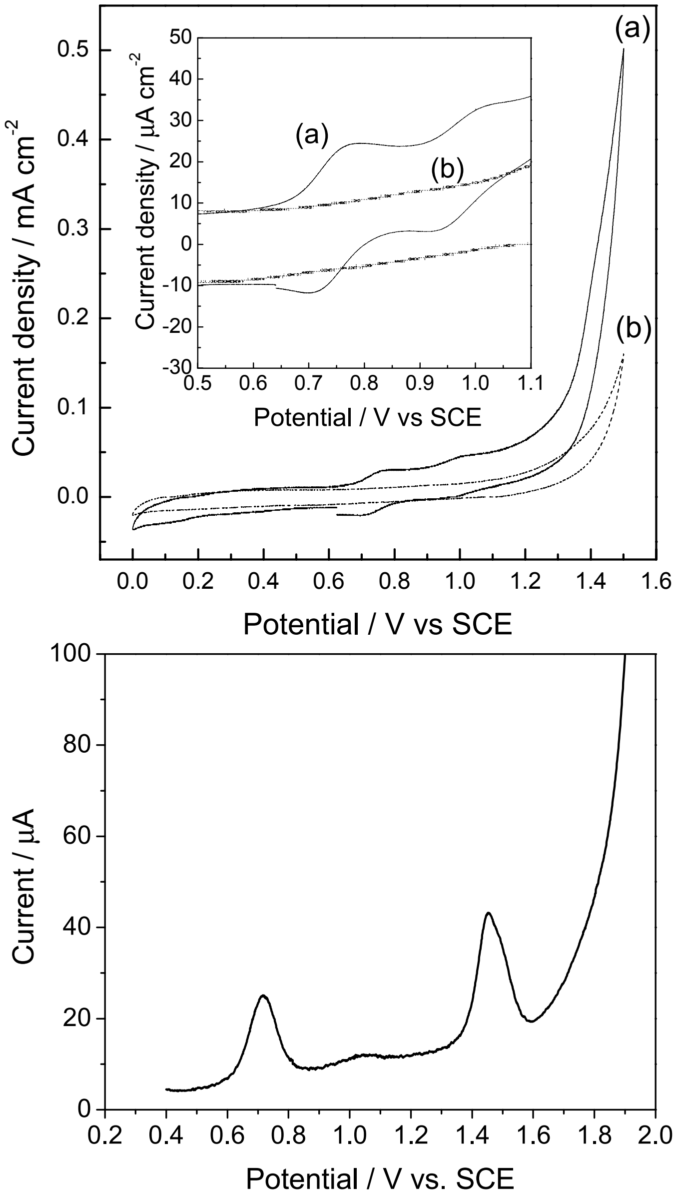

Figure S1 (A) Cyclic voltammograms (CV, upper figure) of (a) 0.5 mM **1a** and (b) without **1a** in a 0.1 M HNO_3 aqueous solution (pH = 1.0) in a potential range from 0.0 to 1.5 V as measured at 25°C and 2 mV s^{-1} of a scan rate. The inset shows CV data in a potential range from 0.5 to 1.1 V. (B) Differential pulse voltammograms (DPV) for **1a** in a 0.1 M KNO_3 aqueous solution (pH = 1.0) in the potential range of 0.0 to 1.9 V vs SCE. pulse amplitude, 50 mV; pulse width, 10 ms; pulse period, 250 ms; scan rate, 5 mV s^{-1}.

5. UV-visible absorption spectral change in pH titration

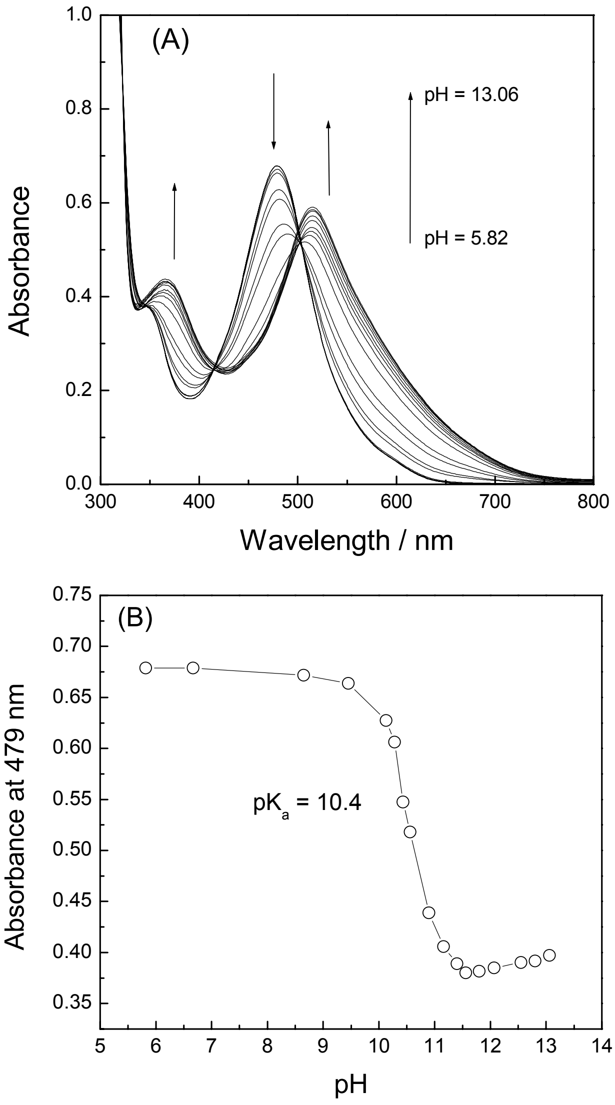

Figure S2 (A) UV-visible absorption spectral change of 0.06 mM **1a** aqueous solution in pH titration with NaOH in a pH range from 5.82 to 13.06 at 25°C. (B) Absorbance change at 479 nm with pH. It provides pK$_a$ = 10.4 by analysis using Henderson-Hasselbalch equation.

6. Kinetic data for O_2 evolution

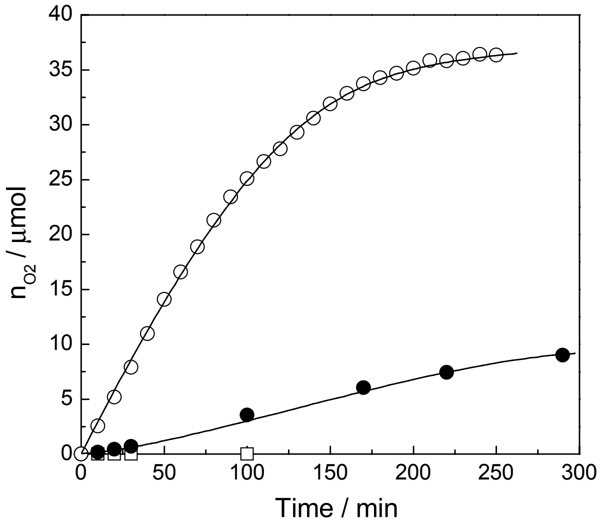

Figure S3 Time courses of the amount (n_{O2} / mol) of O_2 evolved in chemical water oxidation experiments in an aqueous solution at 25˚C using a Ce^{IV} oxidant. Ce^{IV}, 0.1 M (0.5 mmol); **1a**, 20 µM (0.1 µmol); pH = 1.0; liquid volume, 5.0 ml. (○) **1a**, (●) **1** and (□) without complex.

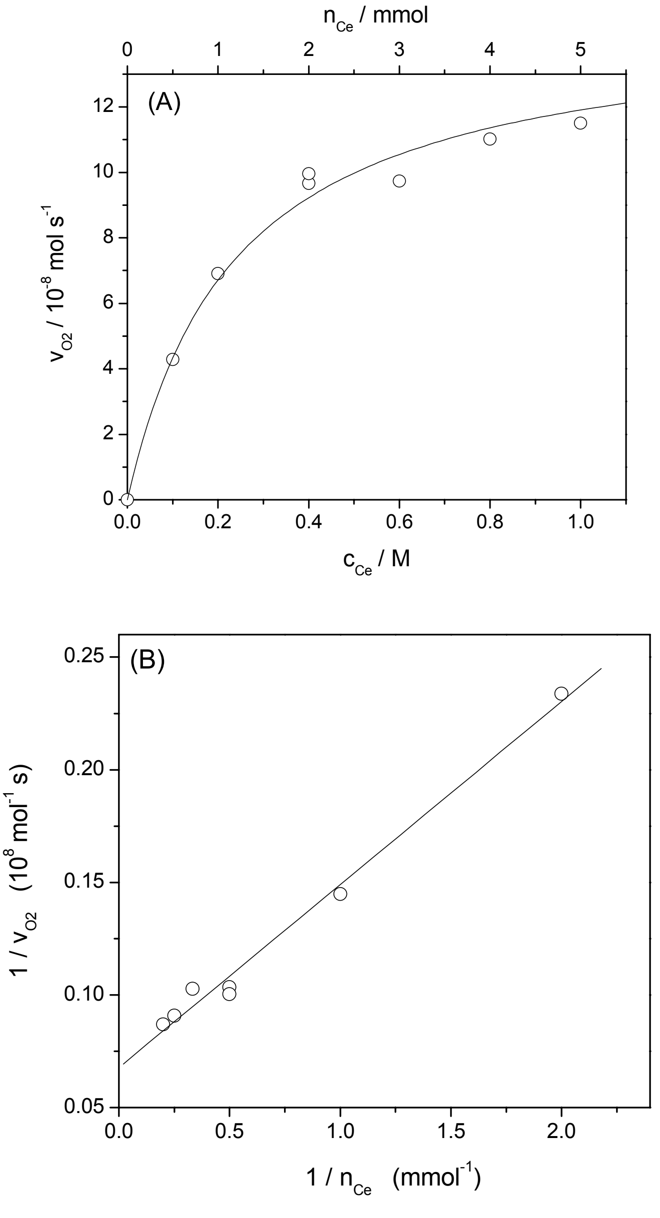

Figure S4 (A) Plots of v_{O2} versus the Ce^{IV} concentration (c_{Ce} / M in chemical water oxidation experiments using 0.2 mM **1a** (5.0 ml water) at 25 ˚C. The corresponding Ce^{IV} amount (n_{Ce} / mol) is indicated on the top axis. The solid line is the simulated curve based on a Michaelis-Menten-like kinetic equation: $v_{O2} = \frac{v_{max} n_{Ce}}{n_{Ce} + K_m}$. (B) Lineweaver-Burk plot based on (A).

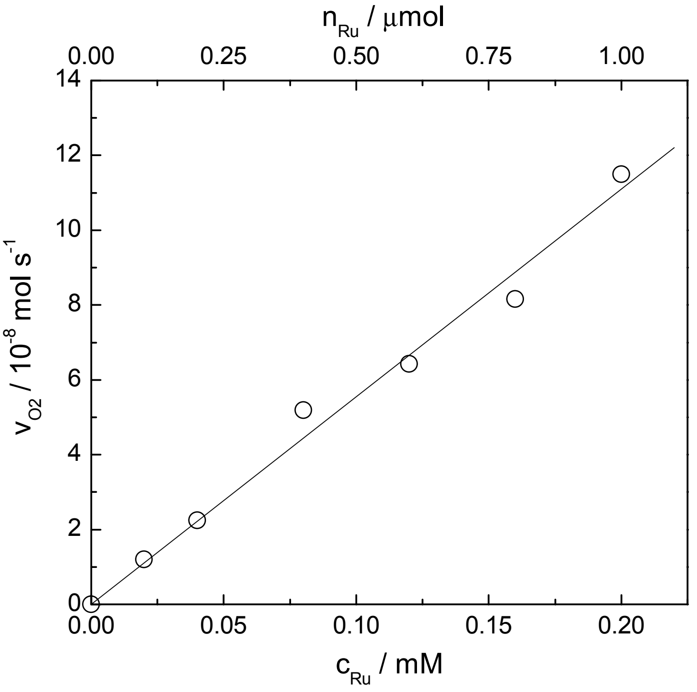

Figure S5 Plots of v_{O2} versus the **1a** concentration (c_{Ru} / M) in chemical water oxidation experiments at 25°C. The corresponding Ru amount (n_{Ru} / mol) is indicated on the top axis. 5.0 mmol Ce^{IV}, 5.0 ml water.