Electronic Supplementary Information

Insights into the direction to increase turnover frequency and turnover number during photochemical water oxidation with molecular Ru catalysts

Indira Pokhrel,^{\$} Guda Dinneswara Reddy,^{\$} Taejin Kwon, Eungyeong Choi, Yu Sung Chun, Sang Tak Lee, Bong June Sung, Duck Hyung Lee, Han Bin Oh, Kyung Byung Yoon*

Department of Chemistry, Sogang University, Seoul 04107, Korea. ^{\$}These authors contributed equally. *e-mail: <u>yoonkb@sogang.ac.kr</u>

Experimental Section

Materials. RuCl₃·3H₂O, pyridine (99.8%), 4-picoline (98%), isoquinoline (97%), *N*-methylimidazole (99%), Ampliflu redTM, and H₂NaPO₄ were purchased from Sigma-Aldrich. Tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate (98%) was purchased from Strem Chemicals. 6,6'-Dibromo-2,2'-dipyridyl (>98%) was purchased from TCI Chemicals. Pyrazole (98%) was purchased from Alfa Aesar. *t*-BuOK was purchased from Fluka. Sodium peroxodisulfate (Na₂S₂O₈) was purchased from Junsei. Na₂HPO₄ was purchased from Duksan Korea. All purchased chemicals were used without further purifications. Solvents used in this study were dried and distilled prior to use. All manipulations were carried out using a standard Schlenk technique.

Synthesis of 6,6'-di(1H-pyrazol-1-yl)-2,2'-bipyridine (T_{pz})

An oven-dried vial was charged with pyrazole (1.08 g, 15.92 mmol, 2.5 eq), *t*-BuOK (1.78 g, 15.92 mmol, 2.5 eq) in DMSO (30 mL), and the mixture was stirred for 10 min at the temperature below 0 °C. Subsequently, 6,6'-dibromo-2,2'-dipyridyl (1) (2 g, 6.36 mmol, 1 eq) was added. The reaction mixture was stirred for 24 h at 140 °C, and subsequently cooled to room temperature. Upon addition of water (50 mL) the product precipitated as a solid. After filtration, pure 6,6'-di(1*H*-pyrazol-1-yl)-2,2'-bipyridine was washed with water. Yield: 1.65 g (90%). ¹H NMR (400 MHz, CDCl₃): 6.52 (s, 2H), 7.78 (s, 2H) 7.98 (t, 2H), 8.04 (d, 2H), 8.37 (d, 2H), 8.75 (d, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): 107.67, 112.54, 118.33, 126.84, 139.55, 142.00, 150.82, 153.51. HR-MS (ESI-MS): m/z = 311.1018 [M+Na], calcd: 311.1021

Synthesis of [6,6'-di(1*H*-pyrazol-1-yl)-2,2'-bipyridine-Ru] Cl₂ Complex ([T_{pz}-Ru^{II}]·Cl₂)

[6,6'-di(1*H*-pyrazol-1-yl)-2,2'-bipyridine-Ru]Cl₂ (denoted as $([T_{pz}-Ru^{II}]\cdot Cl_2)$ was prepared according to the following procedure. A solution, containing RuCl₃·3H₂O (1 g, 1.1 eq) and 6,6'-di(1*H*-pyrazol-1-yl)-2,2'-bipyridine (1 g, 1 eq) in ethanol (15 mL), was refluxed under argon for 12 h. After cooling to room temperature, the resulting dark green solid was filtered, washed with water, and diethyl ether. Yield: 1.20 g (75%).

Synthesis of [Pyr₂T_{pz}-Ru^{II}]·Cl₂

A suspension of $([T_{pz}-Ru^{II}] \cdot Cl_2 \ 0.2 \ g, 1 \ eq)$ was refluxed with pyridine (10 eq) in 4:1 ethanol/water mixture (15 mL) under argon for 12 h. After cooling to room temperature, the red solution was evaporated, and the obtained $[Pyr_2T_{pz}-Ru^{II}] \cdot Cl_2$ was washed with CHCl₃. Yield: 0.210 g (78%). ¹H NMR (400 MHz, CD₃OD): 9.20 (s, 2H), 8.82 (d, 2H, *J*=8.8), 8.31 (t, 2H), 8.24 (d, 2H, *J* = 8.4 Hz), 7.94 (d, 4H, *J* = 6 Hz), 7.60 (t, 2H), 7.09 (t, 4H), 6.95 (s, 2H) ppm. ¹³C NMR (100 MHz, CD₃OD): 157.46, 152.48, 151.38, 146.40, 137.65, 137.62, 132.96, 125.26, 122.73, 111.90, 110.81 (ppm). HR-MS (ESI-MS): m/z = 583.0716 ([M-Cl])⁺, calcd: 583.0699

Synthesis of [4-Pic₂T_{pz}-Ru^{II}]·Cl₂

A suspension of $([T_{pz}-Ru^{II}]\cdot Cl_2, 0.2 \text{ g}, 1 \text{ eq})$ was refluxed with 4-methylpyridine (10 eq) in 4:1 ethanol/water mixture (15 mL) under argon for 12 h. After cooling to room temperature, the brown red solution was evaporated. The crude product washed with CHCl₃. Yield: 0.23g (82%). ¹H NMR (400 MHz, CD₃OD): 9.11 (s, 2H), 8.83 (d, 2H, J = 2.8 Hz), 8.78 (d, 2H, J = 7.6 Hz), 8.28 (t, 2H), 8.21 (d, 2H, J = 8.4 Hz), 7.68(d, 4H, J = 6.4 Hz), 6.94 (s, 2H), 6.91 (d, 4H, J = 5.6 Hz), 2.13 (s, 6H) ppm. ¹³C NMR (100 MHz, CD₃OD): 157.68, 152.66, 150.56, 150.50, 146.34, 137.58, 133.0, 126.25, 122.64, 111.90, 110.96, 19.10 (ppm).

Synthesis of [Iqn2Tpz-Ru^{II}]·Cl2

A suspension of $([T_{pz}-Ru^{II}]\cdot Cl_2, 0.2 \text{ g}, 1 \text{ eq})$ was refluxed with isoquinoline (10 eq) in 4:1 ethanol/water mixture (15 mL) under argon for 12 h. After cooling to room temperature, the pale red solution was evaporated and the crude product was washed with CHCl₃. Yield: 0.25 g (80%).

¹H NMR (400 MHz, CD₃OD): 9.37 (s, 2H), 8.91 (d, 2H, J = 8 Hz), 8.76 (d, 2H, J = 2.4Hz), 8.62 (s, 2H), 8.34 (t, 2H), 8.20 (d, 2H, J = 8.4 Hz), 7.86 (t, 4H), 7.76 (d, 2H, J = 8 Hz), 7.71 (t, 2H), 7.60 (t, 2H), 7.52 (d, 2H, J = 6.4 Hz), 6.92 (s, 2H) ppm. ¹³CNMR (100 MHz, CD₃OD): 157.54, 155.12, 152.52, 146.46, 142.13, 137.56, 134.87, 132.85, 132.38, 128.53, 128.45, 127.00, 125.83, 122.84, 122.16, 111.86, 110.68 (ppm). HR-MS (ESI-MS): m/z = 683.1040 ([M-Cl])⁺, calcd: 683.1012.

Synthesis of [Imd₂T_{pz}-Ru^{II}]·Cl₂

A suspension of $([T_{pz}-Ru^{II}]\cdot Cl_2, 0.2 \text{ g}, 1 \text{ eq})$ was refluxed with methylimidazole (10 eq) in 4:1 ethanol/water mixture (15 mL) under argon for 12 h. After cooling to room temperature, the dark red solution was evaporated. The obtained crude product was washed with CHCl₃. Yield: 0.24 g (88%). ¹H NMR (400 MHz, CD₃OD): 8.93 (d, 2H, J = 3.2 Hz), 8.81(d, 2H, J=1.6 Hz), 8.55 (d, 2H, J = 8 Hz), 8.25 (d, 2H, J = 8.4 Hz), 8.16 (t, 2H), 6.99 (s, 2H), 6.83 (s, 2H), 6.71 (s, 2H), 5.96 (s, 2H), 3.36 (s, 6H) ppm. ¹³C NMR (100 MHz, CD₃OD): 158.09, 152.67, 146.55, 138.21, 136.17, 132.52, 127.36, 121.94, 121.24, 111.38, 110.71, 32.94 (ppm). HR-MS (ESI-MS): m/z = 589.0933 ([M-Cl])⁺, calcd.: 589.0917.

Instrumentation.

¹H NMR spectra were recorded on a Varian (400 MHz). ¹³C NMR spectra were recorded on a Varian (100 MHz), The ¹H NMR chemical shifts were measured relative to tetramethylsilane (TMS), CDCl₃, CD₃OD and CD₃CN as internal references. ¹³C NMR chemical shifts were recorded with CDCl₃, CD₃OD and CD₃CN as the internal standard. High resolution mass spectrum measurements were recorded on a Thermo Fisher Scientic Orbitrap Mass Spectrometer (Model : LTQ Orbitrap XL). The gas chromatograph was a Young-Lin YL6500 GC, equipped with a pulsed discharge detector (PDD). A molecular sieve column (30 m \times 0.53 mm, 25 mm pore) was used, and the oven temperature was kept isothermally at 50 °C. The flow rate of N₂ gas was kept at 6 mL min⁻¹. A standard O₂ gas (0.01% in Ar) was used to calibrate the GC signal intensity. A Cary 5000 UV-vis-NIR spectrophotometer (Varian) was used to record UV-vis spectra. All electrochemical measurements conducted Gamry Reference 600 were on а Potentiostat/Galvanostat/ZRA using a glassy carbon (diameter = 3 mm) electrode. A platinum wire was used as the counter electrode and Ag/AgCl (3 M KCl aqueous solution) was used as the

reference electrode. The pH of the solution was monitored by using pH meter (METTLER TOLEDO, M400pH SET).

Empirical formula	C26H22Cl2N8O8Ru	
Formula weight	746.48	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Phon	
Unit cell dimensions	a = 8 1943(4) Å	$\alpha = 90^{\circ}$
	h = 21, 1329(9) Å	α- 90°. β- 90°
	c = 165/36(6) Å	$p = 90^{\circ}$. $\gamma = 90^{\circ}$
Volume	c = 10.3430(0) IX 2864 8(2) Å ³	<i>i</i> = <i>j</i> 0 .
7	2004.0(2) A	
L Density (coloulated)	4 1.721 Ma/m ³	
Density (calculated)	1.751 Mg/III ⁵	
Absorption coefficient	0.799 mm ⁻¹	
F(000)	1504	
Crystal size	0.440 x 0.240 x 0.130 mm ³	
Theta range for data collection	2.462 to 26.076°.	
Index ranges	-10<=h<=10, -25<=k<=26,	-18<=l<=20
Reflections collected	13411	
Independent reflections	2796 [R(int) = 0.0230]	
Completeness to theta = 25.242°	98.8 %	
Absorption correction	Semi-empirical from equiva	lents
Max. and min. transmission	0.7453 and 0.6497	
Refinement method	Full-matrix least-squares on	F ²
Data / restraints / parameters	2796 / 0 / 204	
Goodness-of-fit on F ²	1.129	
Final R indices [I>2sigma(I)]	R1 = 0.0622, wR2 = 0.1665	
R indices (all data)	R1 = 0.0732, $wR2 = 0.2083$	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.971 and -2.636 e.Å ⁻³	

Table S1 Single crystal data of [Pyr2Tpz-Ru^{II}] (CCDC; 1848578)

Empirical formula	C ₂₈ H ₂₆ N ₈ Ru, 2(F ₆ P), C ₂ H ₃ N	N
Formula weight	906.63	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.2606(4) Å	α= 77.5866(17)°.
	b = 10.7980(5) Å	$\beta = 84.0528(19)^{\circ}.$
	c = 20.5518(10) Å	$\gamma = 84.8406(18)^{\circ}.$
Volume	1776.36(15) Å ³	
Z	2	
Density (calculated)	1.695 Mg/m ³	
Absorption coefficient	0.632 mm ⁻¹	
F(000)	908	
Crystal size	0.220 x 0.140 x 0.050 mm ³	
Theta range for data collection	2.367 to 28.376°.	
Index ranges	-11<=h<=11, -14<=k<=14, -	-27<=l<=27
Reflections collected	63936	
Independent reflections	8864 [R(int) = 0.0593]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equiva	lents
Max. and min. transmission	0.7457 and 0.7094	
Refinement method	Full-matrix least-squares on	F^2
Data / restraints / parameters	8864 / 0 / 526	
Goodness-of-fit on F ²	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0796	
R indices (all data)	R1 = 0.0549, wR2 = 0.0875	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.751 and -0.521 e.Å ⁻³	

Table S2 Single crystal data of $[4-Pic_2T_{pz}-Ru^{II}]$ (CCDC; 1848584)

Empirical formula	$C_{24} H_{24} Cl_2 N_{10} O_8 Ru$	
Formula weight	752.50	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.8962(5) Å	$\alpha = 90^{\circ}$.
	b = 10.2796(3) Å	$\beta = 90.8990(10)^{\circ}$
	c = 15.9597(5) Å	$\gamma = 90^{\circ}.$
Volume	2935.68(15) Å ³	
Z	4	
Density (calculated)	1.703 Mg/m ³	
Absorption coefficient	0.783 mm ⁻¹	
F(000)	1520	
Crystal size	0.240 x 0.200 x 0.130 i	mm ³
Theta range for data collection	2.276 to 28.348°.	
Index ranges	-23<=h<=23, -13<=k<	=13, -21<=l<=21
Reflections collected	44615	
Independent reflections	3670 [R(int) = 0.0336]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from e	quivalents
Max. and min. transmission	0.7457 and 0.7054	
Refinement method	Full-matrix least-squar	es on F ²
Data / restraints / parameters	3670 / 0 / 205	
Goodness-of-fit on F ²	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.	1199
R indices (all data)	R1 = 0.0413, wR2 = 0.	1283
Extinction coefficient	n/a	
Largest diff. peak and hole	1.096 and -0.750 e.Å ⁻³	

Table S3 Single crystal data of $[Imd_2T_{pz}-Ru^{II}]$ (CCDC; 1848580)

Species	Ru ^{II}	Ru ^{III}	Ru ^{IV}	Ru ^{III} -OH ₂	Ru ^v =O	Ru ^Ⅲ -OOH	Ru ^{IV} -OO
$[Pyr_2T_{pz}-Ru^{II}]$	-6.2858	-7.7362	-8.3566	-7.6818	-7.7689	-6.7403	-5.9130
[4-Pic ₂ T _{pz} -Ru ^{II}]	-6.2289	-7.6736	-8.3512	-7.6246	-7.6818	-6.7049	-5.8668
$[Iqn_2T_{pz}-Ru^{II}]$	-6.1852	-7.1947	-7.3308	-7.0940	-7.0913	-6.7103	-5.8967
$[Imd_2T_{pz}-Ru^{II}]$	-5.9539	-7.5158	-7.7607	-7.4641	-7.3852	-6.5579	-5.8397
$S_2O_8^{2-}$	-7.3000						
SO4	-7.5756						
[PS-0] ³⁺	-7.9000						
$[PS-2]^{3+}$	-7.9300						
$[PS-4]^{3+}$	-7.9800						
[PS-6] ³⁺	-8.1500						
H ₂ O	-8.9090						

Table S4 E_{HOMO} values of various species of interest in this work.

•••••••••••	, , , ,	01111						
Species	Ru ^{II}	Ru ^{III}	Ru ^{III} -OH ₂	Ru ^v =O	Ru ^{III} -OOH	Ru ^{IV} -OO	Ru ^{IV} - OO- Ru ^{IV}	Ru ^{IV} -OO [●]
[Lau-Ru]	-6.0599	-7.6029	-7.5702	-7.5702	-6.8654	-7.1158		
[Lau-2(N- O)Ru ^{II}]	-5.8532	-7.5430	-7.2600	-7.8151	-6.5660	-6.6994		
[Sun-Ru ^{II}]	-5.4014	-6.7702	-6.8600	-6.8709	-5.8613	-6.1334	-6.5797	-6.7702

Table S5 E_{HOMO} values of three reported WOCs whose performances and properties were compared in this work.

$[PS-n]^{2+}$	ΔG° (eV)
$[PS-0]^{2+}$	1.1007
$[PS-2]^{2+}$	1.2786
$[PS-4]^{2+}$	1.3356
[PS-6] ²⁺	1.4208

Table S6 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[PS-n]^{2+} + S_2O_8^{2-} \rightarrow [PS-n]^{3+} + SO_4^{2-} + SO_4^{-\bullet}$.

WOC	PS	ΔG° (eV)
	[PS-6] ²⁺	-0.1822
[Dear T. Deall]]	[PS-4] ²⁺	-0.0970
[PyI21 _{pz} Ku]	[PS-2] ²⁺	-0.0399
	[PS-0] ²⁺	0.1379
	[PS-6] ²⁺	-0.3464
	[PS-4] ²⁺	-0.2612
$[4-P1C_2 I_{pz}Ku^{-1}]$	[PS-2] ²⁺	-0.2042
	[PS-0] ²⁺	-0.0263
	[PS-6] ²⁺	-0.2579
	[PS-4] ²⁺	-0.1727
	[PS-2] ²⁺	-0.1157
	[PS-0] ²⁺	0.0622
	[PS-6] ²⁺	-0.4987
[Imd T Dull]	[PS-4] ²⁺	-0.4135
	[PS-2] ²⁺	-0.3564
	[PS-0] ²⁺	-0.1786

Table S7 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[A_2T_{pz}-Ru^{II}] + [PS-n]^{3+} \rightarrow [A_2T_{pz}-Ru^{III}] + [PS-n]^{2+}$.

WOC	ΔG° (eV)
$[Pyr_2T_{pz}Ru^{II}]$	-0.0423
[4-Pic ₂ T _{pz} Ru ^{II}]	0.1122
$[Iqn_2T_{pz}Ru^{II}]$	0.1407
$[Imd_2T_{pz}Ru^{II}]$	0.1202

Table S8 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[A_2T_{pz}-Ru^{III}] + H_2O \rightarrow [H_2O\cdots A_2T_{pz}-Ru^{III}].$

WOC	PS	ΔG° (eV)
$[Pyr_2T_{pz}Ru^{II}]$	[PS-6] ²⁺	-7.123
	$[PS-4]^{2+}$	-6.953
	[PS-2] ²⁺	-6.839
	[PS-0] ²⁺	-6.483
[4-Pic ₂ T _{pz} Ru ^{II}]	[PS-6] ²⁺	-7.174
	[PS-4] ²⁺	-7.003
	[PS-2] ²⁺	-6.889
	[PS-0] ²⁺	-6.533
$[Iqn_2T_{pz}Ru^{II}]$	[PS-6] ²⁺	-7.236
	$[PS-4]^{2+}$	-7.065
	[PS-2] ²⁺	-6.951
	[PS-0] ²⁺	-6.595
$[Imd_2T_{pz}Ru^{II}]$	[PS-6] ²⁺	-7.191
	$[PS-4]^{2+}$	-7.021
	[PS-2] ²⁺	-6.906
	$[PS-0]^{2+}$	-6.551

Table S9 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[H_2O\cdots A_2T_{pz}-Ru^{III}] + 2 [PS-n]^{3+} + 2 OH^- \rightarrow [A_2T_{pz}-1(N-O)-Ru^{IV}] + 2 [PS-n]^{2+} + 2 H_2O.$

WOC	PS	ΔG° (eV)
	[PS-6] ²⁺	12.955
	$[PS-4]^{2+}$	13.123
$[Pyr_2 I_{pz}Ku^{-}]$	[PS-2] ²⁺	13.237
	[PS-0] ²⁺	13.593
	[PS-6] ²⁺	12.902
$\begin{bmatrix} 4 \mathbf{D}_{i_{0}} \mathbf{T} \mathbf{D}_{i_{0}} \mathbf{I} \end{bmatrix}$	[PS-4] ²⁺	13.073
$[4-FIC_2 I_{pz}Ku]$	$[PS-2]^{2+}$	13.187
	[PS-0] ²⁺	13.543
	[PS-6] ²⁺	12.840
$[Ian T P u^{II}]$	$[PS-4]^{2+}$	13.011
	$[PS-2]^{2+}$	13.125
	[PS-0] ²⁺	13.481
	$[PS-6]^{2+}$	12.885
$[Imd_2T_{pz}Ru^{II}]$	$[PS-4]^{2+}$	13.055
	$[PS-2]^{2+}$	13.169
	[PS-0] ²⁺	13.525

Table S10 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[H_2O\cdots A_2T_{pz}-Ru^{III}] + 2 [PS-n]^{3+} \rightarrow [A_2T_{pz}-1(N-O)--Ru^{IV}] + 2 [PS-n]^{2+} + 2 H^+.$

WOC	$\Delta G^{\circ}(\mathrm{eV})$
[Pyr ₂ T _{pz} Ru ^{II}]	-2.583
$[4-Pic_2T_{pz}Ru^{II}]$	-2.577
$[Iqn_2T_{pz}Ru^{II}]$	-2.577
[Imd ₂ T _{pz} Ru ^{II}]	-2.400

Table S11 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[A_2T_{pz}-1(N-O)-Ru^{IV}] + H_2O+OH^- \rightarrow [A_2T_{pz}-Ru^{III}-OOH] + H_2O.$

WOC	$\Delta G^{\circ}(\mathrm{eV})$
[Pyr ₂ T _{pz} Ru ^{II}]	7.455
$[4-Pic_2T_{pz}Ru^{II}]$	7.461
$[Iqn_2T_{pz}Ru^{II}]$	7.461
$[Imd_2T_{pz}Ru^{II}]$	7.638

Table S12 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[A_2T_{pz}-1(N-O)-Ru^{IV}] + H_2O \rightarrow [A_2T_{pz}-Ru^{III}-OOH] + H^+$.

WOC	PS	$\Delta G^{o}(eV)$
	[PS-6] ²⁺	-3.083
	$[PS-4]^{2+}$	-3.541
$[PyI_2I_{pz}Ku^{-}]$	$[PS-2]^{2+}$	-3.048
	$[PS-0]^{2+}$	-3.123
	[PS-6] ²⁺	-2.998
	$[PS-4]^{2+}$	-3.456
$[4-P1C_2 I_{pz}Ku^{-1}]$	$[PS-2]^{2+}$	-2.963
	$[PS-0]^{2+}$	-3.038
	$[PS-6]^{2+}$	-2.941
	$[PS-4]^{2+}$	-3.399
$[Iqn_2 I_{pz} Ku^{-}]$	$[PS-2]^{2+}$	-2.906
	$[PS-0]^{2+}$	-2.981
	[PS-6] ²⁺	-2.763
[Imd T Dull]	$[PS-4]^{2+}$	-3.221
$\begin{bmatrix} 111102 \ I \ pz \ K u^{-1} \end{bmatrix}$	$[PS-2]^{2+}$	-2.728
	[PS-0] ²⁺	-2.803

Table S13 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[A_2T_{pz}-Ru^{III}-OOH] + [PS-n]^{3+} + OH^- \rightarrow [A_2T_{pz}-Ru^{IV}-OO] + [PS-n]^{2+} + H_2O.$

WOC	PS	$\Delta G^{\circ}(\mathrm{eV})$	
	[PS-6] ²⁺	7.275	
	$[PS-4]^{2+}$	6.817	
	[PS-2] ²⁺	7.310	
	[PS-0] ²⁺	7.235	
	[PS-6] ²⁺	7.097	
	$[PS-4]^{2+}$	6.639	
$[4-PIC_2 I_{pz}Ku]$	[PS-2] ²⁺	7.132	
	$[PS-0]^{2+}$	7.057	
	[PS-6] ²⁺	7.040	
Han T. Dull	$[PS-4]^{2+}$	6.582	
	[PS-2] ²⁺	7.075	
	$[PS-0]^{2+}$	7.000	
	[PS-6] ²⁺	6.955	
$[Imd T Du^{II}]$	$[PS-4]^{2+}$	6.497	
[IIIIu21 _{pz} Ku]	[PS-2] ²⁺	6.990	
	$[PS-0]^{2+}$	6.915	

Table S14 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[A_2T_{pz}-Ru^{III}-OOH] + [PS-n]^{3+} \rightarrow [A_2T_{pz}-Ru^{IV}-OO] + [PS-n]^{2+} + H^+.$

WOC	PS	$\Delta G^{o}(eV)$
	[PS-6] ²⁺	-0.4675
	$[PS-4]^{2+}$	-0.3823
[PyI21 _{pz} Ku]	$[PS-2]^{2+}$	-0.3256
	$[PS-0]^{2+}$	-0.1474
	[PS-6] ²⁺	-0.1204
$[4 \text{ Dia}, \mathbf{T} \text{ Du}^{\text{H}}]$	$[PS-4]^{2+}$	-0.0352
$[4-r]C_2T_{pz}Ku$	$[PS-2]^{2+}$	0.0218
	[PS-0] ²⁺	0.1997
	[PS-6] ²⁺	-0.5797
[Ion T Dull]	$[PS-4]^{2+}$	-0.4945
	$[PS-2]^{2+}$	-0.4375
	[PS-0] ²⁺	-0.2596
	[PS-6] ²⁺	-0.7056
[Imd.T. Dull]	$[PS-4]^{2+}$	-0.6204
	$[PS-2]^{2+}$	-0.5634
	[PS-0] ²⁺	-0.3855

Table S15 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[A_2T_{pz}-Ru^{IV}-OO] + [PS-n]^{3+} \rightarrow [A_2T_{pz}-Ru^{III}] + [PS-n]^{2+} + O_2$.

$[PS-n]^{2+}$	$\Delta G^{\circ} (eV)$
$[PS-0]^{2+}$	0.7569
$[PS-2]^{2+}$	0.9348
$[PS-4]^{2+}$	0.9918
[PS-6] ²⁺	1.0770

Table S16 Gibbs free energy changes (ΔG^o) calculated by DFT calculations for $[PS-n]^{2+} + SO_4^{-\bullet} \rightarrow [PS-n]^{3+} + SO_4^{2-}$.

WOC ^a	PS	O ₂ (µmol)	$TOF_{max}(S^{-1})$	TON
	[PS-6] ²⁺	82.6	5.41	12,665
	$[PS-4]^{2+}$	41.6	2.58	6,929
$[Pyr_2 I_{pz}-Ku^{-1}]$	$[PS-2]^{2+}$	29.1	1.63	4,844
	$[PS-0]^{2+}$	0.0	0.00	0
	[PS-6] ²⁺	74.7	5.33	11,345
	$[PS-4]^{2+}$	44.1	2.87	7,351
[4-P1c ₂ I _{pz} -Ru ⁿ]	$[PS-2]^{2+}$	43.0	2.85	7,169
	$[PS-0]^{2+}$	0.0	0.00	0
	[PS-6] ²⁺	30.3	2.58	3,960
	$[PS-4]^{2+}$	11.2	1.01	1,867
$[Iqn_2I_{pz}-Ru^n]$	$[PS-2]^{2+}$	11.2	0.80	1,861
	$[PS-0]^{2+}$	0.0	0.00	0
	[PS-6] ²⁺	17.6	1.44	1,838
[Imd ₂ T _{pz} -Ru ^{II}]	$[PS-4]^{2+}$	3.1	0.54	517
	$[PS-2]^{2+}$	3.8	0.47	633
	[PS-0] ²⁺	0.0	0.00	0

Table S17 The effect of the nature of photosensitizer (PS) on the catalytic activity of $[A_2T_{pz}-Ru^{II}]$.^a

^a[Cat] = 0.2 μ M. ^b[PS] = 0.4 mM .^c[Na₂S₂O₈] = 20 mM, ^d15 mM, pH = 8.^eIn ClO₄⁻ salt. The photocatalytic reactions were carried under the standard reaction condition, where each reaction was carried out in 30 mL of 15 mM phosphate buffer (pH = 8.0). The concentrations of WOC, PS, and Na₂S₂O₈ were 0.2 μ M, 0.4 mM, and 20 mM, respectively. A solar simulated light (1 Sun, AM 1.5, 100 mW) was used as the light source.

No	Catalyst	[Cat] ²	[Ce ^{IV}] ³	Solvent	pН	TON	TOF (s ⁻¹) References
1	C1-a	62.50	0.365	2% aq. CF ₃ SO ₃ H	1	24,000	1,000	Sun., Chem. Commun., 2014, 50 , 12947-12950.
2	C1-b	62.50	0.365	2% aq. CF ₃ SO ₃ H	1	100,000	380	Sun., Chem. Commun., 2014, 50, 12947-12950.
3	C2	0.022	0.48	CF ₃ SO ₃ H	1	8,360	300	Sun., Nat. Chem., 2012, 4, 418-423.
4	C3	0.005	0.365	CF ₃ SO ₃ H	1	55,400	286	Sun., PNAS, 2012, 109, 15584-15588.
5	C4	0.0329	0.05	CF ₃ SO ₃ H	1	86,498	40	Sun., Dalton Trans., 2016, 45, 3814-3819.
6	C5	0.025	0.01	CF ₃ SO ₃ H	1	42,840	40	Sun., Angew. Chem. Int. Ed., 2013, 52, 3398-3401.
7	C6	16.7	0.083	CF ₃ SO ₃ H	1	680	0.32	Sun., Inorg. Chem., 2012, 51, 3388-3398.
8	C7	50	0.900	CF ₃ SO ₃ H	1	4,319	11.2	Sun., Chinese J. Catal., 2013, 34, 1489-1495.
9	C8	3.33	0.18	CF ₃ SO ₃ H	1	1,200	4.5	Sun., Angew. Chem. Int. Ed., 2011, 50, 445-449.
10	C9	2.5	0.10	HNO ₃	1	-	2.2	Thummel., J. Am. Chem. Soc., 2015, 137, 13260-13263.
11	C10	0.05	0.005	CF ₃ SO ₃ H	1	10,500	1.2	Sun., Angew. Chem. Int. Ed., 2010, 49, 8934-8937.
12	C11	55.6	0.083	HNO ₃	1	54	0.165	Sun., Inorg. Chem., 2013, 52, 2505-2518.
13	C12-a	3.33	0.17	CF ₃ SO ₃ H	1	310	0.10	Sun., Angew. Chem. Int. Ed., 2011, 50, 445-449.
14	C13	66.70	0.320	CF ₃ SO ₃ H	1	450	0.092	Sun., ChemSusChem, 2011, 4, 238-244.
15	C12-b	3.33	0.17	CF ₃ SO ₃ H	1	336	0.09	Sun., Angew. Chem. Int. Ed., 2011, 50, 445-449.

Table S18 Performances of the WOCs shown in Fig S23-24 evaluated under the chemical water oxidation condition.¹

 1For structures see Fig S22 - S23. $^2In~\mu M.$ $^3In~M.$

No	Catalyst	[Cat] ²	$[Ce^{IV}]^3$	Solvent	pН	TON	TOF (s ⁻¹)	References ¹
16	C14-a	25.00	0.250	CF ₃ SO ₃ H	1	293	0.082	Lau., Angew. Chem. Int. Ed., 2014, 126, 14696- 14699.
17	C12-c	3.33	0.170	CF ₃ SO ₃ H	1	190	0.04	Sun., Angew. Chem. Int. Ed. 2011, 50, 445-449.
18	C14-b	25.00	0.250	CF ₃ SO ₃ H	1	707	0.032	Lau., Angew. Chem. Int. Ed., 2014, 126, 14696- 14699.
19	C14-c	25.00	0.250	CF ₃ SO ₃ H	1	576	0.025	Lau., Angew. Chem. Int. Ed., 2014, 126, 14696- 14699.
20	C14-d	25.00	0.250	CF ₃ SO ₃ H	1	219	0.017	Lau., Angew. Chem. Int. Ed., 2014, 126, 14696- 14699.
21	С14-е	25.00	0.250	CF ₃ SO ₃ H	1	327	0.017	Lau., Angew. Chem. Int. Ed., 2014, 126, 14696- 14699.
22	C15	20.00	0.200	HNO ₃	1	-	0.016	Thummel., Faraday Discussion., 2015, 185, 87-104.
23	C16	10000	0.304	CF ₃ SO ₃ H	1	3,200	-	Thummel., J. AM. CHEM. SOC., 2005, 127, 12802-12803.
24	C17	33.30	0.167	CF ₃ SO ₃ H	1	550	0.23	Sun., Chem. Eur. J. 2010, 16, 4659 – 4668.
25	C18	0.20	0.005	CF ₃ SO ₃ H	1	4500	0.10	Sun., Chem. Eur. J., 2011, 17, 9520-9528.
26	C19	0.25	0.046	CF ₃ SO ₃ H	0.8	1,700	-	Sun., Inorg. Chem., 2009, 48, 2717-2719.

Table S19 Performances of the WOCs shown in Fig S25-26 evaluated under the chemical water oxidation condition.¹

 ^1For structures see Fig S24-S25. $^2\text{In}\,\mu\text{M}.$ $^3\text{In}\,\text{M}.$

Step	Basic	Acidic
1	0.1518	0.1518
2	-1.7293	8.3087
3	-3.5899	6.4481
3'	-1.8606	-1.8606
4	-0.0865	-0.0865
5	-1.9471	-1.9471
6	1.3439	1.3439
7	-5.1540	4.8840
8	-2.5966	7.4414
9	-3.0832	6.9548
10	-0.2853	-0.2853
11	-0.1335	-0.1335

Table S20 Gibbs free energy changes for the steps in the catalytic cycles shown in Fig. 31.



Fig. S1 ¹H-NMR of T_{pz} .



Fig. S2 13 C-NMR of T_{pz}.



Fig. S3 ¹H-NMR of $[Pyr_2T_{pz}-Ru^{II}]$.



Fig. S4 ¹³C-NMR of [Pyr₂T_{pz}-Ru^{II}].







Fig. S6 13 C-NMR of [4-Pic₂T_{pz}-Ru^{II}].



Fig. S7 ¹H-NMR of $[Iqn_2T_{pz}-Ru^{II}]$.



Fig. S8 ¹³C-NMR of [Iqn₂T_{pz}-Ru^{II}].



Fig. S9 ¹H-NMR of $[Imd_2T_{pz}-Ru^{II}]$.



Fig. S10 $^{13}\text{C-NMR}$ of [Imd_2T_{pz}-Ru^{II}].



*** [High Resolution] Orbitrap Mass Spectrometer (Model : LTQ Orbitrap XL / Company : ThermoFisher Scientific)

Fig. S11 HR-MS (ESI) of T_{pz} in positive mode with methanol as solvent.



Fig. S12 HR-MS (ESI) of $[Pyr_2T_{pz}-Ru^{II}]$ in positive mode with methanol as solvent.



*** [High Resolution] Orbitrap Mass Spectrometer (Model : LTQ Orbitrap XL / Company : ThermoFisher Scientific)

Fig. S13 HR-MS (ESI) of $[Iqn_2T_{pz}-Ru^{II}]$ in positive mode with methanol as solvent.



*** [High Resolution] Orbitrap Mass Spectrometer (Model : LTQ Orbitrap XL / Company : ThermoFisher Scientific)

Fig. S14 HR-MS (ESI) of $[Imd_2T_{pz}\text{-}Ru^{II}]$ in positive mode with methanol as solvent.

Datablack RuPy - ellipsoid plot



Fig. S15 Single crystal structure of $[Pyr_2T_{pz}-Ru^{II}]$ (CCDC; 1848578).



Fig. S16 Single crystal structure of $[4-Pic_2T_{pz}-Ru^{II}]$ (CCDC; 1848584).

Datablock No1 - ellipsoid plot



Fig. S17 Single crystal structure of $[Imd_2T_{pz}-Ru^{II}]$ (CCDC; 1848580).



Fig. S18 ¹H NMR of [Lau-Ru^{II}].



Fig. S19¹³C NMR of [Lau-Ru^{II}].



Fig. S20 ¹H NMR of [Sun-Ru^{II}].



Fig. S21 ¹³C NMR of [Sun-Ru^{II}].





Fig. S22 Reported WOCs collected from the references shown in Table S18.



C8



C10

C11



Fig. S23 Reported WOCs collected from the references shown in Table S18.





C14-a

Fig. S24 Reported WOCs collected from the references shown in Table S19.



C15

C16

C17



Fig. S25 Reported WOCs collected from the references shown in Table S19.



Fig. S26 Plot of accumulated amounts of O₂ with respect to time during the photochemical evaluation of $[Pyr_2T_{pz}-Ru^{II}]$ (0.2 μ M) with $[PS-6]^{2+}$ as the common photosensitizer (0.4 mM) in the absence and presence of Hg (0.4 mL). Na₂S₂O₈ was used as the common sacrificial electron acceptor (20 mM) in sodium phosphate buffer (15 mM) whose pH was 8.



Fig. S27 HR-MS (ESI) of $[Pyr_2T_{pz}-Ru^{II}]$ fragment at different interval of time during th e course of reaction (at 0 min, 10 min, 30 min & 120 min) in buffer.



Peak at *m/z* 245.0-252.0

Fig. S28 HR-MS (ESI) of [Pyr₂T_{pz}-Ru^{II}] fragment at different interval of time during the course of reaction (at 0 min, 10 min, 30 min & 120 min) in buffer.



Fig. S29 HR-MS (ESI) of [PS-6]²⁺ fragment at 120 min of reaction in buffer.



Fig. S30 HR-MS (ESI) of [PS-6]²⁺ fragment at 120 min of reaction in buffer.



Fig. S31 HR-MS (ESI) of $[PS-6]^{2+}$ fragment at different interval of time during the course of reaction (at 30 min & 120 min) in buffer.



Fig. S32 HR-MS (ESI) of [PS-6]²⁺ fragment at 120 min of reaction in buffer.



Fig. S33 Ground-state structures of (a) $[Pyr_2T_{pz}-Ru^{II}]$, $[Pyr_2T_{pz}-Ru^{III}]$, (b) $[4-Pic_2T_{pz}-Ru^{III}]$, $[4-Pic_2T_{pz}-Ru^{III}]$, (c) $[Iqn_2T_{pz}-Ru^{II}]$, $[Iqn_2T_{pz}-Ru^{III}]$ and (d) $[Imd_2T_{pz}-Ru^{II}]$, $[Imd_2T_{pz}-Ru^{III}]$.



Fig. S34 Two views of the ground-state structures of (a) $[Pyr_2T_{pz}-Ru^{III}-OH_2]$, (b) [4-P ic₂ $T_{pz}-Ru^{III}-OH_2]$, (c) $[Iqn_2T_{pz}-Ru^{III}-OH_2]$ and (d) $[Imd_2T_{pz}-Ru^{III}-OH_2]$, The Ru-O dist ances (in Å) are show in red and O-H hydrogen bond distances (< 3 Å) are shown in blue.



Fig. S35 Ground-state structures of (a) $[Pyr_2T_{pz}-Ru^V=O]$, (b) $[4-Pic_2T_{pz}-Ru^V=O]$, (c) $[Iqn_2T_{pz}-Ru^V=O]$ and (d) $[Imd_2T_{pz}-Ru^V=O]$. The Ru-O distances (in Å) are shown in red and O-H hydrogen bond distances with the distances below 3 Å are shown in blue.



Fig. S36 Two different views of the ground-state structures of (a) $[Pyr_2T_{pz}-Ru^{III}-OOH]$, (b) $[4-Pic_2T_{pz}-Ru^{III}-OOH]$, (c) $[Iqn_2T_{pz}-Ru^{III}-OOH]$ and (d) $[Imd_2T_{pz}-Ru^{III}-OOH]$. The Ru-O dis tances (Å) are shown in red, O-H hydrogen bonds (<3 Å) are shown in blue.



Fig. S37 Two different views of the ground-state structures of (a) $[Pyr_2T_{pz}-Ru^{IV}-OO]$, (b) $[4-Pic_2T_{pz}-Ru^{IV}-OO]$, (c) $[Iqn_2T_{pz}-Ru^{IV}-OO]$ and (d) $[Imd_2T^{pz}-Ru^{IV}-OO]$. The Ru-O distances (Å) are shown in red, O-H hydrogen bonds (<3 Å) are shown in blue.



a. Electrocatalytic (Acidic, pH < 6.5)



b. Electrocatalytic (Basic, pH > 6.5)

c. Photocatalytic (Basic, pH > 6.5)



Fig. S38 Proposed alternative schemes of the catalytic cycles for $[Pyr_2T_{pz}-Ru^{II}]$ under the (a) electrocatalytic acidic, (b) electrocatalytic basic, and (c) photocatalytic conditions.



Fig. S39 Optimized structures of (a,b) $[Ru^{II}-OH_2]^{2+}$ in two different views and (c,d) the common structures of $[Ru_p-OH]^{n+}$ For p = II, III, IV, and V and n = 1, 2, 3, and 4. The corresponding bond lengths (*a*, *b*, and *c*) are shown under the structures.



Fig. S40 Plots of the calculated Gibbs free energy changes (ΔG°) for each step shown in the reaction schemes under three different conditions: (a) the electrocatalytic and acidic, (b) electrocatalytic and basic, and (c) photocatalytic and basic.



Fig. S41 The chart that shows E_{HOMO} values of various species of interest (as indicated) in this work.

To explain the slope of -0.057 V pH⁻¹ of the first oxidation peak in the acidic region, the $[Ru^{II}]^{2+}$ in the solution was forced to form a loosely bound aqua complex of $[Ru^{II}]^{2+}$ (denoted as $[Ru^{II} \cdot \cdot OH_2]^{2+}$) (eq S1) so that it can undergo PCET.

$$[\operatorname{Ru}^{\mathrm{II}}]^{2+} + \operatorname{H}_2 O \longrightarrow [\operatorname{Ru}^{\mathrm{II}} \cdots O \operatorname{H}_2]^{2+}$$
(S1)

The structure of $[Ru^{II} \cdots OH_2]^{2+}$ is likened to the loosely bound aqua complex of $[Pyr_2T_{pz}-Ru^{III}]$, $[H_2O\cdots Pyr_2T_{pz}-Ru^{III}]$, shown in Fig. S34. Thus, in the pH region between 2.0 and 6.0, the first oxidation is PCET from $[Ru^{II} \cdots OH_2]^{2+}$ to $[Ru^{III}-OH]^{2+}$ (eq S2).

$$[\operatorname{Ru}^{\operatorname{II}} \cdots \operatorname{OH}_2]^{2+} + \operatorname{OH}^+ - e^- \longrightarrow [\operatorname{Ru}^{\operatorname{III}} - \operatorname{OH}]^{2+} + \operatorname{H}_2 0$$
(S2)

The second oxidation is the 1-e⁻ oxidation from $[Ru^{III}-OH]^{2+}$ to $[Ru^{IV}-OH]^{3+}$ (eq S3), and the third oxidation is the 1-e⁻ oxidation from $[Ru^{IV}-OH]^{3+}$ to $[Ru^{V}-OH]^{4+}$ (eq S4).

$$[Ru^{III}-OH]^{2+} - e^{-} \longrightarrow [Ru^{IV}-OH]^{3+}$$
(S3)

$$[Ru^{IV}-OH]^{3+} - e^{-} \longrightarrow [Ru^{V}-OH]^{4+}$$
(S4)

Since the oxidation in the pH region between 6.0 and 10 is not affected by pH, $[Ru^{II} \cdots OH_2]^{2+}$ should exist in the hydroxide form, $[Ru^{II} - OH]^+$, under the basic condition, according to eq S5.

$$[Ru^{II} \cdots OH_2]^{2+} + OH^- \leftrightarrows [Ru^{II} - OH]^+ + H_2O$$
(S5)

However, when the pH of the solution was decreased to below 6.0, the DPV again showed the pH-dependent voltammograms that are similar to those shown in Fig. 30a in the main text, indicating that $[Ru^{II}...OH_2]^{2+}$ is reproduced, and eventually indicating that eq S5 is a reversible equilibrium reaction. The repetition of pH shuttling between low and high pHs for several cycles

did not give any sign of WOC deterioration, showing that $[Pyr_2T_{pz}-Ru^{II}]$ is stable under the above pH conditions.

Based on the facts that the intensity of the second peak increases sharply as pH increases in the pH region between 6.0 and 10, that the intensities of second peaks in the basic pH region is much higher than those of the first peak, and that the intensity of the second oxidation peak cannot be higher than that of the first oxidation peak in a voltammogram, the intense second peak is concluded to be the direct 2-e⁻ oxidation of [Ru^{II}-OH]⁺ to [Ru^{IV}-OH]³⁺ (eq S6) and the much weaker first peak is concluded to be the 1-e⁻ oxidation of [Ru^{II}-OH]⁺ to [Ru^{III}-OH]²⁺ (eq S7), which takes place slowly. The produced [Ru^{IV}-OH]³⁺ then undergoes third 1-e⁻ oxidation (eq 24).

$$[Ru^{II}-OH]^+ - 2 e^- \longrightarrow [Ru^{IV}-OH]^{3+}$$
(S6)

$$[Ru^{II}-OH]^+ - e^- \longrightarrow [Ru^{III}-OH]^{2+}$$
(S7)

The Pourbaix-based electrocatalytic cycle under the acidic condition is shown in Fig. S38a. Thus, the added $[Ru^{II}]^{2+}$ undergoes a loose aquation (step 1) to give $[Ru^{II} \cdots OH_2]^{2+}$. The loose aqua complex [Ru^{II}...OH₂]²⁺ undergoes PCET to [Ru^{III}-OH]²⁺ (step 3), which subsequently undergoes 1-e⁻ oxidation to $[Ru^{IV}-OH]^{3+}$ (step 4), which, in turn, undergoes 1-e⁻ oxidation to $[Ru^{V}-OH]^{4+}$ (step 5). $[Ru^{V}-OH]^{4+}$ undergoes deprotonation to give $[Ru^{V}=O]^{3+}$ (step 6), which subsequently undergoes WNA/deprotonation to give hydroperoxy complex, [Ru^{III}-OOH]²⁺ (step 7). The hydroperoxy complex undergoes PCET to give peroxy complex, [Ru^{III}-OO]²⁺ (step 8), which undergoes a simultaneous O₂ expulsion and loose aquation to restore the starting loose aqua complex (step 9). Alternatively, the peroxy complex, $[Ru^{III}-OO]^{2+}$, undergo O₂ repulsion (step 9') to restore the original WOC precursor [Ru^{II}]²⁺, which subsequently undergoes loose aquation (step 1) to give the starting loose aqua complex, $[Ru^{II} \cdots OH_2]^{2+}$. While step 9 is a one-step restoration of the loose aqua complex, the combined two steps (step 9' and step 1) form a two-step stepwise restoration of the loose aqua complex. However, while the one-step pathway (step 9) is an exergonic process, the two-step pathway (step 9' and step 1) needs to go through the endergonic step 1, as will be discussed in detail in the later part of this work. Therefore, the one-step pathway (step 9) is likely to be major pathway for the overall catalytic cycle.

The corresponding scheme for the above electrocatalytic cycle under the basic condition is shown in Fig. S38b. Under this condition, the loose aqua complex deprotonation (step 2) to give the corresponding hydroxide complex [Ru^{II}-OH]⁺, which also returns to the loose aqua complex by protonation (step 2'). Thus, step 2 and step 2' form an equilibrium. Since the pKa value of $[Ru^{II}]$. $(\cdot OH_2)^{2+}$ observed from the Pourbaix diagram is 6.0, $[Ru^{II} \cdots OH_2]^{2+}$ is an weak acid. Therefore, even under the basic condition, a certain portion of $[Ru^{II} \cdots OH_2]^{2+}$ will always exist, indicating that the conversion of $[Ru^{II} \cdots OH_2]^{2+}$ to $[Ru^{III} - OH]^{2+}$ by the direct PCET step (step 3) will also exist to a certain degree unless the pH of the solution is very high. Under the basic condition, in addition to step 3, step 3', the 1-e⁻ oxidation of [Ru^{II}-OH]⁺ to [Ru^{III}-OH]²⁺ also exists. However, because the intensities of first oxidation peaks are very weak under the basic condition (Fig. 30b in the main text) step 3' takes place very reluctantly. By the same analogy, based on the fact that the intensities of the second oxidation peaks are very strong, the direct two electron oxidation from $[Ru^{II}-OH]^+$ to $[Ru^{IV}-OH]^{3+}$ takes place very actively under the electrochemical catalytic reaction with [Ru^{II}]²⁺ as a WOC in the basic environment. The rest of the steps in catalytic cycle are the same. However, since the reaction is taking place under the basic condition, the deprotonation steps (steps 6 and 7) and the PCET steps (steps 3 and 8) will be highly promoted.

The proposed our WOC-specific scheme for the photocatalytic cycle under the basic condition or under our photocatalytic reaction condition is shown in Fig. S38c, which is basically the same with that of Fig. S38b, except the absence of step 4', which exists under the electrochemical reaction condition. The proposed reason for the absence of step 4' in the scheme of Fig. S38c is the requirement of two molecules of the auxiliary oxidant [PS-6]³⁺ to fulfill the direct two-electron oxidation, whose probability is very low arising from fact that photon flux of the 1 Sun AM1.5 solar simulated light as discussed in the earlier part of this work. Thus, the catalytic cycle shown in Fig. S38c represents the mechanism of $[Pyr_2T_{pz}-Ru^{II}]$. Other $[A_2T_{pz}-Ru^{II}]$ WOCs (A = 4-Pic, Iqn, and Imd) could be proposed to catalyze water oxidation in the same manner.

The calculated energy-minimized structures for $[Ru^{II}...OH_2]^{2+}$ and $[Ru^p-OH]^{n+}$, where p = II, III, IV, and V, n = 1, 2, 3, and 4, respectively, are shown in Fig. S39. These results show that even $[Ru^{II}]^{2+}$ forms a loose aqua complex $[Ru^{II}...OH_2]^{2+}$ as was the case of $[Ru^{III}]^{2+}$ discussed in Section 3.15.3 in the text (see also Fig. S34). In $[Ru^{II}...OH_2]^{2+}$, the O-Ru distance is 4.436 Å, which is longer than that (4.181 Å) in $[H_2O...Pyr_2Tpz-Ru^{III}]$. This phenomenon is likely to arise from the fact that the electron affinity of Ru^{II} is lower than that of Ru^{III} . In the case of $[Ru^{II}...OH_2]^{2+}$, the O atom also forms H bonds with the nearby electron-deficient, H⁺-like H atoms, which are placed next to the N atoms in the pyrazole units (Fig. S39b). The O-H distances of 2.401 and 2.400 Å are longer than those observed from $[H_2O...Pyr_2Tpz-Ru^{III}]$, that are 2.291 and 2.294 Å (Fig. S34b). This result coincides with the observed increase in O-Ru distance from 4.181 to 4.436 Å upon decreasing the oxidation state on Ru from III to II.

In the cases of $[Ru^p-OH]^{n+}$, the Ru-O distances are 2.068, 1.935, 1.918, and 1.906 Å, respectively, for p = II, III, IV, and V and n = 1, 2, 3, and 4, respectively. Thus, the Ru and the O atom of OH unambiguously form a direct bond between the two atoms (Ru and O), and as expected, the Ru-O bond distance decreases as the oxidation state of Ru increases. In the case of $[Ru^p-OH]^{n+}$, the O atom also forms H bonds with the electron deficient H atoms placed next to the N atom of each pyrazole ring. The bond distances are between 2.272 and 2.441 Å, and in most cases the O-H bond distances are shorter than those of $[Ru^{II}-OH]^{2+}$. This indicates that the OH groups are also stabilized by the nearby pyrazole rings through H bonds.

The ΔG^0 values for the steps that appear in the three our WOC-specific catalytic cycles were calculated (Table S20) and plotted in Fig. S40. The ΔG^0 of the loose aquation (step 1) is 0.1518 eV (14.6 kJ mol⁻¹ or 3.5 kcal mol⁻¹), which is slightly positive. Under the acidic condition (Fig. S40a), the ΔG^0 values of steps 3, 6, 7, and 8 are highly positive (4.88-7.45 eV), indicating that the acidic condition is highly unfavorable for the catalytic reaction. Fig. S40a once again explains why TON and TOF became very low at pH < 6 (Fig. 12 in the main text). Under the basic condition, the ΔG^0 values of all steps are negative with the values ranging between -0.0865 and -5.1540 eV, except that of step 5, which is significantly positive (1.3439 eV). This indicates that step 5, or the oxidation of [Ru^{IV}-OH]²⁺ to [Ru^{IV}-OH]²⁺, is RDS in the new catalytic cycle under the basic condition (Fig. S40bc).

We also compared the E_{HOMO} values of the intermediates that undergo oxidation with those of $[PS-n]^{3+}$ (n = 0, 2, 4, and 6) (Fig. S40) since the intermediates should be oxidized by $[PS-n]^{3+}$. The results show that the E_{HOMO} values of all oxidizable intermediates are more positive than those of $[PS-n]^{3+}$ (n = 0, 2, 4, and 6), except that of $[Ru^V-OH]^{4+}$. This result also indicates that step 5 is unfavorable. However, because ΔG^0 of the subsequent deprotonation step is highly exergonic, we propose that the immediate deprotonation step (step 6) drives the overall reaction cycle despite

that step 5 is unfavorable. Fig. S40 also shows that the difference in E_{HOMO} between $[Ru^{IV}-OH]^{4+}$ and $[PS-n]^{3+}$ is very small compared to those between other intermediates and $[PS-n]^{3+}$. In such a case, the oxidation power of each individual $[PS-n]^{3+}$ is crucial for the oxidation. Since this step is RDS, the increase in TOF and TON with increasing *n* in $[PS-n]^{3+}$ is also explained from this respect, the increase in oxidation power, as well as the increase in *f* as *n* in $[PS-n]^{3+}$ increases.

Most importantly, the above scheme (Fig. S38c and Fig. S40c) matches well with the experimentally observed secondary KDIE (Fig. 13 in the main text), which indicates that RDS does not involve deprotonation. The above good match between the experimental results and the DFT calculation-based reaction schemes shows that the real mechanism can also be proposed simply based on the DFT calculations.