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Supporting Information for:

Redox-active ligand assisted electrocatalytic water oxidation by a mononuclear cobalt complex

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Sample preparation for SEM and EDX experiment

The FTO surface was cleaned with deionised water prior to SEM and EDX analysis. The FTO electrode was then used for CPE and then again washed with deionised water and dried. The dried FTO was then analysed by SEM and EDX.

Calibration of Ag/AgCl with respect to NHE

The Ag/AgCl reference electrode was calibrated using linear sweep voltammetry technique. The LSV was taken using a Pt-disk (2 mm diameter) in H_2 saturated 0.1M phosphate buffer (pH 8) at a scan rate of 1 mV/sec using the Ag/AgCl (satd KCl) reference electrode in the potential region 0 to -1 V. The potential where the voltammogram crosses 0 (zero) current was considered the potential of the Ag/AgCl vs RHE.¹



Figure S1: LSV plot for Ag/AgCl reference electrode calibration. Pt-disk was used as working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode in H₂-saturated 0.1 M phosphate buffer (pH 8) solution using scan rate of 1 mV/s.



Figure S2: ESI-MS spectra of complex **[1^{II}1^{III}].3ClO**₄ in acetonitrile.



Figure S3: ORTEP representations of the two Co units, $[Co^{II}(dpaq)(H_2O)]^+$, $[1^{II}]^+$ and $[Co^{III}(dpaq)(H_2O)]^{2+}$, $[1^{III}]^{2+}$ (ellipsoids were drawn at 30% probability and the counter anions, hydrogens were omitted for clarity). Full crystallographic details are given in Table S1 and Table S2.



Figure S4: ESI-MS spectra of complex **1** in water.



Figure S5: ¹H NMR spectrum of the complex $\mathbf{1}$ in D₂O (top) and H-dpaq in CDCl₃ (bottom) using a Bruker 400 MHz spectrometer.

Crystal data		
CCDC reference number	CCDC-1573631	
Empirical formula	$Co_2C_{46}H_{47}N_{10}O_{17}Cl_3$	
Moiety formula	CoC ₂₃ H ₂₃ N ₅ O ₂ ,	
	$CoC_{23}H_{22}N_5O_2$, 3(ClO ₄), H ₂ O	
Formula weight	1236.15	
Crystal system	Monoclinic	
Space group	P 21/c	
Colour, habit	Purple, rod	
Size, mm	0.22 × 0.18 × 0.16	
Unit cell dimensions		
	a = 12.563(5)Å $\alpha = 90^{\circ}$	
	b = 18.556(8)Å β = 94.530(6)°	
	$c = 23.167(10)$ Å $\gamma = 90^{\circ}$	
Volume Å ³	5384(4)	
Z	4	
Density (calculated), Mg/m ³	1.525	
Absorption coefficient, mm ⁻¹	0.844	
F(000)	2536	
Data collection		
Temperature, K	293(2)	
Theta range for data	1.96° to 25.58°	
collection		
Index ranges	$-13 \le h \le 15$	
	$-22 \le k \le 22$	
	-23 ≤ <i>l</i> ≤ 28	
Reflections collected	25953	
Unique reflections	9816	
Observed reflections	5566	
(>2 <i>\sigma(l)</i>)		
$R_{\rm int}$	0.0765	
Completeness to θ, %	25.58°. 97.2	
Absorption correction	Multi-scan (SADABS; Bruker, 2000)	
	$T_{\rm min}$ = 0.834, $T_{\rm max}$ = 0.873	
Refinement		
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints /	9816 / 1 / 711	
parameters	$1/(-2)(E^2) + (0.1E(0,2))^2 + 0.0000E^2$	
Calculated weights, w	$1/[\sigma^2(F_0^2) + (0.1592P)^2 + 0.0000P]$ where $P = (F_0^2 + 2F_0^2)/3$	
Goodness-of-fit on <i>F</i> ²	1.018	
Final R indices [I > $2\sigma(I)$]	$R_1 = 0.0873$, w $R_2 = 0.2292$	
R indices (all data)	$R_1 = 0.1482$, w $R_2 = 0.2688$	
Largest diff. peak and hole	1.642 and -0.865 e.Å ⁻³	

Table S1 Crystal data collection and structure refinement for $[1^{II}1^{II}].3ClO_4$

Bond lengths (Å)							
Co(1)-O(2)	1.937(4)	Co(2)-O(4)	1.920(4)				
Co(1)-N(1)	1.924(6)	Co(2)-N(6)	1.941(5)				
Co(1)-N(2)	1.879(5)	Co(2)-N(7)	1.885(5)				
Co(1)-N(3)	1.952(6)	Co(2)-N(8)	1.942(5)				
Co(1)-N(4)	1.939(5)	Co(2)-N(9)	1.936(5)				
Co(1)-N(5)	1.944(5)	Co(2)-N(10)	1.939(5)				
N(2)-C(10)	1.369(8)	N(7)-C(33)	1.325(8)				
O(1)-C(10)	1.224(7)	O(3)-C(33)	1.259(7)				
	Bond angles (°)						
0(2)-Co(1)-N(1)	96.3(2)	0(4)-Co(2)-N(6)	95.1(2)				
O(2)-Co(1)-N(3)	93.2(2)	O(4)-Co(2)-N(8)	95.3(2)				
0(2)-Co(1)-N(4)	88.94(19)	O(4)-Co(2)-N(9)	90.5(2)				
O(2)-Co(1)-N(5)	89.2(2)	O(4)-Co(2)-N(10)	87.06(19)				
N(2)-Co(1)-N(1)	84.0(2)	N(7)-Co(2)-N(6)	84.2(2)				
N(2)-Co(1)-N(3)	86.5(2)	N(7)-Co(2)-N(8)	85.4(2)				
N(2)-Co(1)-N(4)	91.3(2)	N(7)-Co(2)-N(9)	91.6(2)				
N(2)-Co(1)-N(5)	90.5(2)	N(7)-Co(2)-N(10)	91.0(2)				
N(1)-Co(1)-N(4)	95.7(2)	N(6)-Co(2)-N(9)	94.1(2)				
N(1)-Co(1)-N(5)	96.1(2)	N(6)-Co(2)-N(10)	96.9(2)				
N(3)-Co(1)-N(4)	84.8(2)	N(8)-Co(2)-N(9)	83.7(2)				
N(3)-Co(1)-N(5)	83.6(2)	N(8)-Co(2)-N(10)	85.7(2)				

Table S2Selected bond lengths (Å), bond angles (°) and torsion angles (°) for $[1^{II}1^{III}].3ClO_4$

$\begin{array}{llllllllllllllllllllllllllllllllllll$		
CCDC reference numberCCDC-1573631Empirical formulaCoC23H32N5Q2Cl2Moiety formula weight 608.40 Crystal systemTriclinicSpace groupP -1Colour, habitClear dark brown, PlateSize, mm $0.22 \times 0.11 \times 0.05$ Unit cell dimensions $a = 8.7167(6)$ Å $a = 8.7167(6)$ Å $a = 112.930(7)^{\circ}$ $b = 13.2069(8)$ Å $\beta = 92.528(7)^{\circ}$ $c = 13.7214(12)$ Å $\gamma = 108.905(6)^{\circ}$ Volume Å31349.76(17)Z2Density (calculated), Mg/m31.260Absorption coefficient, mm ⁻¹ 0.855F(000)524Data collection 3.00° to 25.00°Index ranges $-10 \le h \le 10$ $-15 \le k \le 15$ $-12 \le l \le 16$ Reflections collected7284Unique reflections (> $2\sigma(I)$)3277 R_{int} 0.0935Completeness to $0, \%$ 25.00°, 99.4Absorption correctionMulti-scan $T_{min} = 0.891, T_{max} = 0.957$ RefinementFull-matrix least-squares on F^2 Data / restraints / parameters $4725 / 0 / 290$ Calculated weights, w $1/[\sigma^2(F_o^2) + (0.1260P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$ 1.009Final R indices (11 2 $2\sigma(I)$) $R_1 = 0.0899, WR_2 = 0.2221$ R indices (all data) $R_1 = 0.1057, WR_2 = 0.2417$ Largest diff. peak and hole0.870 and -1.004 e.År-3	Crystal data	
Empirical formula $CoC_{26}H_{32}N_5O_4(Cl_2$ Moiety formula weight608.40Crystal systemTriclinicSpace groupP-1Colour, habitClear dark brown, PlateSize, mm0.22 × 0.11 × 0.05Unit cell dimensions $a = 8.7167(6)$ Å $a = 8.7167(6)$ Å $a = 112.930(7)^{\circ}$ $b = 13.2069(8)$ Å $\beta = 92.528(7)^{\circ}$ $c = 13.7214(12)$ Å $\gamma = 108.905(6)^{\circ}$ Volume Å ³ 1.349.76(17)Z2Density (calculated), Mg/m ³ 1.260Absorption coefficient, mm ⁻¹ 0.855F(000)524Data collection 3.00° to 25.00°Index ranges $-10 \le h \le 10$ $-15 \le k \le 15$ $-12 \le l \le 16$ Reflections collected7284Unique reflections (> $2\sigma(I)$)3277 R_{int} 0.0935Completeness to θ , %25.00°, 99.4Absorption correctionMulti-scan $T_{min} = 0.891, T_{max} = 0.957$ RefinementFull-matrix least-squares on F^2 Data / restraints / parameters4725 / 0 / 290Calculated weights, w $1/[c^2(F_o^2) + (0.1260P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$ 1.009Final R indices [1 > $2\sigma(I)$] $R_1 = 0.0899, wR_2 = 0.2221$ R indices (all data) $R_1 = 0.1057, wR_2 = 0.2417$ Largest diff. peak and hole0.870 and -1.004 e.År ³	CCDC reference number	CCDC-1573631
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Space group Colour, habitP -1Colour, habitClear dark brown, PlateSize, mm $0.22 \times 0.11 \times 0.05$ Unit cell dimensions $a = 8.7167(6)$ Å $b = 13.2069(8)$ Å $c = 13.7214(12)$ Å $c = 13.7214(12)$ Å $c = 13.7214(12)$ Å $F(000)$ $a = 112.930(7)^{\circ}$ $c = 13.7214(12)$ Å $F(000)$ Z2Density (calculated), Mg/m³ Absorption coefficient, mm ⁻¹ $C(00)$ 0.855 $F(000)$ Temperature, K293(2)Theta range for data collection $-15 \le k \le 15$ $-12 \le l \le 15$ $-12 \le l \le 16$ Reflections collected Unique reflections 7284 25.00° , 99.4 Absorption correction $Multi-scan$ $T_{min} = 0.891$, $T_{max} = 0.957$ Refinement Refinement method Data / restraints / parameters Calculated weights, wFull-matrix least-squares on F^2 $4725 / 0 / 290$ Refinement method Prinal R indices [$1 > 2\sigma(1)$] R indices ($1 > 2\sigma(1)$] R indices ($1 > 2\sigma(1)$] R indices ($1 > 0.099$; R indices ($1 > 0.097$; R indices ($1 > 2\sigma(1)$]Refine get (alta) R indices ($1 > 0.097$; R indices ($1 > 0.007$]Refine fine ($1 > 2\sigma(1)$] R indices ($1 > 0.007$]Rest ($1 > 0.007$)Rest (Crystal system	Triclinic
Colour, habitClear dark brown, PlateSize, mm $0.22 \times 0.11 \times 0.05$ Unit cell dimensions $a = 8.7167(6)$ Å $a = 8.7167(6)$ Å $\beta = 92.528(7)^{\circ}$ $b = 13.2069(8)$ Å $\beta = 92.528(7)^{\circ}$ $c = 13.7214(12)$ Å $\gamma = 108.905(6)^{\circ}$ Volume Å ³ 1.349.76(17)Z2Density (calculated), Mg/m ³ 1.260Absorption coefficient, mm ⁻¹ 0.855F(000)524Data collection3.00° to 25.00°Index ranges $-10 \le h \le 10$ $-15 \le k \le 15$ $-12 \le l \ge 16$ Reflections collected7284Unique reflections4725Observed reflections (> $2\sigma(I)$)3277 R_{int} 0.0935Completeness to θ , %25.00°, 99.4Absorption correctionMulti-scan $T_{min} = 0.891, T_{max} = 0.957$ RefinementFull-matrix least-squares on F^2 Data / restraints / parameters $1/(5^2(F_o^2) + (0.1260P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_o^2)/3$ Goodness-of-fit on F^2 1.009Final R indices [$1 > 2\sigma(I)$] $R_1 = 0.0899,$ w $R_2 = 0.2221$ R indices (all data) $R_1 = 0.1057,$ w $R_2 = 0.2417$ Largest diff. peak and hole0.870 and -1.004 e.Å ⁻³	Space group	P -1
Size, mm $0.22 \times 0.11 \times 0.05$ Unit cell dimensions $a = 8.7167(6)$ Å $a = 8.7167(6)$ Å $\beta = 92.528(7)^{\circ}$ $c = 13.7214(12)$ Å $\gamma = 108.905(6)^{\circ}$ Volume Å ³ 1349.76(17) Z 2 Density (calculated), Mg/m ³ 1.260 Absorption coefficient, mm ⁻¹ 0.855 F(000) 524 Data collection - Temperature, K 293(2) Theta range for data collection 3.00° to 25.00° Index ranges $-10 \le h \le 10$ $-15 \le k \le 15$ $-12 \le l \le 16$ Reflections collected 7284 Unique reflections 4725 Observed reflections (> $2\sigma(l)$) 3277 R_{int} 0.0935 Completeness to θ , % 25.00°, 99.4 Absorption correction Multi-scan $T_{min} = 0.891, T_{max} = 0.957$ Refinement Full-matrix least-squares on F^2 Data / restraints / parameters $4725 / 0 / 290$ Calculated weights, w $1/[\sigma^2(F_o^2) + (0.1260P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$ 1.009	Colour, habit	Clear dark brown, Plate
Unit cell dimensions $a = 8.7167(6)$ Å $\alpha = 112.930(7)^{\circ}$ $b = 13.2069(8)$ Å $\beta = 92.528(7)^{\circ}$ $c = 13.7214(12)$ Å $\gamma = 108.905(6)^{\circ}$ Volume Å ³ 1349.76(17) Z 2 Density (calculated), Mg/m ³ 1.260 Absorption coefficient, mm ⁻¹ 0.855 F(000) 524 Data collection 3.00° to 25.00° Theta range for data collection 3.00° to 25.00° Index ranges $-10 \le h \le 10$ $-15 \le k \le 15$ $-12 \le l \le 16$ Reflections collected 7284 Unique reflections 4725 Observed reflections (> $2\sigma(l)$) 3277 R_{int} 0.0935 Completeness to θ , % 25.00°, 99.4 Absorption correction Multi-scan $T_{min} = 0.891, T_{max} = 0.957$ Refinement Full-matrix least-squares on F^2 Data / restraints / parameters 4725 / 0 / 290 Calculated weights, w $1/[\sigma^2(F_o^2) + (0.1260P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$ 1.009 Goodness-of-fit on F^2 1.009 Final R indices [1	Size, mm	0.22 imes 0.11 imes 0.05
$\begin{array}{c} a = 8.7167(6) \bed{A} & \alpha = 112.930(7)^{\circ} \\ b = 13.2069(8) \bed{A} & \beta = 92.528(7)^{\circ} \\ c = 13.7214(12) \bed{A} & \gamma = 108.905(6)^{\circ} \\ \hline Volume \bed{A}^3 & 1349.76(17) \\ \hline Z & 2 \\ \hline Density (calculated), Mg/m^3 & 1.260 \\ Absorption coefficient, mm^{-1} & 0.855 \\ \hline F(000) & 524 \\ \hline Data collection \\ \hline Temperature, K & 293(2) \\ \hline Theta range for data collection & 3.00^{\circ} to 25.00^{\circ} \\ Index ranges & -10 \le h \le 10 \\ -15 \le k \le 15 \\ -12 \le l \le 16 \\ \hline Reflections collected & 7284 \\ \hline Unique reflections (>2\sigma(l)) & 3277 \\ R_{int} & 0.0935 \\ \hline Completeness to \ \theta, \% & 25.00^{\circ}, 99.4 \\ \hline Absorption correction & Multi-scan \\ T_{min} = 0.891, T_{max} = 0.957 \\ \hline Refinement \\ Refinement \\ Refinement method \\ Data / restraints / parameters \\ Calculated weights, w & 1/[\sigma^2(F_o^2) + (0.1260P)^2 + 0.0000P] \\ where P = (F_o^2 + 2F_c^2)/3 \\ \hline Goodness-of-fit on \ F^2 \\ Inidices (all data) \\ R_1 = 0.1057, wR_2 = 0.2417 \\ Largest diff. peak and hole \\ \hline 0.870 and -1.004 e \begar{A}^{-1}$	Unit cell dimensions	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	a = 8.7167(6)Å	$\alpha = 112.930(7)^{\circ}$
$\begin{array}{c} c = 13.7214(12) \mbox{Å} & \gamma = 108.905(6)^{\circ} \\ \mbox{Volume $ \mbox{Å}^3$} & 1349.76(17) \\ \mbox{Z} & 2 \\ \mbox{Density (calculated), Mg/m}^3 & 1.260 \\ \mbox{Absorption coefficient, mm}^{-1} & 0.855 \\ \mbox{F(000)} & 524 \\ \mbox{Data collection} \\ \mbox{Temperature, K} & 293(2) \\ \mbox{Theta range for data collection} & 3.00^{\circ} to 25.00^{\circ} \\ \mbox{Index ranges} & -10 \leq h \leq 10 \\ -15 \leq k \leq 15 \\ -12 \leq l \leq 16 \\ \mbox{Reflections collected} & 7284 \\ \mbox{Unique reflections} & 4725 \\ \mbox{Observed reflections} (>2\sigma(l)) & 3277 \\ \mbox{R_{int}} & 0.0935 \\ \mbox{Completeness to } \theta, \% & 25.00^{\circ}, 99.4 \\ \mbox{Absorption correction} & Multi-scan \\ \mbox{T_{min}} = 0.891, T_{max} = 0.957 \\ \mbox{Refinement} \\ \mbox{Refinement method} & Full-matrix least-squares on F^2 \\ \mbox{Data / restraints / parameters} & 4725 / 0 / 290 \\ \mbox{Calculated weights, w} & 1/[\sigma^2(F_o^2) + (0.1260P)^2 + 0.0000P] \\ \mbox{$where $P = (F_o^2 + 2F_c^2)/3$} \\ \mbox{Goodness-of-fit on F^2} \\ \mbox{Induces (all data)} & R_1 = 0.0899, $wR_2 = 0.2221$ \\ \mbox{R indices (all data)} & R_1 = 0.1057, $wR_2 = 0.2417$ \\ \mbox{$Largest diff, peak and hole} & 0.870 and -1.004 e. \mbox{Λ^{-3}} \\ \end{tabular}$	b = 13.2069(8)Å	$\beta = 92.528(7)^{\circ}$
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Z	2
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$\begin{array}{cccc} -15 \leq k \leq 15 \\ -12 \leq l \leq 16 \\ \hline \ \mbox{Reflections collected} & 7284 \\ \hline \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	Index ranges	$-10 \le h \le 10$
$\begin{array}{cccc} -12 \leq l \leq 16 \\ \mbox{Reflections collected} & 7284 \\ \mbox{Unique reflections} & 4725 \\ \mbox{Observed reflections} (>2\sigma(l)) & 3277 \\ \mbox{R_{int}} & 0.0935 \\ \mbox{Completeness to } \theta, \% & 25.00^{\circ}, 99.4 \\ \mbox{Absorption correction} & Multi-scan \\ \mbox{T_{min}} = 0.891, T_{max} = 0.957 \\ \mbox{Refinement} \\ \mbox{Refinement method} & Full-matrix least-squares on F^2 \\ \mbox{Data / restraints / parameters} & 4725 / 0 / 290 \\ \mbox{Calculated weights, w} & 1/[\sigma^2(F_o^2) + (0.1260P)^2 + 0.0000P] \\ \mbox{$where $P = (F_o^2 + 2F_c^2)/3$ \\ \mbox{Goodness-of-fit on F^2} \\ \mbox{Indices [I > 2\sigma(I)]} & R_1 = 0.0899, $wR_2 = 0.2221$ \\ \mbox{$R_1 = 0.1057, $wR_2 = 0.2417$} \\ \mbox{Largest diff. peak and hole} & 0.870 \text{ and } -1.004 e.Å^{-3} \\ \end{tabular}$		$-15 \le k \le 15$
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Largest diff. peak and hole 0.870 and -1.004 e.Å ⁻³	R indices (all data)	$R_1 = 0.1057, wR_2 = 0.2417$
	Largest diff. peak and hole	0.870 and -1.004 e.Å ⁻³

Bond lengths (Å)							
Co(1)–Cl(1)	2.2668(13)	Co(1) - N(3)	1.947(4)				
Co(1) - N(1)	1.931(4)	Co(1) - N(4)	1.962(4)				
Co(1) - N(2)	1.895(4)	Co(1) - N(5)	1.950(4)				
Bond angles (°)							
Cl(1)–Co(1)–N(1)	94.41(12)	N(2)-Co(1)-N(4)	89.59(17)				
Cl(1)-Co(1)-N(3)	95.04(12)	N(2)-Co(1)-N(5)	90.21(17)				
Cl(1)-Co(1)-N(4)	88.99(11)	N(1)-Co(1)-N(4)	96.48(18)				
Cl(1)-Co(1)-N(5)	91.56(12)	N(1)-Co(1)-N(5)	95.5(2)				
N(2)-Co(1)-N(1)	84.00(16)	N(3)-Co(1)-N(4)	84.11(19)				
N(2)-Co(1)-N(3)	86.56(17)	N(3)-Co(1)-N(5)	83.9(2)				

 Table S4 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for 1.



Figure S6: CV of complex **1** (0.5mM) (Red) and $[Zn(dpaq)]^+$ (0.5 mM) (Black) in 0.1 M phosphate buffer (pH=8) at a scan rate of 100 mVs⁻¹ using a GC working electrode.



Figure S7: CV of complex **1** in 0.1 M phosphate buffer (pH=8) having different concentration (0.05mM purple, 0.1mM violet line, 0.15mM navy line, 0.2mM green line, 0.25mM magenta line, 0.3mM blue line, 0.4mM red line and 0.5mM black line) at a scan rate of 100 mVs⁻¹ using a GC working electrode. Inset shows the plot of catalytic peak current (1.45 V) vs [catalyst].



Figure S8: (top) Formation of oxygen indicated by the appearance of oxygen bubbles at the GC electrode surface. (bottom). CV of complex **1** (1.0 mM) in pH 8 0.1 M phosphate buffer recorded after multiple anodic scans when bubbles appeared at the electrode surface (black line). After the oxidative scans potential was reversed towards cathodic potentials where a broad reductive wave at -0.33 V (*vs.* NHE) appeared showing the reduction of oxygen. When the same was done before going to the catalytic wave no such reductive wave can be seen (grey line). This indicates the generation of oxygen due to water oxidation catalyzed by complex **1**. Glassy carbon working electrode, scan rate 100 mVs⁻¹.



Figure S9: 15 consecutive CV cycles of complex 1 (0.3mM) in pH 8 0.1 M phosphate buffer and the inset shows the first CV cycle of the multiple scan (black line) and CV of the same electrode in blank buffer medium after 15 scans which was rinsed with water but not polished.



Figure S10: SEM image and EDX spectra of the FTO electrode used in CPE experiment after 3 hours of electrolysis.



Figure S11: UV visible spectra of complex 1 (0.2 mM) before (black line) and after (red line) control potential electrolysis.

Electrochemical kinetic analysis by FOWA

CVs at different scan rate as well as at different catalyst concentrations were used to determine the kinetic parameters for water oxidation. We have applied FOWA methodology for the WNA and I2M mechanisms, for kinetic analysis using the following two equations²,

For WNA

$$i / ip = \frac{4 \times 2.24 \sqrt{\left(\frac{RT}{F\vartheta}\right)kWNA}}{1 + exp^{[m]}\left\{\left(\frac{F}{RT}\right)(E0 - E)\right\}}$$

For I2M

$$i/ip = \frac{4 \times 2.24 \sqrt{\left(\frac{RT}{F\vartheta}\right)kDC0Cat}}{\left[1 + \exp\left\{\left(\frac{F}{RT}\right)(E0 - E)\right\}\right]^{3/2}}$$

And TOF was calculated using the following equation

$$TOF = \frac{kWNA}{1 + exp[m] \{F(E0 - EH2O/O2 - \eta)\}}$$

Where, C_{cat}^{o} : initial bulk concentration of catalyst; E^o: standard potential for the Co^{IV/V} couple; $E_{H2O/O2}$: standard potential of oxidation of water at the working pH; F: Faradaic constant; η : overpotential; i: CV current intensity; i_p : peak current intensity of one-electron redox process of the catalyst; k_1 : apparent WNA rate constant; k_{WNA} : apparent WNA pseudo-rate constant ($k_1[H_2O]$); k_D : apparent dimerization constant; R: gas constant; T: temperature.



Figure S12: Plot of i/ip vs $1+\exp\{(F/RT)(E^o-E)\}$ for foot of the wave analysis at different catalyst concentration.

Electrochemical kinetic analysis by following the classical Shain et al. methodology³

The linear dependency of catalytic peak current for water oxidation, i_{cat} , with the bulk concentration of the catalyst (Figure S7) is consistent with single-site cobalt catalysis and therefore, the peak current of the catalytic process should obey the following equation,

$$i_{\text{cat}} = n_{\text{cat}} FA[\mathbf{Co}](k_{\text{cat}} \mathbf{D}_1)^{1/2}$$
(1)

where i_{cat} is the peak current of the catalytic wave, $n_{cat} = 4$ is the number of electrons transferred in each catalytic cycle of water oxidation, A is the electrode surface area in cm⁻², F is the Faraday constant, [**Co**] is the bulk concentration of the catalyst (in mol/L), and D₁ is the diffusion coefficient of the catalyst in 0.1 M phosphate buffer at pH 8. Moreover, as evident from Inset Figure S13, the peak current for the Co(III/IV) couple at 0.7 V *vs.* NHE varies linearly with the square root of the scan rate ($v^{1/2}$), which is consistent with the Randles-Sevcik equation,

$$i_{\rm d} = 0.496 n_{\rm d} F A [Co] (n_{\rm d} F v D_1 / RT)^{1/2}$$
 (2)

where, $n_d = 1$ is the number of electrons transferred in the diffusion controlled Co(III/IV) process and T is the absolute temperature. The ratio of Eq. 1 and 2 provides a relationship between i_{cat} and i_d (Eq. 3) allowing us to evaluate the rate constants for water oxidation.

$$i_{\text{cat}}/i_{\text{d}} = 0.359 \,(n_{\text{cat}}/n_{\text{d}})^{3/2} (k_{\text{cat}})^{1/2} (1/v^{1/2})$$
 (3)

Thus, catalytic currents at 1.45 V vs NHE (i_{cat}) were normalized to the Co^{III}/Co^{IV}wave at 0.7 V (i_d) and i_{cat}/i_d was plotted against $v^{-1/2}$. From the slope of the plot of i_{cat}/i_p vs $v^{-1/2}$ (Figure S13), k_{cat} was calculated to be 85 s⁻¹ in 0.1M phosphate buffer at pH 8.



Figure S13: (left) Scan rate dependent CVs of **1** (0.5mM) in 0.1M phosphate buffer pH=8 using a GC working electrode, Pt counter electrode and Ag/AgCl reference electrode (black line 50mVs⁻¹, red line 25 mVs⁻¹, blue line 10 mVs⁻¹ and pink line 5 mVs⁻¹). (inset) Plot of $i_p vs. v^{1/2}$ for electrocatalytic water oxidation in 0.1M phosphate buffer at pH=8 (black circles). (right) Background corrected plot of $i_{cat}/i_p vs$ $1/v^{1/2}$ for electrocatalytic water oxidation in 0.1M phosphate buffer at pH=8 (black circles). (right) Background corrected plot of rate constant (black circles).



Figure S14: CV of complex **1** (0.3 mM) in pH 8 phosphate buffer (0.1 M) in H_2O (red line) and D_2O (black line) at GC working electrode. All the CVs were recorded at a scan rate of 100 mVs⁻¹.



Figure S15: CV of complex 1 (0.3mM) in different concentration of HPO_4^- and the ionic strength was maintained by adding NaClO₄.



Figure S16: CV of complex **1** (0.2 mM) in pH 8 0.1 M phosphate buffer with (black line) and without KCl (red line).



Figure S17: (top) ESI-MS spectra of $[Zn(dpaq)]^+$ in acetonitrile. (bottom) UV-Vis spectra of the Zn(complex) (25 µM) in acetonitrile.

Reference:

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