

Electronic Supplementary Information

A mononuclear cobalt complex for water oxidation:

New controversies and puzzles

Rasoul Safdari,^a Mohammad Reza Mohammadi,^{b,c} Małgorzata Hołyńska,^d Petko Chernev,^{b,e}
Holger Dau^b and Mohammad Mahdi Najafpour^{*a,f,g}

^a*Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanzan, 45137-66731, Iran*

^b*Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany*

^c*University of Sistan and Baluchestan, Department of Physics, Zahedan, Iran, 98167-45845*

^d*Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften (WZMW), Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany*

^e*Uppsala University, Department of Chemistry - Ångströmlaboratoriet, Lägerhyddsvägen 1, 75120 Uppsala, Sweden*

^f*Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanzan, 45137-66731, Iran*

^g*Research Center for Basic Sciences & Modern Technologies (RBST), Institute for Advanced Studies in Basic Sciences (IASBS), Zanzan 45137-66731, Iran*

**Corresponding author;*

Phone: (+98) 24 3315 3201; E-mail: mmnajafpour@iasbs.ac.ir

Experimental

Materials

All reagents and solvents were purchased from commercial sources and were used without further purification. Di(2-pyridyl)ketone, cobalt(II) perchlorate hexahydrate and fluorine-doped tin oxide coated glass (FTO) were purchased from the Sigma-Aldrich Company. Sodium carbonate was purchased from Merck Company.

Synthesis of **1**

1 was synthesized by the previously reported method ^[1].

Solution 1: $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) was dissolved in 4 mL of acetonitrile.

Solution 2: Na_2CO_3 (0.5 mmol) and di(2-pyridyl)ketone (1.0 mmol) (1:2) were dissolved in a mixture of distilled water and acetonitrile ($V_{\text{water}}:V_{\text{acetonitrile}} = 1:1$, 8mL) and the mixture was stirred until a clear solution was formed.

Subsequently, the **solution 1** was slowly added dropwise to the **solution 2** under strong stirring. The solution was strongly stirred for 3 hours and then filtered. The filtrate was kept in a 20 mL flask to allow slow evaporation at room temperature and the dark-red crystals of **1** were obtained after 5 days.

Characterization

Electrochemical experiments were performed using an EmStat³⁺ device from PalmSens (Netherlands). Cyclic voltammetry studies were carried out with a conventional three-electrode setup in which FTO, $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ and a platinum rod served as the working,

reference and auxiliary electrodes, respectively. The distance between the two opposite sides of the FTO electrode was measured with a digital caliper MarCal 16ER model (Mahr, Germany). The temperature was measured with the Laserliner 082 device (Germany).

XAS experiments

After the bulk electrolysis of **1** for one hour at 1.20 V (vs. Ag|AgCl|KCl_{sat}) using an FTO electrode we investigated this FTO electrode (**FTO-A**) in XAS experiments. The electrode was frozen by immersion in liquid nitrogen.

XAS measurements at the cobalt K-edge were performed at the KMC-3 beamline at the BESSY II synchrotron facility (Helmholtz-Zentrum Berlin, Germany) at 20 K in a liquid-helium cooled cryostat (Oxford-Danfysik). The angle between the film surface and the incident beam was approximately 45°. Fluorescence-detected X-ray absorption spectra at the cobalt K-edge were collected using a 13-element Ge detector (Ultra-LEGe, Canberra) installed perpendicular to the X-ray beam.

X-ray diffraction studies

Single crystal in form of an orange block was mounted on a Bruker Quest D8 diffractometer with CMOS detector. A multi-scan absorption correction was applied. Basic crystallographic data are collected in Table S1.

Refinement

The crystal structure was solved by direct methods in SHELXS and refined with a full-matrix technique in SHELXL-2014. O-bonded H atoms were found on difference Fourier map and subsequently, the cation hydroxyl H atoms were constrained with AFIX 147 constraints.

Additional maxima appearing in the vicinity of perchlorate O atoms were interpreted as a disorder of this anion. In this disorder the Cl1-O8 moiety position does not change, whereas the remaining three O atoms adopt two positions related by a rotation along the Cl1-O8 axis. The refined occupancies are 0.89(1) and 0.11(1), respectively. The minor-occupancy component was refined isotropically. SADI restraints were applied to keep the Cl-O bond lengths similar. On the final difference Fourier map the highest maximum of 0.48 e/Å³ is located in the middle of C12-C13 bond.

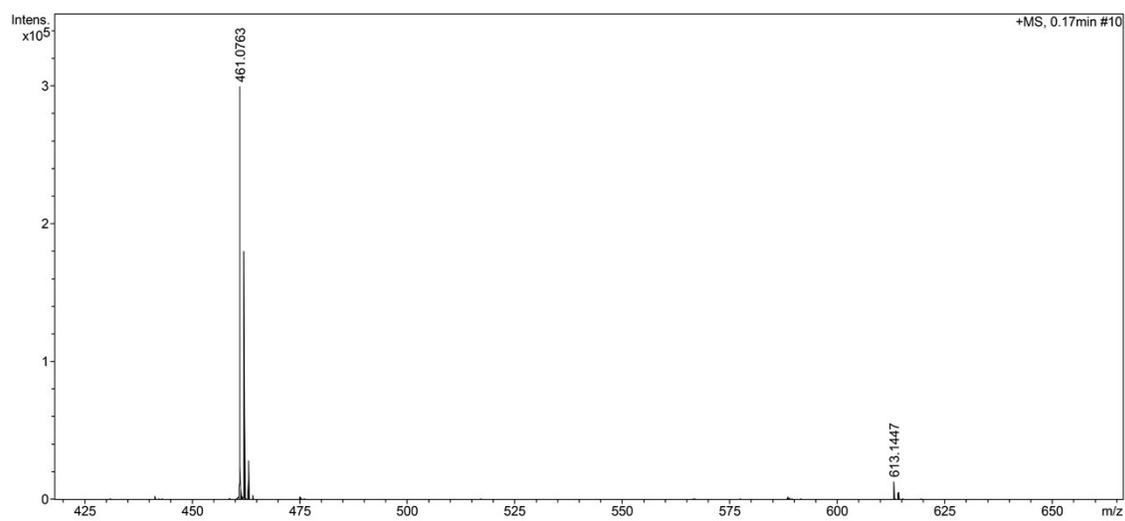


Fig. S1 ESI-Mass spectrum for **1**.

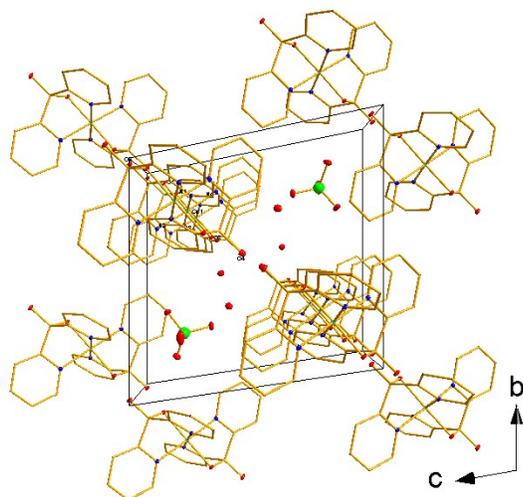


Fig. S2 Cation columns formed along the *a* direction. The disordered anion minor component and H atoms are omitted for clarity.

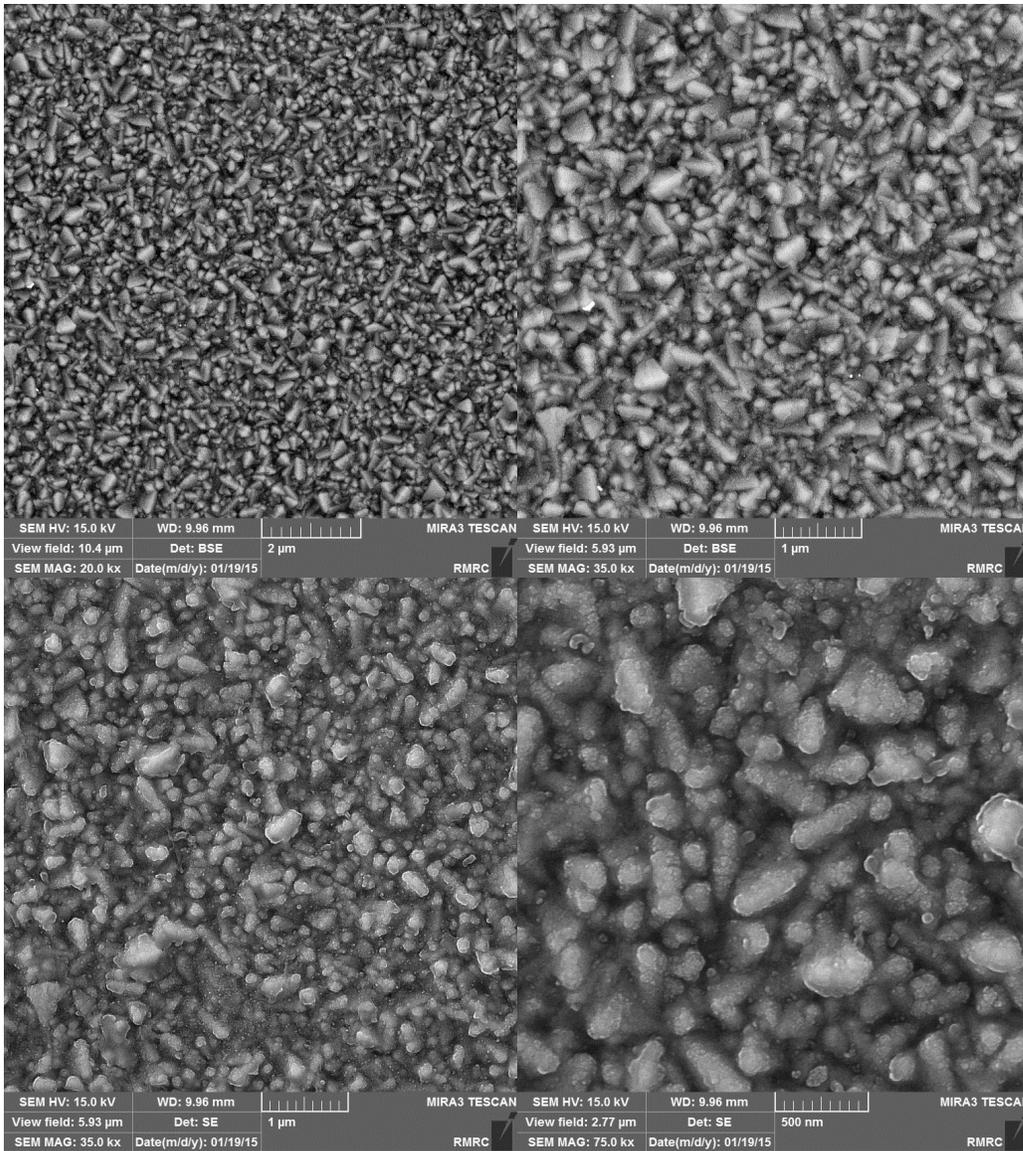


Fig. S3 SEM images for the fresh FTO.

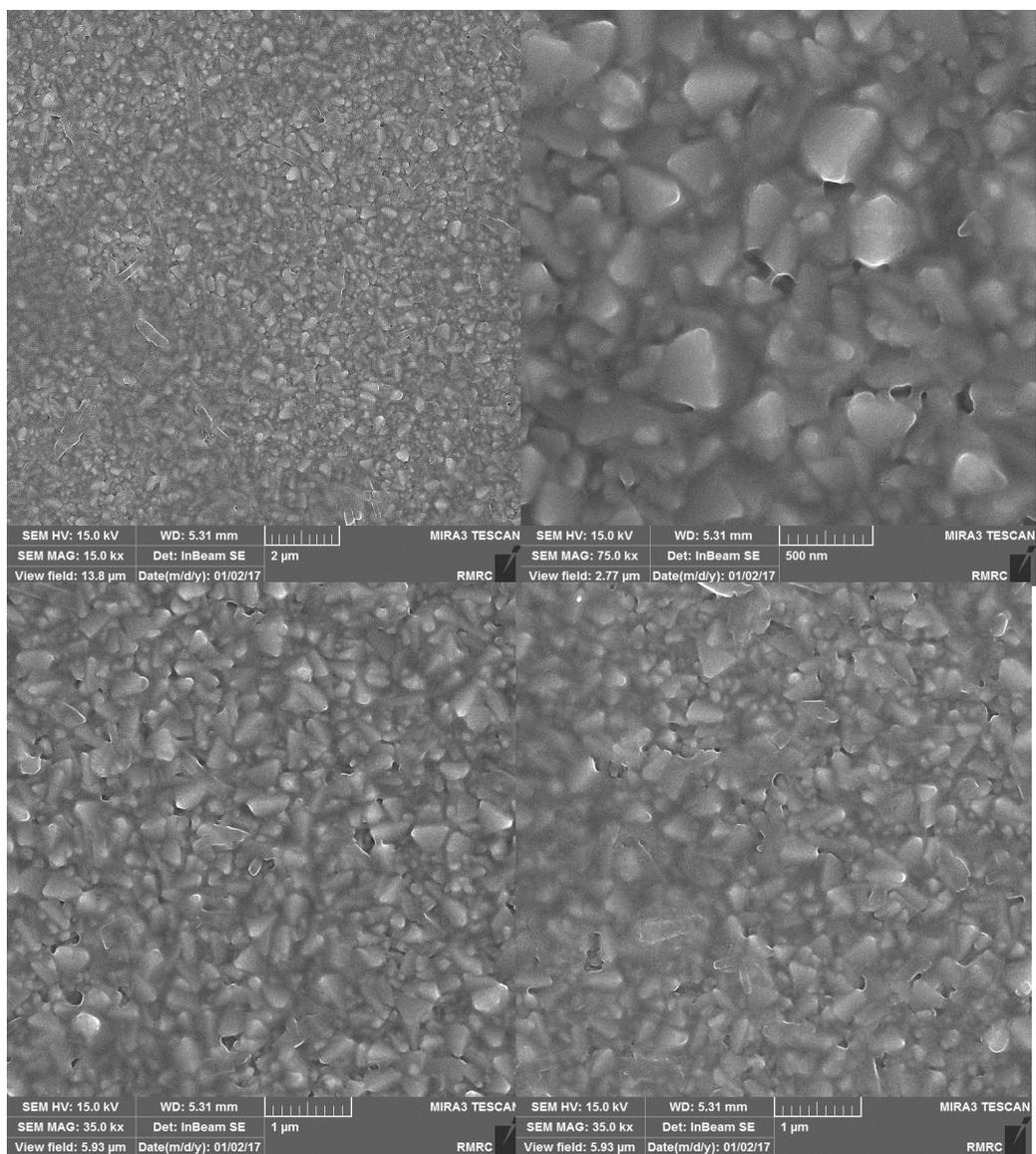


Fig. S4 SEM images for the film formed on the **FTO-A** electrode after 5.0 hours of electrolysis of **1** at (1.20 V vs. vs. Ag/AgCl) in 100.0 mL of sodium borate buffer solution (pH 9.0, 80 mM).

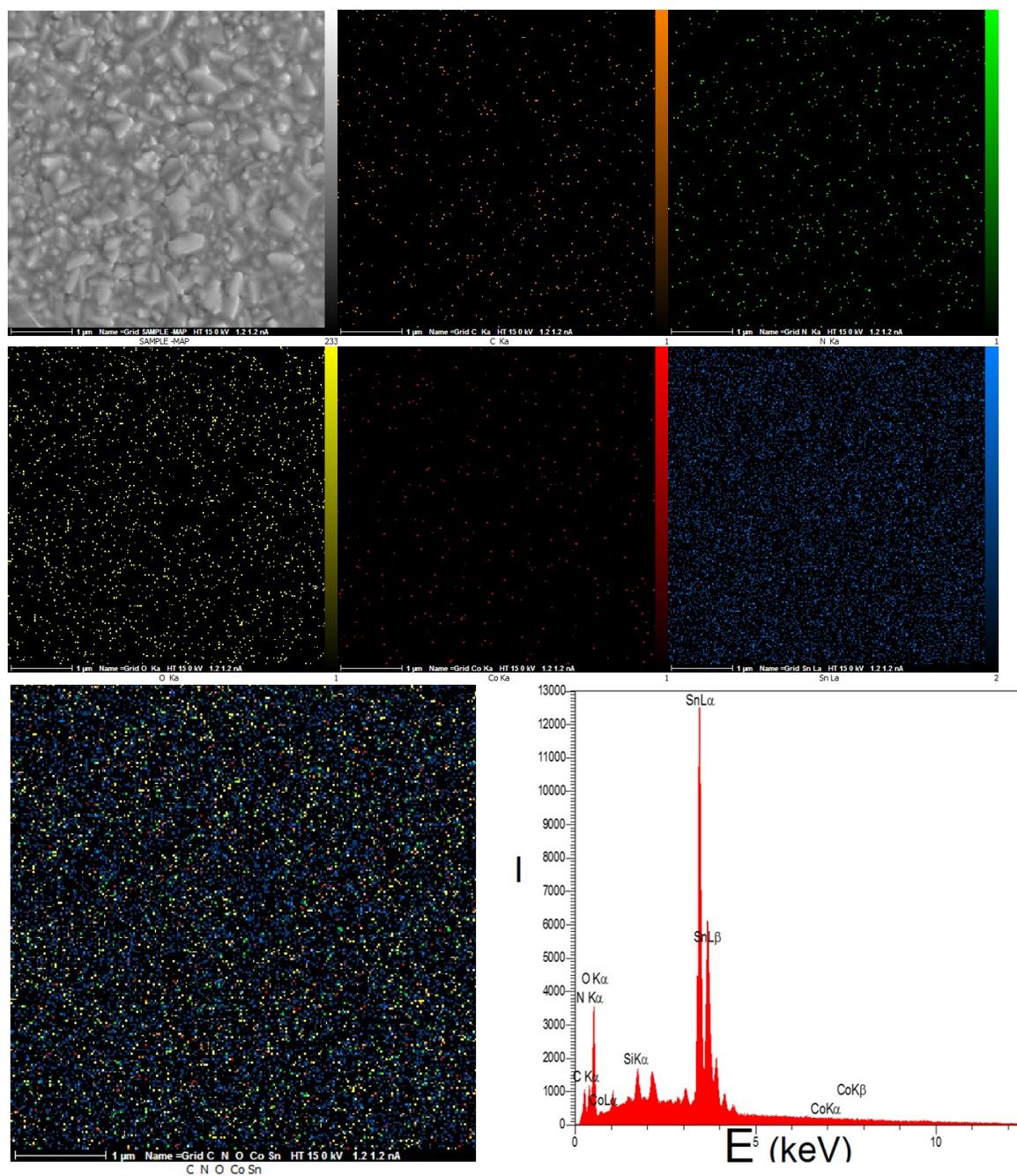
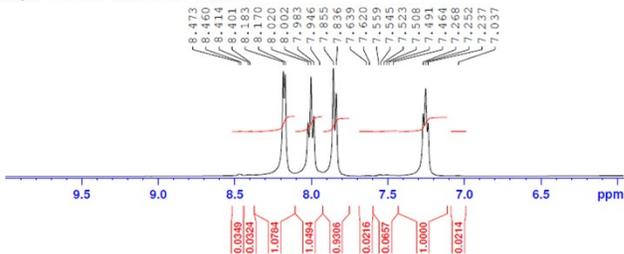
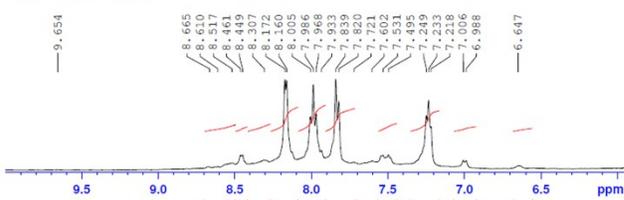


Fig. S5 EDX-SEM results for the film formed on the **FTO-A** electrode after 5.0 hours of electrolysis of **1** at (1.20 V vs. vs. Ag/AgCl) in 100.0 mL of sodium borate buffer solution (pH 9.0, 80 mM).

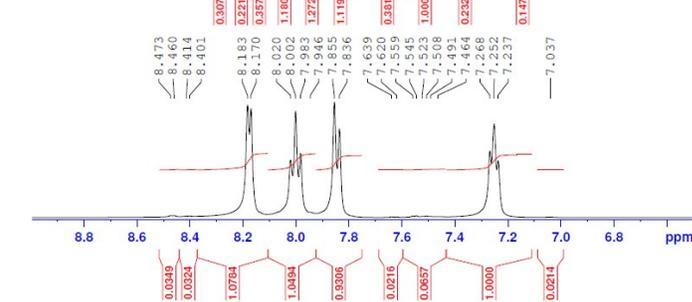
Sample code:Co-DPK in D2O (safdari)



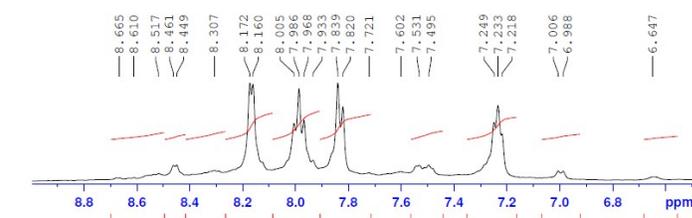
Sample code:Co-DPK t=0 in D2O (safdari)



Sample code:Co-DPK t=0 in D2O (safdari)



Sample code:Co-DPK t=0 in D2O (safdari)



Sample code:Co-DPK t=0 in D2O (safdari)



Sample code:Co-DPK t=0 in D2O (safdari)

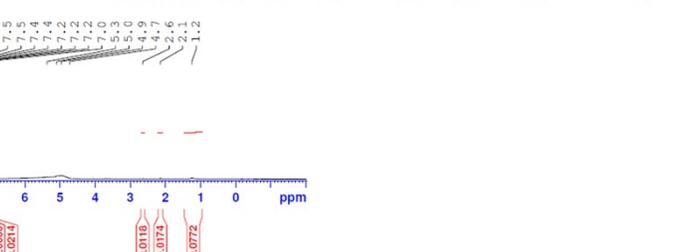
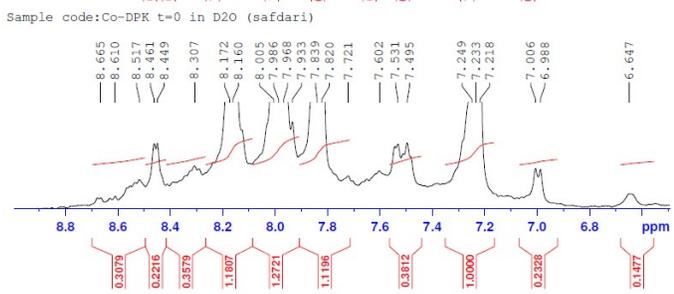
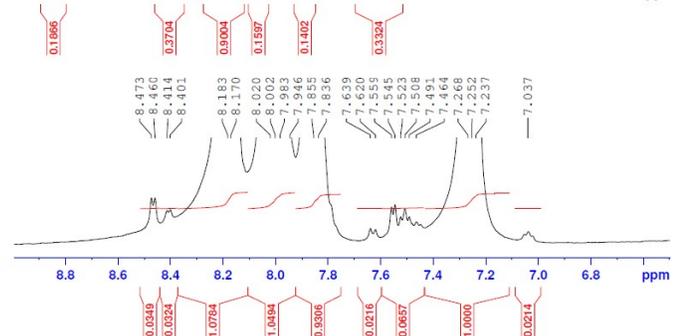
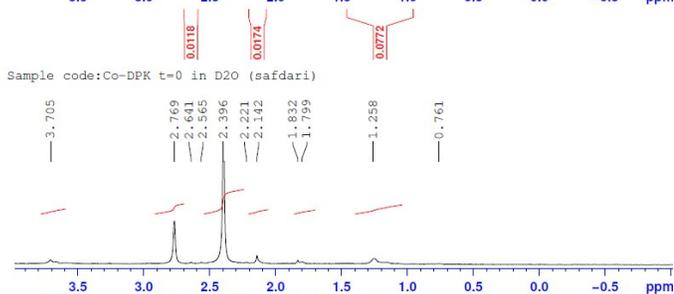
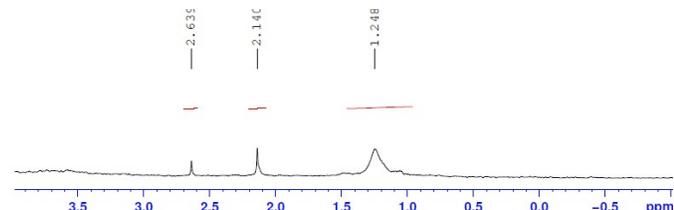
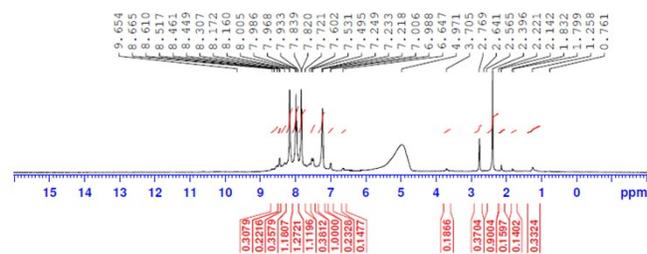


Fig. S6 ¹H NMR spectra for **1** before (below) and after 5.0 hours (top) amperometry (1.20 V vs. Ag/AgCl) of **1** (20.0 mg) in 100.0 mL of sodium borate buffer¹ solutions (pH 9.0, 80 mM).

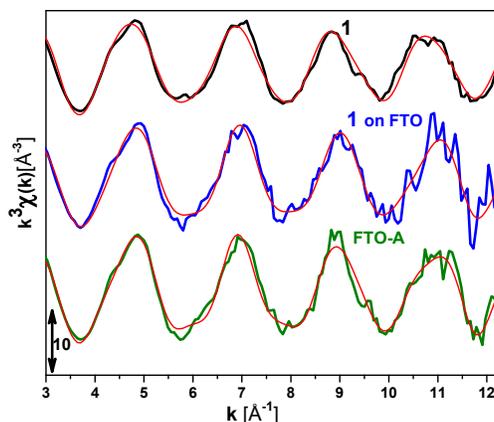


Fig. S7 k^3 -weighted $\chi(k)$ of **1** and **1** adsorbed on FTO as well as the operated compound on FTO (**FTO-A**) at 1.20 V for 5.0 hour in 100.0 mL of sodium borate buffer solutions (pH 9.0, 80 mM) and the simulation results (red lines). XANES of adsorbed **1** on FTO and **FTO-A** at 1.2 V in 100.0 mL of sodium borate buffer solutions (pH 9.0, 80 mM). The fit parameters are given in **Table 1**.

EXAFS simulations

Simulations were performed using the in-house software package SimX^[2] and SimXLite. An EXAFS spectrum $\chi(k)$ is given by the sum of the contributions of n_{shell} 'atomic shells'. A 'shell' is a group of elements with identical atomic number and similar distances from the X-ray absorbing atom (e.g., six oxygen atoms surrounding the absorbing manganese ion). The EXAFS equation is mathematically defined by the following equation^[3, 4]:

$$\chi(k) = S_o^2 \sum_i^{n_{shell}} A(R_i, k)_i N_i \exp(-2\sigma_i^2 k^2) \sin(2kR_i + \phi_i)$$

where S_o^2 is the amplitude reduction factor, $A(R_i, k)_i$ is a factor that includes the scattering amplitude and mean-free-path of the photo-electron, ϕ_i the phase correction, N_i the number of atoms in the i^{th} atomic shell, σ_i the Debye-Waller parameter of the i^{th} atomic shell, and R_i the (average) distance between the X-ray

absorbing atom and the atoms of the i^{th} atomic shell. The functions A and ϕ were obtained herein from ab-initio calculations using Feff 9.05 [5], using coordinates from the molecular structure of **1**.

For conversion of the energy axis to a k-vector axis, an E_0 of 7709 eV was used. Curve-fitting of the data was accomplished within a k-range of 2.5 \AA^{-1} to 13 \AA^{-1} . The amplitude reduction factor, S_o^2 , was 0.7. Parameter error estimation was performed as described in Ref. 6.

As it is well known, distance R is not an independent parameter but strongly coupled with the ΔE_0 value. Similarly, the coordination numbers N and Debye-Waller parameters σ are also coupled and need to be separated from each other. Therefore, we first determined ΔE_0 and σ from a fit to the initial compound **1** in which the coordination numbers were fixed to the values expected from the molecular structure of **1** (sum of N for Co- $O_{\text{short}}/N_{\text{short}}$ shells equal to 6, and sum of N for Co-C shells equal to 10). We then used these ΔE_0 and σ values for the fit of the sample after operation.

Table S1 Basic crystallographic data.

	1
Formula	C ₂₂ H ₁₈ CoN ₄ O ₄ ·ClO ₄ ·2(H ₂ O)
Formula weight	596.81
Temperature [K]	100(2)
λ [Å]	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	8.445 (3)
b [Å]	11.908 (3)
c [Å]	12.414 (4)
α [°]	99.74 (3)
β [°]	103.51 (3)
γ [°]	90.24 (3)
V [Å ³]	1195.1 (7)
Z, ρ _{calc} [g cm ⁻³]	2, 1.658
μ [mm ⁻¹]	0.90
F(000)	612
Crystal size [mm]	0.64 × 0.24 × 0.15
θ range[°]	2.2–30.1
reflns: total /unique	60965/7036
Abs. corr.	multi-scan
Min., max. transmission factors	0.600, 0.876
Data/restraints/params	7036/21/376
GOF on F ²	1.02
R ₁ [I > 2σ(I)]	0.026
wR ₂ (all data)	0.076
Max., min. Δρ _{elect} [e Å ⁻³]	0.48, -0.54

Table S2 Selected bond lengths and bond angles [Å, °].

Co1—O3	1.8859 (11)	Co1—N3	1.9302 (12)
Co1—O1	1.8902 (11)	O1—C6	1.4047 (14)
Co1—N4	1.9133 (12)	O2—C6	1.3759 (14)
Co1—N1	1.9159 (11)	O3—C17	1.4062 (14)
Co1—N2	1.9238 (12)	O4—C17	1.3799 (14)
O3—Co1—O1	178.44 (3)	N4—Co1—N2	178.45 (4)
O3—Co1—N4	83.33 (5)	N1—Co1—N2	87.92 (5)
O1—Co1—N4	95.36 (5)	O3—Co1—N3	82.91 (5)
O3—Co1—N1	95.90 (5)	O1—Co1—N3	97.93 (5)
O1—Co1—N1	83.26 (5)	N4—Co1—N3	88.82 (5)
N4—Co1—N1	90.78 (5)	N1—Co1—N3	178.78 (4)
O3—Co1—N2	97.65 (5)	N2—Co1—N3	92.49 (5)
O1—Co1—N2	83.64 (5)		

Table S3 Hydrogen bonding parameters [\AA , $^\circ$].

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1W1\cdots O8^i$	0.81 (3)	2.15 (3)	2.942 (2)	167 (2)
$O2W-H1W2\cdots O3^i$	0.78 (2)	1.90 (2)	2.6706 (16)	172 (2)
$O2W-H2W2\cdots O8$	0.77 (3)	2.12 (3)	2.8938 (18)	179 (3)
$O2-H2O\cdots O1^{ii}$	0.84	1.78	2.6181 (14)	174
$O4-H4O\cdots O2W$	0.84	1.76	2.5929 (15)	173
$C2-H2\cdots O1W^i$	0.95	2.65	3.344 (2)	130
$C4-H4\cdots O2^{iii}$	0.95	2.63	3.225 (2)	121
$C10-H10\cdots O6^i$	0.95	2.62	3.142 (3)	115
$C11-H11\cdots O6^i$	0.95	2.42	3.048 (2)	124
$C12-H12\cdots O7^{iv}$	0.95	2.63	3.529 (2)	158
$C12-H12\cdots O66^{iv}$	0.95	2.59	3.110 (14)	115
$C12-H12\cdots O2^{ii}$	0.95	2.59	3.2171 (17)	124
$C15-H15\cdots O4^v$	0.95	2.60	3.498 (2)	159
$C19-H19\cdots O1W^v$	0.95	2.66	3.252 (2)	121
$C22-H22\cdots O7^{vi}$	0.95	2.37	3.314 (2)	174
$C22-H22\cdots O77^{vi}$	0.95	2.45	3.356 (13)	158

(i) $-x+1, -y+1, -z+1$

(ii) $-x+1, -y+2, -z+2$

(iii) $-x+2, -y+2, -z+2$

(iv) $x, y, z+1$

(v) $-x, -y+1, -z+1$

(vi) $-x+1, -y+2, -z+1$

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