

## **Electronic Supplementary Information**

# **Homogeneous or heterogeneous electrocatalysis: Reinvestigation of a cobalt coordination compound for water oxidation**

Amirreza Valizadeh,<sup>a</sup> Rahman Bikas,<sup>b</sup> Subhajit Nandy,<sup>c</sup> Tadeusz Lis,<sup>d</sup> Keun Hwa Chae,<sup>c</sup> and  
Mohammad Mahdi Najafpour<sup>\*a,e,f</sup>

<sup>a</sup>Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

<sup>b</sup>Department of Chemistry, Faculty of Science, Imam Khomeini International University, 34148-96818, Qazvin, Iran

<sup>c</sup>Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

<sup>d</sup>Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, Wrocław 50-383, Poland

<sup>e</sup>Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

<sup>f</sup>Research Center for Basic Sciences & Modern Technologies (RBST), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

\*Corresponding author: Tel: (+98) 24 3315 3201; E-mail: [mmnajafpour@iasbs.ac.ir](mailto:mmnajafpour@iasbs.ac.ir) (MMN)

## Experimental

### Materials

All reagents and solvents were purchased from commercial sources and were used without further purification. Cobalt(II) nitrate, H<sub>2</sub><sup>18</sup>O, and fluorine-doped tin oxide coated glass slide (FTO; surface resistivity ~7 Ω/sq) were purchased from the Sigma-Aldrich Company. Sodium salt of 4-(2-Hydroxy-1-naphthylazo) benzenesulfonate was purchased from the Merck Company. For the experiments, milli-Q water (18-20 MΩ•cm<sup>-1</sup> at 27 °C) was used.

### Characterization

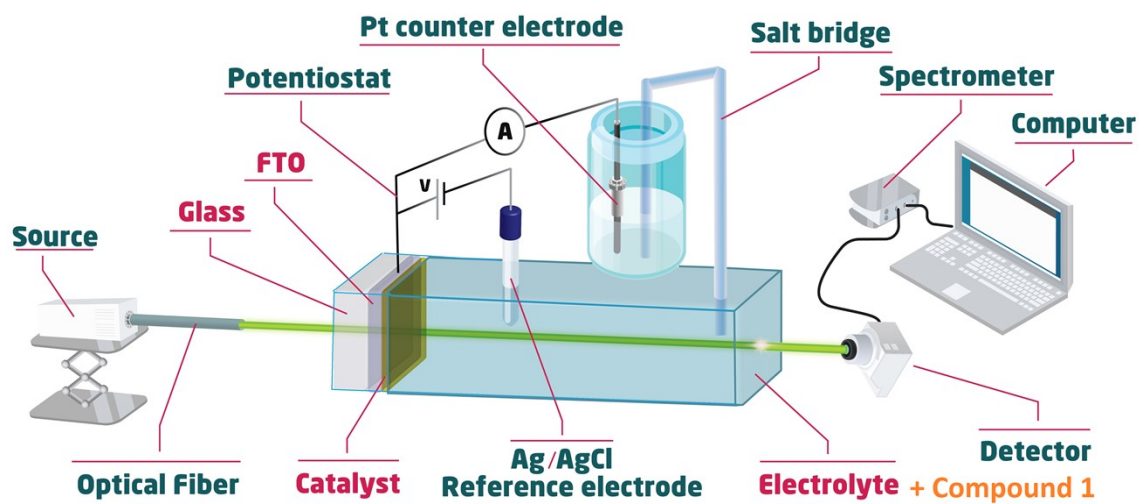
SEM and EDX were carried out with VEGA\TESCAN-XMU. HRTEM and TEM were carried out using a FEI Tecnai G<sup>2</sup> F20 transmission electron microscope, TF20 (200 kV). Electrochemical experiments were performed using an EmStat<sup>3+</sup> from PalmSens (Netherlands). Voltammetry studies were carried out with a conventional three-electrode setup, in which FTO (1.0 cm<sup>2</sup>) or glassy carbon (GC, 0.0314 cm<sup>2</sup>), Ag|AgCl (KCl: 3.0 M), and a platinum foil served as working, reference, and auxiliary electrodes, respectively. All potentials in this project were reported vs. the reversible hydrogen electrode (RHE). To convert the measured potential to RHE, it is determined by cyclic voltammetry (CV) in the range of hydrogen evolution/oxidation at a Pt electrode in H<sub>2</sub>-saturated electrolyte, using a H<sub>2</sub> generation, with the scan rate of 10 mV/s under stirrer at zero current. The distance between two opposite sides of the FTO electrode was measured by a digital caliper MarCal 16ER model (Mahr, Germany). The temperature was measured by Laserliner 082 (Germany). The visible spectra were recorded by a mini spectrophotometer (Pooyesh Tadbir Karaneh (Phystec), Iran). X-ray photoelectron spectroscopy (XPS, K-ALPHA, Thermo Scientific) was used to analyze the samples surface. All spectra were collected using Al-K<sub>α</sub> radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot at 3 mA × 12 kV. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements. XPS data were analyzed with Advantage software. A smart background function was used to approximate the experimental backgrounds and surface elemental composition were calculated from background-subtracted peak areas. Charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. The penetration depth is around 3 nm. The X-ray powder diffraction patterns were recorded with a Bruker D8 Advance (Germany) diffractometer (CuK<sub>α</sub> radiation). Raman spectra were collected from the electrode surface before and after consecutive CVs (range: 1.16-1.66 V, scan rate: 10 mV/s). Raman spectra were collected by XploRA ONE™ Raman Microscope from Horiba Company using 750 nm laser. The deconvolution plots were calculated by Origin software using Gauss function. The Raman spectra were performed by the software " LabSpec 6 from" from Horiba Company. It has an auto-calibration software-ensures the data is always accurate.

### **Details of single crystal X-ray analysis**

The crystals of compound **1** were obtained by thermal gradient method in methanol during a week. Data collection was performed on an Xcalibur CCD diffractometer with graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 100 K. The structure was solved by direct methods and refined by the full-matrix least-squares method on  $F^2$  with the use of SHELX2013 program packages [1]. The analytical absorption corrections were applied (CrysAlis version 171.39.46 package of programs [2]). Positions of hydrogen atoms have been found from the electron density maps and hydrogen atoms were constrained during refinement with the appropriate riding model as implemented in SHELX during refinement. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, no. 2056677.

### **Details of X-ray absorption spectroscopy**

The extended X-ray absorption fine structure (EXAFS) measurements for reported materials and references (Co metal, CoO, and Co<sub>2</sub>O<sub>3</sub>) were performed at the 1D XAS KIST-PAL beamline at Pohang Light Source (PLS), operating at 3.0 GeV with a storage current of 250 mA top-up mode. The beamline is a bending magnet X-ray scattering (XRS) beamline which uses a Si(111) double crystal monochromator to give a wide range of monochromatic energies (4 - 16 keV). To measure the EXAFS spectra of the materials, higher harmonics were removed by detuning the incident beam intensity to 60% of the maximum intensity. Three ionization chambers filled with He and N<sub>2</sub> gases were used to record the intensity of the incident and the transmitted X-rays, respectively. These materials are placed between the first and second ionization chamber, while reference foil (Co) for energy calibration is placed between the second and the third ionization chamber. Under stationary conditions, extended X-ray absorption fine-structure (EXAFS) measurements were performed around the Co K-edge in the step scanning mode. The obtained data are processed by using ATHENA [3].



Scheme S1 Setup for operando visible spectroscopy.

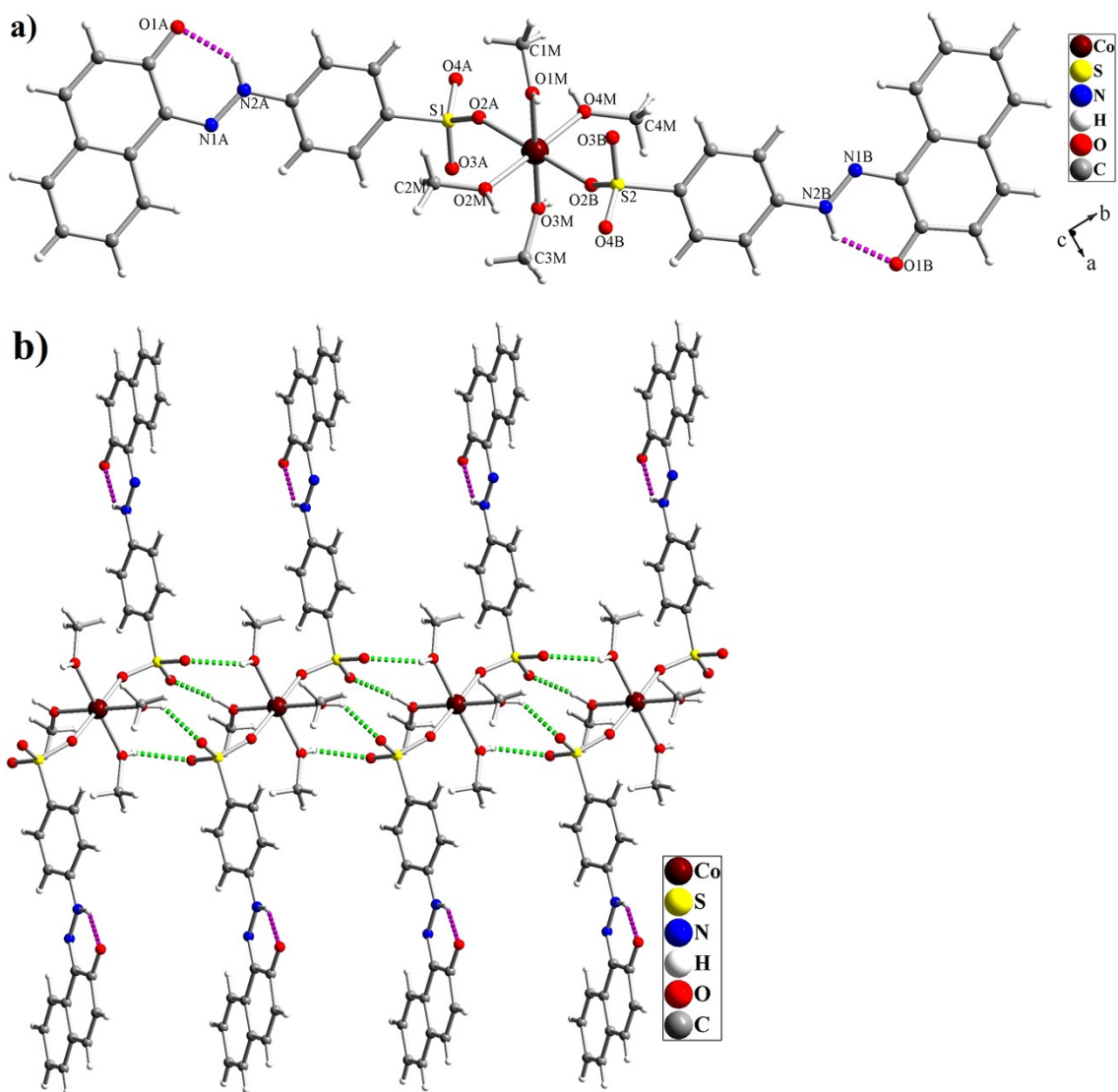


Figure S1 Molecular structure of compound **1** (a); 1D polymeric network obtained by intermolecular hydrogen bond interactions in the crystal structure of compound **1**. Pink and green dashed lines show intramolecular and intermolecular hydrogen bond interactions, respectively (b).

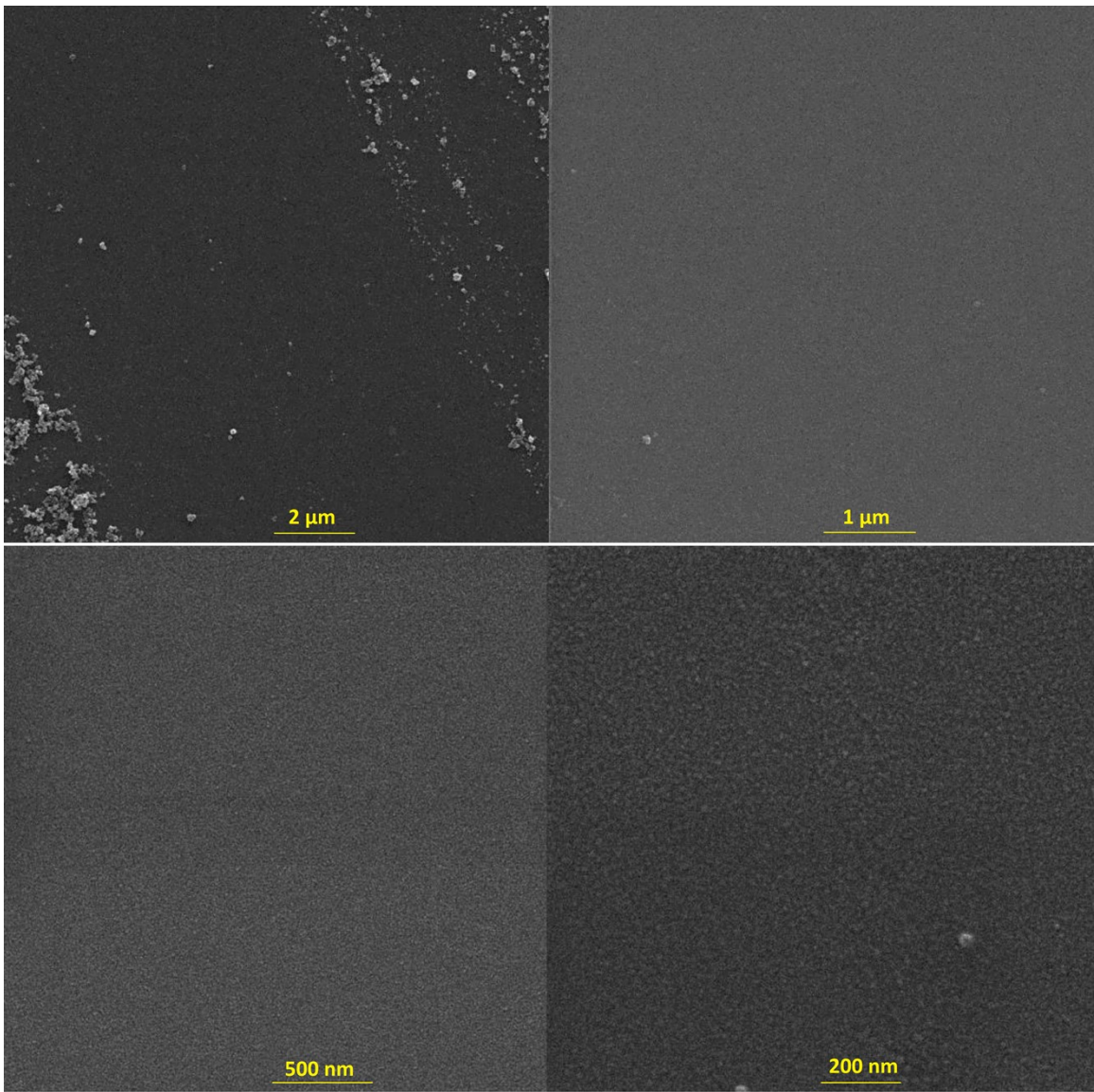


Figure S2 SEM images of a bare glassy carbon electrode at different magnifications.



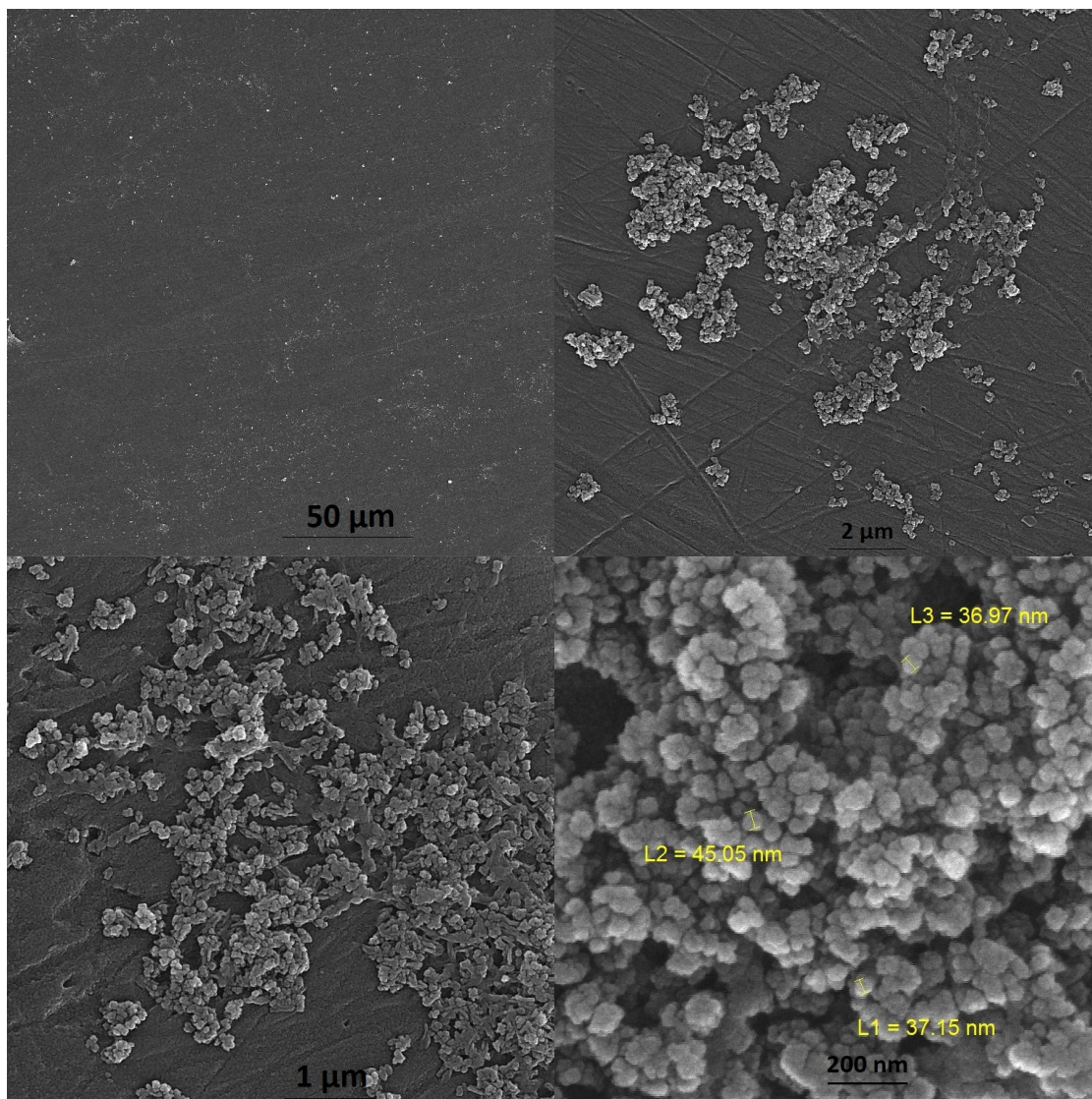


Figure S3 SEM images in the presence of compound **1** (60.0 μM) after 250 consecutive CVs using GC in a three-electrode system (0.25 M, pH = 9; scan rate: 100 mV/s).



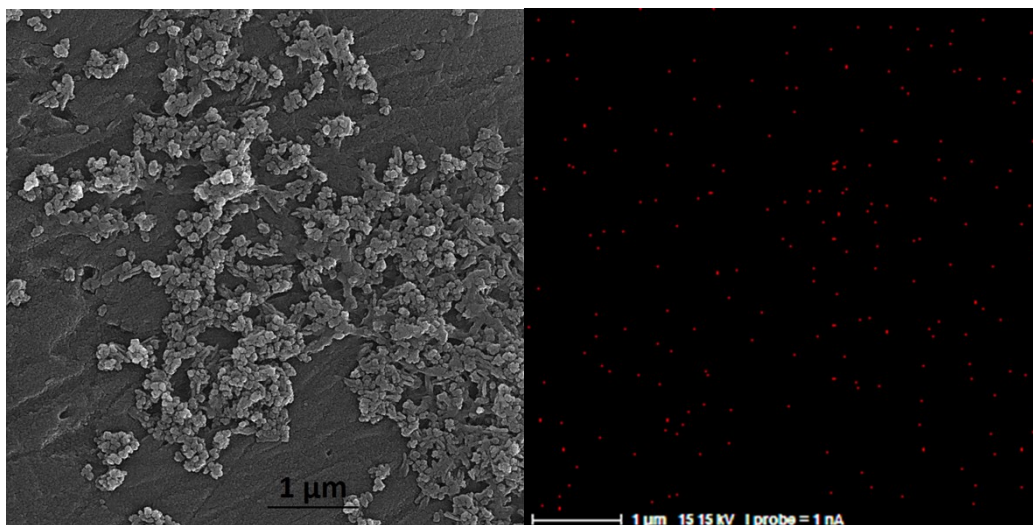


Figure S4 SEM-EDX Mapping for Co in the presence of compound **1** (60.0  $\mu\text{M}$ ) after 250 consecutive CVs using GC as working electrode in a three-electrode system (0.25 M, pH = 9; scan rate: 100 mV/s).

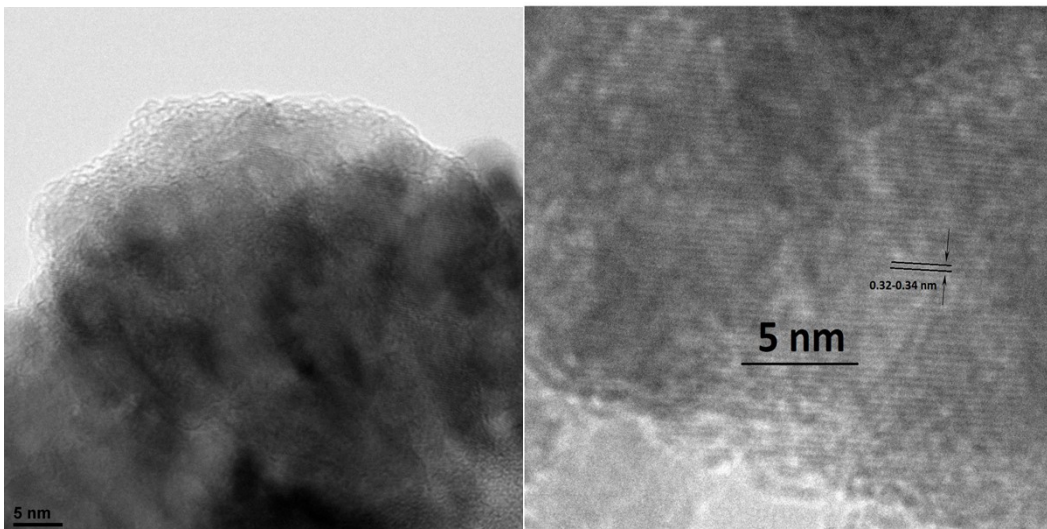


Figure S5 HRTEM images for Co in the presence of compound **1** (60.0  $\mu\text{M}$ ) after 250 consecutive CVs using carbon paper as working electrode in a three-electrode system (0.25 M, pH = 9; scan rate: 100 mV/s). Patterns in HRTEM are related to carbon paper.

Table S1. Crystallographic information of compound **1**

Compound	<b>1</b>
net formula	C <sub>36</sub> H <sub>38</sub> CoN <sub>4</sub> O <sub>12</sub> S <sub>2</sub>
$M_r$ /g mol <sup>-1</sup>	841.75
crystal size/ mm	0.20 × 0.03 × 0.03
T/K	100
crystal colour	Red
crystal system	Monoclinic
space group	<i>P2<sub>1</sub>/n</i>
Absorption correction	Analytical
$a/\text{Å}$	15.333(3)
$b/\text{Å}$	34.67(2)
$c/\text{Å}$	7.035(2)
$\beta/\text{Å}$	104.94(5)
$V/\text{Å}^3$	3613(3)
$Z$	4
$D_x/\text{Mg m}^{-3}$	1.547
$\mu/\text{mm}^{-1}$	0.66
$F(000)$	1748
measured reflections	10470
independent reflections	10470
reflections with $I > 2\sigma(I)$	2962
Parameters	345
$R_{\text{int}}$	0.029
$\theta$ range	3.2–25.5
$T_{\text{min}}, T_{\text{max}}$	0.917, 1.000
	$h, k, l$ -18 → 18, -42 → 42, -8 → 5
$R[F^2 > 2\sigma(F^2)]$	0.077
$R_w(F^2)$	0.089
$S$	0.83
Shift/error <sub>max</sub>	< 0.001
max electron density/e Å <sup>-3</sup>	0.64
min electron density/e Å <sup>-3</sup>	-0.69

Table S2. Selected bond lengths and angles in the crystal structure of compound **1**.

Bond	Length/Å	Bond	Angle/°
Co—O3M	2.038(5)	O3M—Co—O1M	177.9(3)
Co—O1M	2.053(6)	O3M—Co—O2B	86.5(2)
Co—O2B	2.058(7)	O1M—Co—O2B	91.6(3)
Co—O2A	2.092(7)	O3M—Co—O2A	93.1(2)
Co—O4M	2.115(6)	O1M—Co—O2A	88.8(2)
Co—O2M	2.124(6)	O2B—Co—O2A	179.0(3)
S1—O4A	1.460(7)	O3M—Co—O4M	90.0(2)
S1—O3A	1.464(6)	O1M—Co—O4M	89.2(2)
S1—O2A	1.476(7)	O2B—Co—O4M	93.4(2)
S1—C10A	1.785(9)	O2A—Co—O4M	85.8(3)
S2—O3B	1.464(6)	O3M—Co—O2M	90.9(2)
S2—O4B	1.464(7)	O1M—Co—O2M	89.9(2)
S2—O2B	1.466(7)	O2B—Co—O2M	87.3(3)
S2—C10B	1.756(9)	O2A—Co—O2M	93.5(2)
N1A—N2A	1.324(10)	O4M—Co—O2M	178.9(2)
N1B—N2B	1.303(10)		

## References

- [1] G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
- [2] CrysAlis 171.38.43 package of programs. Rigaku Oxford Diffraction, 2015.
- [3] B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537–541.