Supplementary Information

A tetraCo(II/III) complex with an open cubane Co_4O_4 core and square-pyramidal Co(II) and octahedral Co(III) centres: bifunctional electrocatalytic activity towards water splitting at neutral pH

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Section S1
Quantitative Estimation of Electrocatalytically Produced Hydrogen/Oxygen

The quantitative estimation of the evolved gas was performed by constant current electrolysis (CCE) with a locally designed and constructed electrolysis cell, where the working electrode and the counter electrode were placed in two separate chambers (image on the left). Bulk electrolysis at a constant current of –500 μA (for HER) or 500 μA (for OER) was carried out for 6 h using the two electrode system and 0.1 M sodium phosphate buffer of pH 7 as the

electrolyte. Surface coated (with $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, carbon-black and Nafion) FTO electrode with surface area of 0.5 cm^2 was used as the working electrode (cathode for HER/anode for OER) and a spiral platinum wire was used as the counter electrode (anode for HER/cathode for OER). The loading of the catalyst on FTO was maintained at 0.6 mg/cm^2. During electrolysis gas bubbles were formed at the surface coated FTO electrode which steadily accumulated in the graduated tube by displacing the electrolyte solution. The cell was designed in such a way that the gas bubbles formed at the counter electrode could no way interfere with those formed at the working electrode.

Section S2
Theoretical Calculations to Determine the Magnetic Anisotropy. The ab initio calculations were performed using the coordinates obtained from X-ray crystal structure without optimization. The diamagnetic Co(III) atoms were replaced by Ga(III) atoms in all the calcualtions. In these calculations, ZORA (zeroth-order regular approximation) was employed for both first principles and ZFS calculations. The basis sets def2-TZVPP for Co, def2-TZVP for Ga, def2-TZVP for N and O, and def2-SV(P) for C and H with the auxiliary basis set def2/JK for all the atoms were used for all calculations. Using the configuration interaction (CI) procedure, 10 quartet and 40 doublet spin states with the active space containing 7 electrons distributed over 5 d-orbitals (CAS 7, 5) were computed. In addition, to introduce the effect of dynamic correlation N-electron valence perturbation theory (NEVPT2) was employed on top of the CASSCF wave function. Further, the spin-orbit coupling was included by using quasi-degenerate perturbation theory (QDPT) approach. Both second-order perturbation theory and an effective Hamiltonian approach (EHA) were used to calculate the ZFS parameters D and E.

The SH parameters obtained from fitting of experimental data and ab initio calculations

Complex	D_{exp} (cm^{-1})	$|E|_{exp}$ (cm^{-1})	g_{exp}	D_{theo} (cm^{-1})	$|E|_{theo}$ (cm^{-1})	g_{theo}
$[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$	–23.59	0.03	2.52	–67.34	0.30	2.47

Section S3
Calculations of the Faradaic Efficiencies for HER and OER using Complex, CB, and Nafion Mixture Coated FTO Electrode

Hydrogen Evolution Reaction (HER). In the CCE experiment (see Section S1 for the procedure and the electrolytic cell setup) for HER, it was found that 1.4 mL of hydrogen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of hydrogen evolved in 1 h = 1.4/(6 x 22400) mol = 10.41 x 10^{-6} mol.

The controlled experiment was performed using carbon-black and Nafion coated FTO electrode keeping all other experimental conditions identical. The total amount of hydrogen evolved in 6 h was ~0.22 mL. Therefore, in terms of number of moles, the amount of hydrogen evolved in 1 h = 0.22/(6 x 22400) mol = 1.63 x 10^{-6} mol.

Thus, the amount of hydrogen actually evolved in 1 h = (10.41 − 1.63) x 10^{-6} mol
$$= 8.78 \text{ x } 10^{-6} \text{ mol}$$

The ideal number of moles of hydrogen expected to be evolved is Q/nF, where Q is the total charge employed, n is the number of electrons involved for H_2 production and F is the Faraday constant. The value of n for HER is 2 as it is a two electron process and since we employed −500 µA current, Q/nF in 1 h = (0.5 x 10^{-3} x 3600)/(2 x 96500) = 9.33 x 10^{-6} mol.

The expression used for the calculation of Faradaic Efficiency is as follows:

$$\text{Faradaic Efficiency} = \frac{\text{Moles of hydrogen evolved experimentally in 1 h}}{\text{Moles of hydrogen ideally expected in 1 h}} \text{ x } 100$$

$$= \{(8.78 \text{ x } 10^{-6})/(9.33 \text{ x } 10^{-6})\} \text{ x } 100 = 94\%$$

Oxygen Evolution Reaction (OER). In the CCE experiment (see Section S1 for the procedure and the electrolytic cell setup) for OER, 0.53 mL of oxygen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of oxygen evolved in 1 h = 0.53/(6 x 22400) mol = 3.94 x 10^{-6} mol.

In the controlled experiment performed using carbon-black and Nafion coated FTO electrode keeping all other experimental conditions identical the amount of oxygen evolved in 6 h was ~0.04 mL. Hence, the number of moles oxygen evolved in 1 h = 0.04/(6 x 22400) mol = 0.3 x 10^{-6} mol.

Hence, the amount of oxygen actually evolved = (3.94 − 0.3) x 10^{-6} mol
$$= 3.64 \text{ x } 10^{-6} \text{ mol}$$

The ideal number of moles of oxygen expected to be evolved is Q/nF, where Q is the total charge employed, n is the number of electrons involved for O_2 production and F is the Faraday constant. The value of n for OER is 4 as it is a four electron process and since we employed 500 µA current, Q/nF in 1 h = (0.5 x 10^{-3} x 3600)/(4 x 96500) = 4.66 x 10^{-6} mol.

The expression used for the calculation of the Faradaic Efficiency is as follows:

$$\text{Faradaic Efficiency} = \frac{\text{Moles of oxygen evolved experimentally in 1 h}}{\text{Moles of oxygen ideally expected in 1 h}} \text{ x } 100$$

$$= \{(3.64 \text{ x } 10^{-6}) / (4.66 \text{ x } 10^{-6})\} \text{ x } 100 = 78\%$$

Section S4

Calculations of Turnover Frequencies (TOF) for HER and OER using Complex, CB, and Nafion Mixture Coated FTO Electrode

Hydrogen Evolution Reaction (HER). The TOF was calculated using the following equation: TOF = I/2mF, where, I (= 2.55 x 10^{-4} A) is the steady state current in the constant potential (−1.05 V) electrolysis (CPE) plot for HER (Fig. S8), F is the Faraday constant (in C mol^{-1}), m is the number of active sites (in mol), and 2 is the number of electrons required to form one hydrogen molecule from two protons.

The number of active sites m can be calculated using the equation, m = Q/2F, where, Q (1.96 x 10^{-4} C) is the charge calculated by integrating the current vs time plot (within the potential range −0.8 to −1.2 V) generated from the cyclic voltammogram trace (in Fig. 6 and also in Fig. S4) recorded using [$Co^{II}Co^{III}$(μ-OAc)(μ_3-OH)(μ-L)]$_2$, carbon-black, and Nafion coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor ½ is for the 2 electron reduction of the catalyst [$Co^{II}Co^{III}$(μ-OAc)(μ_3-OH)(μ-L)]$_2$. Now, replacing m by Q/2F in the equation for TOF (in h^{-1}) we get:

$$TOF \text{ (in } h^{-1}) = (I/2mF) \text{ x } 3600 = (I/Q) \text{ x } 3600$$
$$= \{(2.55 \text{ x } 10^{-4})/(1.96 \text{ x } 10^{-4})\} \text{ x } 3600$$
$$= 4683 = 4.6 \text{ x } 10^{3}$$

Oxygen Evolution Reaction (OER). Here, the equation used for the calculation of TOF was TOF = I/4mF, where, I (= 2.4 x 10^{-5} A) is the steady state current in the constant potential (1.05 V) electrolysis (CPE) plot for OER (Fig. S8), F is the Faraday constant (in C mol^{-1}), m is the number of active sites (in mol), and 4 is the number of electrons required to form one oxygen molecule from two water molecules.

The number of active sites m was calculated using the equation, m = Q/2F, where, Q (3.97 x 10^{-5} C) is the charge calculated by integrating the current vs time plot (within the potential range 0.5 to 1.1 V) generated from the cyclic voltammogram trace (in Fig. 7 and also in Fig. S5) recorded using [$Co^{II}Co^{III}$(μ-OAc)(μ_3-OH)(μ-L)]$_2$, carbon-black, and Nafion coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor ½ is for the 2 electron oxidation of the catalyst [$Co^{II}Co^{III}$(μ-OAc)(μ_3-OH)(μ-L)]$_2$. Now, replacing m by Q/2F in the equation for TOF (in h^{-1}) we get:

$$TOF \text{ (in } h^{-1}) = (I/4mF) \text{ x } 3600 = (I/2Q) \text{ x } 3600$$
$$= \{(2.4 \text{ x } 10^{-5})/(2 \text{ x } 3.97 \text{ x } 10^{-5})\} \text{ x } 3600$$
$$= 1088 = 1.1 \text{ x } 10^{3}$$

Section S5
Calculations of the Faradaic Efficiency and Turnover Frequency (TOF) for OER using Pure Complex Coated FTO Electrode

Faradaic Efficiency. In the CCE experiment (see Section 1 and main text for the procedure and the electrolytic cell setup) for OER, 0.51 mL of oxygen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of oxygen evolved in 1 h = $0.51/(6 \times 22400)$ mol = 3.8×10^{-6} mol.

In the controlled experiment performed using pristine FTO electrode keeping all other experimental conditions identical, the amount of oxygen evolved in 6 h was ~0.05 mL. Hence, the number of moles oxygen evolved in 1 h = $0.05/(6 \times 22400)$ mol = 0.4×10^{-6} mol.

Hence, the amount of oxygen actually evolved = $(3.8 - 0.4) \times 10^{-6}$ mol

$$= 3.4 \times 10^{-6} \text{ mol}$$

The ideal number of moles of oxygen expected to be evolved is Q/nF, where Q is the total charge employed, n is the number of electrons involved for O_2 production and F is the Faraday constant. The value of n for OER is 4 as it is a four electron process and since we employed 500 µA current, Q/nF in 1 h = $(0.5 \times 10^{-3} \times 3600)/(4 \times 96500) = 4.66 \times 10^{-6}$ mol.

$$\text{Faradaic Efficiency} = \frac{\text{Moles of oxygen evolved experimentally in 1 h}}{\text{Moles of oxygen ideally expected in 1 h}} \times 100$$

$$= \{(3.4 \times 10^{-6}) / (4.66 \times 10^{-6})\} \times 100 = 73\%$$

Turnover Frequency. Here, the equation used for the calculation of TOF was TOF = I/4mF, where, I (= 6.8×10^{-5} A) is the steady state current in the constant potential (1.28 V) electrolysis (CPE) plot for OER (Fig. S12), F is the Faraday constant (in C mol^{-1}), m is the number of active sites (in mol), and 4 is the number of electrons required to form one oxygen molecule from two water molecules.
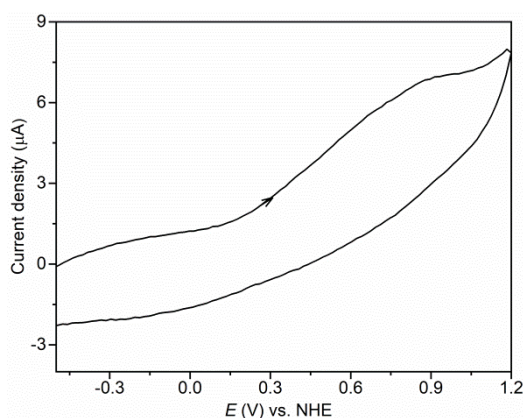
The number of active sites m was calculated using the equation, $m = Q/2F$, where, Q (3.6×10^{-5} C) is the charge calculated by integrating the current vs time plot (within the potential range 0.5 to 1.1 V) generated from the cyclic voltammogram trace (shown at the left) recorded using only [Co^{II}Co^{III}(μ-OAc)(μ_3-OH)(μ-L)]$_2$ coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor ½ is for the 2 electron oxidation of the catalyst [Co^{II}Co^{III}(μ-OAc)(μ_3-OH)(μ-L)]$_2$. Now, replacing m by Q/2F for m in the equation for TOF (in h^{-1}) we get:

TOF (in h^{-1}) = (I/4mF) x 3600 = (I/2Q) x 3600

$$= \{(6.8 \times 10^{-5})/(2 \times 3.6 \times 10^{-5})\} \times 3600$$

$$= 3400 = 3.4 \times 10^{3}$$

Section S6
Calculations of the Faradaic Efficiency and the Turnover Frequency (TOF) for HER using Pure Complex Coated FTO Electrode

In the CCE experiment (see Section S1 and main text for the procedure and the electrolytic cell setup) for HER, it was found that 1.33 mL of hydrogen was evolved at ambient temperature and pressure in 6 h. Therefore, the number of moles of hydrogen evolved in 1 h = 1.33/(6 x 22400) mol = 9.89×10^{-6} mol.

The controlled experiment was performed using pristine FTO electrode keeping all other experimental conditions identical. The total amount of hydrogen evolved in 6 h was ~0.20 mL. Therefore, in terms of number of moles, the amount of hydrogen evolved in 1 h = 0.20/(6 x 22400) mol = 1.48×10^{-6} mol.

Thus, the amount of hydrogen actually evolved in 1 h = $(9.89 - 1.48) \times 10^{-6}$ mol
$$= 8.41 \times 10^{-6} \text{ mol}$$

The ideal number of moles of hydrogen expected to be evolved is Q/nF, where Q is the total charge employed, n is the number of electrons involved for H_2 production and F is the Faraday constant. The value of n for HER is 2 as it is a two electron process and since we employed −500 µA current, Q/nF in 1 h = $(0.5 \times 10^{-3} \times 3600)/(2 \times 96500) = 9.33 \times 10^{-6}$ mol.

The expression used for the calculation of Faradaic Efficiency is as follows:

$$\text{Faradaic Efficiency} = \frac{\text{Moles of hydrogen evolved experimentally in 1 h}}{\text{Moles of hydrogen ideally expected in 1 h}} \times 100$$

$$= \{(8.41 \times 10^{-6})/(9.33 \times 10^{-6})\} \times 100 = 90\%$$

Hydrogen Evolution Reaction (HER).

The TOF was calculated using the following equation: TOF = I/2mF, where, I (= 7.57×10^{-4} A) is the steady state current in the constant potential (−1.28 V) electrolysis (CPE) plot for HER (Fig. S12), F is the Faraday constant (in C mol^{-1}), m is the number of active sites (in mol), and 2 is the number of electrons required to form one hydrogen molecule from two protons. The number of active sites m can be calculated using the equation, m = Q/2F, where, Q (1.77 x 10^{-4} C) is the charge calculated by integrating the current vs time plot (within the potential range −0.8 to −1.2 V) generated from the cyclic voltammogram trace (shown at the left) recorded using
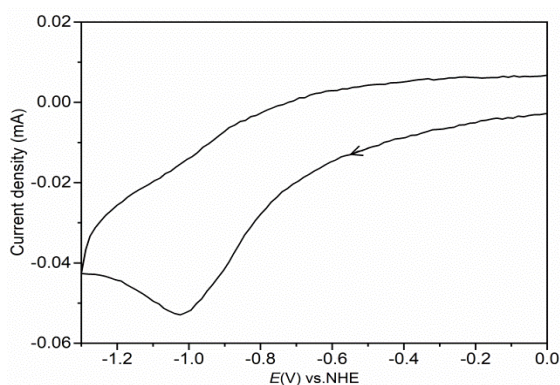

$[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ coated FTO as the working electrode under non-catalytic conditions (THF medium rather than the neutral sodium phosphate buffer medium) and the factor ½ is for the 2 electron reduction of the catalyst $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$. Now, replacing m by Q/2F in the equation for TOF (in h^{-1}) we get:

TOF (in h^{-1}) = (I/2mF) x 3600 = (I/Q) x 3600
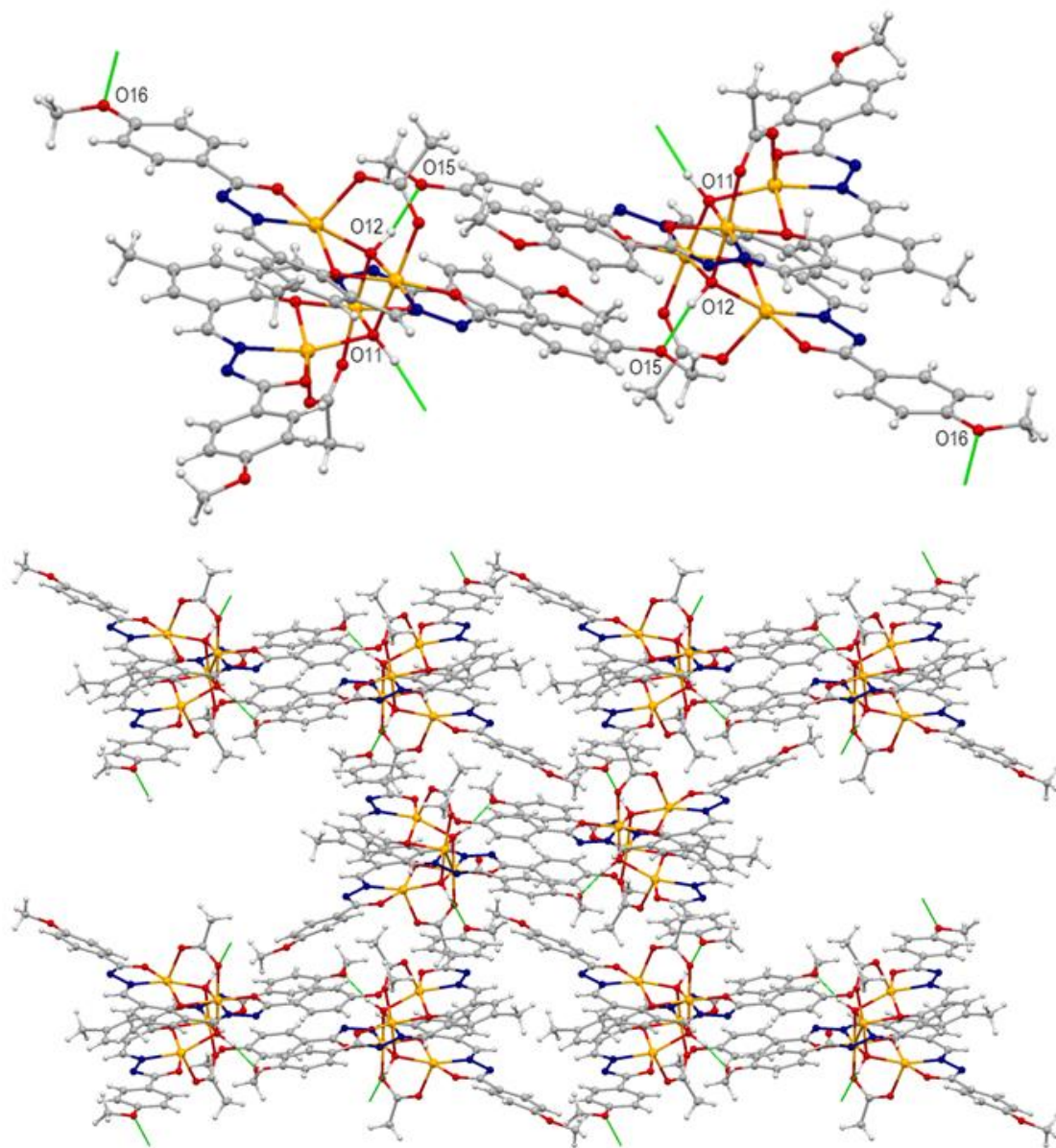$$= \{(7.57 \times 10^{-4})/(1.77 \times 10^{-4})\} \times 3600$$
$$= 15396 = 1.53 \times 10^4$$

Table S1

Continuous shape measurement for Co-centers in $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$.

Metal atom	S. No.	Geometry	Symmetry	CShM value
	1	Hexagon	D_{6h}	30.776
	2	Pentagonal pyramid	C_{5v}	27.439
Co1	**3**	**Octahedron**	**Oh**	**0.426**
	4	Trigonal prism	D_{3h}	14.389
	5	Johnson pentagonal pyramid J2	C_{5v}	31.198
	1	Pentagon	D_{5h}	26.788
	2	**Vacant octahedron (Johnson square pyramid J1)**	**C_{4v}**	**1.791**
Co2	3	Trigonal bipyramid	D_{3h}	6.025
	4	Spherical square pyramid	C_{4v}	1.831
	5	Johnson trigonal bipyramid J12	D_{3h}	8.109
	1	Hexagon	D_{6h}	30.679
	2	Pentagonal pyramid	C_{5v}	25.914
Co3	**3**	**Octahedron**	**Oh**	**0.626**
	4	Trigonal prism	D_{3h}	12.916
	5	Johnson pentagonal pyramid J2	C_{5v}	29.769
	1	Pentagon	D_{5h}	25.170
	2	Vacant octahedron (Johnson square pyramid J1)	C_{4v}	1.971
Co4	3	Trigonal bipyramid	D_{3h}	7.114
	4	**Spherical square pyramid**	**C_{4v}**	**1.864**
	5	Johnson trigonal bipyramid J12	D_{3h}	9.215
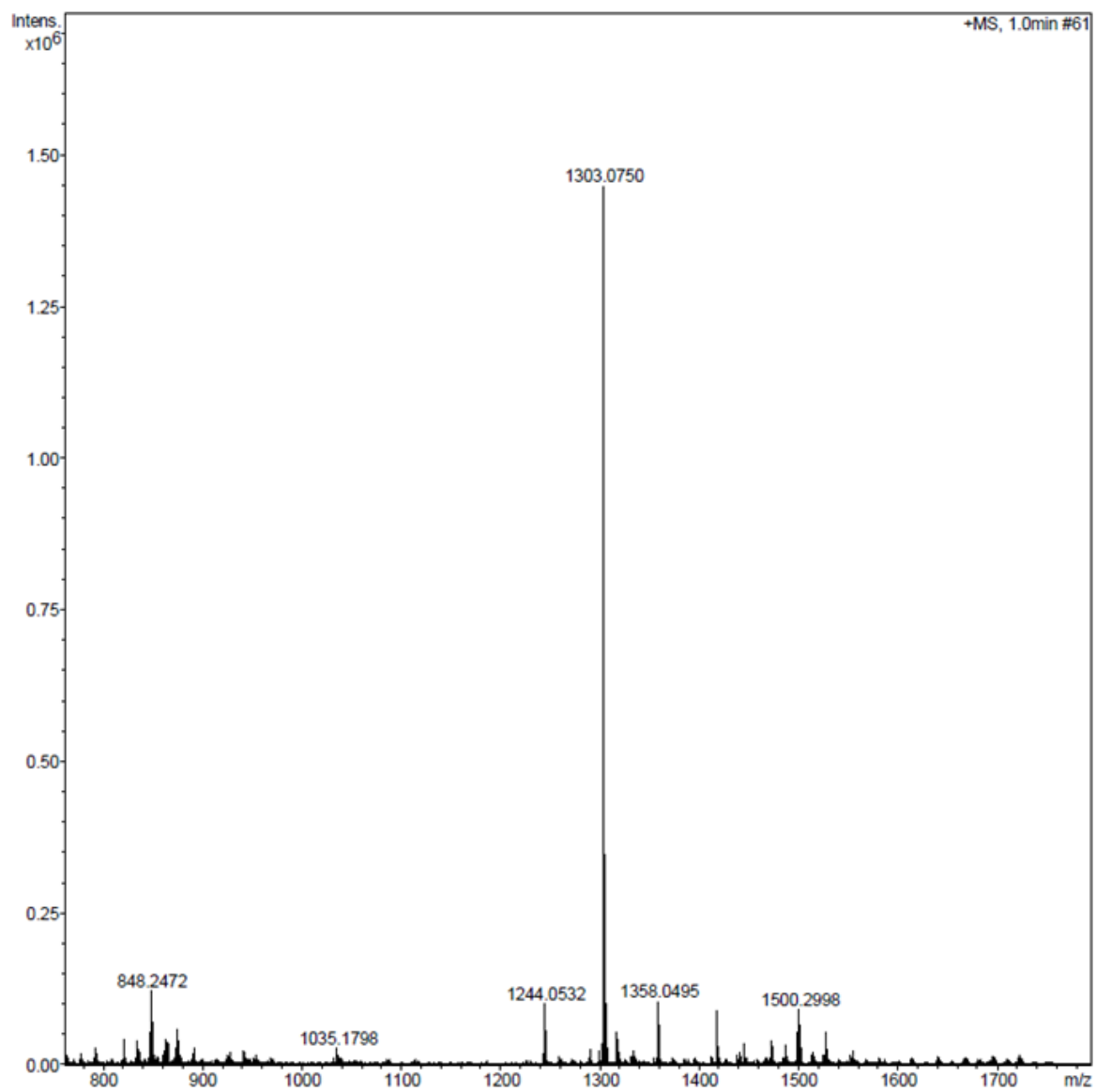
Fig. S1 ESI mass spectrum of [Co^{II}Co^{III}(μ-OAc)(μ_3-OH)(μ-L)]$_2$ in *N,N*-dimethylformamide.

Fig. S2 Hydrogen bonded dimer of $[Co^{II}Co^{III}(\mu\text{-}OAc)(\mu_3\text{-}OH)(\mu\text{-}L)]_2$ (top) and the two-dimensional assembly of these dimeric units viewed along the *a*-axis (bottom).
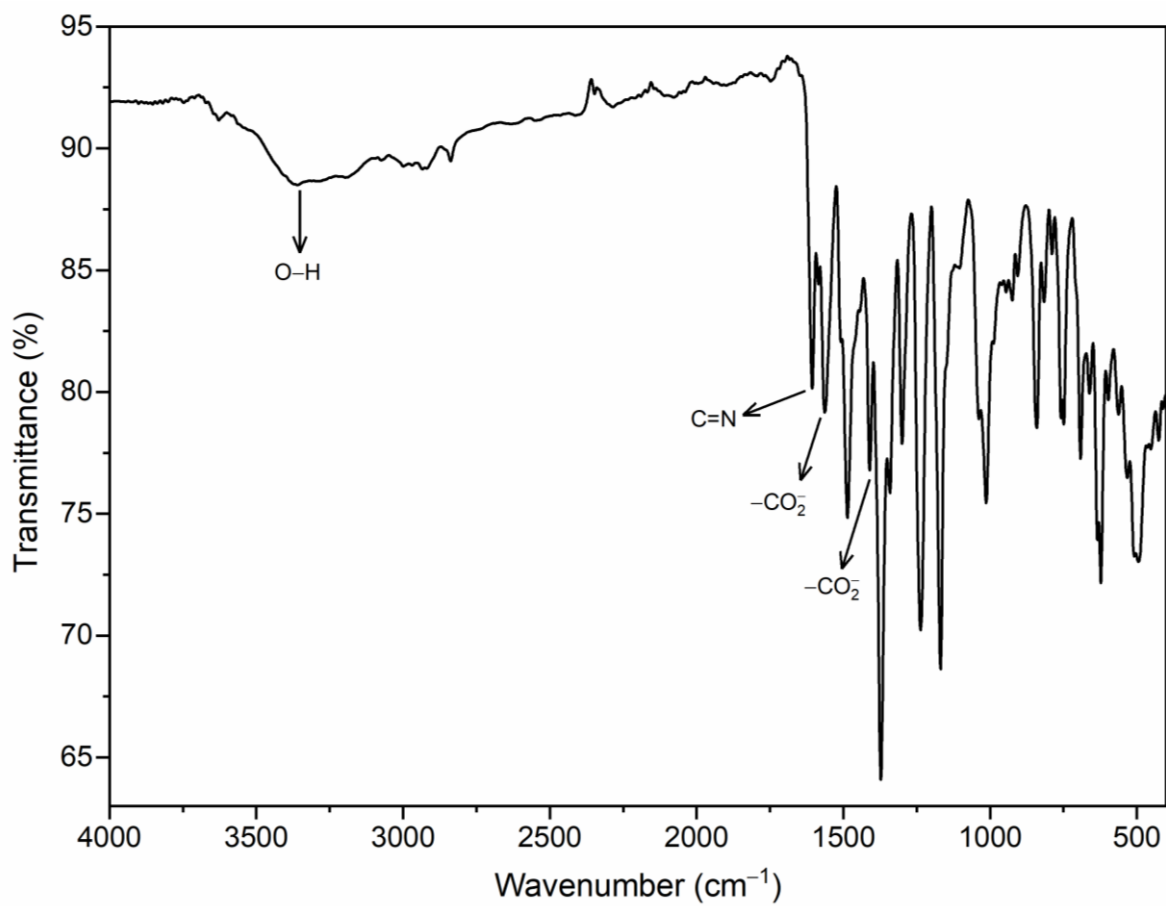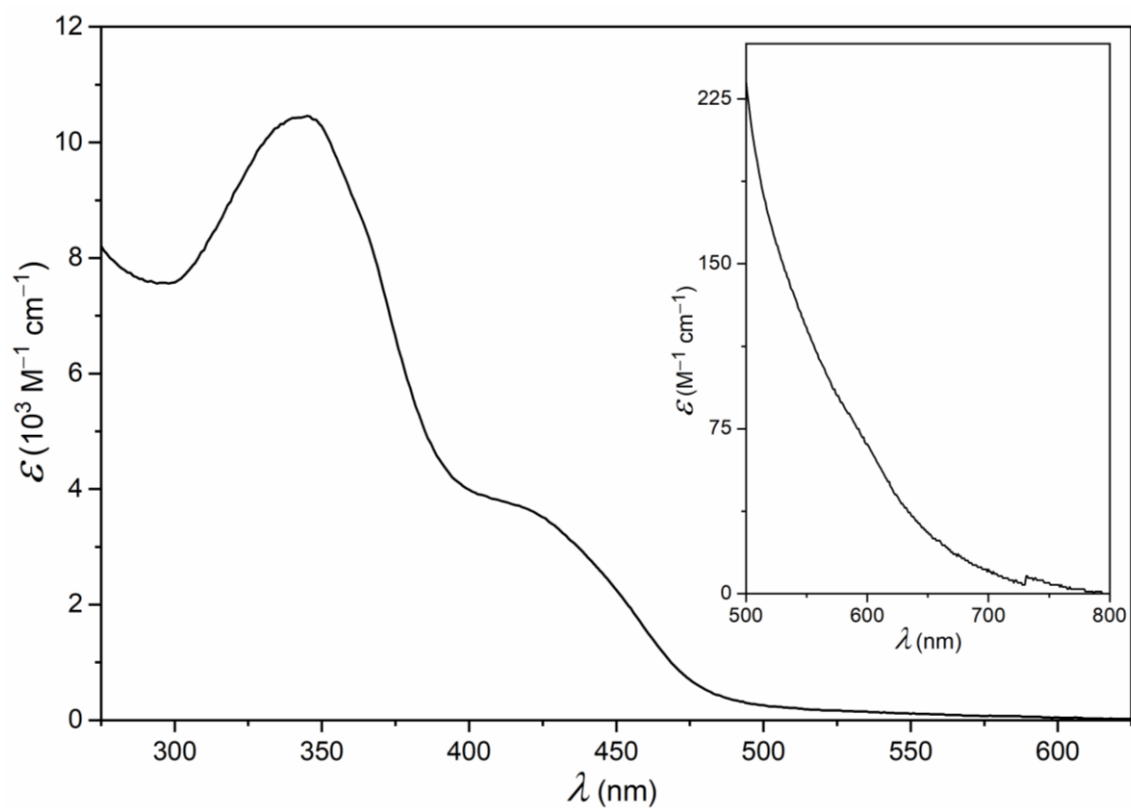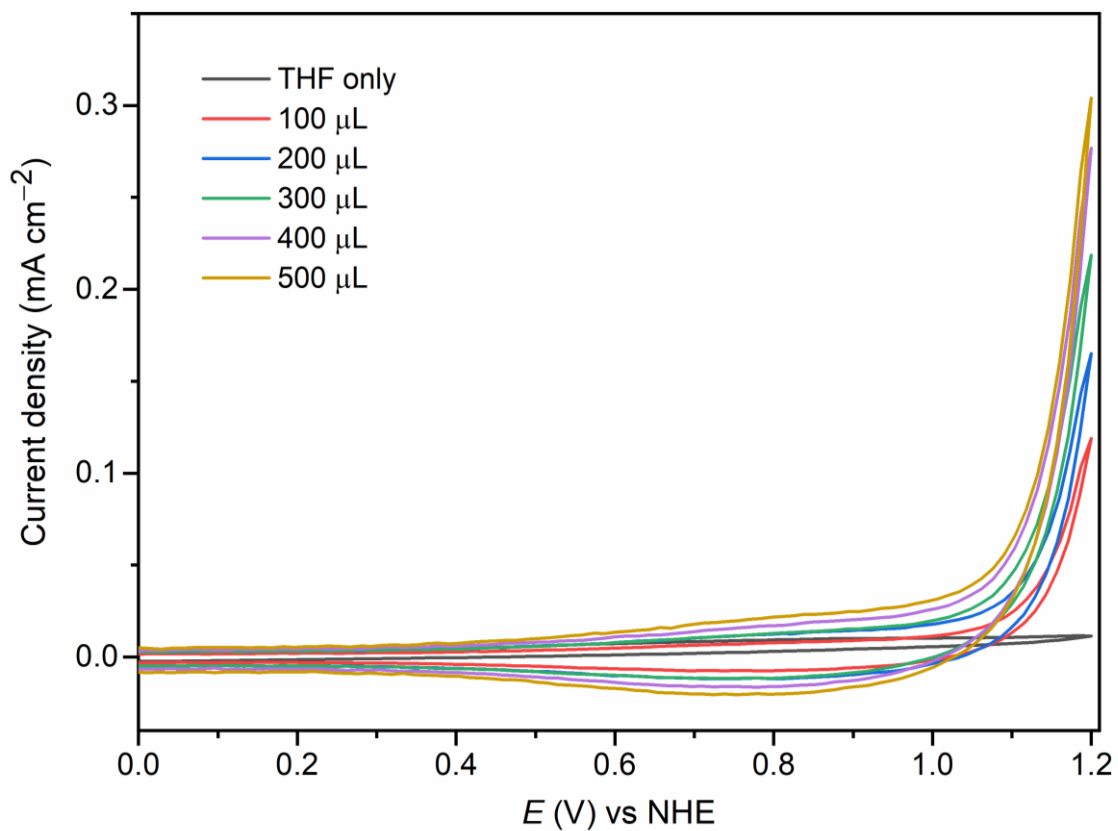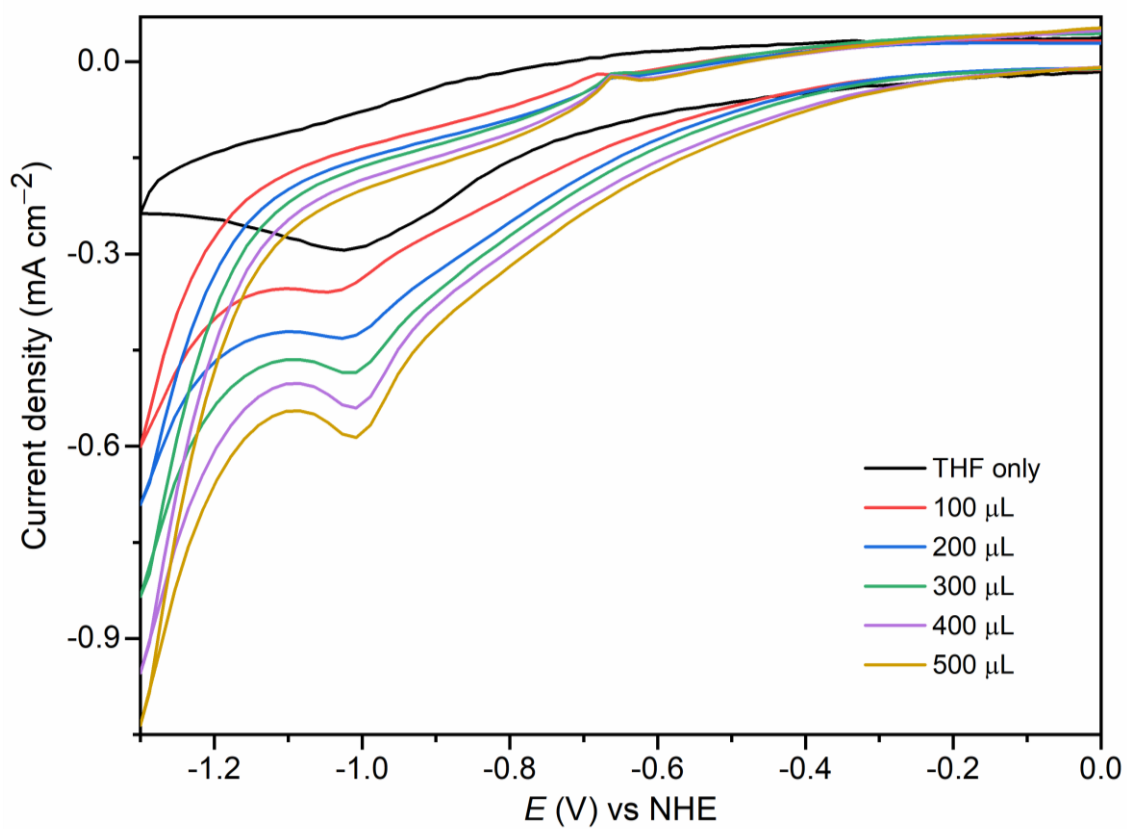
Fig. S3 Infrared spectrum of $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ in powder phase.

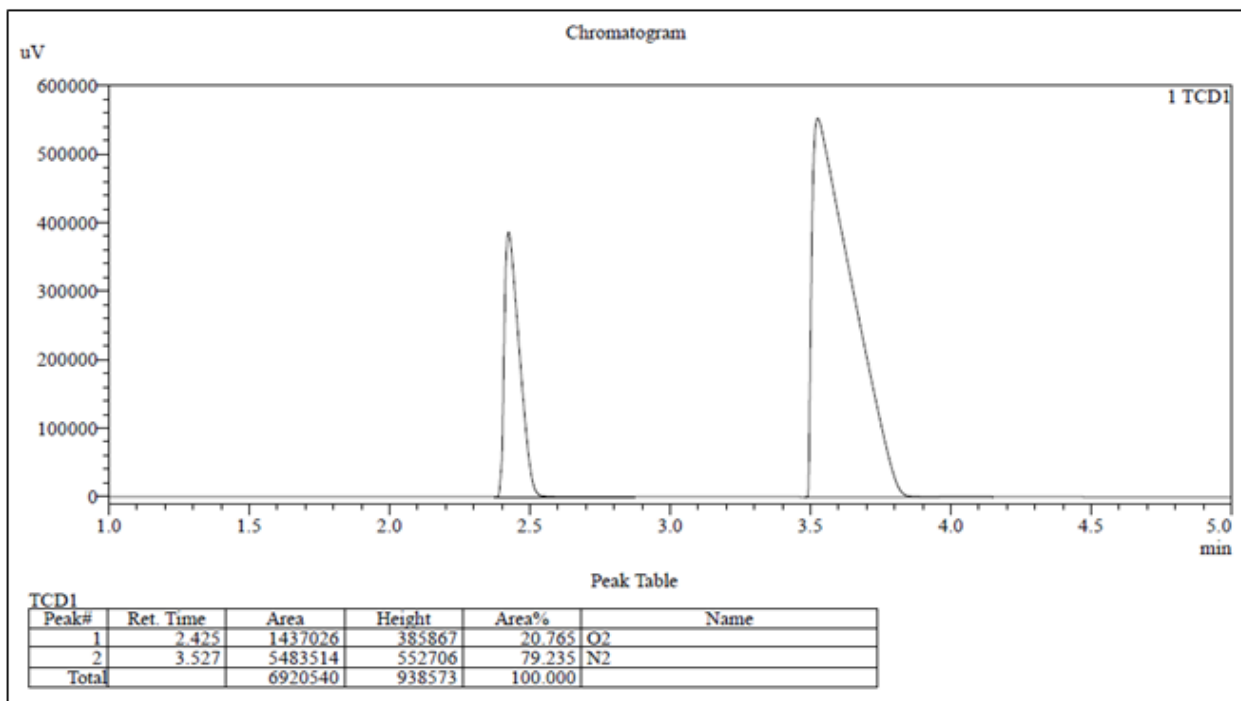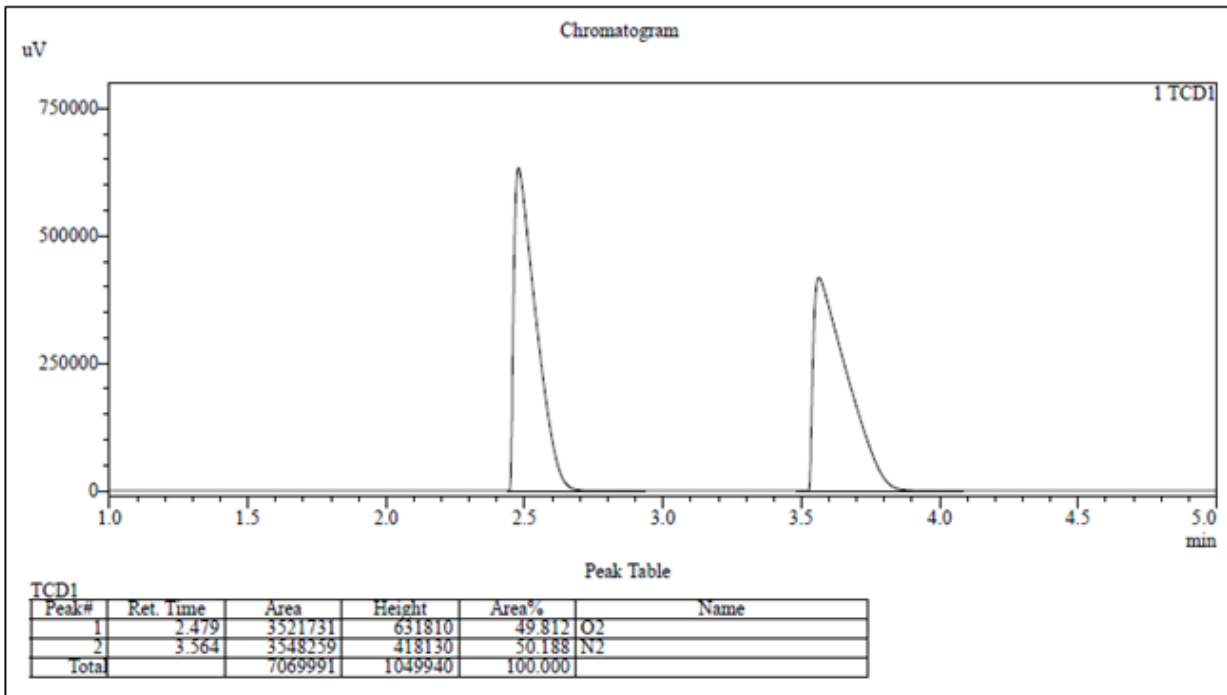**Fig. S4** Electronic spectrum of $[Co^{II}Co^{III}(\mu\text{-}OAc)(\mu_3\text{-}OH)(\mu\text{-}L)]_2$ in *N,N*-dimethylform-amide. Inset: Enlarged low-energy portion.
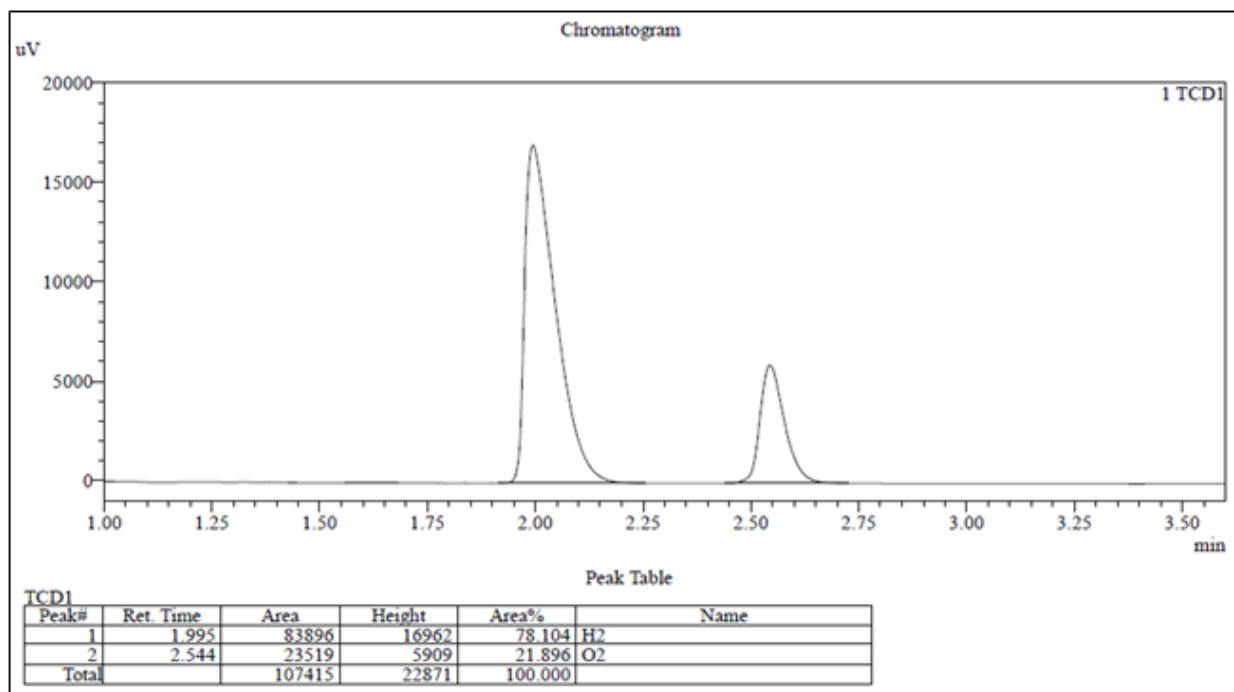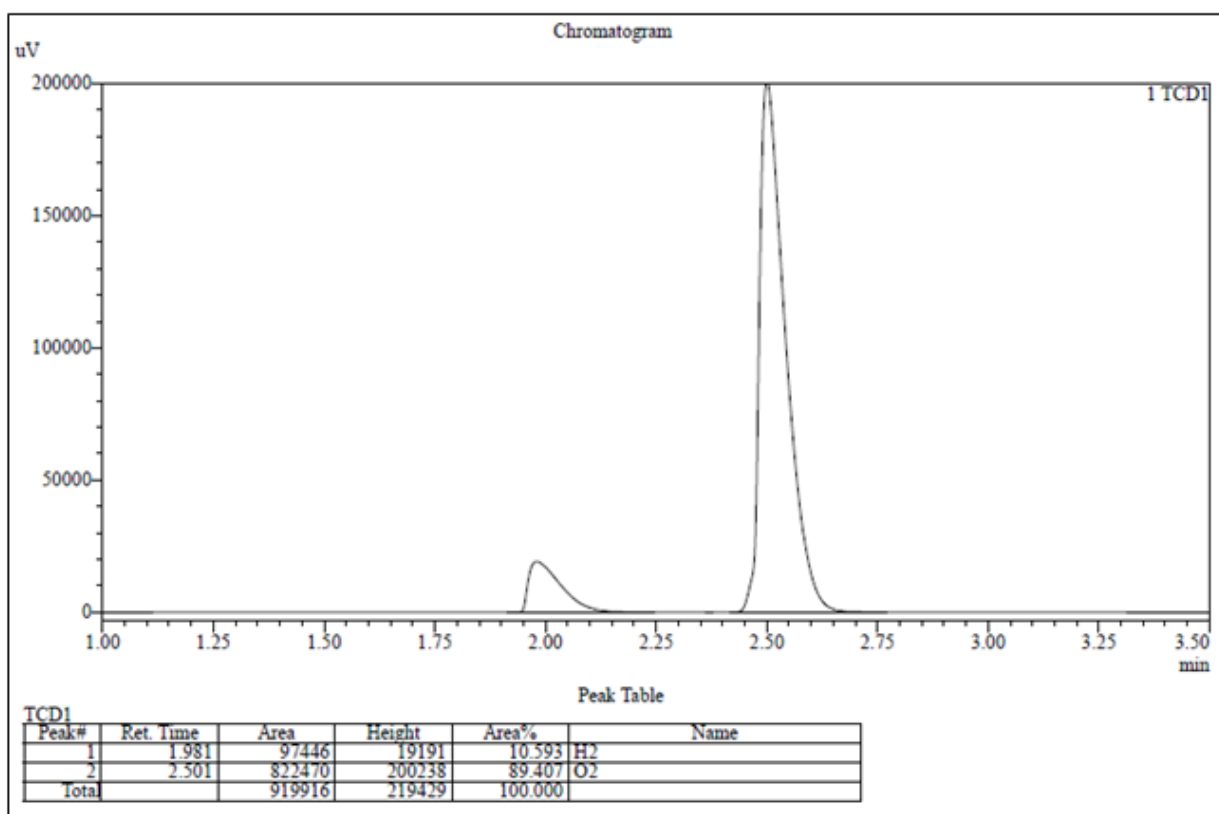
Fig. S5 Electrocatalytic water oxidation in tetrahydrofuran (THF) with gradual addition of aliquots of sodium phosphate buffer of pH 7.

Fig. S6 Electrocatalytic water reduction in tetrahydrofuran (THF) with incremental addition of sodium phosphate buffer of pH 7.

Chromatogram (top)

TCD1

Peak#	Ret. Time	Area	Height	Area%	Name
1	2.479	3521731	631810	49.812	O2
2	3.564	3548259	418130	50.188	N2
Total		7069991	1049940	100.000	

Chromatogram (bottom)

TCD1

Peak#	Ret. Time	Area	Height	Area%	Name
1	2.425	1437026	385867	20.765	O2
2	3.527	5483514	552706	79.235	N2
Total		6920540	938573	100.000	

Fig. S7 Chromatograms of the gas evolved in the oxidative electrolysis (top) and air (bottom). The nitrogen peak in the first chromatogram is due to contamination by air during sample collection.

Chromatogram (top)

Peak Table

TCD1

Peak#	Ret. Time	Area	Height	Area%	Name
1	1.981	97446	19191	10.593	H2
2	2.501	822470	200238	89.407	O2
Total		919916	219429	100.000	

Chromatogram (bottom)

Peak Table

TCD1

| Peak#	Ret. Time	Area	Height	Area%	Name
1	1.995	83896	16962	78.104	H2
2	2.544	23519	5909	21.896	O2
Total		107415	22871	100.000	

Fig. S8 Chromatograms of the gas evolved in the reductive electrolysis (top) and hydrogen (bottom). The oxygen peaks are due to contamination by air during sample collection.
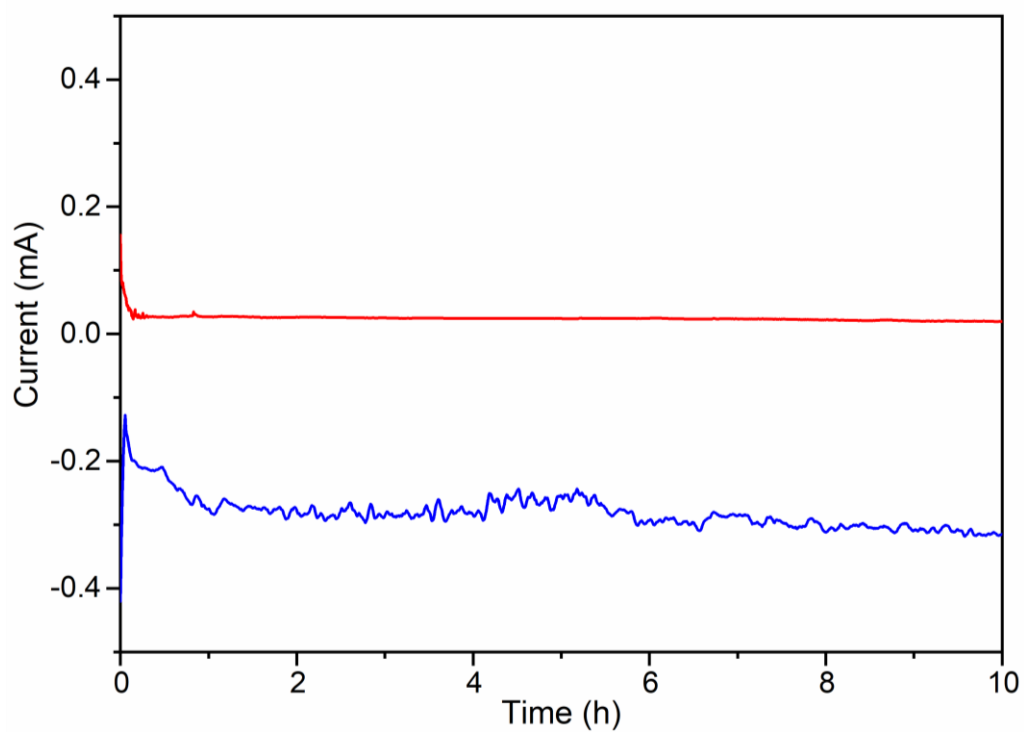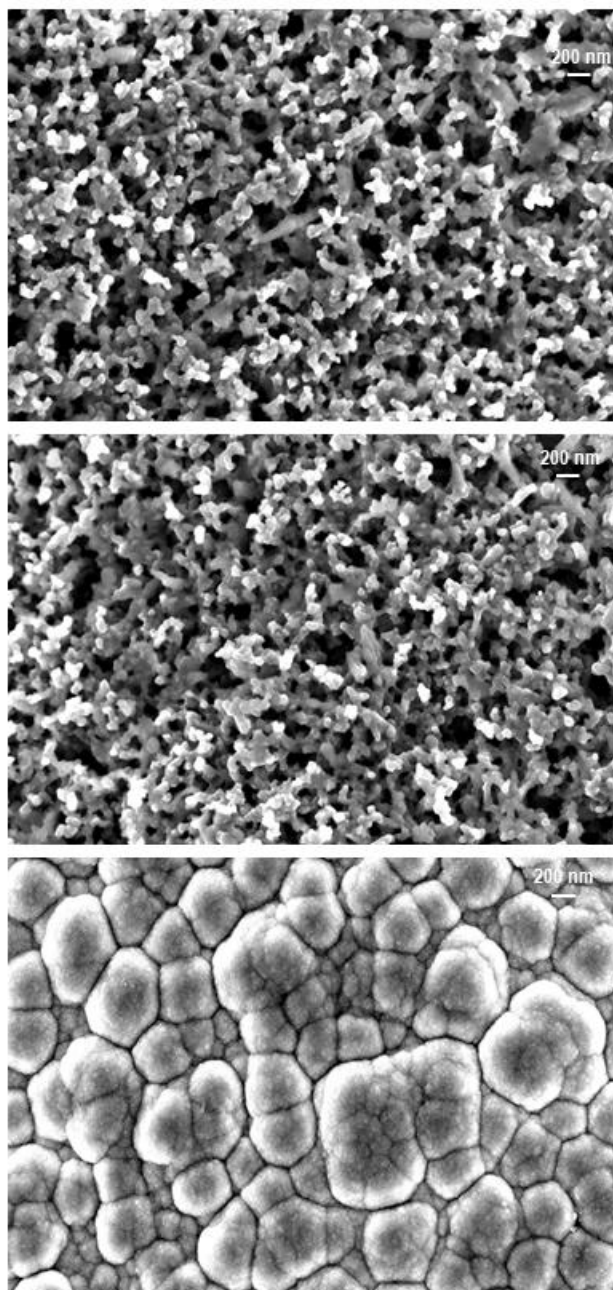
Fig. S9 Constant potential electrolysis (CPE) plots for OER (——) and HER (------) using the $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, CB, and Nafion mixture coated FTO electrode in 0.1 M sodium phosphate buffer of pH 7.
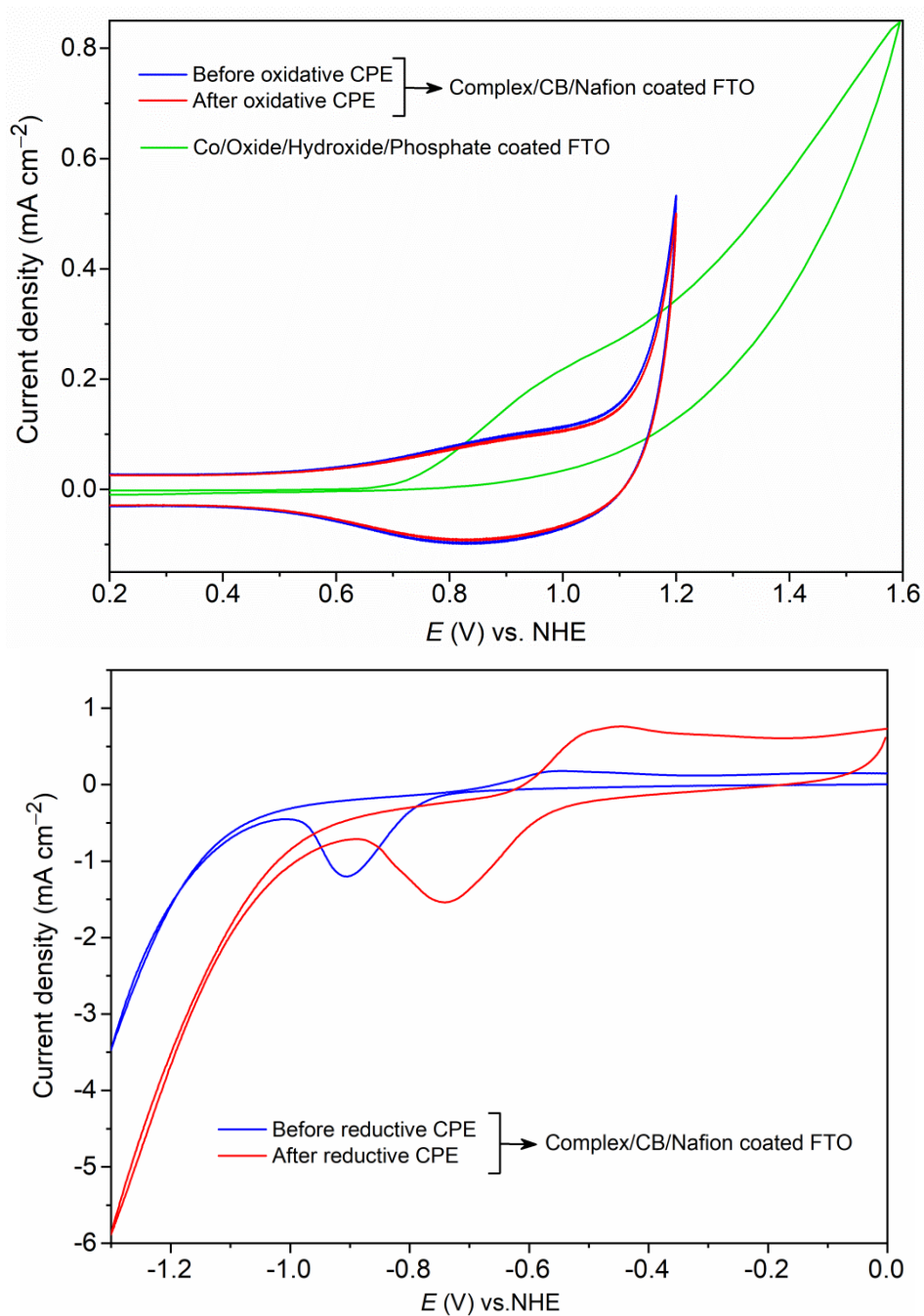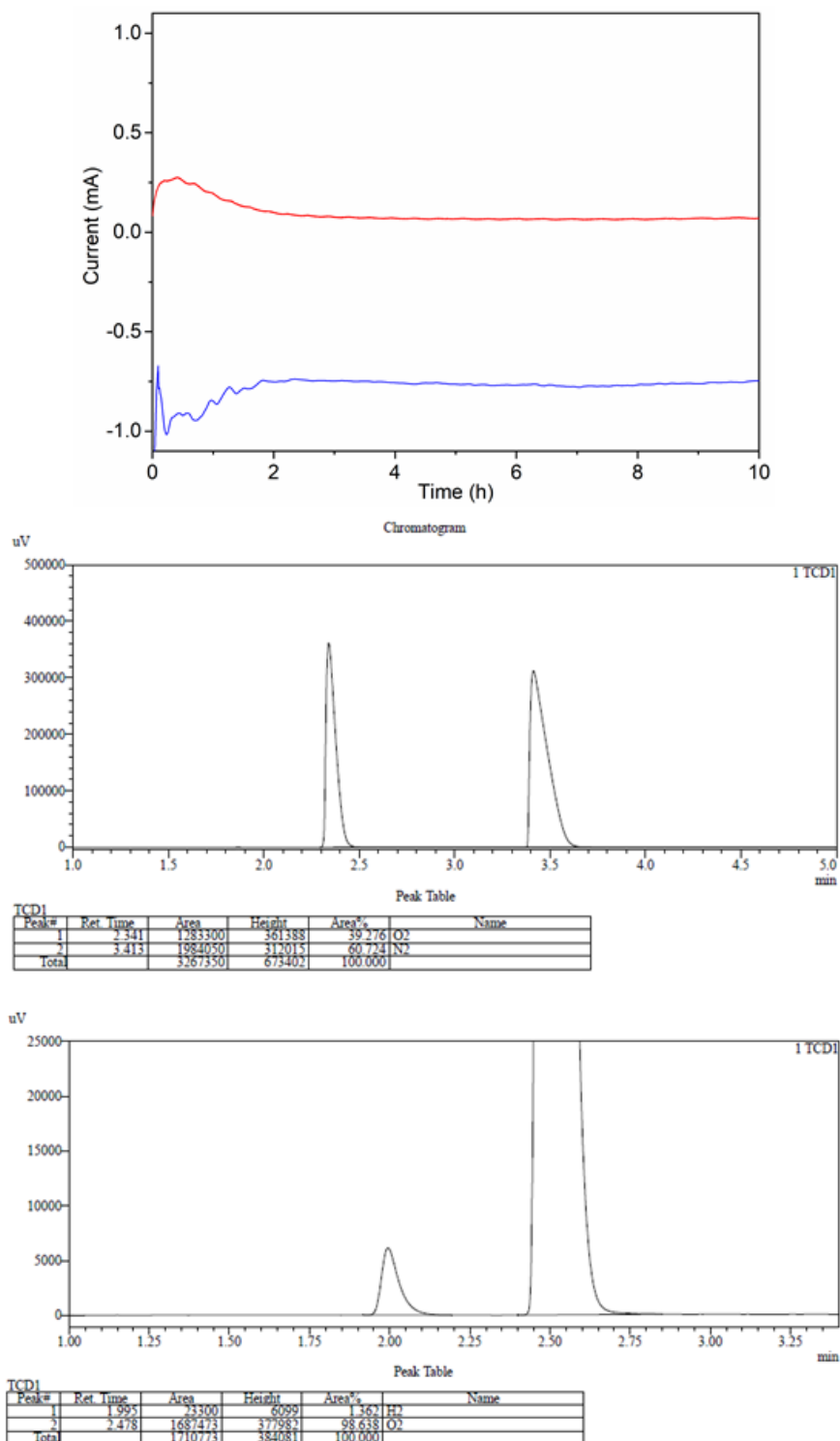
Fig. S10 CVs using $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$, CB, and Nafion mixture coated FTO as working electrode before and after its use in CPE experiments and the CV using cobalt oxide/hydroxide/phosphate coated FTO as working electrode.
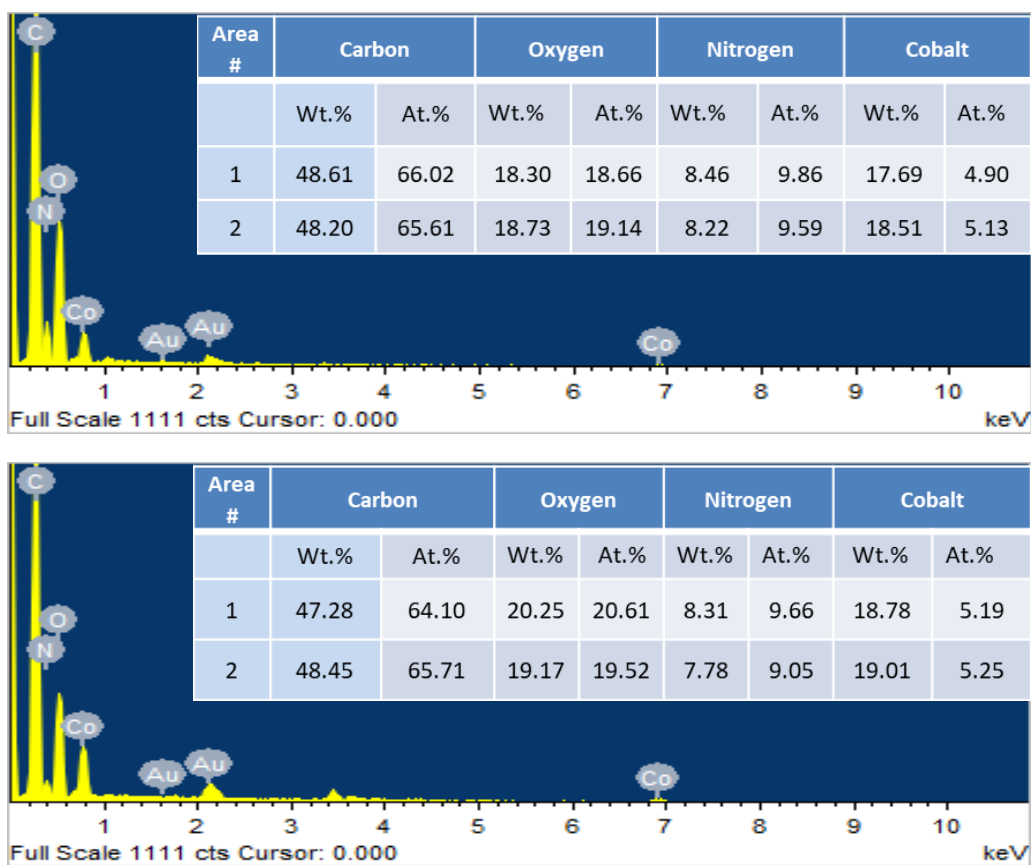
Fig. S11 FESEM images of FTO electrode coatings: CB/Nafion/complex before (top) and after oxidative (middle) CPE and electrodeposited cobalt oxide/hydroxide/phosphate material (bottom).
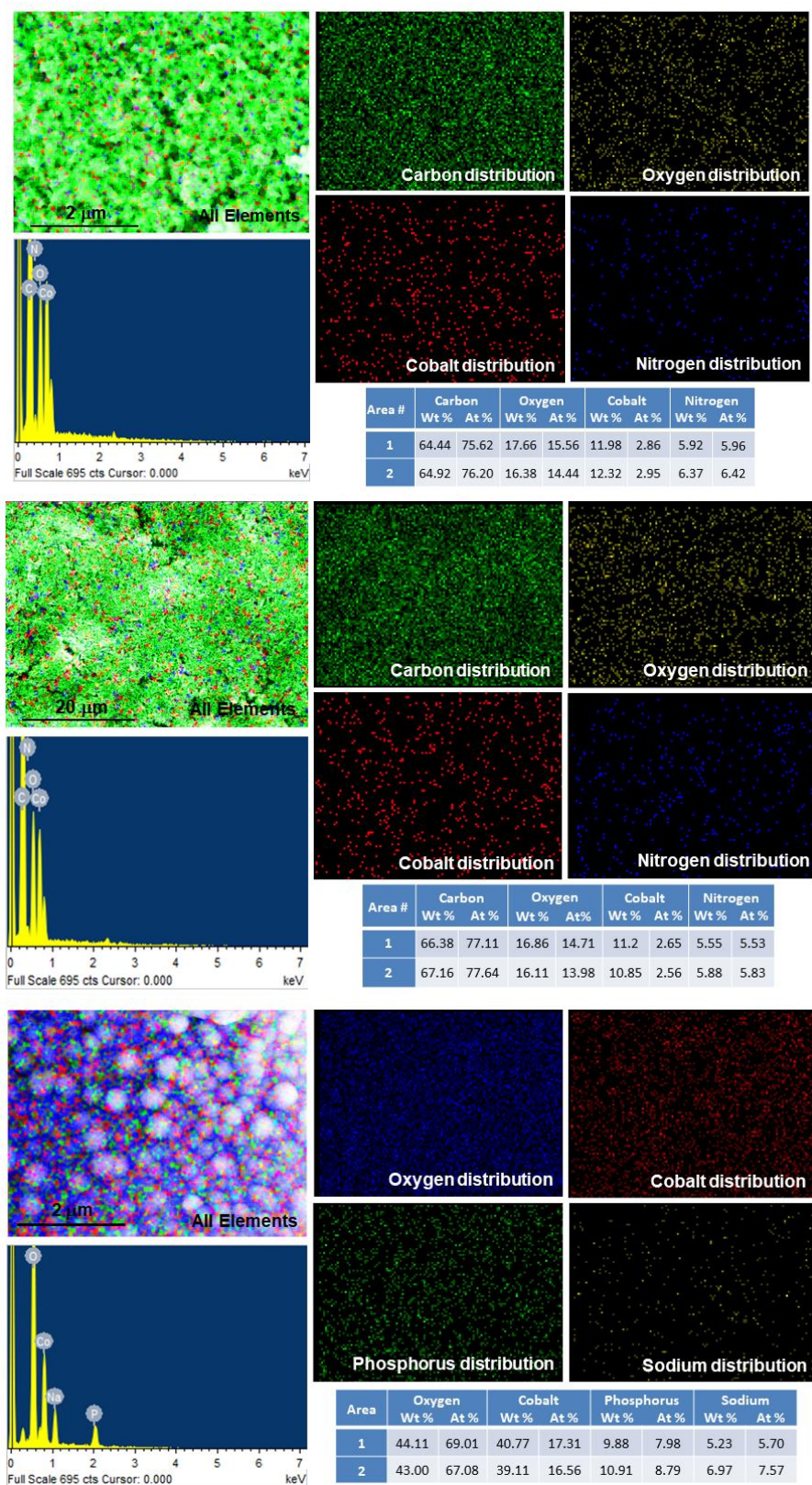
Fig. S12 EDX spectra and elemental compositions of FTO electrode coatings: complex/CB/Nafion before (top) and after oxidative CPE (middle) and the electrodeposited cobalt oxide/hydroxide/phosphate material (bottom).

Chromatogram

uV

TCD1

Peak#	Ret. Time	Area	Height	Area%	Name
1	2.341	1283300	361388	39.276	O2
2	3.413	1984050	312015	60.724	N2
Total		3267350	673402	100.000	

uV

TCD1

Peak#	Ret. Time	Area	Height	Area%	Name
1	1.995	23300	6099	1.362	H2
2	2.478	1687473	377982	98.638	O2
Total		1710773	384081	100.000	

Fig. S13 Constant potential electrolysis (CPE at 1.28 V for OER and at −1.28V for HER) plots for OER (——) and HER (------) using $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ coated FTO electrode in 0.1 M sodium phosphate buffer of pH 7 (top). Chromatograms of the gases evolved in oxidative CPE (middle) and reductive CPE (bottom). The N_2 peak in the 1st chromatogram and the O_2 peak in the 2nd chromatogram are due to contamination by air during collection of samples.

Area #	Carbon		Oxygen		Nitrogen		Cobalt	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
1	48.61	66.02	18.30	18.66	8.46	9.86	17.69	4.90
2	48.20	65.61	18.73	19.14	8.22	9.59	18.51	5.13

Full Scale 1111 cts Cursor: 0.000   keV

| Area #	Carbon		Oxygen		Nitrogen		Cobalt	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
1	47.28	64.10	20.25	20.61	8.31	9.66	18.78	5.19
2	48.45	65.71	19.17	19.52	7.78	9.05	19.01	5.25

Full Scale 1111 cts Cursor: 0.000   keV

Fig. S14 EDX spectra and elemental compositions of the pure complex coated FTO electrode surface: before (top) and after oxidative CPE at 1.28 V (bottom).
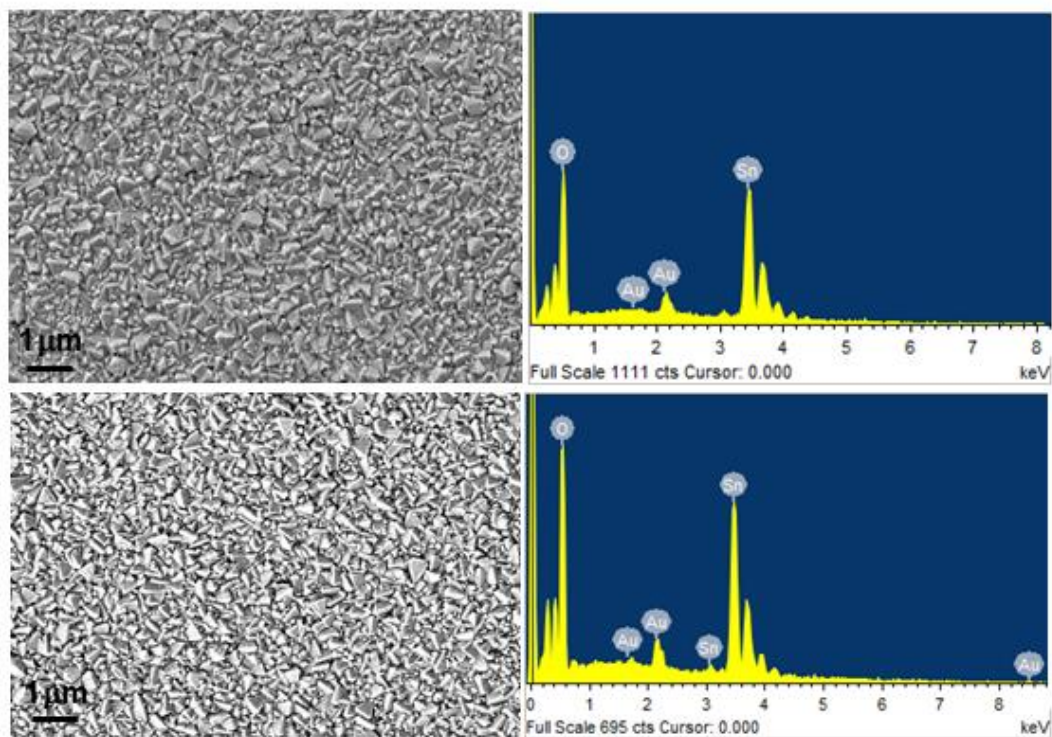
Fig. S15 FESEM images and EDX spectra of water and DMF washed complex coated FTO electrode used in oxidative CPE at 1.28 V (top) and pristine FTO electrode (bottom).
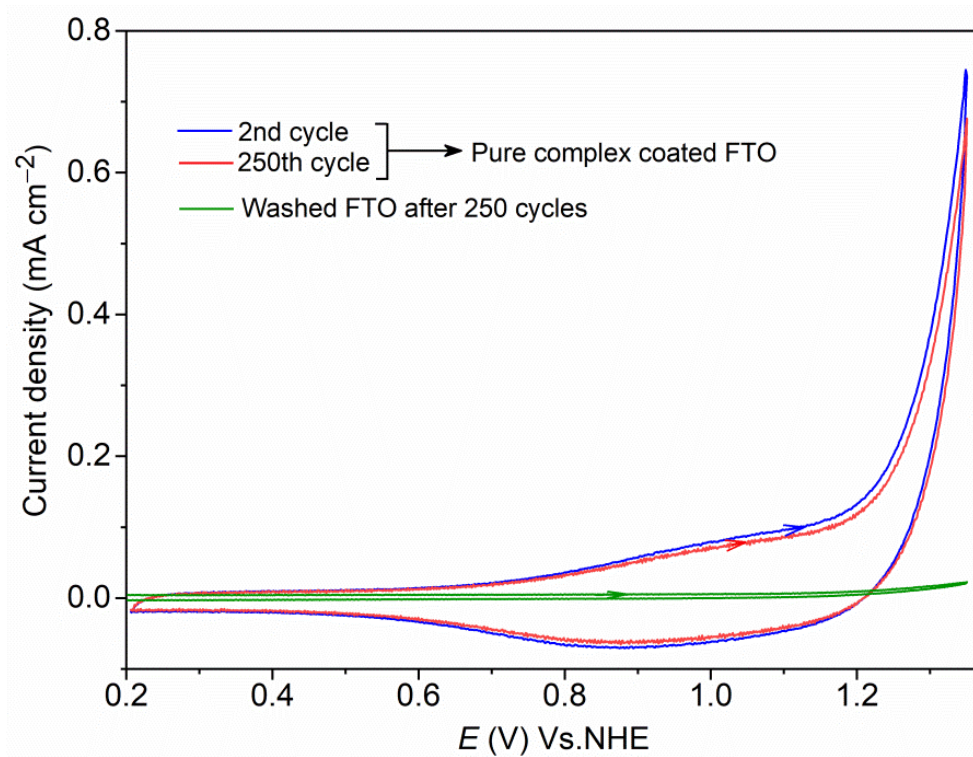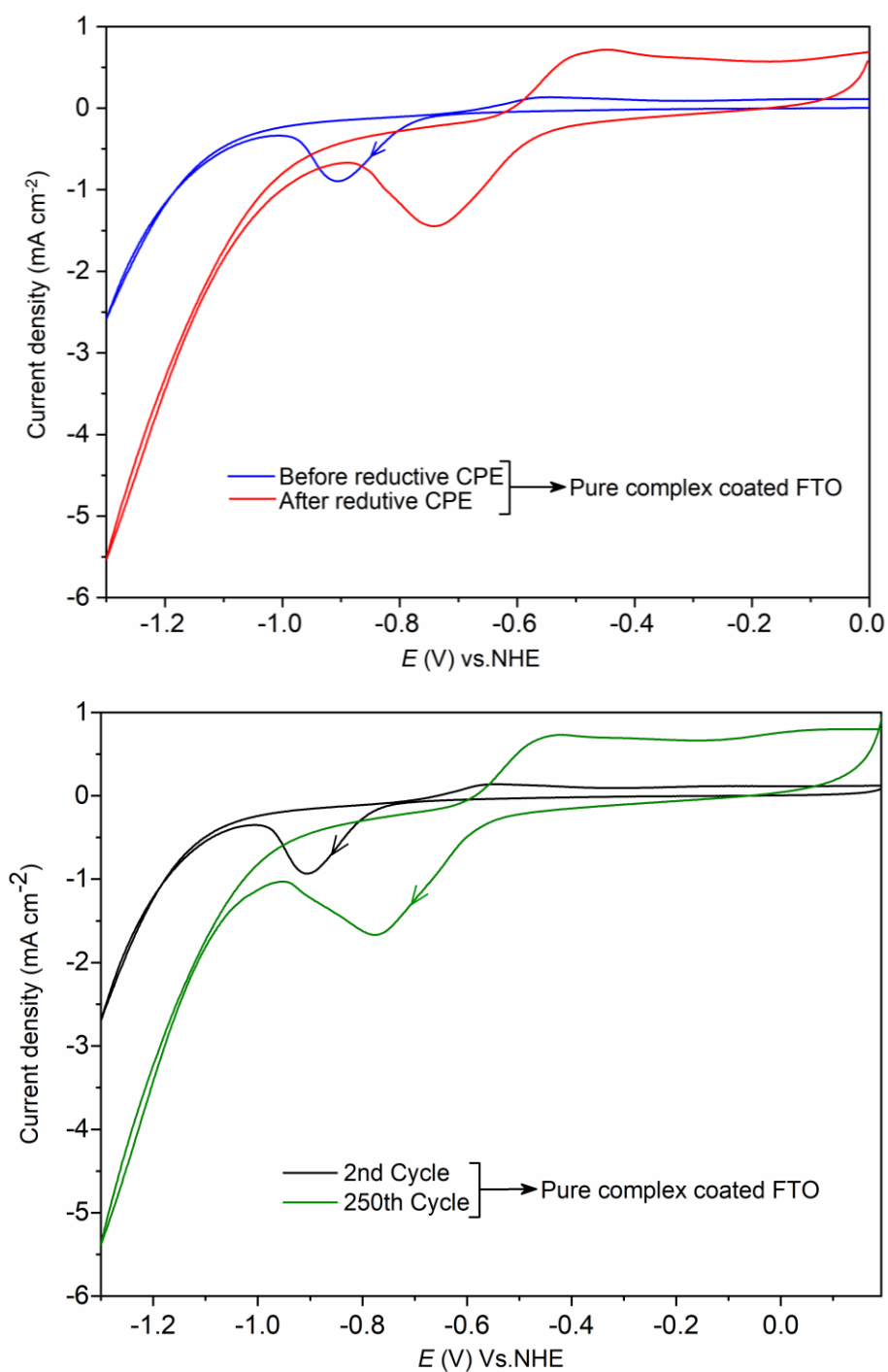
Fig. S16 CVs using $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ coated FTO as working electrode: 2nd and 250th cycles in 250 consecutive CV cycles and water and DMF washed FTO electrode. All CVs were recorded at a scan rate of 100 mV s^{-1}.
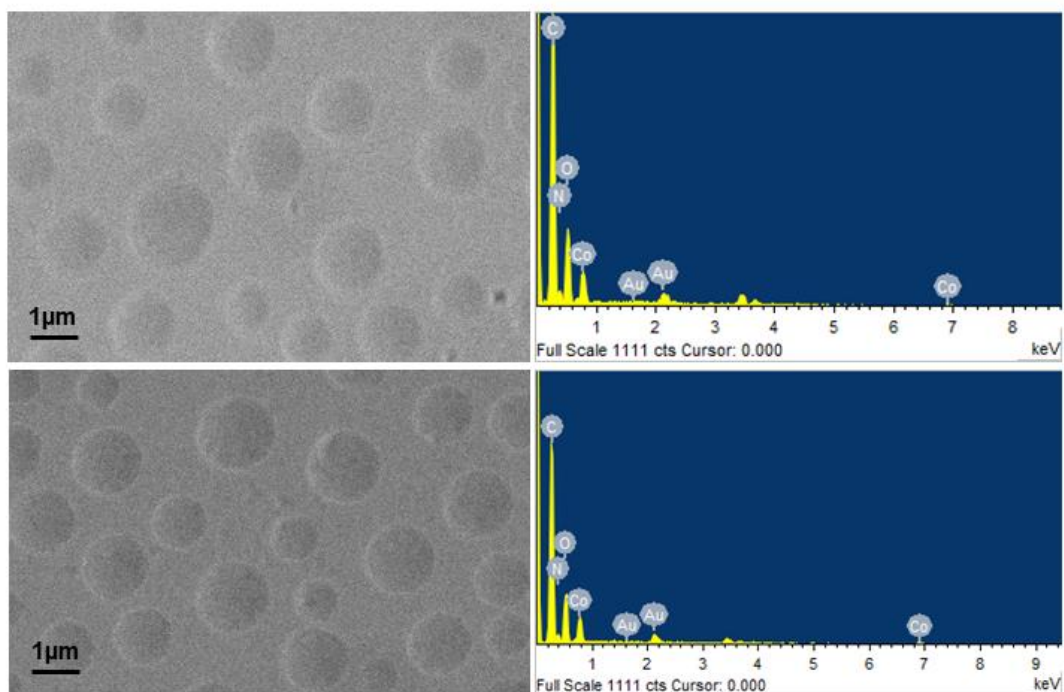
Fig. S17 FESEM images and EDX spectra of pure complex coated FTO electrode before (top) and after (bottom) its use in 250 consecutive CV cycles.

Fig. S18 CVs using $[Co^{II}Co^{III}(\mu\text{-}OAc)(\mu_3\text{-}OH)(\mu\text{-}L)]_2$ coated FTO as working electrode: before and after its use in 10 h reductive CPE (at -1.28 V) (top) and 2nd and 250th cycles in 250 consecutive CV cycles (bottom). All CVs were recorded at a scan rate of 100 mV s^{-1}.
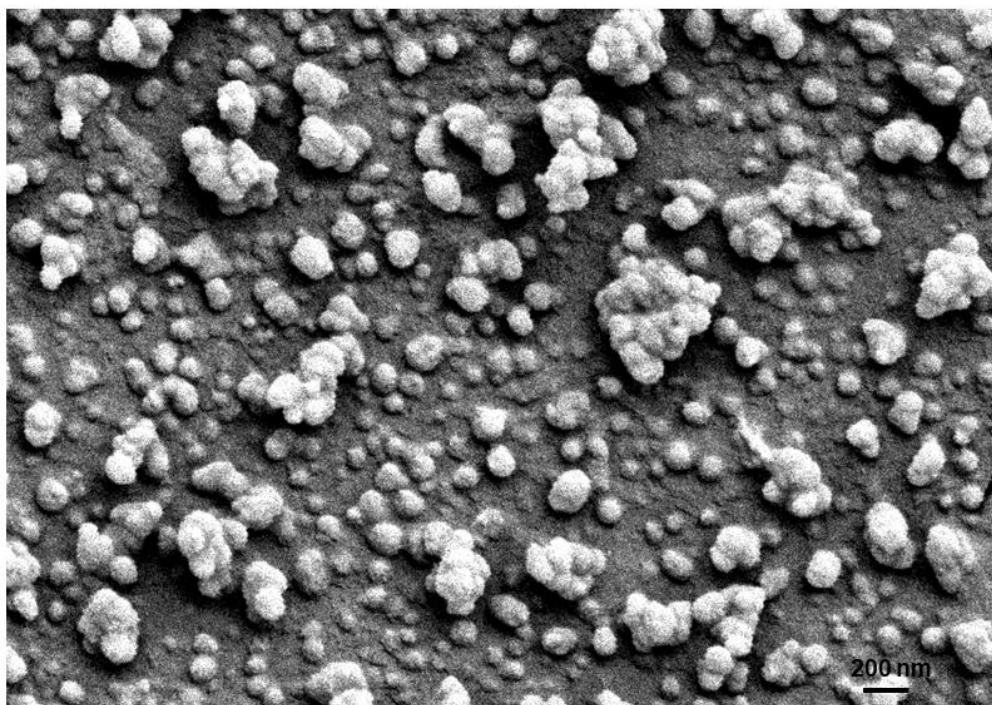
Fig. S19 FESEM image of $[Co^{II}Co^{III}(\mu\text{-OAc})(\mu_3\text{-OH})(\mu\text{-L})]_2$ coated FTO electrode after its use in 10 h reductive CPE (at -1.28 V) and followed by washing with water.