

Electronic Supplementary Information for

## Molecular material based on electropolymerized cobalt macrocycle for electrocatalytic hydrogen evolution

Stéphane Rioual,<sup>1</sup> Benoit Lescop,<sup>1</sup> François Quentel,<sup>2</sup> Frederic Gloaguen<sup>2,\*</sup>

<sup>1</sup>LMB EA 4522, <sup>2</sup>CEMCA UMR 6521, CNRS, Université de Bretagne Occidentale, Brest, France

E-mail: fgloague@univ-brest.fr (FG)

**Fig. S1.** UV-vis absorption spectra of CoTAA in solution in MeCN showing a sharp absorption band at 365 nm and a large absorption band around 505 nm, consistent with previously reported data. {Bailey, 1986 #391}

**Fig. S2.** Voltammograms of CoTAA in N<sub>2</sub>-purged Bu<sub>4</sub>NPF<sub>6</sub>/PhCN. The scan rate was at 0.1 V s<sup>-1</sup> and the electrode surface area 0.071 cm<sup>2</sup>. The redox events at E<sub>1/2</sub> ~ -1.80 V and -0.28 V are metal centered and respectively ascribed to the Co(II)/Co(I) and Co(III)/Co(II) couples, while that at E<sub>1/2</sub> ~ 0.42 V is ligand centered.

**Fig. S3.** Voltammograms recorded upon continuous potential scanning at 0.1 V s<sup>-1</sup> at a GC electrode of ca 0.071 cm<sup>2</sup> in surface area immersed in a solution of about 2 mM CoTAA in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/PhCN: 2nd scan (black trace), 10th scan (red trace), 20th scan (blue trace) and 30th scan (green trace).

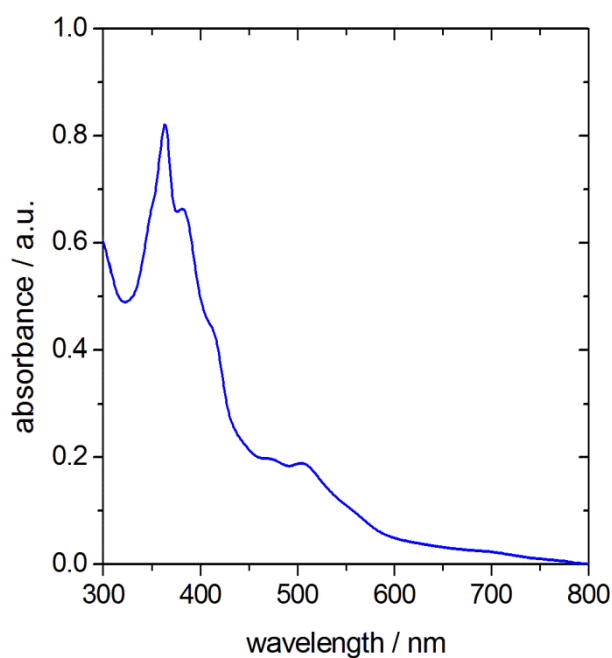
**Fig. S5.** XPS survey spectrum of a poly-CoTAA film electropolymerized on an Au-coated glass slide electrode.

**Fig. S6.** O(1s) and C(1s) XPS signals of poly-CoTAA film (black trace) and Co(II)-tetraphenylporphyrin (red trace) used as a reference compound.

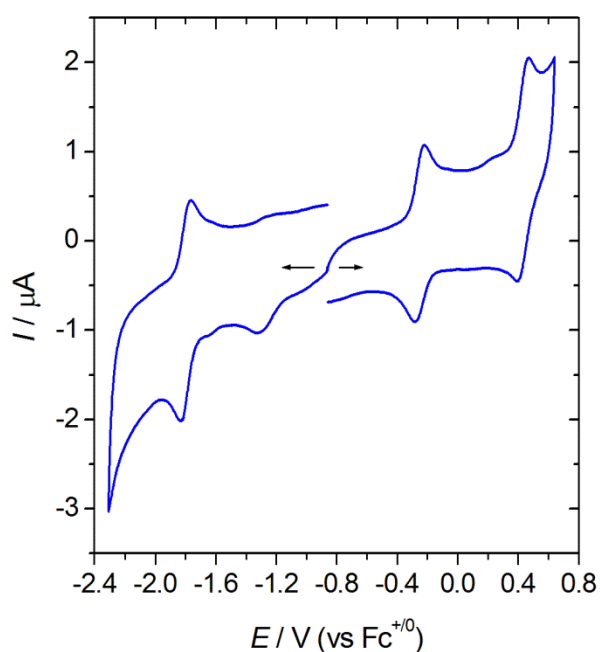
**Fig. S7.** Voltammograms recorded at 5 mV s<sup>-1</sup> and rotation rates ranging from 100 to 500 rpm at a poly-CoTAA modified RDE in 0.1 M NaCl and 6 mM acetate buffer (pH 4.6). The inset shows the corresponding Levich plot: a slope of 0.0354 mA cm<sup>-2</sup> rpm<sup>-1/2</sup> was calculated by linear regression (R<sup>2</sup> = 0.999).

**Fig. S8.** Charge passed versus time for electrolysis at -1.20 V vs. SCE of 0.1 M NaCl containing about 1 mM HCl. The working electrode is a poly-CoTAA modified GC electrode rotating at 500 rpm. The total charge passed during electrolysis of 2 mL of solution is Q<sub>tot</sub> = 0.128 C. This corresponds to the consumption of Q<sub>tot</sub>/F × 500 = 6.63 × 10<sup>-4</sup> M of H<sup>+</sup>. In the meantime, pH has increased from 3.10 to 3.70 corresponding to a decrease of 10<sup>-3.1</sup> - 10<sup>-3.70</sup> = 5.95 × 10<sup>-4</sup> M of H<sup>+</sup>. Comparison of these results allows us to conclude that poly-CoTAA works at Faradaic efficiency of 5.95/6.63 = 90%.

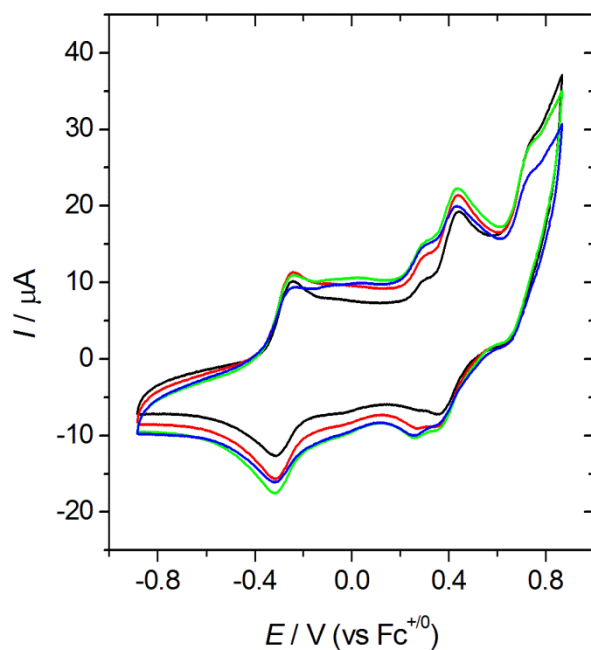
**Fig. S9 .** Tafel plot obtained from the voltammogram recorded at a poly-CoTAA modified RDE in 6 mM acetate buffer solution at pH 4.6 (see Fig. 3). The red line was calculated by linear regression: η = -0.1225 × log [-i<sub>k</sub>] - 0.9397; R<sup>2</sup> = 0.999.



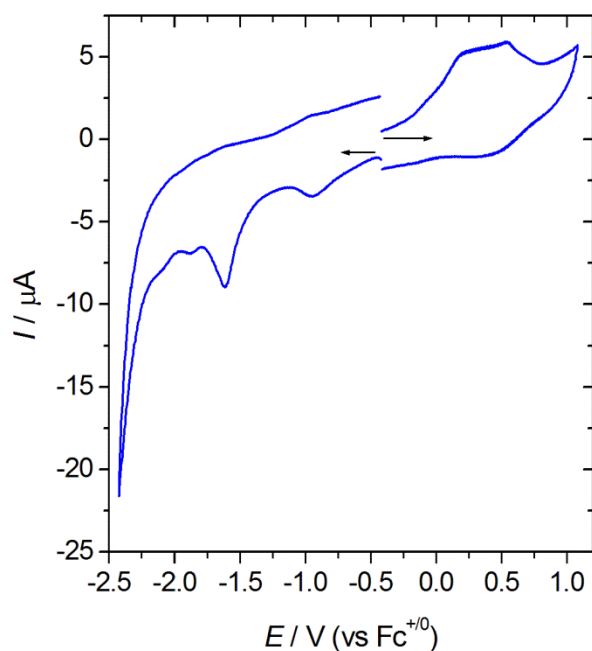
**Fig. S1.** UV-vis absorption spectra of CoTAA in solution in MeCN showing a sharp absorption band at 365 nm and a large absorption band around 505 nm, consistent with previously reported data.{Bailey, 1986 #391}



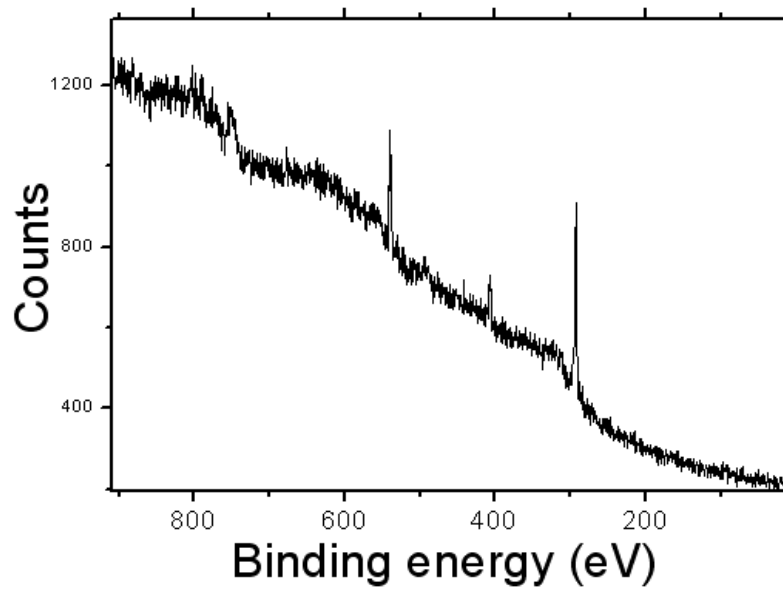
**Fig. S2.** Voltammograms of CoTAA in  $N_2$ -purged  $Bu_4NPF_6/PhCN$ . The scan rate was at  $0.1 \text{ V s}^{-1}$  and the electrode surface area  $0.071 \text{ cm}^2$ . The redox events at  $E_{1/2} \sim -1.80 \text{ V}$  and  $-0.28 \text{ V}$  are metal centered and respectively ascribed to the  $Co(II)/Co(I)$  and  $Co(III)/Co(II)$  couples, while that at  $E_{1/2} \sim 0.42 \text{ V}$  is ligand centered.



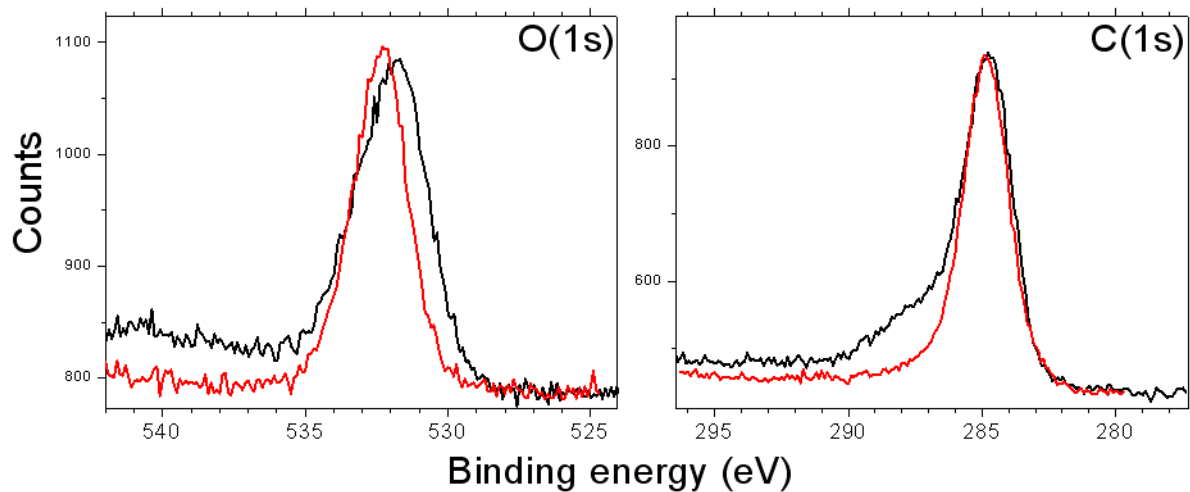
**Fig. S3.** Voltammograms recorded upon continuous potential scanning at  $0.1 \text{ V s}^{-1}$  at a GC electrode of ca  $0.071 \text{ cm}^2$  in surface area immersed in a solution of about 2 mM CoTAA in 0.1 M  $Bu_4NPF_6/PhCN$ : 2nd scan (black trace), 10th scan (red trace), 20th scan (blue trace) and 30th scan (green trace).



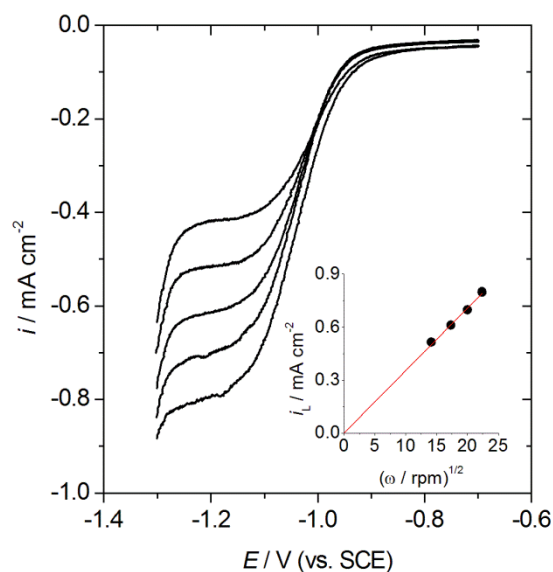
**Fig. S4.** Voltammograms of a poly-CoTAA modified electrode in  $N_2$ -purged  $Bu_4NPF_6/MeCN$ . The scan rate was at  $0.1 \text{ V s}^{-1}$  and the electrode surface area  $0.071 \text{ cm}^2$ .



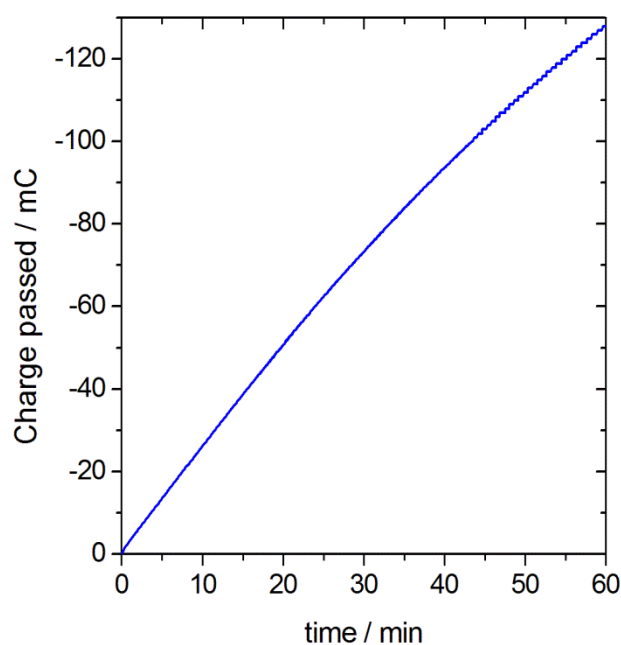
**Fig. S5.** XPS survey spectrum of a poly-CoTAA film electropolymerized on an Au-coated glass slide electrode (see Fig. 1).



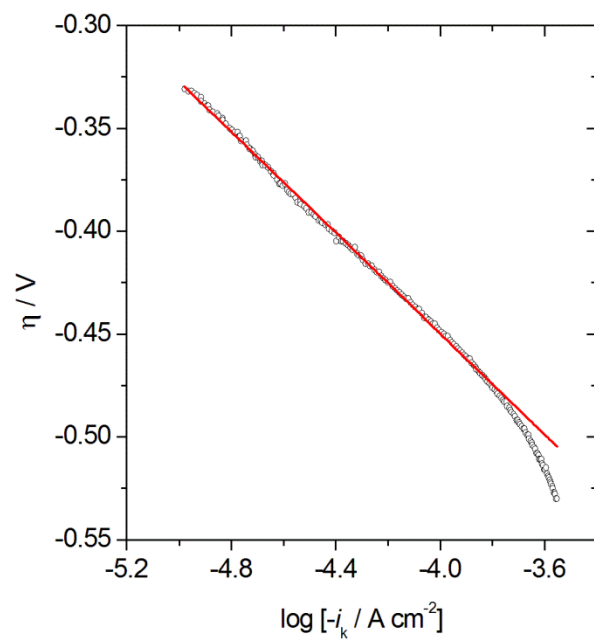
**Fig. S6.** O(1s) and C(1s) XPS signals of poly-CoTAA film (black trace) and Co(II)-tetraphenylporphyrin (red trace) used as a reference compound.



**Fig. S7.** Voltammograms recorded at  $5 \text{ mV s}^{-1}$  and rotation rates ranging from 100 to 500 rpm at a poly-CoTAA modified RDE in 0.1 M NaCl and 6 mM acetate buffer (pH 4.6). The inset shows the corresponding Levich plot: a slope of  $0.0354 \text{ mA cm}^{-2} \text{ rpm}^{-1/2}$  was calculated by linear regression ( $R^2 = 0.999$ ).



**Fig. S8.** Charge passed versus time for electrolysis at  $-1.20 \text{ V vs. SCE}$  of 0.1 M NaCl containing about 1 mM HCl. The working electrode is a poly-CoTAA modified GC electrode rotating at 500 rpm. The total charge passed during electrolysis of 2 mL of solution is  $Q_{\text{tot}} = 0.128 \text{ C}$ . This corresponds to the consumption of  $Q_{\text{tot}}/F \times 500 = 6.63 \times 10^{-4} \text{ M}$  of  $\text{H}^+$ . In the meantime, pH has increased from 3.1 to 3.7 corresponding to a decrease of  $10^{-3.1} - 10^{-3.7} = 5.95 \times 10^{-4} \text{ M}$  of  $\text{H}^+$ . Comparison of these results allows us to conclude that poly-CoTAA works at Faradaic efficiency of  $5.95/6.63 = 90\%$ .



**Fig. S9** . Tafel plot obtained from the voltammogram recorded at a poly-CoTAA modified RDE in 6 mM acetate buffer solution at pH 4.6 (see Fig. 3). The red line was calculated by linear regression:  $\eta = -0.1225 \times \log [-i_k] - 0.9397$ ;  $R^2 = 0.999$ .