

ELECTRONIC SUPPORTING INFORMATION

A Cobalt Complex with a bioinspired molybdopterin-like ligand: a Catalyst for Hydrogen Evolution

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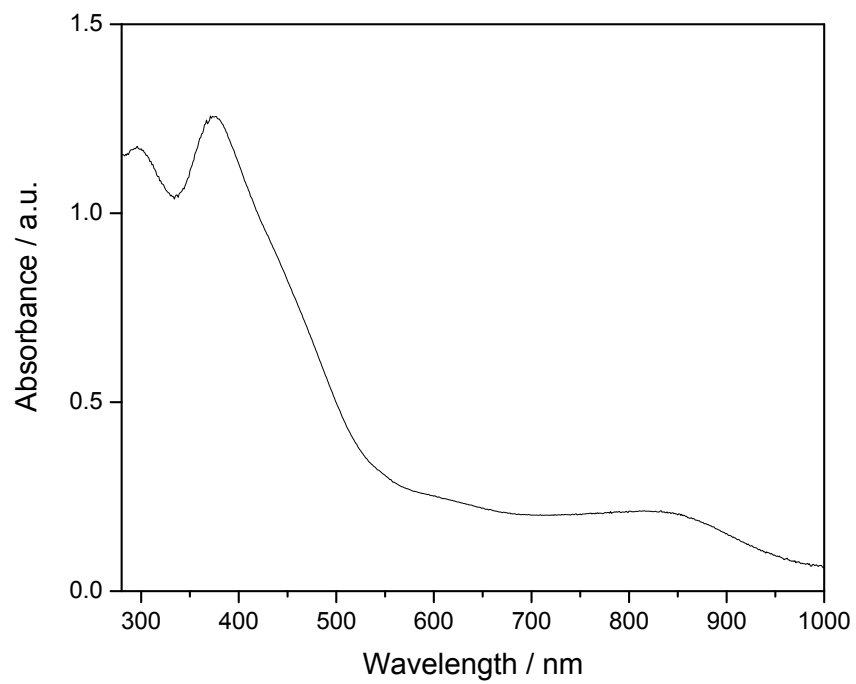


Figure S1. UV/Vis absorption spectrum of $5 \cdot 10^{-5}$ M of complex **2** in CH₃CN.

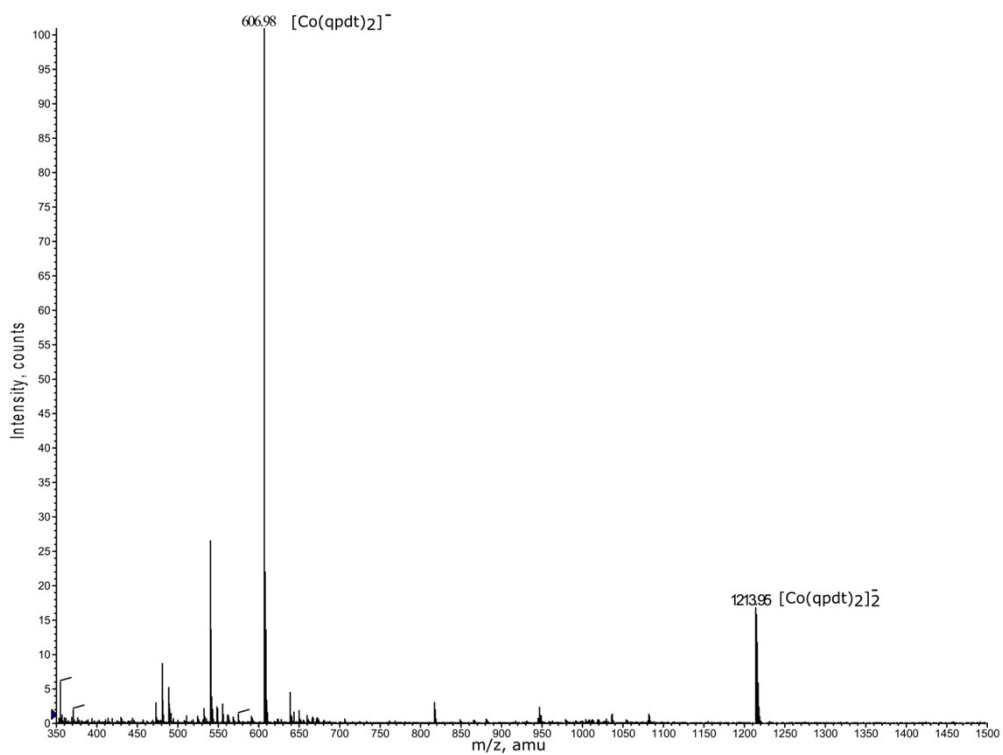


Figure S2. Negative-ion electrospray mass spectrum of **2** in CH₃CN.

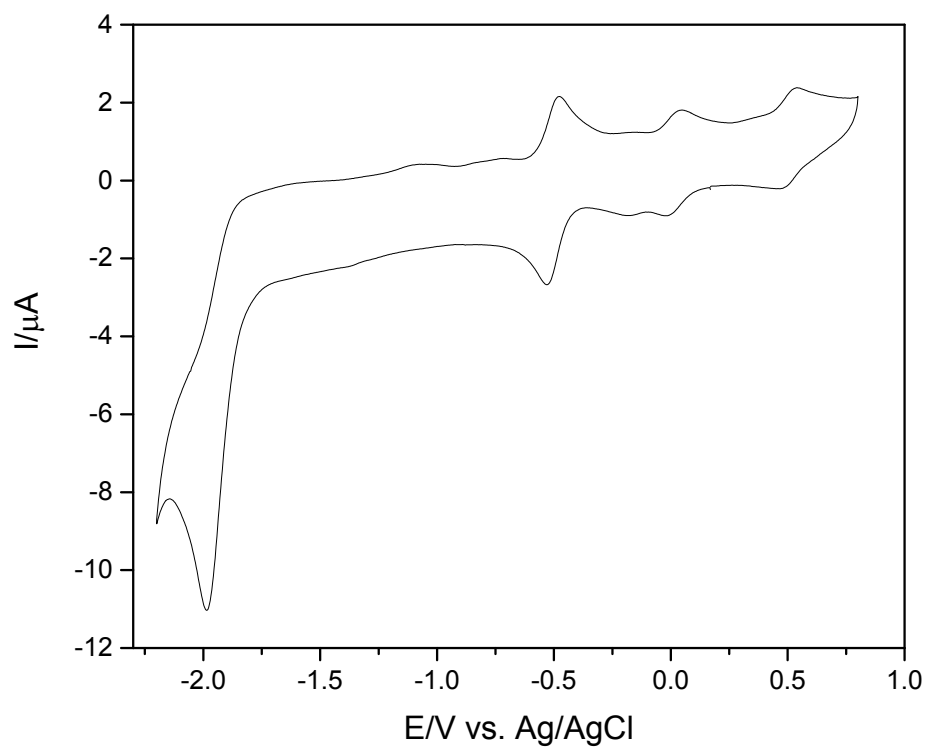


Figure S3. Cyclic voltammogram of 0.5 mM of complex **2** in 0.1 M tetrabutylammonium perchlorate (TBAP) in CH₃CN. Scan rate of 50 mV s⁻¹; glassy carbon electrode of 3 mm diameter; third scan shown.

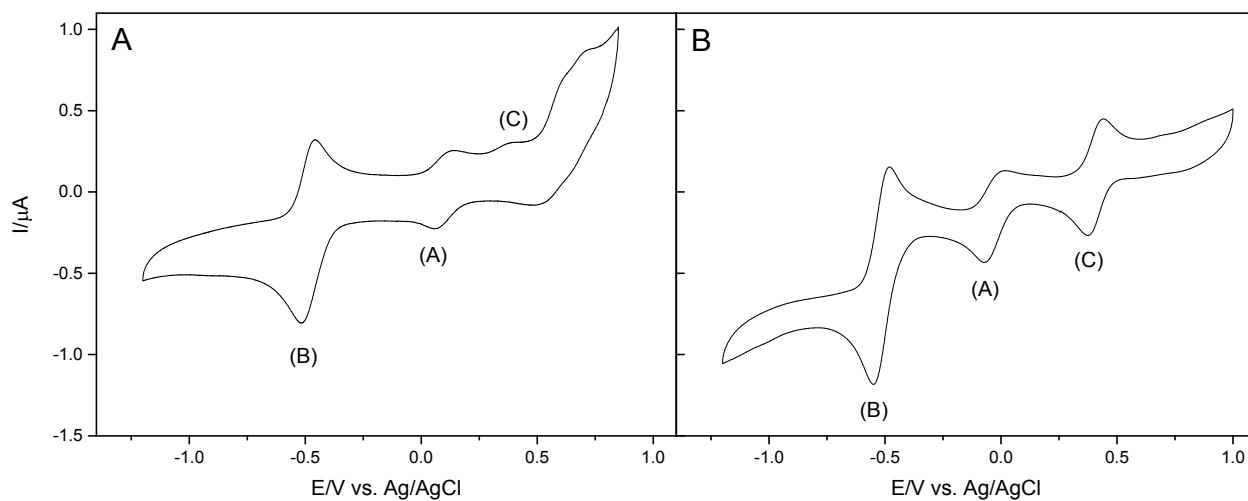


Figure S4. Cyclic voltammogram of 1 mM of complex **2** in 0.1 M tetrabutylammonium perchlorate (TBAP) in DMF (A) and in CH_2Cl_2 (B). Scan rate of 50 mV s^{-1} ; glassy carbon electrode of 1 mm diameter; third scan shown.

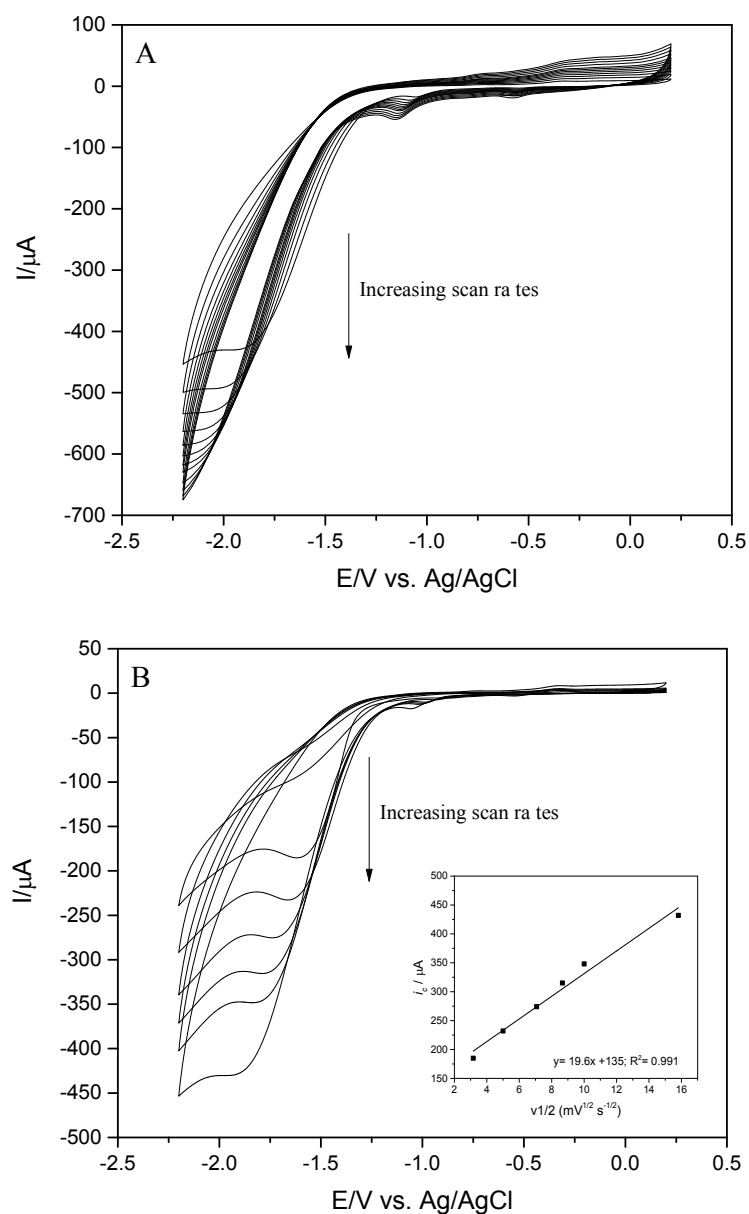


Figure S5. Cyclic voltammograms of 0.5 mM solutions of complex 2 in 0.1 M TBAP in acetonitrile under Ar conditions in the presence of 50 mM AcOH at different scan rates: (A) from 250 mV s^{-1} to 4000 mV s^{-1} and (B) from 10 mV s^{-1} to 250 mV s^{-1} . i_c is independent with the scan rate at a set potential of -1.75 V. Inset of S5B: Plot of the reduction current peak (i_c) at -1.75 V as a function of the square root of scan rate ($v^{1/2}$). Glassy carbon electrode (3 mm diameter); third scan shown.

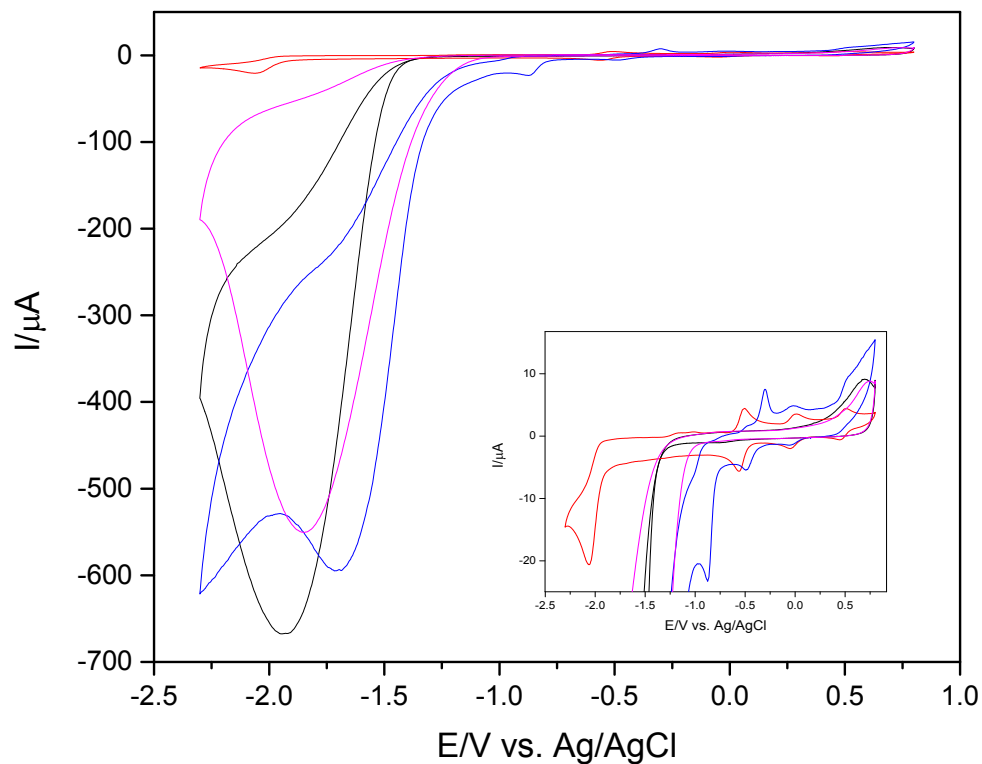


Figure S6. Rinse test. Cyclic voltammograms of 0.5 mM solutions of complex **2** in 0.1 M TBAP in acetonitrile under Ar conditions (red line), in the presence of 100 mM AcOH (blue line) and after the rinse test (magenta line). The rinse test consists on cycling the electrode for multiple CV scans (100 cycles) in the presence of acid and catalyst, then separating it from the reaction mix and rinsing it and finally, obtaining a new CV in a fresh medium that contains only acetic acid. Black line represents the cyclic voltammogram of 100 mM AcOH in the absence of catalyst. Scan rate 50 mV s^{-1} , glassy carbon electrode of 3 mm diameter, third scan is shown.

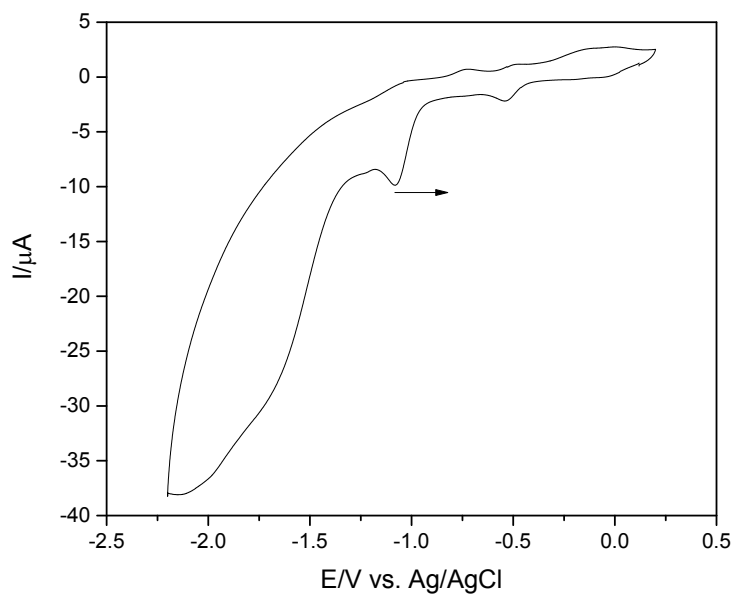


Figure S7. Pre-wave. Cyclic voltammograms of 0.5 mM solutions of complex **2** in 0.1 M TBAP in acetonitrile under Ar conditions in the presence of 2 mM AcOH at 50 mV s^{-1} , glassy carbon electrode of 3 mm diameter, third scan is shown.

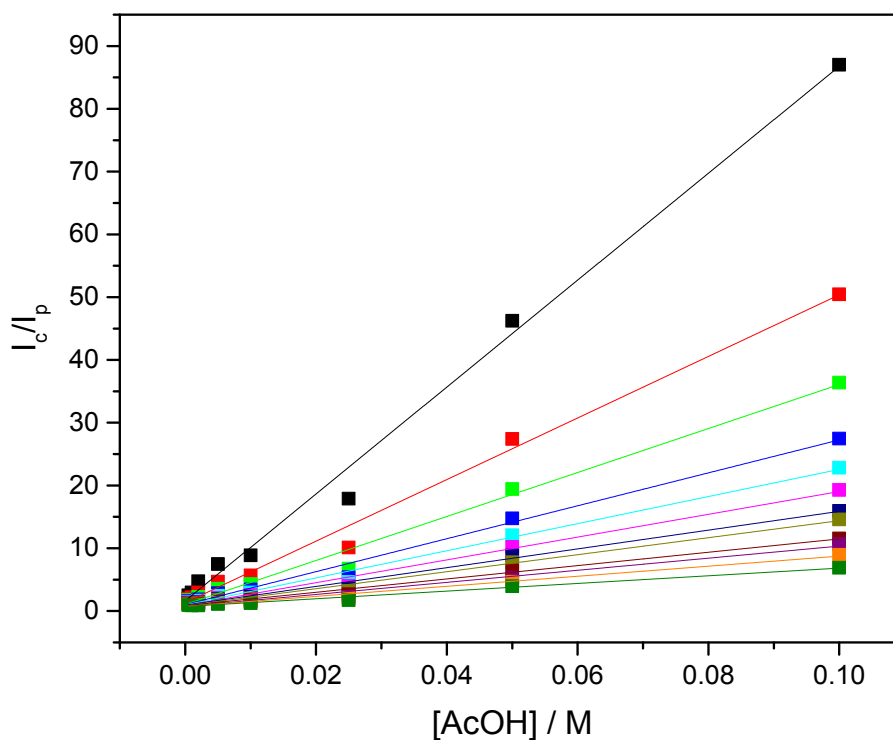


Figure S8. Plot of the i_c / i_p values as a function of AcOH concentration for 0.5 mM of complex **2** in 0.1 M TBAP in acetonitrile at a glassy carbon electrode: 0.25 V s⁻¹ (black), 851.495x +1.617; 0.5 V s⁻¹ (red), 490.466x +1.322; 0.75 V s⁻¹ (green), 350.326x +1.047; 1.0 V s⁻¹ (blue), 262.310x +1.026; 1.25 V s⁻¹ (cyan), 216.019x +0.961; 1.5 V s⁻¹ (magenta) 181.540x +0.885; 1.75 V s⁻¹ (navy) 149.446x +0.932; 2.0 V s⁻¹ (dark yellow) 135.434x +0.848; 2.5 V s⁻¹ (brown) 106.311x +0.859; 3.0 V s⁻¹ (purple) 96.322x +0.714; 3.5 V s⁻¹ (orange) 80.166x +0.731; 4.0 V s⁻¹ (olive) 61.037x +0.733. The slopes of these lines are plotted vs. $v^{-1/2}$ in Figure S7.

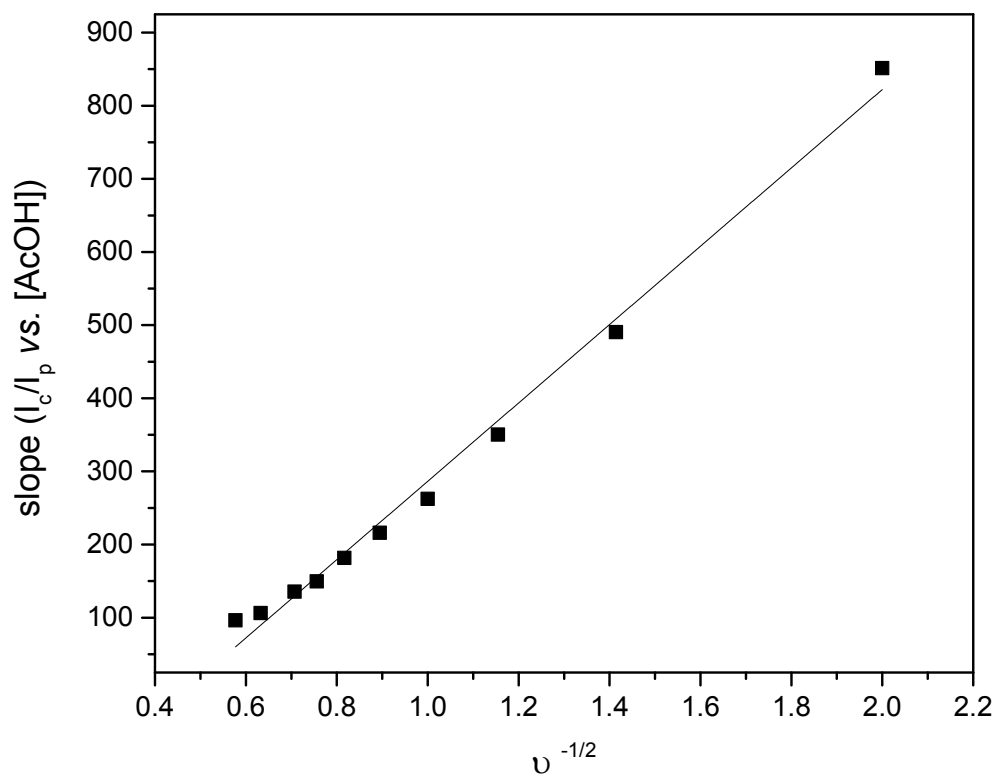


Figure S9. Plot of the slopes from figure S6 vs. $v^{-1/2}$ for complex **2**. The rate constant for hydrogen production, k , can be calculated from the slope to be *ca.* 557000 $M^{-2} s^{-1}$. For 0.1 M of AcOH, this corresponds to a turnover frequency (TOF) of *ca.* 5570 s^{-1} .

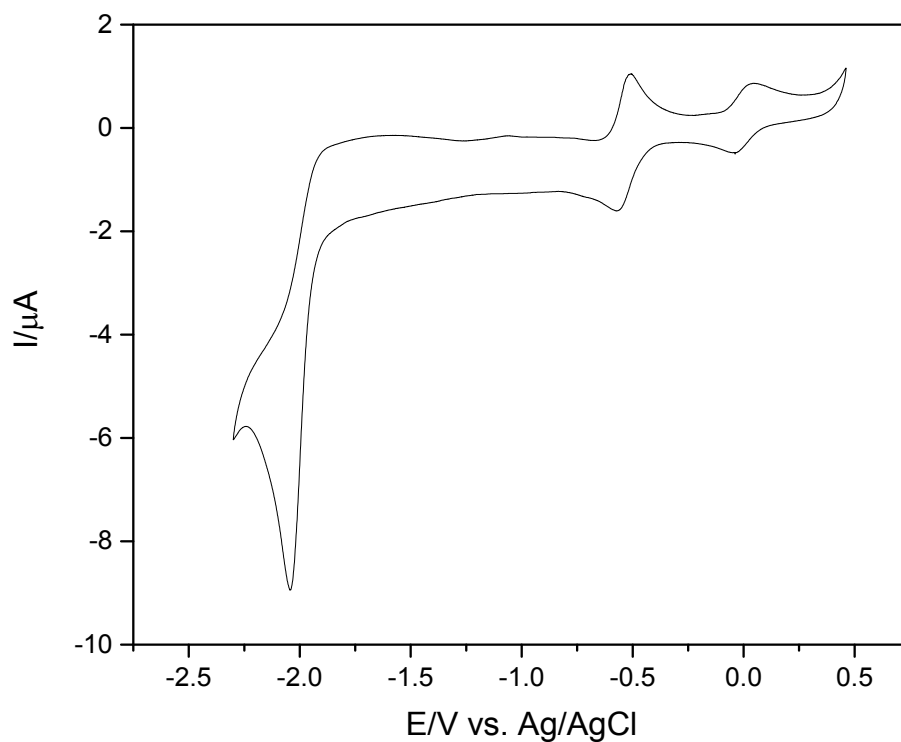


Figure S10. Cyclic voltammogram of 0.5 mM of complex **2** in 0.1 M tetrabutylammonium perchlorate (TBAP) in CH_3CN . Scan rate of 50 mV s^{-1} ; mercury-gold amalgam as the working electrode; third scan shown.

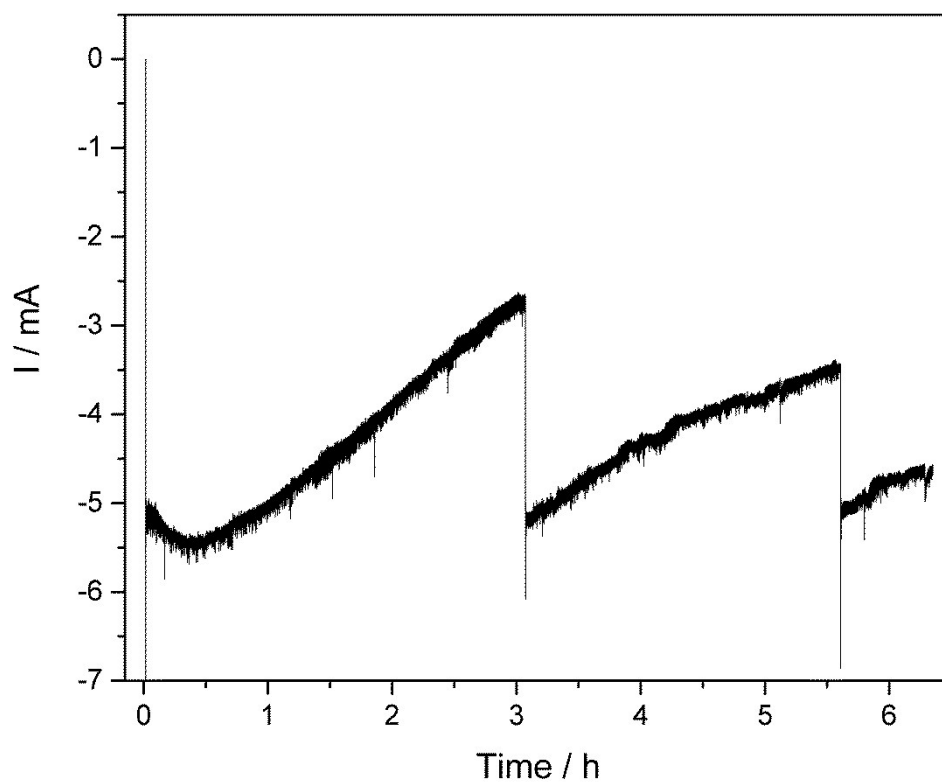


Figure S11. Current passed as a function of time during electrolysis at -1.6 V of 1 mM of complex **2** in the presence of 100 mM AcOH. After 3 h and 5 h 30 min, further additions of 100 mM AcOH were added.

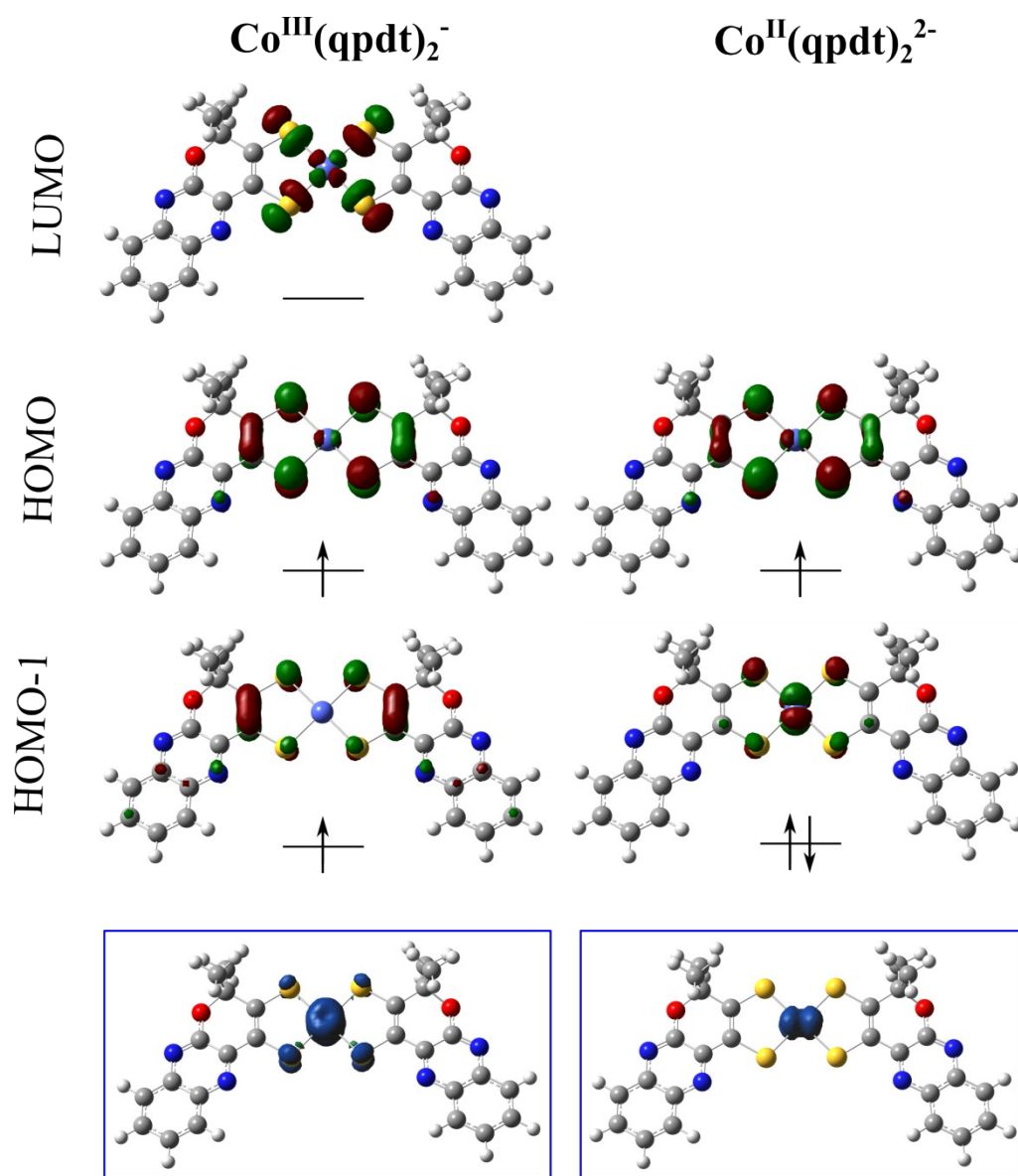


Figure S12. Kohn-Sham frontier molecular orbitals (isovalue 0.05) and the spin density plots (isovalue 0.005) for $\text{Co}^{\text{III}}(\text{qpdt})_2^-$ and its reduced counter-part $\text{Co}^{\text{II}}(\text{qpdt})_2^{2-}$.

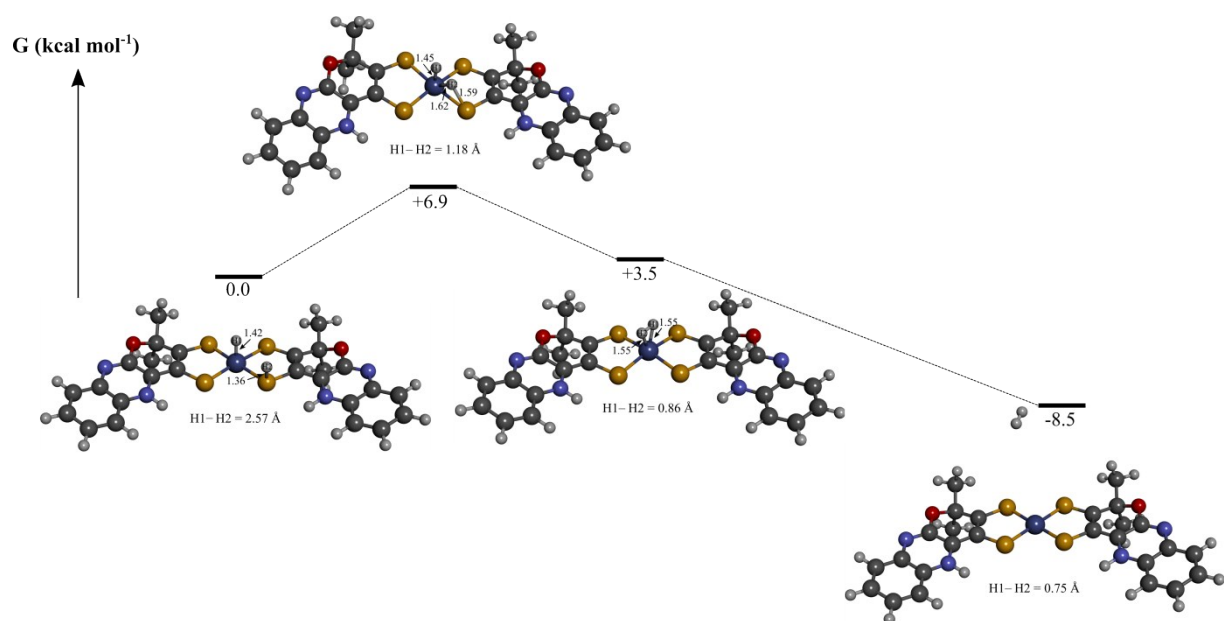


Figure S13. Free energy profile (in kcal mol^{-1}) for the migration of proton from a sulfur atom to the Co-H bond in the quadruply protonated Co^{III} hydride intermediate.

Table S1. Crystal data and structure refinement for $(\text{Et}_4\text{N})_2[\text{Co}(\text{qpdt})_2]_2 \cdot (\text{CH}_2\text{Cl}_2)_2$.

Empirical formula	C70 H84 Cl4 Co2 N10 O4 S8	
Formula weight	1645.61	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 20.2139(5) Å	$\alpha = 90^\circ$.
	b = 17.4564(6) Å	$\beta = 112.140(2)^\circ$.
	c = 23.2027(6) Å	$\gamma = 90^\circ$.
Volume	7583.6(4) Å ³	
Z	4	
Density (calculated)	1.441 Mg/m ³	
Absorption coefficient	7.216 mm ⁻¹	
F(000)	3424	
Crystal size	0.2 x 0.04 x 0.04 mm ³	
Theta range for data collection	3.669 to 62.497°.	
Index ranges	-23 ≤ h ≤ 21, 0 ≤ k ≤ 20, 0 ≤ l ≤ 26	
Reflections collected	11750	
Independent reflections	11750 [R(int) = ?]	
Completeness to theta = 62.497°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.752 and 0.513	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11750 / 65 / 1006	
Goodness-of-fit on F ²	0.937	
Final R indices [I > 2σ(I)]	R1 = 0.0664, wR2 = 0.1444	
R indices (all data)	R1 = 0.1188, wR2 = 0.1636	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.515 and -0.492 e.Å ⁻³	

Table S2. Selected bond lengths [\AA] and angles [$^\circ$] for $(\text{Et}_4\text{N})_2[\text{Co}(\text{qpdt})_2]_2 \cdot (\text{CH}_2\text{Cl}_2)_2$.

Co(1)-S(1)	2.1796(16)
Co(1)-S(2)	2.1889(17)
Co(1)-S(3)	2.1910(16)
Co(1)-S(4)	2.2056(14)
Co(1)-S(5)	2.3671(16)
S(1)-C(1)	1.730(6)
S(2)-C(2)	1.717(5)
S(3)-C(14)	1.757(5)
S(3)-Co(2)	2.3585(16)
S(4)-C(15)	1.719(6)
C(1)-C(2)	1.367(7)
C(14)-C(15)	1.355(7)
Co(2)-S(7)	2.1652(16)
Co(2)-S(5)	2.1896(16)
Co(2)-S(8)	2.2002(17)
Co(2)-S(6)	2.2089(15)
S(5)-C(27)	1.754(5)
S(6)-C(28)	1.721(6)
S(7)-C(40)	1.727(6)
S(8)-C(41)	1.711(6)
C(27)-C(28)	1.347(7)
C(40)-C(41)	1.372(8)
S(1)-Co(1)-S(2)	90.32(6)
S(1)-Co(1)-S(3)	87.82(6)
S(2)-Co(1)-S(3)	171.15(7)
S(1)-Co(1)-S(4)	159.60(7)
S(2)-Co(1)-S(4)	88.71(6)
S(3)-Co(1)-S(4)	90.01(6)
S(1)-Co(1)-S(5)	105.85(5)
S(2)-Co(1)-S(5)	94.87(6)
S(3)-Co(1)-S(5)	93.96(6)
S(4)-Co(1)-S(5)	94.53(6)
C(1)-S(1)-Co(1)	103.87(19)
C(2)-S(2)-Co(1)	104.7(2)
C(14)-S(3)-Co(1)	104.28(19)

C(14)-S(3)-Co(2)	105.07(19)
Co(1)-S(3)-Co(2)	85.86(6)
S(7)-Co(2)-S(5)	86.53(6)
S(7)-Co(2)-S(8)	90.55(6)
S(5)-Co(2)-S(8)	171.26(7)
S(7)-Co(2)-S(6)	159.57(7)
S(5)-Co(2)-S(6)	89.71(6)
S(8)-Co(2)-S(6)	90.17(6)
S(7)-Co(2)-S(3)	102.47(6)
S(5)-Co(2)-S(3)	94.24(6)
S(8)-Co(2)-S(3)	94.44(6)
S(6)-Co(2)-S(3)	97.83(6)
C(27)-S(5)-Co(2)	104.24(19)
C(27)-S(5)-Co(1)	105.71(19)
Co(2)-S(5)-Co(1)	85.68(6)
C(28)-S(6)-Co(2)	103.89(18)
C(40)-S(7)-Co(2)	103.8(2)
C(41)-S(8)-Co(2)	104.0(2)

Symmetry transformations used to generate equivalent atoms.