SUPPLEMENTARY INFORMATION

How to Switch from a Poor PEDOT:X Oxygen Evolution Reaction (OER) to a Good One. A study on Dual Redox Reversible PEDOT/Metallacarborane.

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Synthesis and characterization of Cs[1]-Cl_2: To a solution of 1 equivalent of

Cs[**1**] (148.4 mg) and 2.3 equivalent of N-Chlorosuccinimide (100 mg) in 50 mL of tetrahydrofuran in a 100 mL round bottomed flask was heated for 24 hours at 58°C. Then, the volatiles were removed in the rotavapor and the product wasextracted with diethyl ether (15 mL) and 1 M aqueous HCl three times (3 x 15 mL) to remove all the impurities. After the extraction, the organic layer was dried over $MgSO_4$, filtered and the liquid was evaporated and dissolved in the minimum volumeof water. An aqueous solution containing an excess of CsCl was added, resultingin the formation of an orange precipitate. This Cs[**1**]-Cl_2 was filtered off,washed several times with water and dried. Characterization of Cs[**1**]-Cl_2: ATR-FTIR (cm^{-1}): ν 3051 (w, C_c-H), 2606, 2537 (s, B-H). MALDI-TOF-MS: m/z calc for [**1**]-Cl_2^-: 391; m/z found (%): 368 [**1**]-Cl_1, 1.60%, 392 [**1**]-Cl_2, 96.97% and 427 [**1**]-Cl_3,1.43%. $^1H\{^{11}B\}$ NMR (300.13 MHz, CD_3OCD_3): δ = 4.31 (br s, 4H, C_c-H), 3.42, 3.19, 2.94, 2.77, 2.15, 1.76, 1.70 (br s, 14H, B-H). ^{11}B NMR (96.29 MHz,CD_3OCD_3): δ = 14.27, 1.74, 3.63, -17.23, -23.52.

Figure S1. **Cyclic voltammograms** of a) Cs[**1**], b) Cs[**1**]-Cl_2, c)Cs[**1**]-Cl_4, d) Cs[**1**]-Cl_6 and e) Cs[**1**]-I_6 with ferrocene as internal reference in anhydrous acetonitrile.

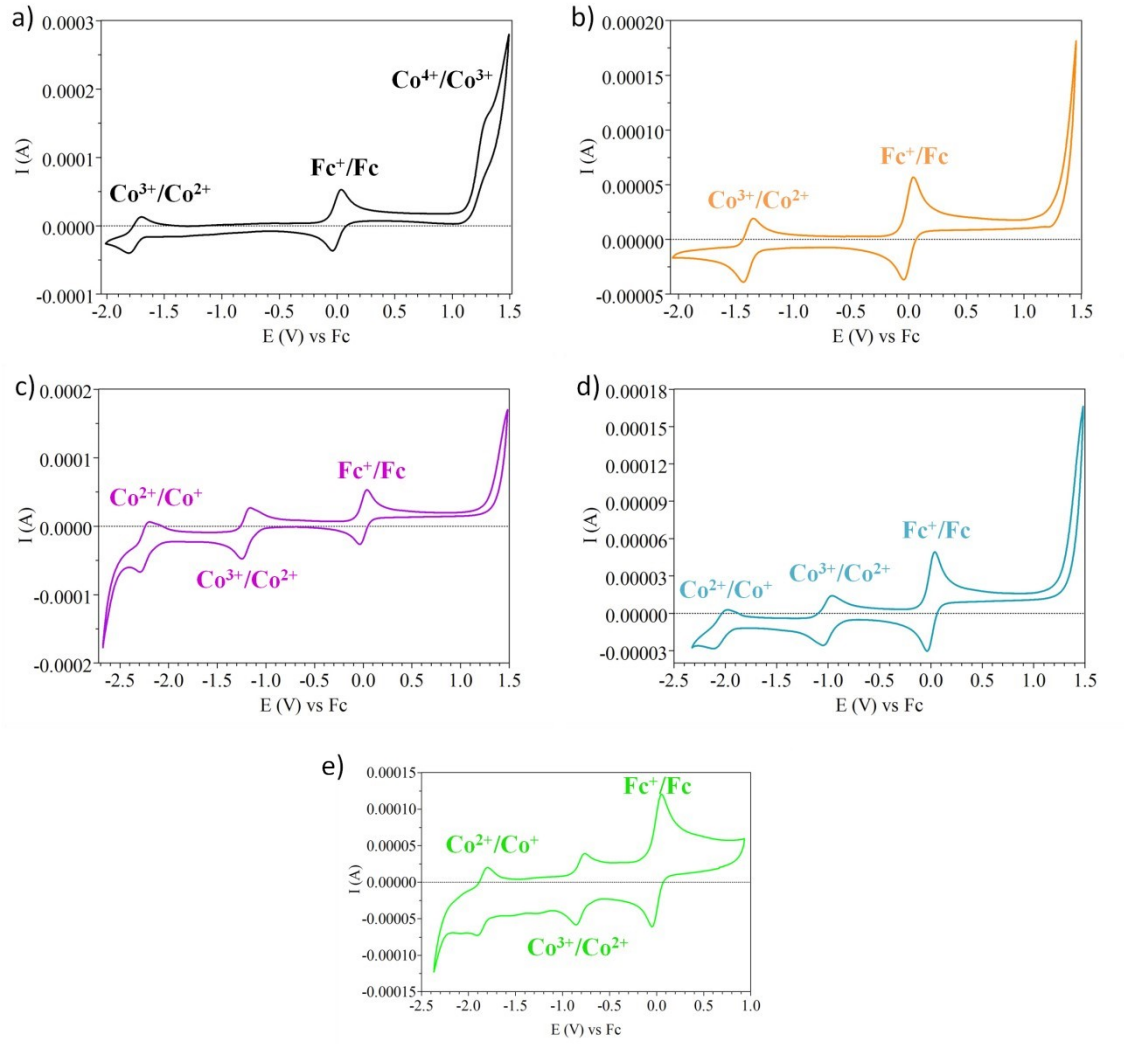

Figure S2. High resolution XPS spectra of [1], PEDOT:[**1**] and PEDOT:[**1**]-Cl_6.

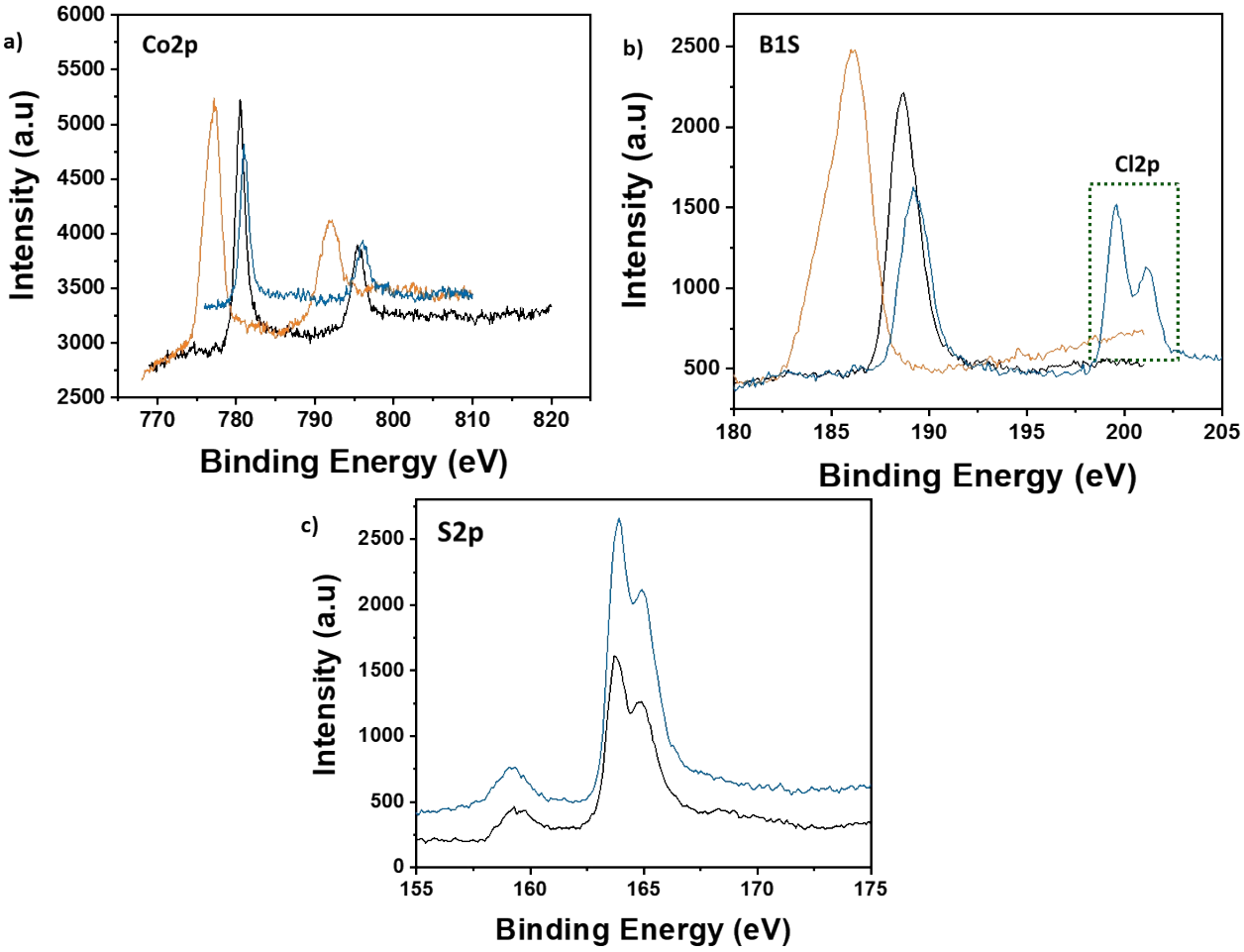

Figure S3. FTIR spectra of PEDOT:[**1**]-Cl_x (x=2,4 and 6), PEDOT:[**1**]-I_6 and PEDOT:PSS.

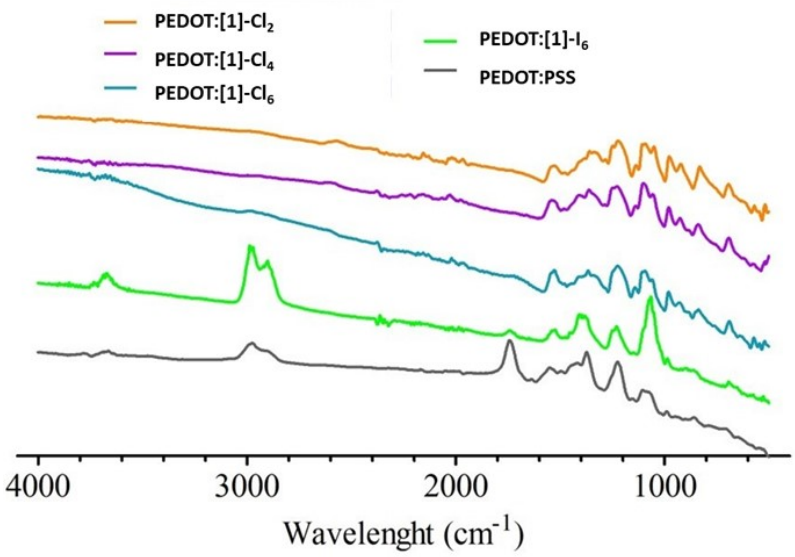

Figure S4. Thermogravimetric analysis of PEDOT:[**1**]-Cl_x (x=2,4 and 6), and PEDOT:PSS from 298-1173K**.**

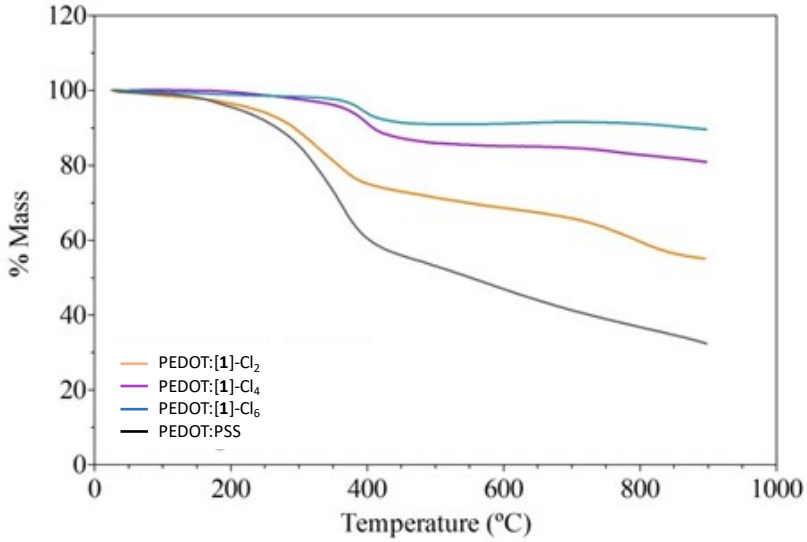

Figure S5. Linear sweep voltammograms of a) PEDOT:[**1**]-Cl_2; b) PEDOT:[**1**]-Cl_4; c) PEDOT:[**1**]-Cl_6, inclusive of the deconvolution of the wave; d) PEDOT:[**1**]-I_6 and e) PEDOT:PSS in 0.1M Na_2SO_4 at 0.5mV/s.

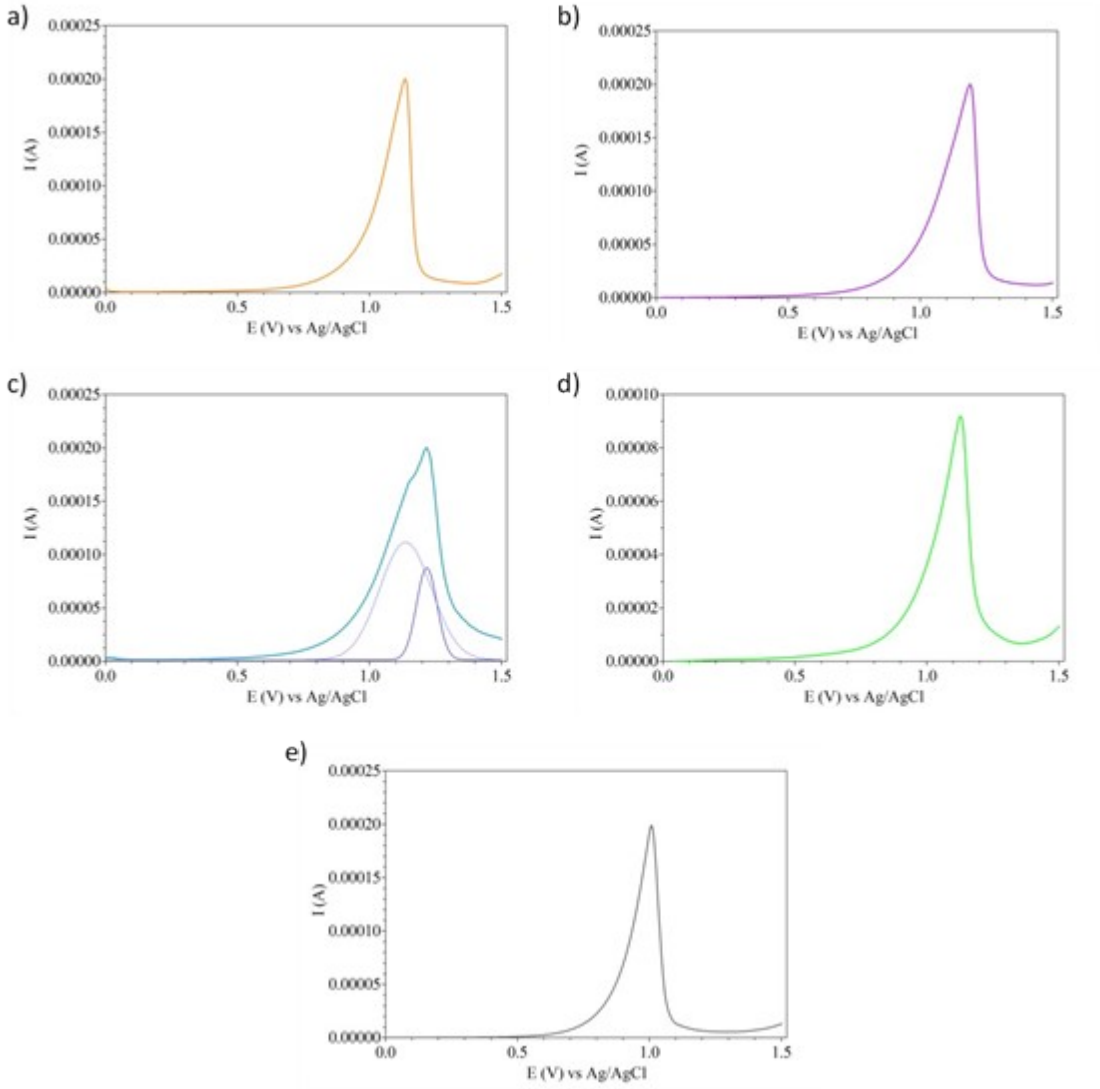

Figure S6. Bode diagrams of a) PEDOT:[**1**]-Cl_2; b) PEDOT:[**1**]-Cl_4; c) PEDOT:[**1**]-Cl_6; d) PEDOT:[**1**]-I_6 and e) PEDOT:PSS at different temperatures from 20-160ºC.

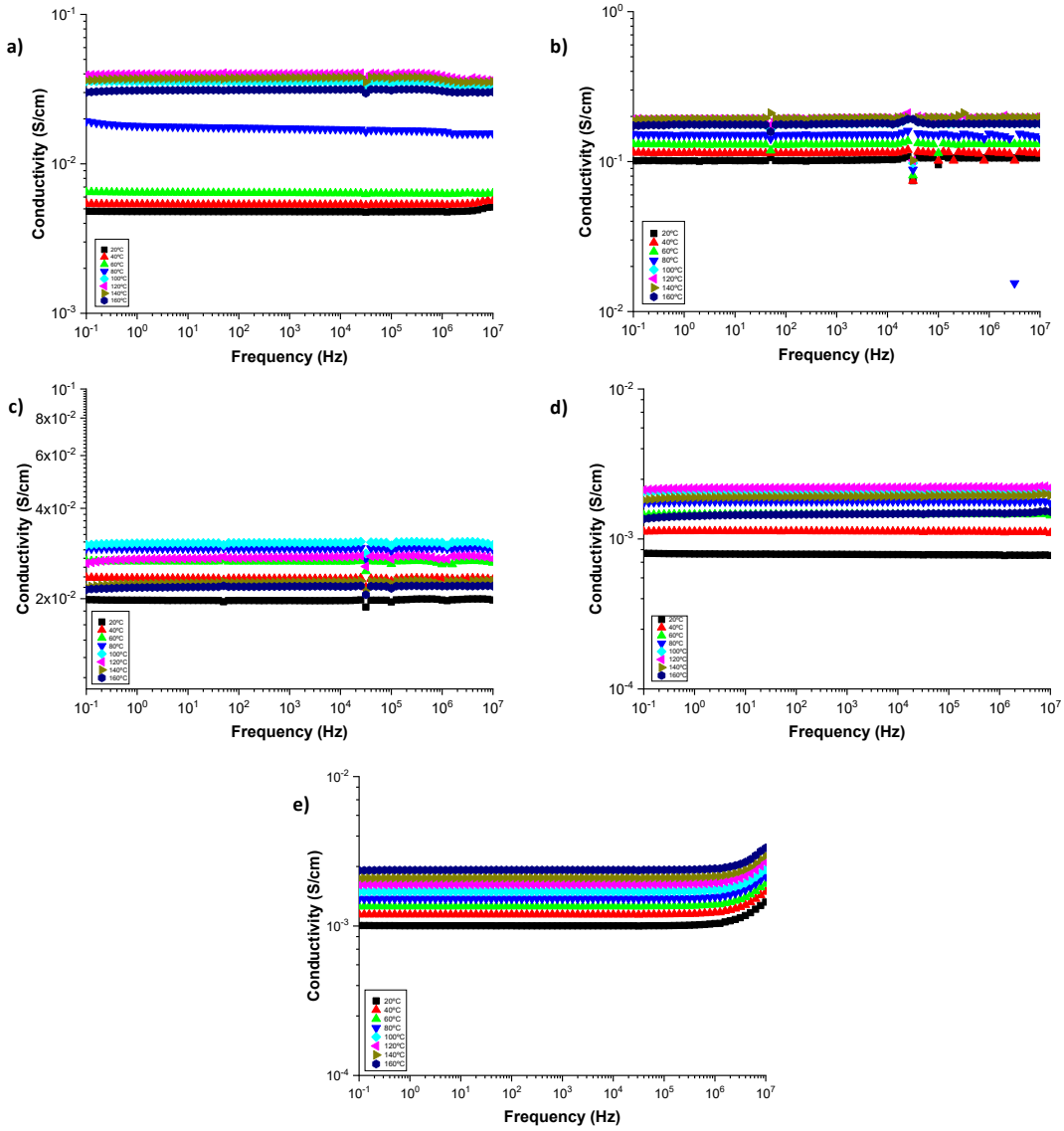

Figure S7. Temperature dependence of conductivity obtained from Bode diagram for a) PEDOT:[**1**]-Cl_2 (◘); b) PEDOT:[**1**]-Cl_4 (❑); c) PEDOT:[**1**]-Cl_6 (⧫); d) PEDOT:[**1**]-I_6 (◆) and e) PEDOT:PSS (■).

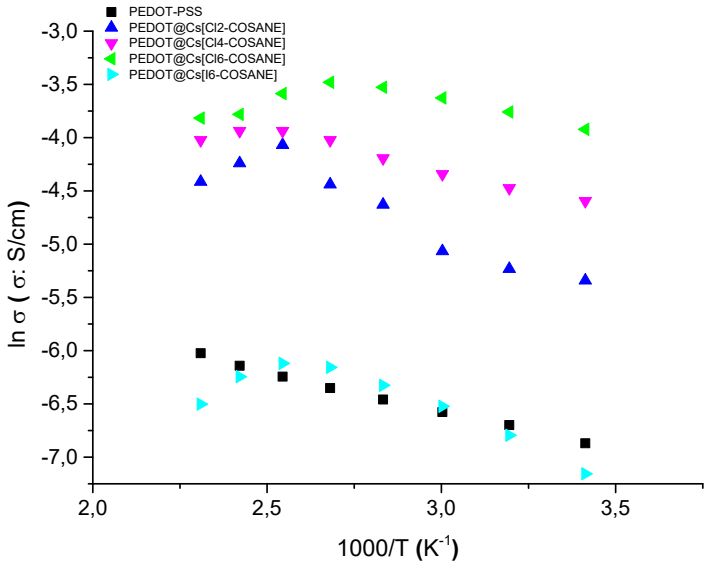

Figure S8. Temperature dependence of the direct-current conductivity a) PEDOT:[**1**]-Cl_2 (◘); b) PEDOT:[**1**]-Cl_4 (❑); c) PEDOT:[**1**]-Cl_6 (♦); d) PEDOT:[**1**]-I_6 (◆) and e) PEDOT:PSS (■), for all the range of temperatures.

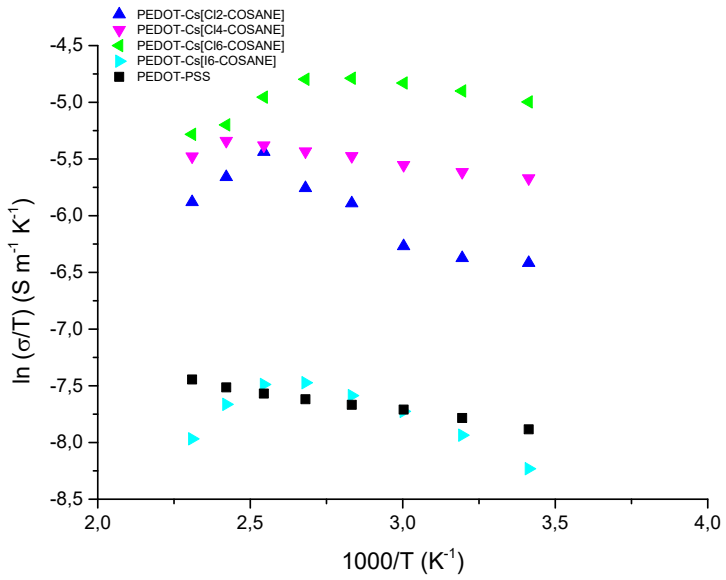

Figure S9. Linear sweep voltammetries of PEDOT:PSS (grey), PEDOT:[**1**], (blue) and PEDOT:[**1**]-Cl_6 (yellow) to compare their water oxidation catalytic power at a) pH=7 and b) pH=13.

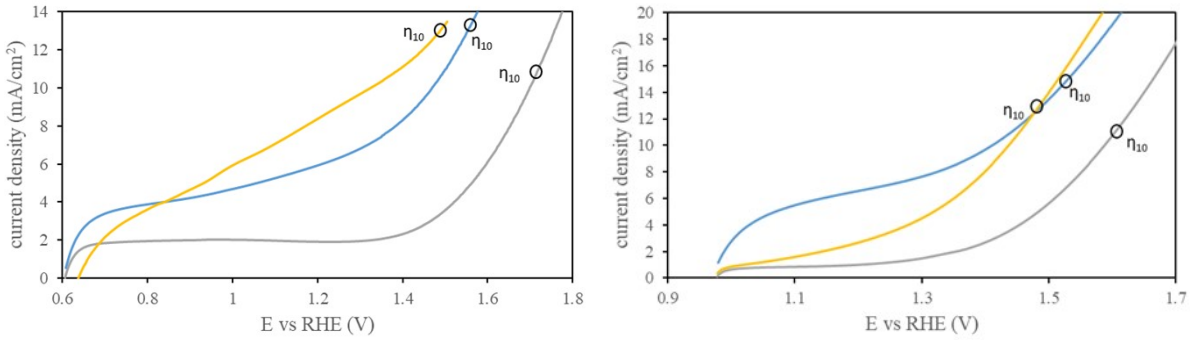

Figure S10. OER confirmation in WOC in pH=7 with 1 mM of fluoresceine using GC-PEDOT:metallacarborane electrode to demonstrate the formation of O_2.

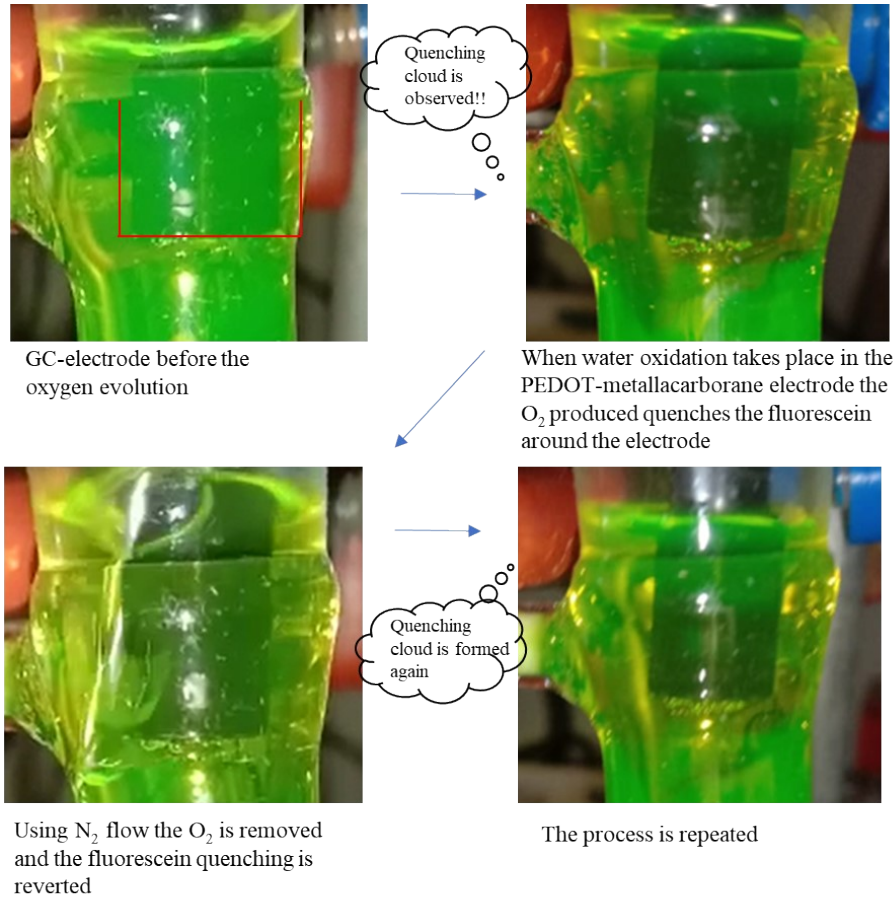

Figure S11: i vs *v* for PEDOT:Cs[*o*-COSAN] at pH=7 for both oxidative and reductive currents.

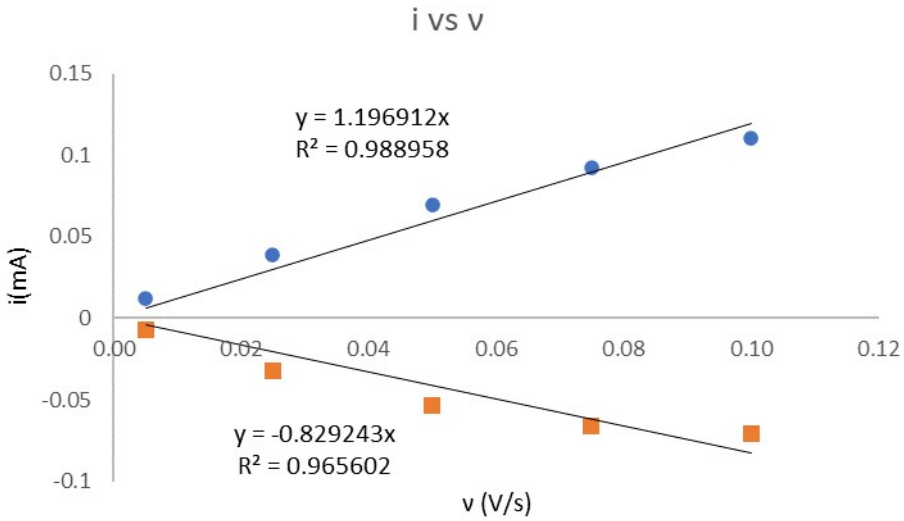

Table S1. Parameters of Gaussian function deconvoluted $Co^{4+/3+}$ oxidation waves as the summatory of square error.

Sample	pH	Peak Value	Area	SD	$\Sigma Error^2$
PEDOT:[**1**]	7	1.2451	1.0626	0.1912	1.5366
PEDOT:[**1**]-Cl_6	7	1.1867	2.139	0.182	22.269
PEDOT:[**1**]	13	1.2331	0.267	0.093	1.4822
PEDOT:[**1**]-Cl_6	13	1.1731	0.1697	0.1020	1.3907