

Supporting Information

Efficient Bio-Inspired Oxygen Reduction Electrocatalysis with Electropolymerized Cobalt-Corroles

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Experimental Procedures

Synthesis of 5,10,15-tris(4-aminophenyl)corroloato cobalt(III) triphenylphosphine, Co-TAC:

This complex was prepared by metalation of the free-base 5,10,15-tris(4-aminophenyl)corrolo (H₃TAC) with Co(OAc)₂·4H₂O in the presence of triphenylphosphine. The H₃TAC was prepared either by reduction of 5,10,15-tris(4-nitrophenyl)corrolo or by reductive-de-metallation of 5,10,15-tris(4-nitrophenyl)corroloato copper(III). 5,10,15-tris(4-nitrophenyl)corrolo was prepared by condensation 2 equivalent of 5-(4-nitrophenyl)dipyrromethane with one equivalent of 4-Nitrobenzaldehyde in acidic methanol/water solution. The procedures in details for the synthesis of Co-TAC complex as well as the precursor materials are as follow:

Synthesis of 5-(4-nitrophenyl)dipyrromethane. 250 mL round-bottom flask was loaded with 100 mL of pre prepared 0.18 M HCl solution (1.5 mL 37% HCl: 98.5 mL H₂O). Pyrrole (3 equiv., 2.75 mL, 0.0397) was added followed by addition of 4-Nitrobenzaldehyde (1 equiv. 2.00 gr, 0.0132 mol.). The reaction mixture was stirred at room temperature and the reaction progress was monitored by TLC. After 2 hr. light yellow solid (slightly sticky) was filtered off and washed several times with water and then with petroleum ether to afford the product (3.42 gr, 97% yield).

MS: (TOF-MS ES detection mode) m/z 367 [M], 366 [M-H].

¹H NMR: (CDCl₃, 400 MHz): δ 8.15 (d, *J* = 9.1 Hz, 2H), 8.04 (br s, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.75 (m, 2H), 6.18 (m, 2H), 5.87 (br s, 2H), 5.58 (s, 1H)

Synthesis of 5,10,15-tris(4-nitrophenyl)corrolo. 5-(4-nitrophenyl)dipyrromethane (2 equiv. 1 mmol, 0.267 gr.) and 4-Nitrobenzaldehyde (1 equiv. 0.5 mmol, 0.0755 gr) were dissolved in 50 mL MeOH previously loaded into 250 mL round-bottom flask. 50 mL of pre prepared 0.60 M HCl solution (2.5 mL 37% HCl: 47.5 mL H₂O) was added and the reaction was stirred at room temperature for 1 hr. this procedure was repeated in 4 flasks simultaneously. The reactions were stirred at room temperature. After 1 hr an orange solid precipitate was filtered off (all 4 flasks together) washed several times with water and then with petroleum ether. The product was dissolved in 200 ml of CH₂Cl₂, dried (Na₂SO₄) filtered, divided to two 1L round-bottom flasks, and diluted to 500mL with CH₂Cl₂. p-chloranil (3 equiv. 3.0 mmol, 738 mg) was added to each, and the mixtures were stirred overnight at room temperature. The reaction mixtures were evaporated to dryness and passed over a silica column (hexane/EtOAc 3:7). An olive green brown

band elutes immediately before the corrole band which starts to elute at ~70% EtOAc. The column must be pretty fast, otherwise the amount of olive green brown product will increase. The corrole fraction was collected and evaporated to dryness. The resulting solid was recrystallized from CHCl_3 /hexane to afford pure corrole. (360 mg, 27 %).

UV-vis: λ_{abs} (nm(log ϵ), DCM): 445(4.21), 570(3.87).

MS: (APCI positive mode) m/z 661 [M], 660 [M-H].

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 9.11 (d, $J = 4.0$ Hz, 2H), 8.90 (d, $J = 4.5$ Hz, 2H), 8.71 (d, $J = 8.2$ Hz, 4H), 8.66 (b, 4H), 8.58 (d, $J = 4.6$ Hz, 2H), 8.55 (d, $J = 8.3$ Hz, 4H), 8.38 (d, $J = 8.4$ Hz, 2H).

Synthesis of 5,10,15-tris(4-nitrophenyl)corrolato Cu(III). To a solution of not clean 5,10,15-tris(4-nitrophenyl)corrole (0.1 mmol, 1equiv.) in THF were added (3 mmol, 3equiv.) of $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and the mixture was stirred at room temperature for 20 min. The reaction mixture was evaporated to dryness and passed over a silica column (DCM: hexane 1:1) the product was obtained as brown solid. This procedure is effective for any amount of started material (tried on maximum 300 mg.)

UV-vis: λ_{abs} (nm(log ϵ), DCM): 424 (4.41), 660 (4.25).

MS: (APCI positive mode) m/z 721 [M].

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.37 (m, 6H), δ 7.99 (b, 2H), δ 7.92 (d, $J = 8.6$ Hz, 4H), δ 7.83 (d, $J = 8.5$ Hz, 2H), δ 7.60 (d, $J = 4.1$ Hz, 2H), δ 7.32 (d, $J = 4.5$ Hz, 2H), δ 7.20 (d, $J = 4.5$ Hz, 2H).

Synthesis of 5,10,15-tris(4-aminophenyl)corrole, H_3TAC .

1. By reductive – demetallation of 5,10,15-tris(4-nitrophenyl)corrolato Cu(III):

To a solution of 5,10,15-tris(4-nitrophenyl)corrolato Cu(III) (1 equiv. 0.05 mmol, 36 mg) in ACN-DCM (2-1; 15mL) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (100 equiv. 5 mmol, 1.1 gr) was added. The resulting mixture was stirred under Ar and heated to gentle reflux. Subsequently, concentrated aqueous HCl (2mL) was added and stirring was continued for 20 min. The solution was culled to room temperature and the transparent fraction was removed (as much as possible). The colored fraction was dissolved in 100 mL of water, 100 mL of EtOAc were added. After neutralization with NaHCO_3 the organic layer was washed several times with water, dried over Na_2SO_4 and the drying agent was filtered off. The solvent was evaporated under reduced pressure and a pure free base corrole was obtained after a flash column chromatography (silica hexane: EtOAc 1:9) (11 mg, 40%).

2. By reduction of 5,10,15-tris(4-nitrophenyl)corrole:

The same procedure as described for Cu corrole was applied on 5,10,15-tris(4-nitrophenyl)corrole (1 equiv. 0.15mmol,100mg) but this time 10 equiv. (1.5 mmol, 0.34 gr) of SnCl₂·2H₂O were used . After purification the product was obtained in 50% yield.

UV-Vis: λ_{abs} (nm(log ϵ), acetone) 429(5.60), 526, (4.80), 637 (4.80)

MS: (APCI positive mode) m/z 570[M-H].

¹H NMR (400 MHz CDCl₃): δ 8.90(br, 4H), 8.58 (br, 4H), 8.19 (d, $J = 7.5$ Hz, 4H), 7.96 (d, $J = 7.8$ Hz, 2H) 7.15 (d, $J = 7.6$ Hz, 4H), 7.08 (d, $J = 7.5$ Hz, 2H).

Synthesis of 5,10,15-tris(4-aminophenyl)corrolato cobalt(III) triphenylphosphine, Co-TAC.

H₃TAC (1equiv., 25 μ mol, 15 mg) was dissolved in 2 mL of EtOAc then 8 mL of EtOH and dry NaOAc (15 equiv., 366 μ mol ,30 mg) were added, the solution was stirred for 5 min. Co(OAc)₂·4H₂O (5 equiv.,120 μ mol, 30 mg) and PPh₃ (8 equiv.,191 μ mol, 50 mg) were added. After 15 min stirring at room temperature and flash silica column chromatography (100% EtOAc) the product was obtained in 80% yield (17mg).

UV-Vis: λ_{abs} (nm (log ϵ), DCM) 410(4.62), 570(3.90)

MS: (APCI positive mode) m/z 627[M].

¹H NMR (-40°C, 500 MHz, CDCl₃): δ 8.63 (d, $J = 4.1$ Hz, 2H), 8.46 (d, $J = 4.6$ Hz, 2H), 8.20 (d, $J = 4.7$ Hz, 2H), 8.08 (d, $J = 4.3$ Hz, 2H), 7.95 (d, $J = 6.7$ Hz, 2H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 3H), 7.07 (t, $J = 7.0$ Hz, 3H), 6.99(m, 5H), 6.89 (d, $J = 7.4$ Hz, 1H),6.71 (t, $J = 6.6$ Hz, 6H), 4.64 (t, $J = 9.7$ Hz, 6H)

³¹P NMR (400 MHz CDCl₃): δ 29.21 (s,1P).

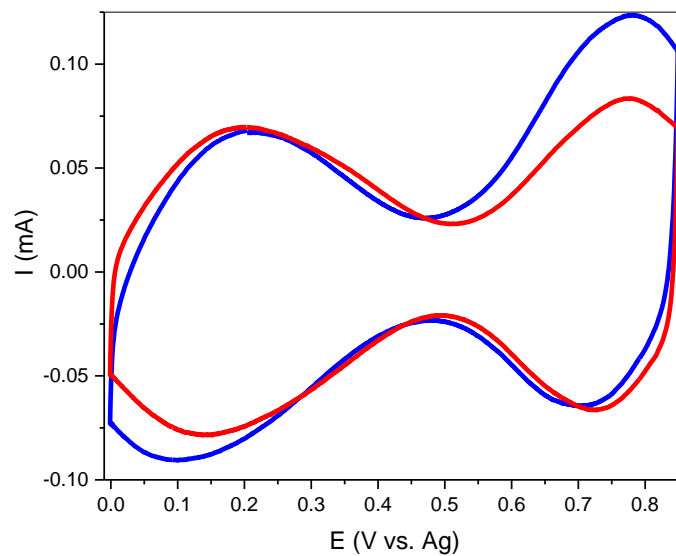


Figure S1. CV of the last cycle of polymerization (blue) and CV of the polymer in monomer free 0.1M TEAT/AN solution (red).

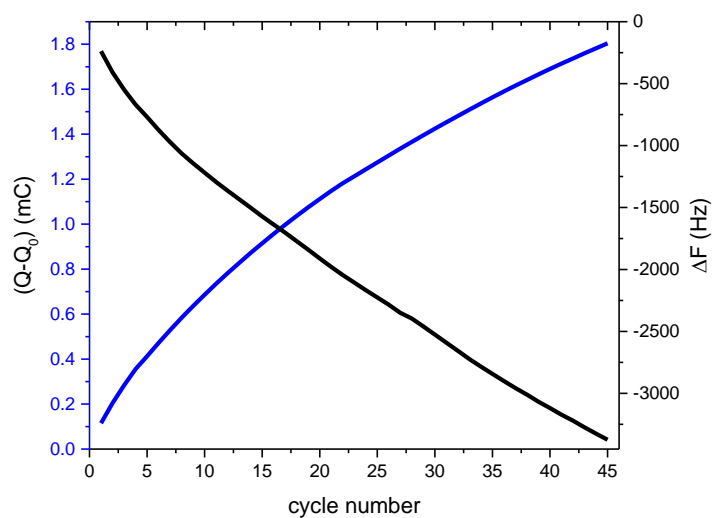


Figure S2. Changes in frequency (black) and accumulated charge per cycle (blue) as function of cycle number in EQCM measurement.

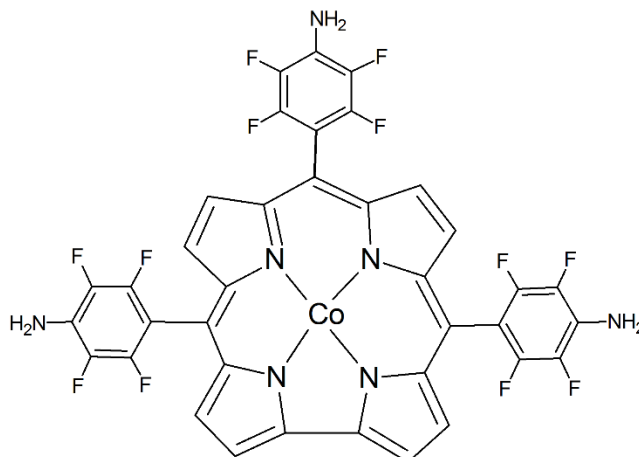
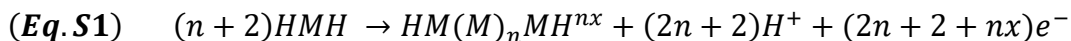


Figure S3. Cobalt(III)-tri(tetrafluoro-p-aminophenyl) corrole (CoTFAC)

For the short term, chain propagation occurs, involving repeated steps of $E(CCE)_n$. The simplified reaction for the polymerization process is:



Where $(2n+2)$ electrons are used for the bond formed at the polymerization process and the additional nx electrons for charging the polymer, where n changing as function of the oxidation level (or doping level) of the polymer.

In the RRDE measurements, the number of transferred electrons (n) was calculated via Levich equation:

$$(Eq. S2) \quad i_{l,c} = -0.201nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_{O_2}^*$$

Where A is the surface area of the electrode disk (0.2475 cm^2), D and $C_{O_2}^*$ are the oxygen diffusion coefficient ($1.5 \cdot 10^{-5} \text{ cm}^2/\text{s}$ in $0.5 \text{ M H}_2\text{SO}_2$ and $1.9 \cdot 10^{-5} \text{ cm}^2/\text{s}$ in 0.1 M KOH) and the bulk concentration of oxygen ($1.3 \cdot 10^{-6} \text{ mol/mL}$ in $0.5 \text{ M H}_2\text{SO}_2$ and $1.1 \cdot 10^{-6} \text{ mol/mL}$ in 0.1 M KOH) respectively, ν is the kinematic viscosity ($0.01 \text{ cm}^2/\text{s}$) and ω is the rotation speed (rpm).

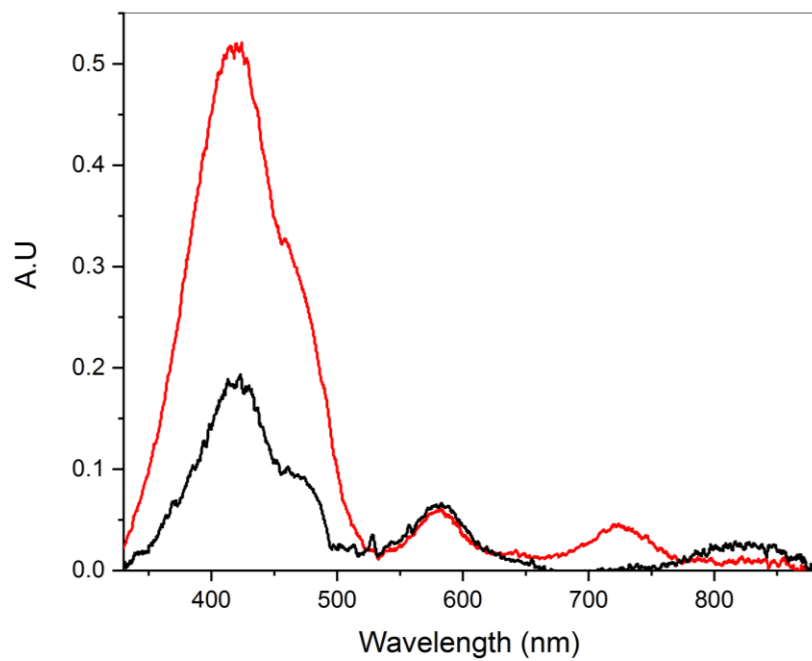


Figure S4. UV-Vis spectrum of CoTAC/ACN solution (black) and polyCoTAC on ITO electrode (red).