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Electro-reduction of Oxygen to Water Mediated by Stable Glassy Carbon Electrodes Modified by Co(II)-porphyrins with Voluminous *Meso*-Substituent.

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Glassy carbon electrodes were modified by physisorption of two different Co(II)-porphyrins, specifically designed and synthesized to study the effect of the substitution pattern (and the resulting steric hindrance) on the electrocatalytic behavior for a characteristic inner-sphere reaction such as the reduction of oxygen. In spite of the change in morphology caused by a change in the relative positions of the *meso* substituents, they showed practically the same behavior toward the electro-reduction of O_2. In both cases, water was obtained as the main product. The modified electrodes were also active toward the electro-reduction of hydrogen peroxide. Both electrodes were found stable for more than a month upon exposure to air and the current for the electro-reduction remained practically the same.

Keywords: Co-porphyrins, electro-reduction of oxygen, modified electrodes, oxygen to water reduction, substitution pattern

1. INTRODUCTION

A vast amount of research has already been conducted on the reduction of oxygen catalyzed by transition metal complexes. Metallophthalocyanines and metalloporphyrins are well-known efficient catalysts for many reactions [1-4], including the reduction of oxygen [5-16]. These kinds of complexes are hence commonly used to modify cheap surface electrodes such as glassy carbon electrodes, creating very active electrocatalysts. The electroactivity is heavily influenced by the metal center [2, 14, 17-18] and also depends on the donor or acceptor nature of the tetrapyrrolic ligand [10, 11, 16].

On the other hand, the reactivity of modified electrodes also depends on the type of modification, which can be done by a wide variety of methods [1, 3-6], although the usual approach is immobilization of the catalyst on the electrode surface via physical adsorption [3, 5, 8, 9, 11, 16]. In the field of oxygen reduction, many reports describe cobalt complexes, due to the oxophilic character of the metal. Normally, the product resulting from the reduction of oxygen is hydrogen peroxide via a two-electron reaction [9, 12, 13] or water via a four-electron process [6, 10, 14]. When cobalt centers can be located at an appropriate distance, the oxygen molecule can react with two metal centers simultaneously, breaking its bond and generating water in one single step. There are also cases where these reactions occur in parallel [9, 16].

According to our knowledge, there are no reports yet concerning to effect of the relative positions of voluminous *meso*-substituents on the metal center activity. For this reason, we have designed and synthesized two new cobalt(II)-porphyrins with 4-aminophenyl and 3,5-di-*tert*-butylphenyl *meso*-substituents positioned either alternating (ABAB-porphyrin) or adjacent (AABB-porphyrin) (Fig. 1). Both complexes have been used for the modification of glassy carbon electrodes through physical adsorption and the resulting electrodes have been analyzed for the reduction of O_2.

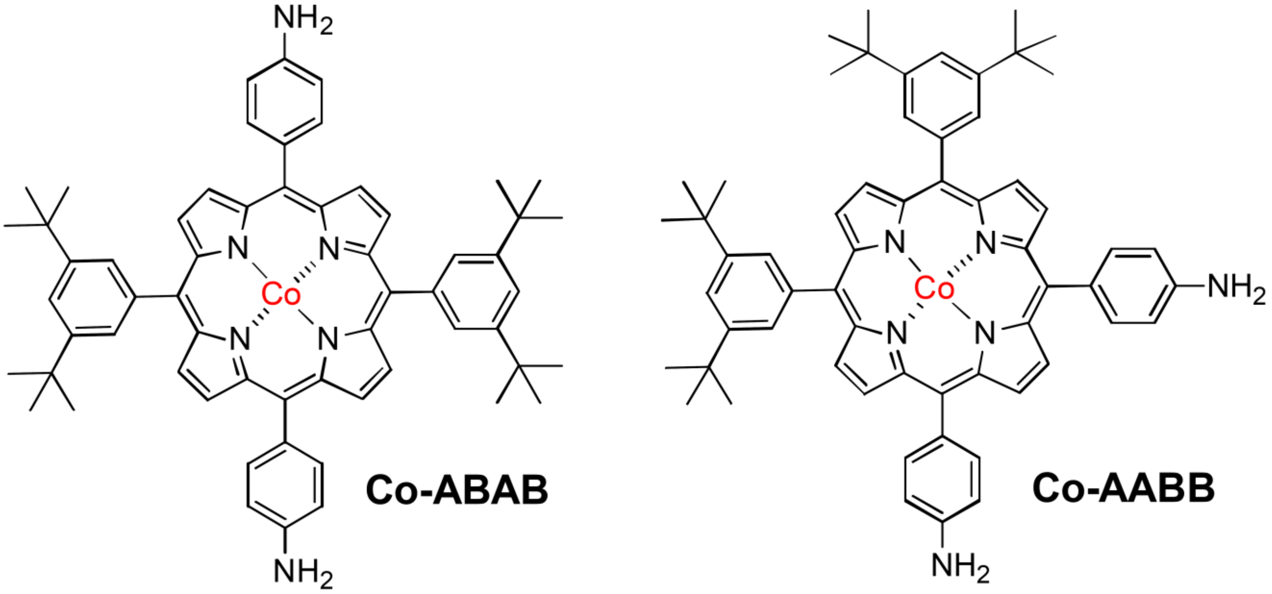

Figure 1. Structures of the applied Co(II)-porphyrins: Co(II)-5,15-bis(4-aminophenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (**Co-ABAB**) and Co(II)-5,10-bis(4-aminophenyl)-15,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (**Co-AABB**).

2. EXPERIMENTAL

2.1. Reagents

Tetrabutylammonium perchlorate (TBAP) (Fluka, 99%), *N*,*N*'- dimethylformamide (DMF) (Merck), CH_2Cl_2 (p.a. Merck). Phosphate buffer solution (PBS), pH 7.4, was prepared from 0.1 M NaCl, 2.6 mM KCl, 0.04 M Na_2HPO_4 and 0.01 M KH_2PO_4) and used as base electrolyte. H_2SO_4 and NaOH (p.a. Merck) were used to change the pH. Chemicals received from commercial sources were used without further purification. THF was dried by distillation over Na/benzophenone.

2.2. Co(II)-porphyrin synthesis:

A_2B_2-aminoporphyrins. Synthesis according to the procedure described by Sauvage *et al.* for the AB_3-porphyrin analogue [19].

A mixture of the A_2B_2-nitroporphyrins (~6:1 ratio *trans*:*cis*) (100 mg, 0.108 mmol) and $SnCl_2{\cdot}2H_2O$ (245 mg, 1.08 mmol, 10 equiv) was carefully mixed in a mortar and dissolved in ethanol (10 mL). To the resulting solution, concentrated HCl (aq) (10 mL) was added and the mixture was stirred at 70 °C for 30 min, after which complete reduction was monitored by TLC and ESI-MS. The mixture was cooled down to 0 °C and neutralized with NH_4OH, then diluted with $CHCl_3$, and the organic layer was washed with water, dried over $MgSO_4$, filtered and evaporated to dryness. The desired aminoporphyrins Fb-ABAB (61 mg) and Fb-AABB (11 mg) (resp.) were obtained as purple solids after column chromatographic purification (silica, eluent CH_2Cl_2−ethyl acetate, gradient 100−0 to 95−5). Yield: 76%.

5,15-Bis(4-aminophenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (Fb-ABAB). Data identical to that reported in the literature [20]. MS (ESI) calcd for $C_{60}H_{64}N_6$: 868.5; found: *m/z* 870.1 $[M + H]^+$; ^1H NMR (300 MHz, $CDCl_3$) δ 8.93−8.85 (dd_{AB}, 8H, H_β-porph.), 8.08 (d, ^4J = 1.8 Hz, 4H), 8.00 (d, ^3J = 8.2 Hz, 4H), 7.79 (s, 2H), 7.05 (d, ^3J = 8.2 Hz, 4H), 4.00 (s_{br}, 4H, NH_2), 1.53 (s, 36H), -2.70 (s_{br}, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 146.1, 141.5, 135.7 (CH), 132.9, 132.0−130.5 (br, CH_β), 130.1 (CH), 121.3, 121.0 (CH), 120.3, 113.6 (CH), 35.2, 31.9 (CH_3).

5,20-Bis(4-aminophenyl)-10,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (Fb-AABB). MS (ESI) calcd for $C_{60}H_{64}N_6$: 868.5; found: *m/z* 870.1 $[M + H]^+$; ^1H NMR (300 MHz, $CDCl_3$) δ 8.94−8.84 (m, 8H, H_β-porph.), 8.07 (s, 4H), 7.99 (d, ^3J = 8.2 Hz, 4H), 7.78 (s, 2H), 7.03 (d, ^3J = 8.2 Hz, 4H), 3.96 (s_{br}, 4H, NH_2), 1.52 (s, 36H), -2.69 (s_{br}, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 146.0, 141.5, 135.7 (CH), 132.8, 132.0−130.5 (br, CH_β), 130.0 (CH), 121.2, 121.1 (CH), 120.4, 113.6 (CH), 35.2, 31.9 (CH_3).

Co-insertion. According to a procedure adapted from previous work by Zhang *et al.* [21]. The respective free base A_2B_2-porphyrin (50 mg, 57.5 μmol) and anhydrous $CoCl_2$ (60 mg, 460 μmol, 8 equiv) were placed in an oven-dried round-bottom flask under Ar, and dry THF and 2,6-lutidine (25 mg, 230 μmol, 4 equiv) were added via a syringe. The mixture was heated at reflux temperature with stirring for 1 h and THF was removed *in vacuo*. Reaction completion was monitored by TLC and ESI-MS. $CHCl_3$ and a few drops of pyridine (to ensure solubility) were added, and the solution was washed with water (centrifugation/decantation, 3x) to remove the excess of metal salt and subsequently dried over $MgSO_4$. The solvents were evaporated *in vacuo* and the Co-porphyrin derivatives were quantitatively obtained as red-brown solids.

5,15-Bis(4-aminophenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinato cobalt(II) (Co-ABAB). MS (ESI) calcd for $C_{60}H_{62}CoN_6$: 925.4; found: *m/z* 926.0 $[M + H]^+$.

5,20-Bis(4-aminophenyl)-10,15-bis(3,5-di-*tert*-butylphenyl)porphyrinato cobalt(II) (Co-AABB). MS (ESI) calcd for $C_{60}H_{62}CoN_6$: 925.4; found: *m/z* 926.0 $[M + H]^+$.

2.3. Electrochemical experiments

The conventional three electrodes system consisted of a glassy carbon working electrode (GC) (geometrical area 0.07 cm^2, CHI instrument), Ag/AgCl (3 M KCl) reference electrode, and a platinum wire as counter electrode. Before each experiment, the working electrodes were polished with 1200 and 2400 microns sandpaper. After this treatment, they were polished with alumina slurry (particle size 0.3 μm) on soft leather Struers OP-NAP. Afterward, the electrodes were washed with Milli-Q water and cycled in the electrolyte solution until a stable voltammetric response was reached. Rotating disk electrode experiments were carried out using the same glassy carbon electrodes (Metrohm, Autolab, RDE80462). Rotating ring-disk measurements were achieved using a Pt-GC electrode.

2.4. Equipment

Electrochemical measurements were carried out using an Autolab potentiostat-galvanostat (PGSTAT30), AMEL Instruments (Mod. 7050) and Mod. 273 A from EG&G PARC. Rotating disk measurements were carried out using a motor controller from Autolab. Rotating ring-disk experiments were achieved with an AFMSRCE Modulated Speed Rotator (MSR) from Pine Instruments. Rotating disk and Rotating ring-disk experiments were performed with a CHI604C CH-Instrument Electrochemical Analyser.

Scanning Electron Microscopy (SEM) images were obtained using a Scanning Electron Microscope of resolution 3,5 nm JEOL JSM 6300 with a microanalyzer X-ray energies Oxford Instruments Microanalysis Group 6699 ATW with a software of processing analytical information ‘Labbook’ and quantitative analysis ‘SEMQUANT’.

NMR spectra were acquired on a commercial instrument (Bruker Avance 300 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (TMS) (^1H) or the carbon signal of $CDCl_3$ (^{13}C). Mass spectra were run using a Thermo Finnigan LCQ Advantage apparatus (ESI). For column chromatography 70-230 mesh silica 60 (E.M. Merck) was used as the stationary phase.

2.5. Modification of the electrodes

Two drops of a 1.08 mM Co(II)-porphyrin solution in DMF were deposited on the GC electrode surface and exposed to air until solvent evaporation. After the evaporation of the solvent, the surface was thoroughly washed with Milli-Q water.

3. RESULTS AND DISCUSSION

The redox behavior of the novel cobalt(II)-porphyrins was studied using cyclic voltammetry (CV) in DMF on glassy carbon electrodes (GCs). Figure 2 shows the cyclic voltammograms of the porphyrins in a 0.1 M DMF/TBAP solution.

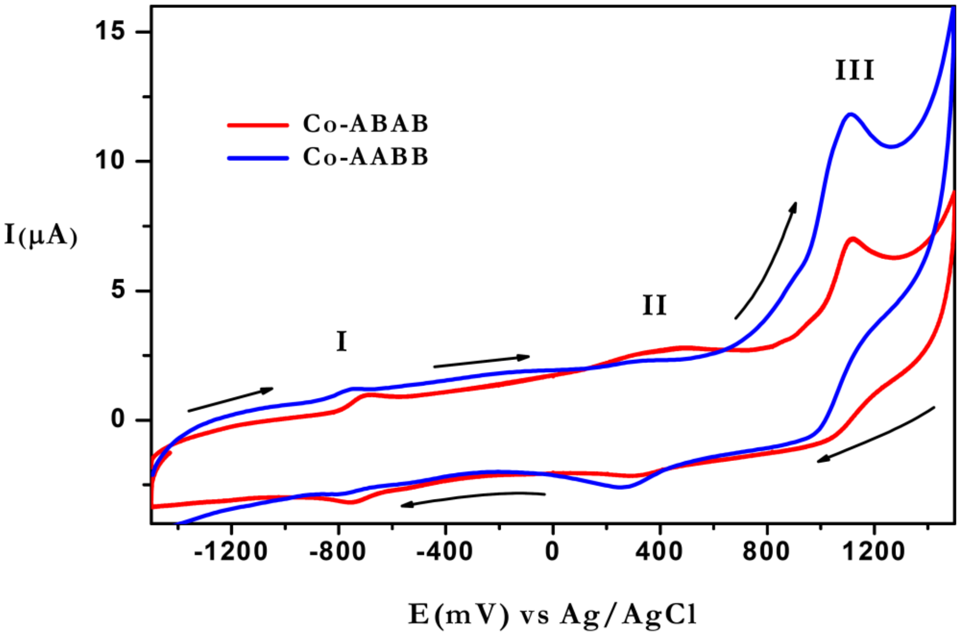

Figure 2. CVs of the Co(II)-porphyrins (Co-AABB and Co-ABAB) in a 0.1 M DMF/TBAP solution (scan rate 0.1 V-s^{-1}).

The voltammograms are quite similar, in spite of the change of the relative positions of the substituents that can affect the properties [22-24]. For both metalloporphyrins, peak I (-0.7 V) is a quasi-reversible peak corresponding to the Co (II)/Co(I) couple [25]. Peak II at ca. 0.25 V is not reversible and could be related to the Co (III)/Co(II) couple [25]. Indeed, the anodic current is not related with the cathodic current and the cathodic peak does not appear when the limits of the potential for the cycles are changed to 0.0 and 0.5V. This behavior is not entirely clear for cobalt-porphyrins but it has been described that the reduction of Co(III) can involve lose of an axial ligand.

Although the potential which cobalt (II) reduction occurs are generally not dependent on the solvent and supporting electrolyte, it can be affected by the donor or acceptor nature of the substituent groups [26]. Peak III is attributed to the oxidation of the amino groups [27].

The redox properties of the cobalt-porphyrins adsorbed by dropping a solution (1.08 mM in DMF) on the GC electrodes were studied in a phosphate buffer solution (pH 7.4) using cyclic voltammetry (CV). No redox couple was depicted for the central metal or the porphyrin ring, which is a usual behavior in aqueous solution for modified electrodes with porphyrin.

The modified electrodes were tested using the ferri-ferrocyanide redox couple (Figure 3). In both cases, the conductivity decayed showing an important increase in the irreversibility of the couple.

This behavior is commonly observed because normally, when a porphyrin is adsorbed on the electrode surface, the current decreases due to the loss of conductivity of the electrode.

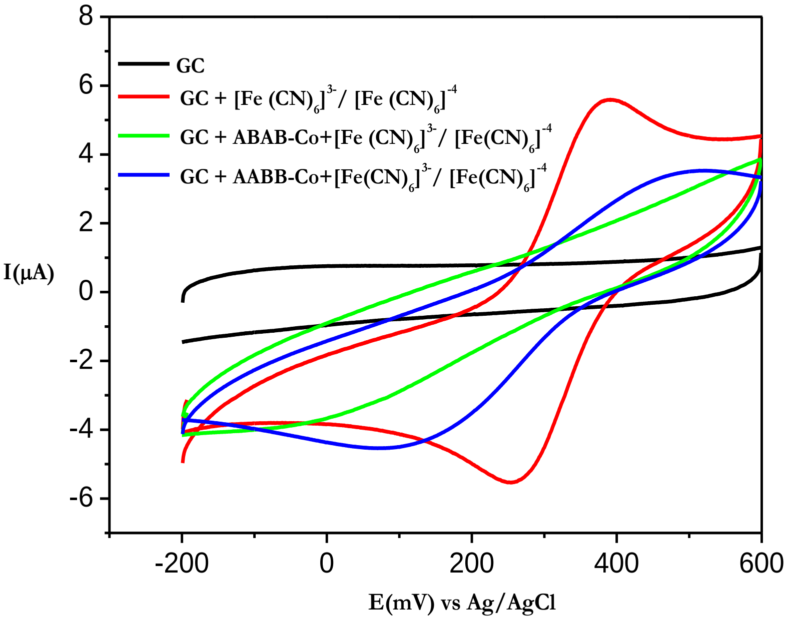

Figure 3. CVs of Co(II)-porphyrins -modified electrodes in 0.4 mM $K_3[Fe(CN)_6]$/PBS solution (scan rate: 0.1 V-s^{-1}).

Figure 4 shows the voltammograms corresponding to oxygen electro-reduction on a bare GC and on Co-porphyrin-modified electrodes.

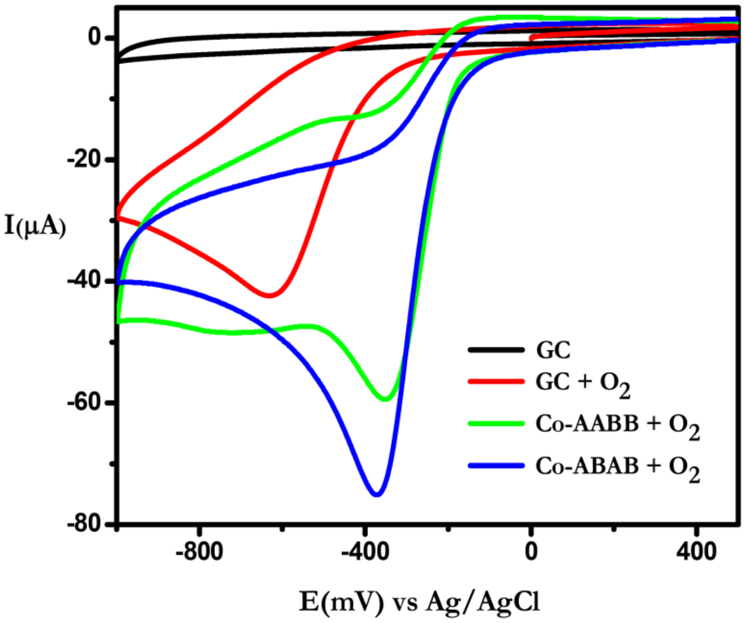

Figure 4. CVs of Co(II)-porphyrins -modified electrodes against oxygen reduction in PBS solution (scan rate: 0.1 V-s^{-1}).

As can be observed, both modified electrodes are very active toward the reduction of oxygen, shifting the potential ca. 200 mV to more positive values compared to the bare GC. However, the response is different for each porphyrin. The AABB-porphyrin shows a unique cathodic wave, whereas the Co-ABAB porphyrin shows a reduction wave at very similar potential but also a “plateau” zone from -0.5 to -1.0 V. The second cycle (not shown) depicts a very similar response for both modified electrodes, but a low decrease in current (less than 5%) is observed for the Co-ABAB porphyrin. The responses remained unchanged for at least one month, exposing the electrodes to air, demonstrating the high stability of both electrodes. These results clearly indicate the existence of an electrocatalytic process in PBS solution saturated with dioxygen at the different modified electrodes. It is interesting that both modified electrodes are stable and catalytic toward the reduction of oxygen at acid (pH 0 and 3) and basic (pH 12) media. However, in this work we elucidate products and electrons transferred at pH 7.4.

In order to determine if one of the reduction waves corresponds to the reduction of hydrogen peroxide, a drop of a solution containing peroxide was added to the oxygen-satured PBS solution (Figure 5). In each case, a current increase of the wave at ca. -0.2 to -0.5 V was observed indicating that this wave corresponds to the simultaneous reduction of oxygen to hydrogen peroxide and hydrogen peroxide to water. The electro-reduction of H_2O_2 in deoxygenated PBS solution is also catalyzed by both modified electrodes.

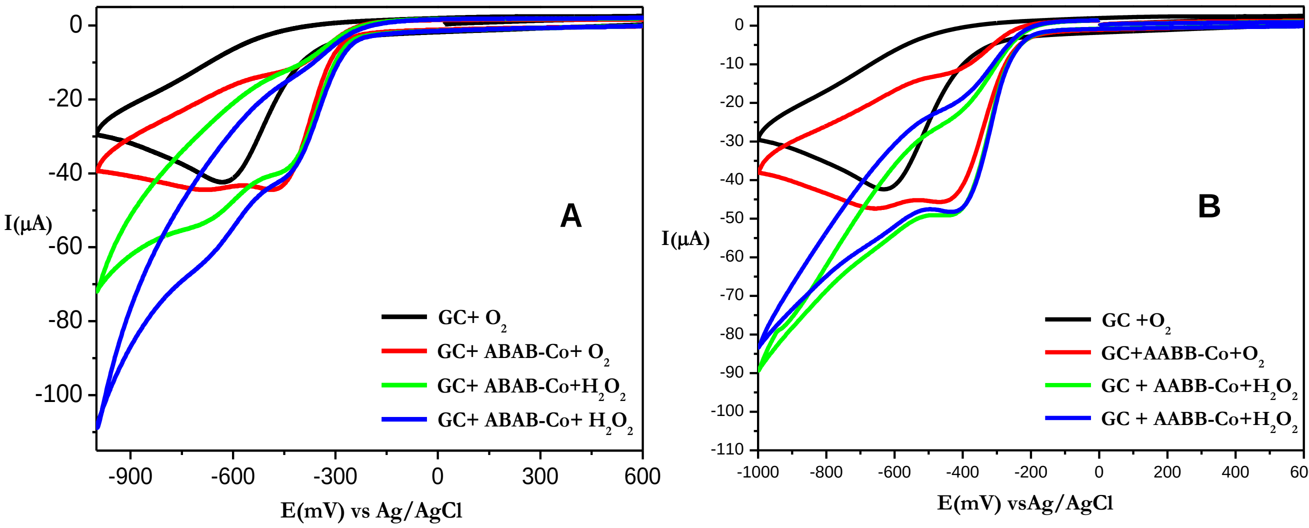

Figure 5. CVs of Co(II)-porphyrins -modified electrodes (cobalt-porphyrins adsorbed by dropping a solution (1.08 mM in DMF) on the GC electrodes) against oxygen reduction in PBS solution adding small quantities of H_2O_2. Green line is the first scan and blue line the second scan (scan rate: 0.1 V-s^{-1}).

In both cases a clear reduction wave (with a current value of about ten times higher than that detected by the bare GC) was obtained near the first potential reduction peak shown in Figure 4.

Two experiments were then carried out to elucidate the process of electro-reduction of oxygen. Rotating Disk Electrode (RDE) and Rotating Ring-Disk Electrode (RRDE) techniques were used. Figure 6(A) depicts I vs. E curves obtained at different rotation rates for a potential scan rate of 0.005 $V \cdot s^{-1}$ for the AABB-Co-porphyrin and Figure 6(B) shows the Koutecky-Levich plots (K-L) comparing the experimental values with the theoretically expected 2-electron or 4-electron curves from equation 1 (K-L plots for the ABAB-Co-porphyrin were similar and are therefore not shown).

$$\frac{1}{i}=\frac{1}{i_K}+\frac{1}{i_{l,c}}=\frac{1}{i_K}+\frac{1}{0.62nFAD_O^{1/2}\omega^{1/2}\nu^{-1/6}C_O^*} \qquad \text{(eq. 1)}$$

in which I is the disk current, i_K is the kinetic current, $i_{l,c}$ is the Levich current, $D_\mathbf{o}$ is the diffusion coefficient of O_2 (1.9E-5 cm^2s^{-1} [19, 28]), ν is the kinematic viscosity of the electrolyte solution (0.01 cm^2s^{-1} [29, 30]), A is the electrode area (0.0634 cm^2), ω is the rotation rate and C^*_O is the concentration of dissolved O_2 (1.2E-6 mol/cm^{-3} [29-30]). From the analysis of the K-L plots (I^{-1} versus $\omega^{-1/2}$), n can be obtained, the number of transferred electrons.

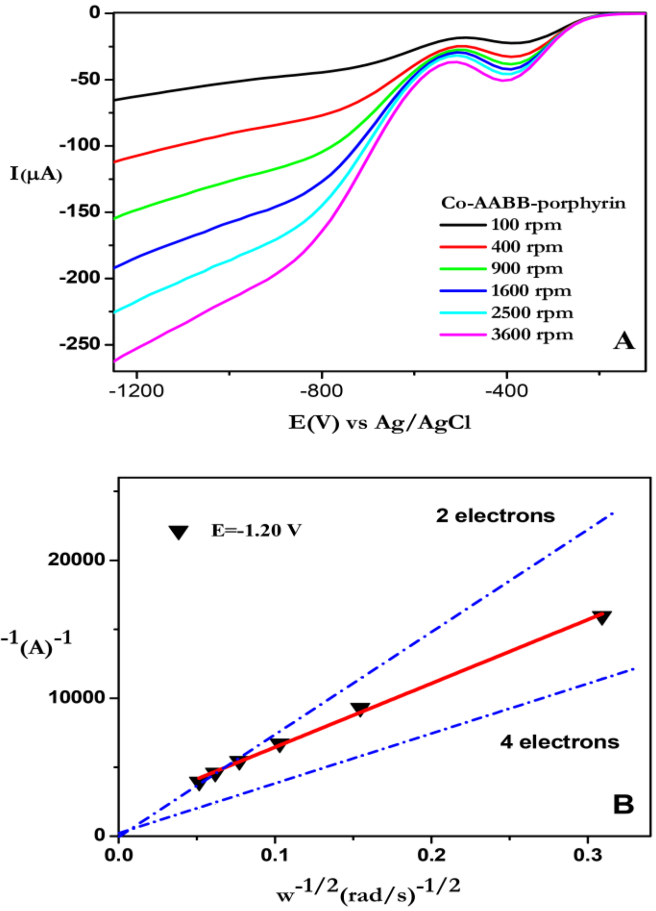

Figure 6. (A) Current-potential curves for the AABB-Co-porphyrin adsorbed on a rotating graphite disk electrode at rotation rates of 100, 400, 900, 1600, 2500 and 3600 rpm, recorded in an oxygen-saturated PBS solution (scan rate 0.005 $V \cdot s^{-1}$). (B) Koutecky–Levich plot using data from Fig. 6(A) at an electrode potential of -1.2 V. The theoretical lines are calculated according to Levich equation (eq.1) for 2- and 4-electron O_2 reduction processes.

It is clear from Fig. 6(B) that the slope of the K-L plot is similar to that of a 4-electron O_2 reduction, indicating that the AABB-Co-porphyrin can catalyze the 4-electron oxygen reduction reaction. The experimentally calculated number of transferred electrons was 3.8 for the ABAB-Co-porphyrin and 3.2 for the AABB-Co-porphyrin. It is necessary to point out here that these numbers were obtained at a fixed potential of -1.2 V, beyond the second peak in the case of the AABB-Co-porphyrin. However, at this potential, the transferred electrons are quite close to 4. If a 2+2 reaction takes place, at this potential only the second reaction was measured. Then, if the product is peroxide and peroxide becomes water after the first reaction (reduction of oxygen to give peroxide), the number of transferred electrons expected from eq. 1 is 2.

RRDE experiments for O_2 reduction (current-potential curves recorded) for the modified electrodes in PBS solution and acid solution showed that the current of the ring was zero (Figure 7). This is indicative of the fact that peroxide is not formed during the electroreduction and in both cases a 4-electron reduction of oxygen to water was obtained.

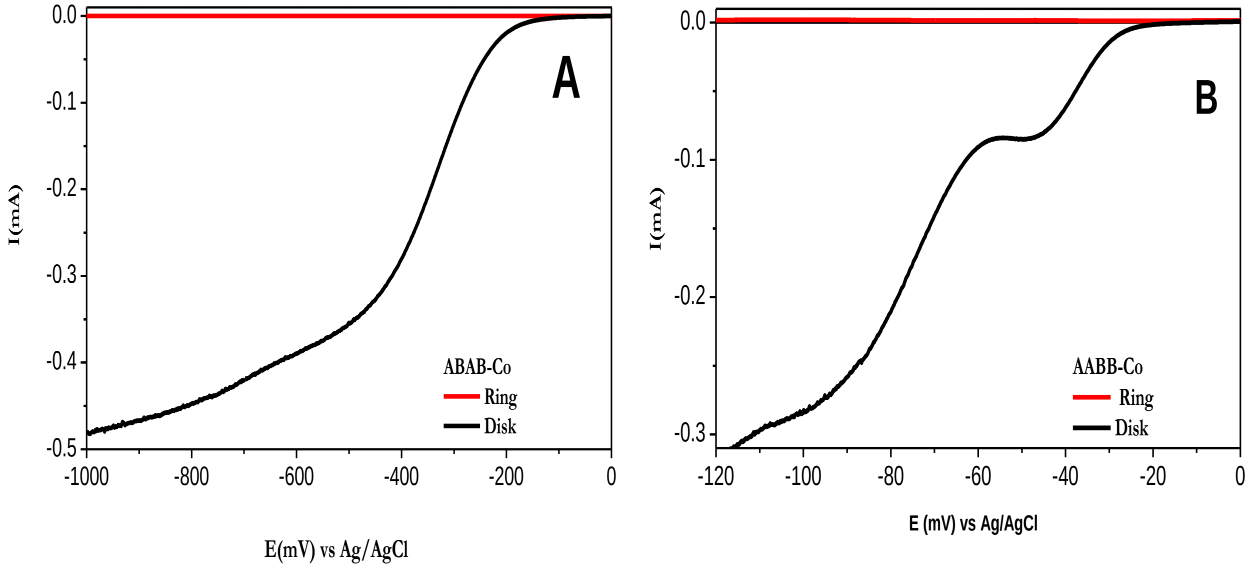

Figure 7. Current-potential curves for ABAB-Co-porphyrin (Fig. A) and AABB-Co-porphyrin (Fig. B) adsorbed on a rotating graphite disk electrode during the reduction of O_2. The platinum ring electrode was held at 1.2 V to oxidize any H_2O_2 that was generated at the disk electrode and swept to the concentric ring by the rotation of the electrode. The electrode was rotated at 900 rpm. Scan rate: 5 mVs^{-1}.

However, it is possible that in the first region of the potential for the reduction of oxygen, that is 0 to -0.5 V, two parallel reactions are occurring [16]. Indeed, at this potential, it is possible that a part of the active sites give water and another part gives peroxide, that immediately becomes water. This means there are two kinds of active sites in the porphyrins or two ways to form an adduct between the metal center and oxygen. Water as the direct product of the reduction was found to be due to the interaction between O_2 and the Co metal centers [9]. This interaction can effectively weaken the O-O bond. Face-to-face di-Co-N_4 complexes favor a 4-electron transfer pathway, depending on the Co-Co distance in the molecules [31, 32]. The number of transferred electrons for the AABB-Co-porphyrin indicates that a small amount of H_2O_2 is formed, which could be due to a mixed 2- or 4-electron transfer in the O_2 reduction pathway, but this is not the case for the ABAB-Co-porphyrin. Alternatively, it is possible that porphyrin aggregates formed on the electrode surface could have a range of compositions/structures that yield porphyrin-O_2 adducts with differing reduction potentials. Whatever their origin, the presence of differing forms of the adsorbed catalyst seems to be necessary to account for the two-step reduction of O_2 evident in Figure 4.

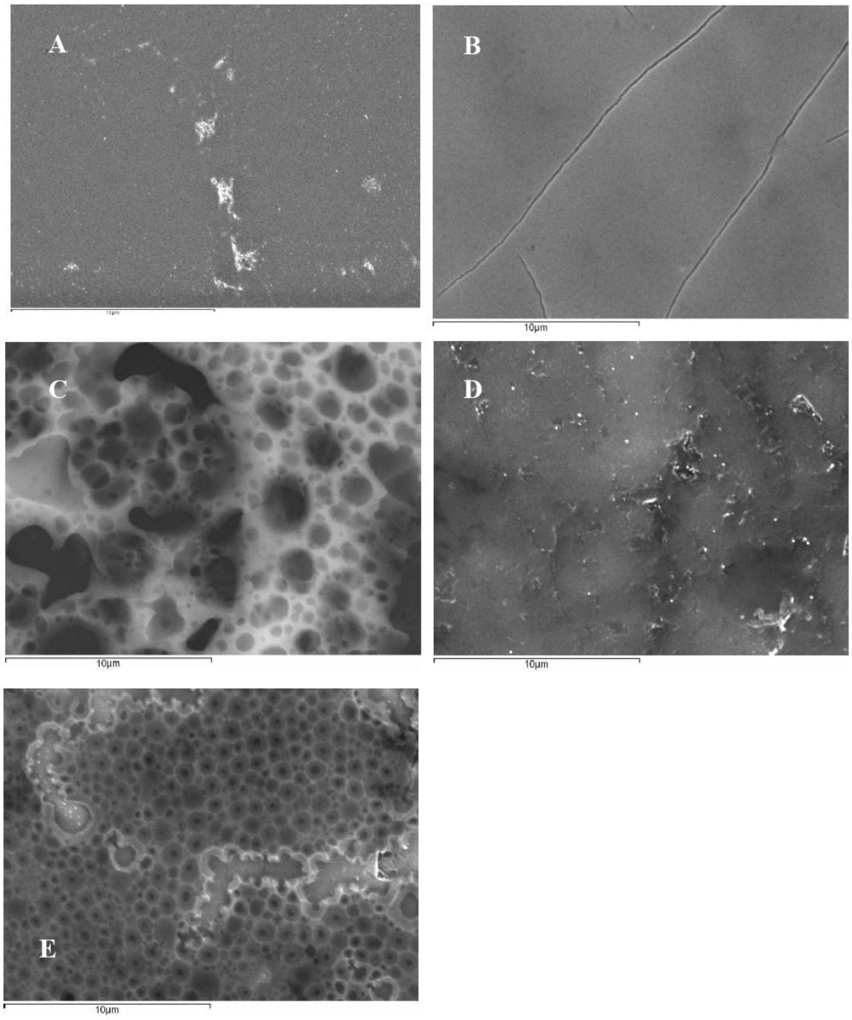

Figure 8. SEM images of : A) GC, B.) ABAB-Co-porphyrin adsorbed on GC, C) AABB-Co-porphyrin adsorbed on GC, D) ABAB-Co-porphyrin adsorbed on GC after electro-reduction of oxygen in PBS solution (scan rate: 0.1 Vs^{-1}), E) AABB-Co-porphyrin adsorbed on GC after electro-reduction of oxygen in PBS solution (scan rate: 0.1 Vs^{-1}); Scale bar: 20 µm.

In the RDE measurements we found that the transfer numbers (*n*) were close to 4. Furthermore, the 4-electron transfer pathway was further confirmed by the RRDE measurements. The substituents on the macrocycles affect the O_2 reduction catalytic activity of the Co-porphyrins, possessing electron donating substituents that can increase the binding energy between O_2 and the metal center, and can strongly and irreversibly adsorb on a GC electrode [16].

Finally, we studied the change in morphology of the deposited porphyrins before and after reduction. Figure 8 shows the SEM images of the modified glassy carbon electrodes before the reduction (Figure 8B and 8C), where the differences between the two porphyrins are large. In the case of the AABB-Co-porphyrin, a very globular coverage is obtained. In the case of the ABAB-Co-porphyrin, a homogeneous thin coverage appears.

After various oxygen reduction cycles, both modified electrodes show different morphologies. In fact, the AABB-Co-porphyrin shows little homogeneous pores and ABAB-Co-porphyrin shows a less homogeneous coverage. The reason for those differences is not well-understood at this point. It is worth to mention that the first reduction causes the modification of the surfaces and subsequent cycles do not change these surfaces any further. Indeed these changes in morphology do not change activity because the electrodes are very stable. Energy dispersive X-ray spectroscopy (EDX) measurements of the modified surfaces after of electro reduction of oxygen in PBS solution (not shown) showed peaks corresponding to the C and O atoms (at ca. 0.28 and 0.53 keV, respectively) and also three peaks characteristic of Co (at ca. 0.70, 6.89 and 7.68 keV) that confirmed the modification of the surfaces with metalloporphyrins [33] before and after the electrocatalytic reaction.

4. CONCLUSIONS

Our results show that non-cofacial porphyrins can give water in a unique 4e-step as the main product. In this case, the modified electrodes showed electrocatalytic activity for O_2 electroreduction, but the relative position of the substituents (with neighboring substituents causing steric hindrance) on the macrocyclic rings did not affect the O_2 reduction reaction catalytic activity, but affect the morphology of the modified surfaces. The modified electrodes of both Co-porphyrins maintained their electrocatalytic properties after repeated voltammetric cycles, showing high stability. The complexes can strongly and irreversibly been adsorbed on a graphite electrode surface to form a monolayer or multilayers of O_2 reduction catalysts.

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