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Influence of the supramolecular arrangement of iron phthalocyanine thin films on catecholamine oxidation

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Abstract

The versatility of iron phthalocyanine (FePc) to form distinct supramolecular arrangements in thin films, characterized by their thickness, molecular organization, morphology, and crystallinity, can be used to tune the electrochemical oxidation of catecholamines, becoming a promising material for sensing applications. Here, Langmuir-Schaefer (LS) and electrodeposition (ED) techniques have been used to produce thin films of FePc with different supramolecular arrangements on ITO electrodes. Both types of modified electrode were evaluated for the electrochemical oxidation of L-Dopa, dopamine (DA), norepinephrine (NEp), and epinephrine (Ep) in aqueous solution. The effect of scan rate, potential range, presence of oxygen, and pH were also evaluated, having an influence on the electrochemical oxidation of catecholamines. The FePc/ED modified electrodes showed two distinct peaks in the presence of mixtures of DA/L-Dopa and DA/Ep, while for FePc/LS modified electrodes an overlap of the oxidation waves was observed. This behaviour reveals the influence of the supramolecular arrangement of FePc on catecholamine oxidation. The FePc/LS modified electrodes showed a limit of detection of 0.024 µmol L^{-1} for DA and 0.168 µmol L^{-1} for L-Dopa, while FePc/ED showed limits of detection of 0.288 µmol L^{-1} and 0.564 µmol L^{-1}, respectively. The FePc films showed suitable properties for future application as catecholamine sensors.

Keyword: catecholamines**,** iron phthalocyanine, Langmuir-Schaefer, electrodeposition.

1. Introduction

Catecholamines are substances possessing amine and catechol groups and include L-3,4-dihydroxyphenylalanine (L-Dopa), dopamine (DA), norepinephrine (NEp), and epinephrine (Ep). These substances are a class of neurotransmitters, which play an important role in the human body, principally in the central nervous system [1,2]. The depletion of DA in the brain can be associated with Parkinson's disease [3], the treatment being the administration of drugs based on L-Dopa [4,5], an immediate precursor of DA. The L-Dopa crosses the blood-brain barrier and, by decarboxylation, is converted into DA. Consequently, to improve the efficiency, drug formulations usually contain L-Dopa together with a decarboxylase inhibitor (such as benserazide or carbidopa) [5]. Therefore, the determination of catecholamines such as L-Dopa and DA in drugs and also in biological fluids is very important. Methods such as HPLC [6,7], electrophoresis [8], and electrochemical [9,10] have been applied to determine this catecholamine in both drugs and biological fluids. Electrochemical techniques are widely applied due to their fast response, high sensitivity, selectivity, and only needing small samples. However, as sensor devices, electrodes usually require surface modification, in order to improve the sensitivity and selectivity.

Among the organic compounds used for modification of electrode substrate surfaces, metal phthalocyanine complexes (MPc) have been used as electron mediators in electrochemical sensors [11–14], as well as electroactive materials in chemical sensors [15–18]. A large number of studies report the influence of the deposition technique on morphology [12,19], structural organization [12,15,20], conductivity [21,22], and optical properties [20] of such thin films. Based on this, the aim of this work is to tune the electrochemical properties of electrodes modified with iron phthalocyanine (FePc) films for application to the electrochemical oxidation of catecholamines. Indium tin oxide (ITO) electrodes were modified using Langmuir-Schaefer (LS) deposition and electrodeposition techniques. The electrodes modified with FePc/LS and FePc/ED films were evaluated in inert electrolyte and in DA-containing solution. Electrochemical parameters such as potential range, oxygen, and pH were investigated in the presence of catecholamines in solution.

2. Experimental

2.1 Reagents and solutions

Thin films were formed from FePc (Kodak, MM = 568.38 g mol^{-1}). The electrochemical characterization of the FePc films and of catecholamine oxidation was performed in aqueous solutions of the catecholamines: L-tyrosine (Ty, Sigma Aldrich), 3,4-dihydroxy-L-phenylalanine (L-Dopa, Sigma), dopamine hydrochloride (DA, Fluka), (-)-Norepinephrine (NEp, Sigma) and (-)-Epinephrine (Ep, Sigma), with 0.1 mol L^{-1} potassium chloride (KCl, Sigma Aldrich) as supporting electrolyte. The pH values of unbuffered KCl solution were adjusted by adding small amounts of 1 mol L^{-1} HCl or NaOH, as needed. All aqueous solutions were prepared with Millipore Milli-Q nanopure water (resistivity ≥ 18 MΩ cm). Scheme 1 shows the molecular structure of the catecholamines and of the FePc complex.

<Scheme 1>

2.2 FePc film deposition

The FePc thin films were deposited on indium tin oxide electrodes (ITO, Aldrich, resistivity 8-12 Ω/sq) with a 1 cm^2 geometric area using either electrodeposition (ED) at constant potential or the Langmuir-Schaefer (LS) technique (Fig. 1). The ED films were formed using a 1.0 mmol L^{-1} FePc solution prepared in 1,2-

dichloromethane (DCM, Sigma-Aldrich) containing 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP, Fluka) as supporting electrolyte. The FePc thin films were electrodeposited at a constant potential of -1.5 V *vs*. Ag/AgCl, during 3600 s controlled by an *µ*-Autolab type III (Metrohm-Autolab), with a platinum wire as a counter electrode and Ag/AgCl/3M KCl electrode as reference. More details about the electrodeposition parameters are given in [23].

The LS films were grown using a KSV Langmuir trough model 2000 (Biolin Scientific). The Langmuir film was formed on an ultrapure water subphase by spreading 500 µL of a 0.5 mg mL^{-1} FePc solution dissolved in DCM, with symmetric compression at 10 mm min^{-1} and keeping the surface pressure at 24 mN m^{-1}. The LS film deposition was carried out using the horizontal contact of the substrate surface to the air/water interface (manually). LS films were deposited with 20 layers.

<Figure 1>

2.3 Electrochemical measurements

Characterisation of the electrochemical behaviour of ITO electrodes modified with FePc thin films was carried out in an aqueous solution of 0.1 mol L^{-1} KCl (pH ~5.6) as supporting electrolyte, to which 1.2×10^{-4} mol L^{-1} of catecholamine was added to study catecholamine oxidation. The catecholamines were Ty, L-Dopa, NEp, and Ep. The study of the influence of dissolved oxygen was carried out in normal conditions with dissolved oxygen present in solution and also under a nitrogen atmosphere, in order to remove dissolved oxygen. All other electrochemical measurements were performed in the presence of dissolved oxygen.

3. Results and Discussion

3.1 Characteristics of FePc thin films in KCl and catecholamine solution

FePc films were prepared using two different deposition methods (LS and ED) and their activities toward catecholamine electrooxidation were investigated. Recently, it was demonstrated that film formation does not depend on either the electrochemical deposition method (potentiostatic or potentiodynamic mode) or on the identity of the electrode substrate (glassy carbon or ITO electrode), and that FePc electrodeposited films show promising application for DA electrooxidation [23].

On the other hand, the supramolecular arrangement, i.e., thickness, molecular organization, morphology, and crystallinity, of FePc films deposited by different techniques showed an impact on both electrochemical and catalytic properties [12,24]. The supramolecular arrangement of FePc films formed by LS deposition and by electrodeposition was fully characterized using Uv-vis, micro-Raman, FTIR, SEM, AFM, and cyclic voltammetry in supporting electrolyte [24]. This revealed that the two deposition techniques led to FePc thin films with distinct supramolecular arrangements, and distinct electrochemical properties. The FePc/ED films showed a flat-on macrocycle organization with compact structure, homogeneous surface, and smaller energy gap, while the FePc/LS showed a slight tilt in macrocycle organization with the presence of aggregates, which leads to a higher energy gap and a less homogeneous surface [24].

Here, the results suggest that the electrode modified with FePc by electrodeposition and LS present different behaviour in supporting electrolyte and in catecholamine-containing solution. Thus, we observed the deposition method influences not only the kinetics of the FePc redox process in 0.1 mol L^{-1} KCl solution but also the catacholamine oxidation. Fig. 2 shows cyclic voltammograms of FePc/ED and FePc/LS modified electrodes at 5 and 25 mV s^{-1} scan rate in 0.1 mol L^{-1} KCl + 1.2 x 10^{-4} mol L^{-1} DA solution.

<Figure 2>

At the lower scan rate (5 mV s^{-1}) both films showed a well-defined cathodic peak ascribed to oxygen reduction [24]. Indeed, the FePc complexes show interaction with molecular oxygen through the metal centre and π* orbital of O_2 [25]. However, for the FePc/LS films, a peak at -0.79 V was also observed, attributed to phthalocyanine ring reduction ($[Fe^{I}Pc^{3-}]^{-2}/[Fe^{I}Pc^{2-}]^{-1}$) [24]. On the other hand, at 25 mV s^{-1} (both films), the FePc redox process becomes more evident. The FePc/ED film showed a redox couple ascribed to $[Fe^{I}Pc^{3-}]^{-2}/[Fe^{I}Pc^{2-}]^{-1}$ (phthalocyanine ring process) and $[Fe^{I}Pc^{2-}]^{-1}/[Fe^{II}Pc^{2-}]$ (metal centre process), while for the FePc/LS film an overlap of both redox couples was observed [24]. The peak potential values and their respective attributions are summarized in Table 1. The redox process for FePc/LS films becomes more irreversible with increase of scan rate, but for FePc/ED is almost unaffected (Fig. S1 in supplementary material). The peak current was linearly proportional to the scan rate (Fig. S1) at the FePc/ED modified electrode, corresponding to a surface confined process. However, FePc/LS modified electrodes showed peak currents linear with the square root of the scan rate, indicating diffusion control. The FePc redox process for both films shows the influence of scan rate, at 5 mV s^{-1} scan rate the peak attributed to oxygen reduction being predominant, and at higher scan rate, 25 mV s^{-1}, the phthalocyanine process becoming more significant.

Table 1: Attribution of peak potentials at ITO electrodes modified with FePc/ED and FePc/LS films in 0.1 mol/L KCl solution at 5 and 25 mV s^{-1} scan rate

Modified electrode	**Scan rate (mV s^{-1})**	**$[Fe^IPc^{3-}]^{-2}/[Fe^IPc^{2-}]^{-1}$**		**$[Fe^IPc^{2-}]^{-1}/[Fe^{II}Pc^{2-}]$**		**O_2 reduction**
		E_{pa} / V	E_{pc} / V	E_{pa} / V	E_{pc} / V	E_{pc} / V
FePc/ED	5	-	-	-	-	-0.59
	25	-0.65	-0.76	-0.38	-	-0.61
FePc/LS	5	-	-0.79	-	-	-0.53
	25	-0.53*	-0.80*	*	*	-0.54

*potential corresponding to overlap of both FePc redox processes

In DA solution, the cyclic voltammograms recorded at 5 mV s^{-1} reveal that both types of film show a similar DA oxidation potential. At this scan rate, the peak currents of the phthalocyanine ring reduction and DA oxidation are lower than observed at 25 mV s^{-1}. The phthalocyanine ring reduction is irreversible and the DA process (dopamine/dopamine quinone) is reversible. However, at 25 mV s^{-1} both modified electrodes showed better performance, with the DA oxidation peak current at ~0.19 V vs. Ag/AgCl (Table 2) being three times higher for FePc/ED than for FePc/LS films (Fig. 2D) or at bare ITO electrodes. A similar enhancement of peak current at FePc/ED relative to FePc/LS was also seen for L-Dopa, Nep, and Ep, as summarized in Table 2 and shown in Fig. S2 in supplementary material. Neither of the FePc modified electrodes showed any oxidation peak for Ty in solution.

Table 2: Peak potential and peak current for catecholamine oxidation using ITO electrodes modified with FePc/ED and FePc/LS films. v = 25 mV s^{-1}

Catecholamine	FePc/ED		FePc/LS	
	E_{pa} / V	j_{pa} /μA cm^{-2}	E_{pa} /V	j_{pa} /μA cm^{-2}
Ty	-	-	-	-
L-Dopa	0.245	30.2	0.201	7.41
DA	0.193	32.1	0.190	9.97
NEp	0.216	22.0	0.204	9.91
Ep	0.216	24.0	0.215	12.5

The differences in the oxidation potential of DA at FePc/ED and FePc/LS may be explained through their surface morphology (Fig. 1). In previous studies, we reported that the FePc/ED film is compact, with lower surface roughness (11.6 nm), while the FePc/LS film has aggregates, leading to higher roughness (22.4 nm) and, consequently, to higher surface area [24]. Thus, the difference in the electrooxidation potentials of catecholamines can indicate a difference in the interactions of catecholamine molecules with the film/electrode interface. The morphology of FePc/ED can be regarded as the most suitable for DA oxidation, a higher electrocatalytic current being promoted by compact films and with low roughness. Nevertheless, the high roughness arising from of a large number of aggregates can influence the adsorption of analyte molecules on the film surface. This was demonstrated by multicycle cyclic voltammetry in supporting electrolyte in 1.2 x 10^{-4} mol L^{-1} DA solution at 25 mV s^{-1}. After potential cycling in catecholamine solution, both modified electrodes were washed with ultrapure water and were cycled in supporting electrolyte (0.1 mol/L KCl) in the absence of analytes. After two potential cycles the anodic peak attributed to catecholamine oxidation despair completely to FePc/ED modified electrode, while FePc/LS modified electrodes the redox couple from catecholamine oxidation at 0.19 V vs Ag/AgCl decreases only for a higher number of potential cycles.

3.2 Influence of experimental conditions on DA oxidation

3.2.1 Potential range

The potential corresponding to DA oxidation is influenced by the oxidation-reduction of FePc films on the modified electrode surface. Fig. 3 shows three successive potential cycles of an electrode modified with FePc film immersed in DA solution. The first cycle, starting at 0.0 V, shows a reversible redox process of DA at a more positive potential ($\Delta E = E_{pa} - E_{pc}$ = 0.303 V for FePc/ED and 0.234 V for FePc/LS modified electrodes) than in subsequent cycles (Table 2) and the redox process becomes irreversible (decrease of the DA cathodic current). This is confirmed when cycling the FePc film in DA solution between 0.0 and 0.7 V (inset in Fig. 3). In this potential range, DA oxidation is observed at more positive potentials. A similar behaviour was also observed using differential pulse voltammetry (DPV). The DA oxidation peak occurs at a more positive potential when the DPV scan starts at 0.0 V, than when starting at a negative potential (-1.0 V) when two DA oxidation processes are observed. The influence of potential range indicates that an “activation” of both modified electrodes is necessary for DA oxidation to occur at lower potential values. The same behaviour was observed for the other catecholamines studied (supplementary material– Fig. S3).

<Figure 3>

3.2.2 Influence of dissolved oxygen

Fig. 4 shows cyclic voltammograms of modified electrodes immersed in DA solution in the presence and absence of dissolved oxygen. The peak current and potential of DA oxidation were influenced by the presence of oxygen, indicating its interaction with DA. Moreover, in the presence of dissolved oxygen, the peak current of DA oxidation was lower at the FePc/LS modified electrode than at the FePc/ED modified electrode.

< **Figure 4>**

DA in solution can undergo a two-step oxidation process, which produces an semi-dopamine-quinone (semi-DAQ) intermediate species that acts as a free radical [26]. Ming La et. al. [27], through in vitro studies, report that the intermediate species can be formed from reduction of Fe(III) to Fe(II), and formation of complexes with free Fe(II) ions. In the presence of oxygen, the complex Fe(II)/semi-DAQ can also form a ternary complex, that, in general, accelerates DA oxidation in solution. They also showed that oxidation of semi-DAQ by dissolved O_2 can lead to the formation of DAQ, H_2O_2, and O_2•-. Based on this, the lower DA oxidation current at FePc/LS modified electrodes can be ascribed to the formation of intermediate species such as semi-DAQ and consequent complexation with FePc aggregates at the modified electrode surface. The semi-DAQ can then undergo chemical oxidation to dopamine-ortho-quinone (DAQ), catalyzed by dissolved O_2. Thus, the net amount of electrochemical oxidation is less.

The direct electrooxidation of DA to DAQ at 0.198 V vs. Ag/AgCl without formation of intermediate species can be favoured at the FePc/ED modified electrode. This effect can be related to a greater homogeneity (lower number of aggregates and lower roughness), which decreases the amount of possible complexation and stabilization of intermediate species. Besides this, a higher DA oxidation current was observed at FePc/ED than at FePc/LS modified electrodes, which suggests that the organization of FePc molecules parallel to the electrode surface [24] observed on the FePc/ED films favours electron transfer from the analyte to the electrode surface. Thus, the greater homogeneity of FePc/ED modified electrode surfaces and of the FePc molecular organization both favour the electrooxidation of DA in solution.

In the absence of dissolved oxygen (under a continuous flow of nitrogen gas), both modified electrodes showed a DA oxidation peak at more positive potential values. This indicates that dissolved oxygen can assist the chemical oxidation and the electrooxidation of DA. Based on the better electrochemical performance in the presence of dissolved oxygen, all previous (and following) electrochemical measurements were carried out without nitrogen gas flow.

3.2.3 Influence of pH

In most cases, electrocatalytic dopamine oxidation is a pH-dependent reaction, involving two electrons and two protons [28,29]. It was found that the peak potential shifts negatively with increase of solution pH, but not in a linear fashion, as shown in Fig. 5. Thus, other equilibria need to be taken into account. The variation of DA oxidation current also showed a nonlinear dependence on pH (Fig. 5C).

<Figure 5>

The modified electrode performance can also be explored taking into account the DA species distribution as a function of pH, the pK_a values being 8.9 (pK_{a1}), 10.4 (pK_{a2}) and 13.1 (pK_{a3}) [30]. FePc/LS and FePc/ED modified electrodes showed a similar behaviour between pH 3.0 and 7.0. However, for pH up to 7.0, the DA unprotonated showed a better interaction with the FePc/LS modified electrode leading to a decrease of oxidation potential as well as an increase of peak current.

3.3 Separation of electrochemical response of DA in the presence of L-Dopa, NEp, and Ep at FePc modified electrodes.

DA, L-Dopa, NEp, and Ep have similar molecular structures (Scheme 1), the principal similarity being the catechol group. Because of this, they have similar oxidation potentials at conventional electrodes, and an overlap of the signal is expected. Therefore, FePc modified electrodes were evaluated for the simultaneous voltammetric measurements of DA in mixtures with L-Dopa, NEp or Ep. Fig. 6 presents cyclic voltammograms of 1.2 x 10^{-4} mol L^{-1} DA in mixtures with 1.2 x 10^{-4} mol L^{-1} of L-DOPA. As can be seen, the FePc/LS modified electrode showed an overlap of oxidation peak in mixtures, which makes it impossible to identify and quantify each of the catecholamines. The same behaviour was observed for a mixture of DA/NEp and DA/Ep (supplementary material– Fig. S4).

<Figure 6>

FePc/ED modified electrodes showed two peaks in the presence of mixtures of DA/L-Dopa (Fig. 6B) and DA/Ep (supplementary material– Fig. S4), suggesting that each peak corresponds to one catecholamine in solution. However, an overlap of the oxidation peak of DA/NEp at FePc/ED modified electrodes was observed, which can be ascribed to the similarity of the molecular structure of DA and NEp.

The overlap or separation of oxidation peaks is due to the possible interaction of catecholamine structure and the FePc film surface. In the cyclic voltammograms, DA oxidation at FePc modified electrodes occurred at a lower potential than that of L-Dopa, NEp, and Ep (Table 2). This can be ascribed to the direct interaction of the amine group with the iron metal centre of the FePc molecules, which favours the catechol group oxidation [31]. The L-Dopa, NEp, and Ep molecules have oxygen-containing groups (hydroxyl or carboxylic groups) and not only the amine group in the alkyl chain. Additionally, the Ep molecule is a catecholamine with a secondary amine. The presence of amine groups can lead to a decrease of direct interaction between the catecholamine and the FePc metal centre, and consequently an increase of oxidation potential.

In catecholamine mixtures, the possibility of different interactions with FePc film surfaces may lead to separation of the oxidation peaks at FePc/ED modified electrodes. The overlap of catecholamine oxidation at FePc/LS modified electrodes can be ascribed to high levels of aggregates on the film surface. The aggregates increase the rate of adsorption and prevent a selective electrochemical response.

3.4 Effect of DA and L-Dopa concentration

The effect of DA and L-Dopa concentration at FePc modified electrodes was carried out using DPV in 0.1 mol L^{-1} KCl solution (pH 5.4). The calibration curve for DA and L-DOPA showed differences in the linear range when using FePc/LS, and FePc/ED modified electrodes, as shown in Fig. 7 and Table 3.

Table 3: Analytical parameters for DA and L-Dopa calibration curves using FePc/ED and FePc/LS modified electrodes

Film	Analyte	Linear response / µM	Limit of detection / µM	Sensitivity / A/M^{-1}*
FePc/LS	DA	2-80	0.024	0.141
	L-Dopa	2-40		0.037
		40-120	0.168	0.020
FePc/ED	DA	2-20	0.288	0.654
		20-80		0.332
	L-Dopa	2-20	0.564	0.334
		20-120		0.087

*ampere/mol L^{-1}, limit of detection was calculated according to 3*x*SD/slope criterion. The increase of current of DA and L-Dopa using DPV was observed at -0.9 V and 0.13 V at FePc/LS and FePc/ED modified electrodes, respectively.

<Figure 7>

The calibration curves at FePc/LS modified electrodes for L-DOPA addition and FePc/ED modified electrodes for DA, and L-DOPA addition showed two linear ranges (Table 3). This behaviour may be due to the influence of analyte adsorption onto the film surface causing a change in the mechanism. For low DA concentrations (first linear range of concentration), both modified electrodes showed a slope higher than that observed at high DA concentrations (second linear range of concentration). This supports the hypothesis of a changing mechanism, first controlled by adsorption (active sites on the film surface > concentration of analyte molecules at the solution/interface) and at higher concentrations by diffusion (active sites on the film surface < concentration of analyte molecules at the solution/interface) [32]. Based on these results, the single linear range of DA concentration observed at FePc/LS modified electrodes can be ascribed to a surface-controlled mechanism being followed for all DA concentrations via adsorption of DA on FePc aggregates through amine group/metal centre interactions.

The deposition technique also had an influence on the sensitivity and limit of detection of catecholamines at FePc modified electrodes. The FePc/ED modified electrodes showed higher sensitivity than FePc/LS modified electrodes, but a lower limit of detection. Tables 4 and 5 show the analytical parameters for similar types of modified electrode used to determine DA and L-DOPA, respectively, by electrochemical techniques.

Table 4: Analytical parameters for different films described in the literature for DA detection

Film	**Linear range / µM**	**Limit of detection /µM**	**Ref.**
ICDACH-GCE [a]	11.8-90	0.186	[32]
Pyrolytic carbon film	18-270	2.300	[33]
PANI/FeTsPc[b]	250-8000	10.00	[34]
PAH/FePc/AgNp[c]	2-97	0.860	[35]
Poly(CTAB)/GCE[d]	0.5-100	0.110	[36]

[a] *N,N'*-bis(indol-3-carboxaldimine)-1,2-diaminecyclehexane thin films electrodeposited onto glassy carbon electrode (GCE).

[b] Films containing 20 bilayers Layer-by-Layer (LbL) from polyaniline (PANI) and tetrasulfonated iron phthalocyanine (FeTsPc), deposited onto ITO electrode.

[c] Films containing 5 trilayers Layer-by-Layer (LbL) from polyallylamine hydrochloride (PAH), FePc and silver nanoparticles (AgNp), deposited onto ITO electrode.

[d] cetyl-trimethyl-ammonium bromide (CTAB) films electrodeposited onto GCE.

Table 5: Analytical parameters for different films described in the literature for L-Dopa detection

Film	**Linear range / µM**	**Limit of detection/µM**	**Ref.**
SWNT-GCE[a]	0.5-20	0.30	[37]
Nafion/Ca(OH)$_2$-MWCNTs/CILE[b]	0.25-10	0.120	[38]
	15-225		
Ppy-CNT-GCE[c]	1-100	0.10	[39]
[VO(salen)] [d]	1-100	0.80	[40]
Poly(XO)MCPE[e]	2-120	52.4	[41]

*a*Single-wall carbon nanotubes (SWNT) deposited onto GCE.
*b*Multi-walled carbon nanotubes (MWCNTs) modified with calcium hydroxide (Ca(OH)$_2$) deposited onto liquid ionic carbon electrode previous modified with Nafion membrane.
*c*Polypyrrole (Ppy) films and carbon nanotubes (CNT) deposited onto GCE.
d oxide vanadium *N,N'*-ethylene-bis(salycilydenoiminate) ([VO(salen)]) films deposited onto polyurethane graphite electrode.
eCarbon paste electrode (MCPE) modified with orange poly-xylenol (poly(OX)).

Reproducibility, repeatability, stability in DA solution

Reproducibility was investigated using three modified electrodes independently with FePc/LS and FePc/ED films. A standard deviation of 11.3% and 4.8% for FePc/LS and FePc/ED, respectively, was observed for 1.2 x 10^{-4} mol L^{-1} DA in solution, an acceptable reproducibility. The high standard deviation for LS films can be attributed to the film fabrication procedure by manual deposition of LS layers. The repeatability was also evaluated by conducting 15 consecutive assays in 1.2 x 10^{-4} mol L^{-1} of DA solution, the standard deviation being 4.8% and 4.9% for FePc/LS and FePc/ED, respectively. Both modified electrodes showed excellent stability and were used after several months of storage at room temperature in air, without changes in the electrochemical behaviour in supporting electrolyte and DA solution.

4. Conclusions

The electrochemical behaviour of the FePc film modified electrodes in inert electrolyte and in catecholamine solutions depends directly on the supramolecular arrangement of the FePc films on the electrode surface and on the catecholamine structure. The FePc/LS modified electrode showed overlapping oxidation peaks in catecholamine mixtures. This overlap can be ascribed to high levels of aggregates on the film surface, which increase the amount of adsorption and prevent a selective electrochemical response. However, the FePc/ED modified electrodes show two distinct peaks in mixtures of DA/L-Dopa and DA/Ep, that can be associated with different interactions with FePc film surfaces. Additionally, the higher oxidation current observed at FePc/ED modified electrodes suggests the organization of FePc molecules parallel to the electrode surface favours electron transfer from the analyte to the electrode surface.

Scan rate, potential range, dissolved oxygen and pH showed influence on the catecholamine oxidation potential for both FePc modified electrodes. At higher scan rate, both types of modified electrode showed better performance to catecholamine oxidation than at slower scan rates, but the Fe(III)/Fe(II) redox process for FePc/LS films becomes more irreversible, but with FePc/ED it is almost unaffected. The influence of potential range applied indicates that an “activation” of modified electrodes is necessary for oxidation at lower potential for all catecholamines studied. Dissolved oxygen assists the chemical oxidation and electrooxidation of catecholamines. Both FePc films showed a similar influence of pH between 3.0 and 7.0, the best electrooxidation conditions being between 5.0 and 7.0.

Using optimized electrochemical parameters, two linear concentration ranges for DA and L-Dopa are observed, which can be ascribed to different mechanisms, the first being controlled by adsorption and the second by diffusion. FePc/LS modified electrodes showed a lower limit of detection for DA and L-Dopa than FePc/ED modified electrodes, with acceptable reproducibilities.

The deposition technique is shown to be a possible tool for tuning the electrochemical properties of FePc modified electrodes for subsequent application as catecholamine sensors.

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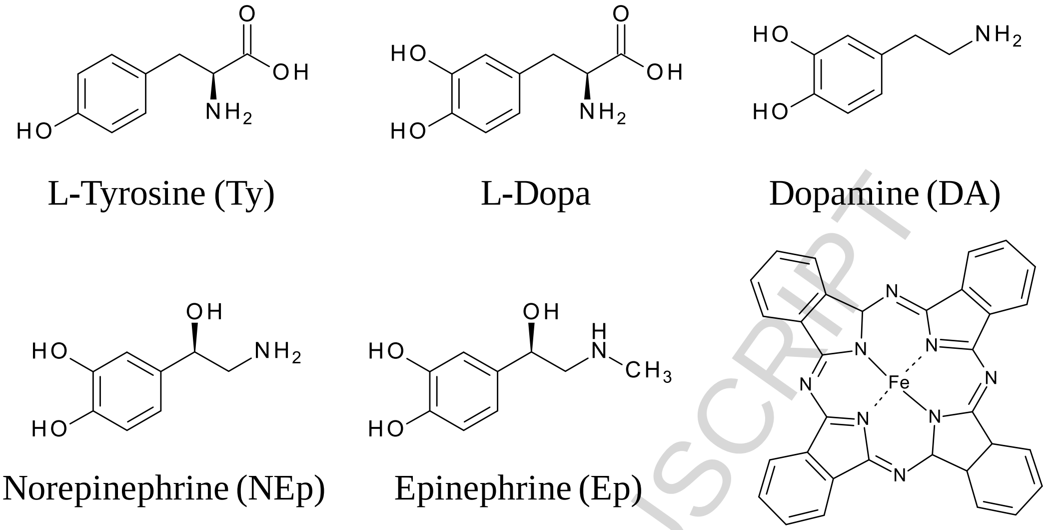
Scheme Captions

Scheme 1: representation of the molecular structure of Ty, L-Dopa, DA, NEp, Ep, and FePc.

Scheme 1 – Martin et. al



L-Tyrosine (Ty)

L-Dopa

Dopamine (DA)

Norepinephrine (NEp)

Epinephrine (Ep)

Iron phthalocyanine (FePc)

Figure Captions

Fig. 1. Representation of FePc deposition onto an ITO electrode surface. SEM micrographs for bare ITO electrode (A), ITO electrode covered with FePc/ED (B) and FePc/LS films (C).

Fig. 2. Cyclic voltammograms for ITO modified electrodes with FePc/ED and FePc/LS films in 0.1 mol L^{-1} KCl at (A) 5 and (B) 25 mV s^{-1}. Cyclic voltammograms for ITO modified electrode with FePc/ED and FePc/LS films in 1.2 x 10^{-4} mol L^{-1} DA + 0.1 mol L^{-1} KCl solution at (C) 5 and (D) 25 mV s^{-1}.

Fig. 3. Three potential cycles at ITO electrodes modified with (A) FePc/ED and (B) FePc/LS films immersed in 1.2 x 10^{-4} mol L^{-1} DA + 0.1 mol L^{-1} KCl solution in the range -1.0 to +1.0 V vs Ag/AgCl. *Insert*: cyclic voltammogram (3rd cycle) of modified electrode in the range -1.0 to +0.7 V vs Ag/AgCl.

Fig. 4. Cyclic voltammograms at ITO electrodes modified with (A) FePc/ED and (B) FePc/LS films immersed in 1.2 x 10^{-4} mol L^{-1} DA + 0.1 mol L^{-1} KCl solution, in the presence and absence of O_2 (N_2 atmosphere). v = 25 mV s^{-1}.

Fig. 5. Cyclic voltammograms at ITO electrodes modified with (A) FePc/ED and (B) FePc/LS films immersed in 1.2 x 10^{-4} mol L^{-1} DA + 0.1 mol L^{-1} KCl solution at different pH values (2 to 8.5). Magnifications of the potential range -0.1 to 1.0 V are also shown as (A’) and (B’). v = 25 mV s^{-1}. Plots of (C) anodic peak potential and (D) peak current density as a function of pH at both FePc modified electrodes (FePc/ED and FePc/LS).

Fig. 6. Cyclic voltammograms at ITO electrodes modified with FePc/ED (A) and FePc/LS films (B) immersed in 1.2 x 10^{-4} mol L^{-1} DA + 0.1 mol L^{-1} KCl solution (black curve) and in a mixture of 1.2 x 10^{-4} mol L^{-1} of DA and L-Dopa + 0.1 mol L^{-1} KCl solution (red curve). v = 25 mV s^{-1}.

Fig. 7. Calibration curves for (A) DA and (B) L-Dopa using FePc/ED and FePc/LS modified electrodes.

Figure 1 – Martin et. al

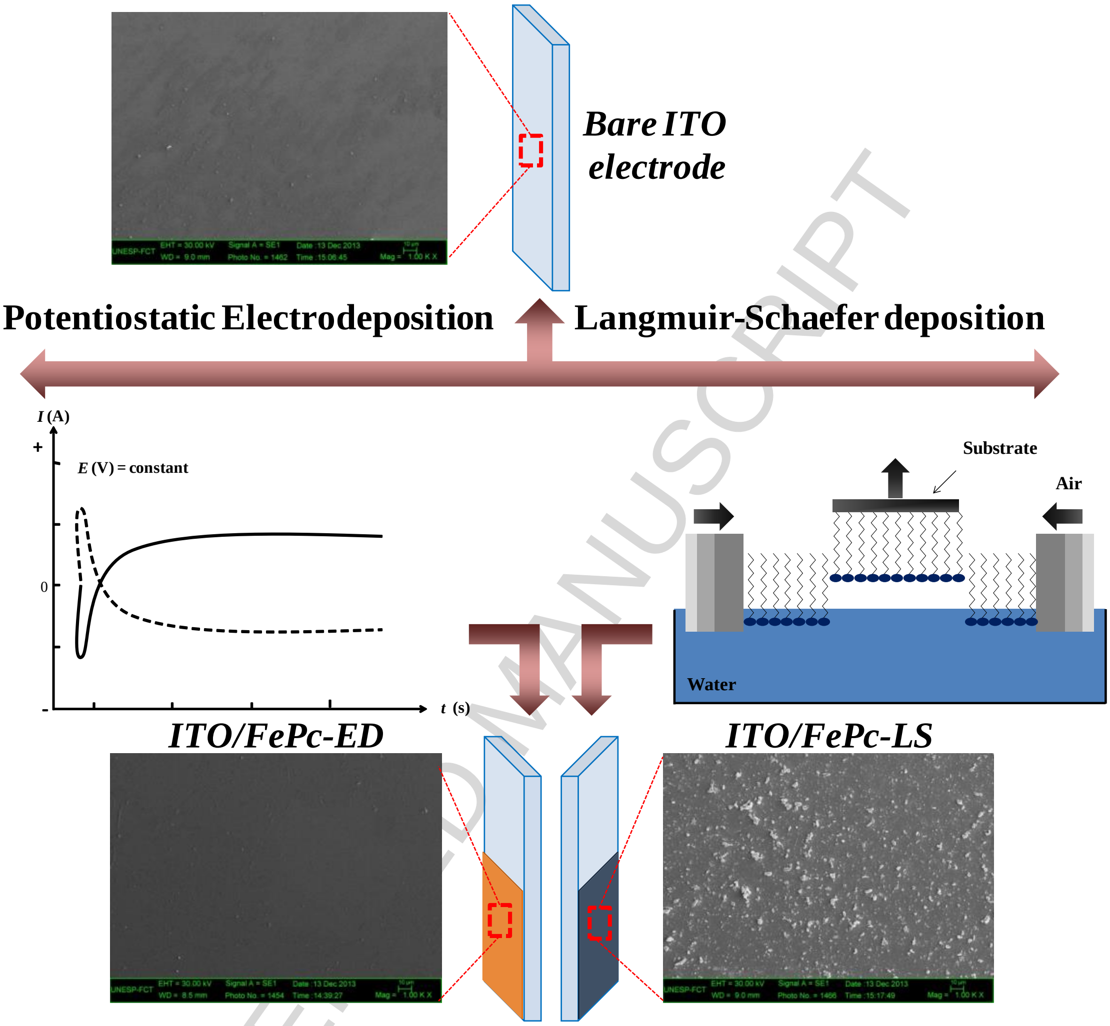


Figure 2 – Martin et. al

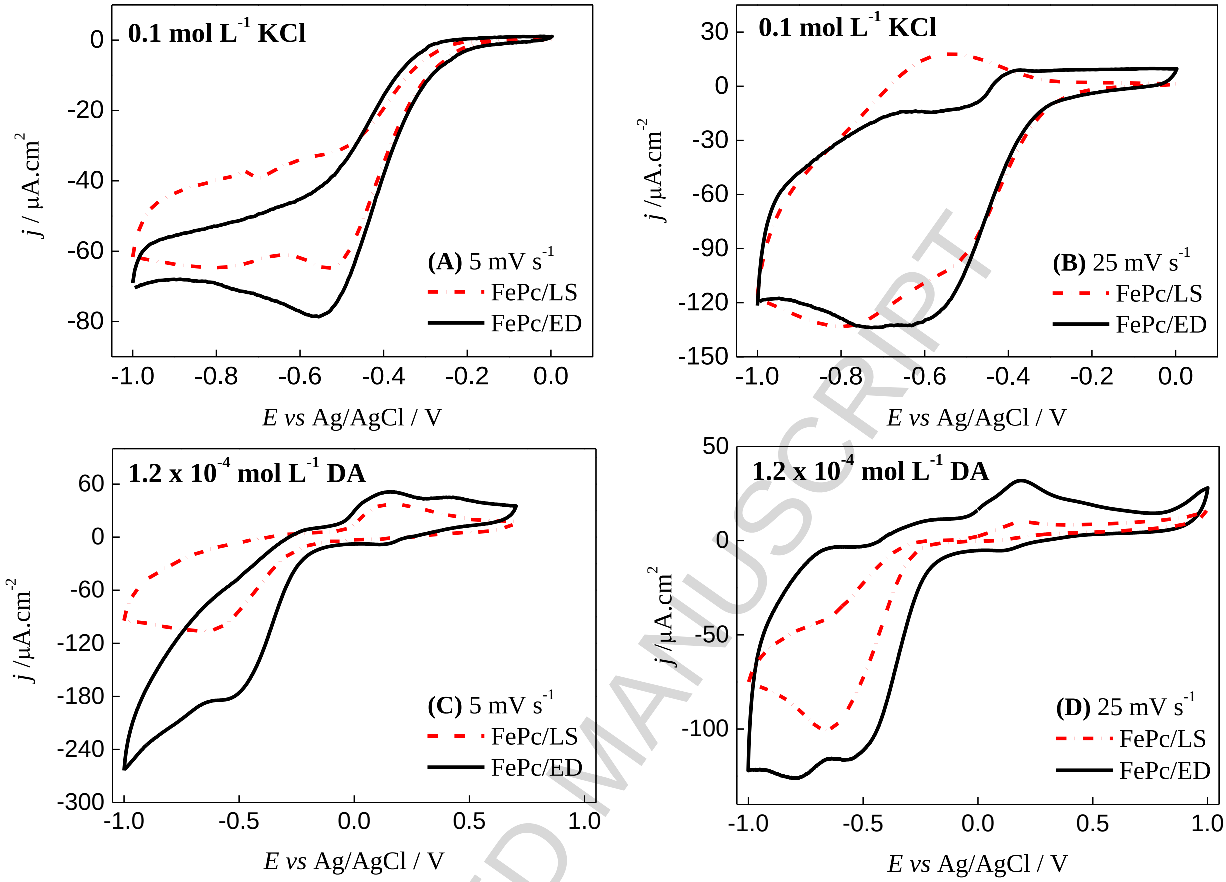


Figure 3 – Martin et. al

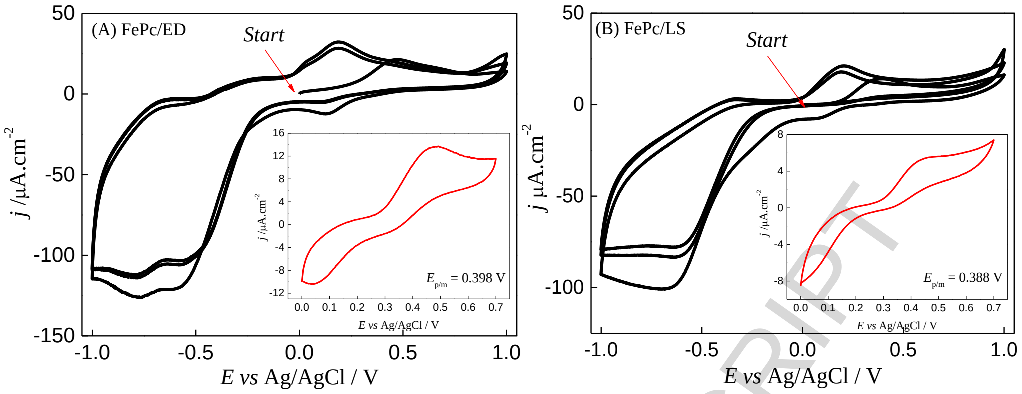


Figure 4 – Martin et. al

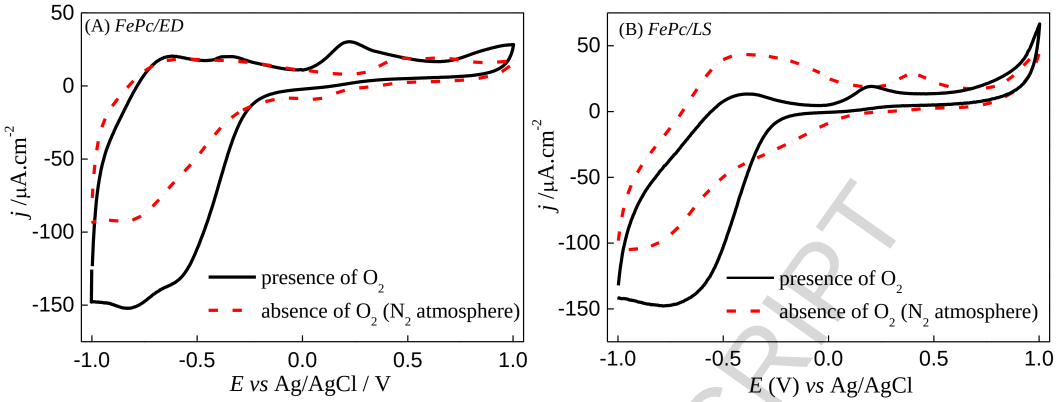


Figure 5 – Martin et. al

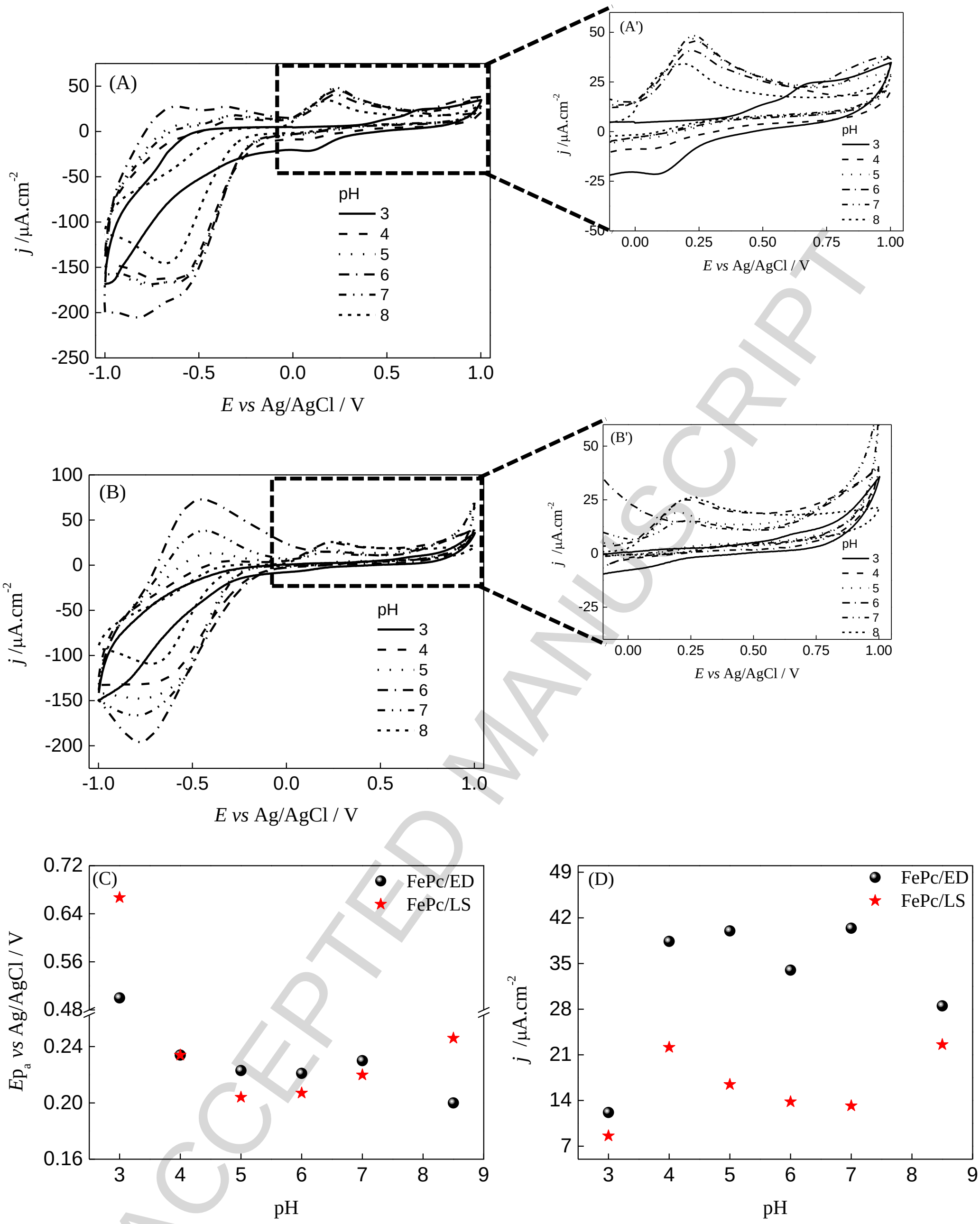


Figure 6 – Martin et. al

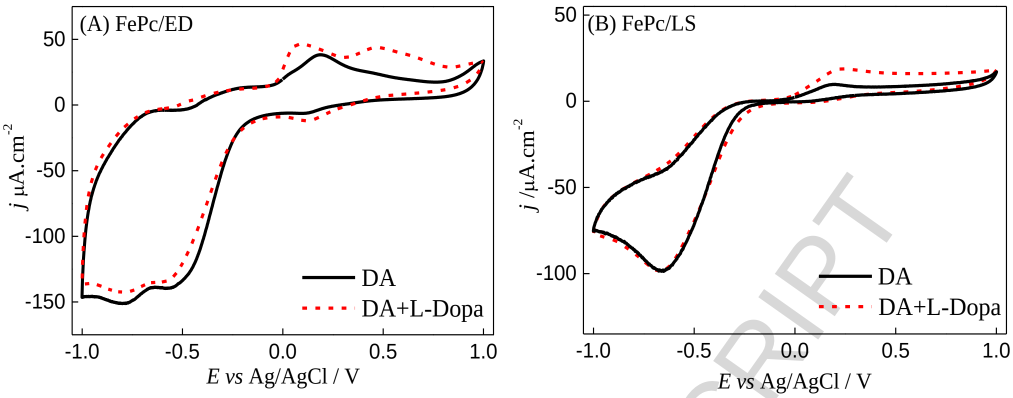
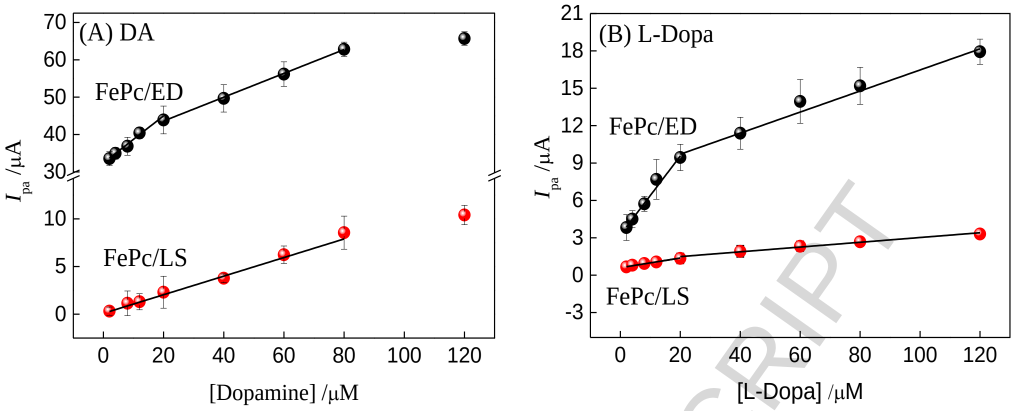
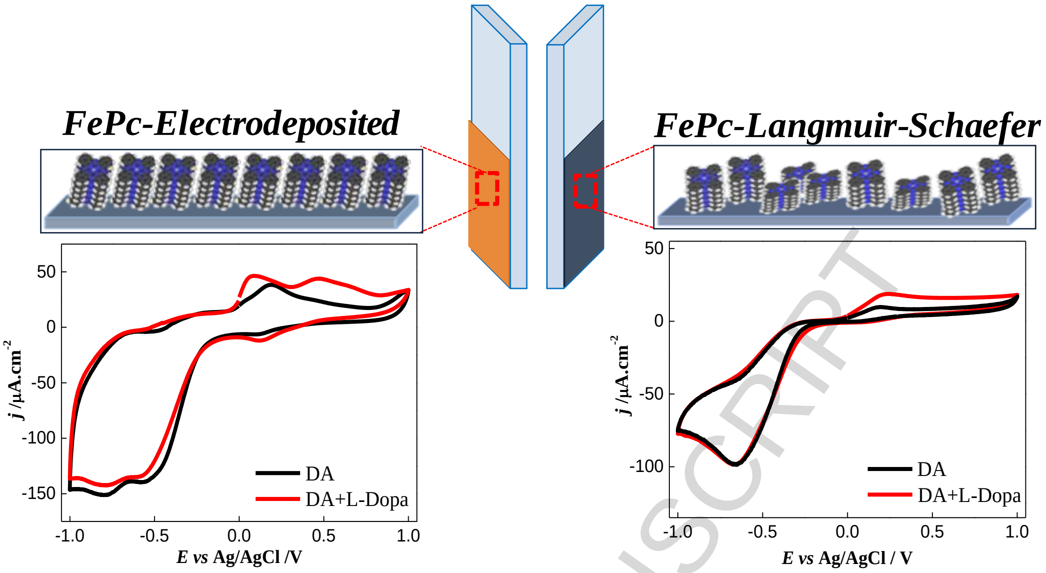


Figure 7 – Martin et. al



Graphical Abstract



Highlights

- Electrodes are modified with FePc by Langmuir-Schaefer method and electrodeposition
- FePc modified electrodes have good performance as catecholamine voltammetric sensor
- The FePc supramolecular arrangement influences the catecholamine oxidation
- The electrodeposited film can separate dopamine, L-Dopa, and epinephrine
- Langmuir-Schaefer films showed a lower limit of detection for dopamine and L-Dopa

Supplementary material

Influence of the supramolecular arrangement of iron phthalocyanine thin films on catecholamine oxidation

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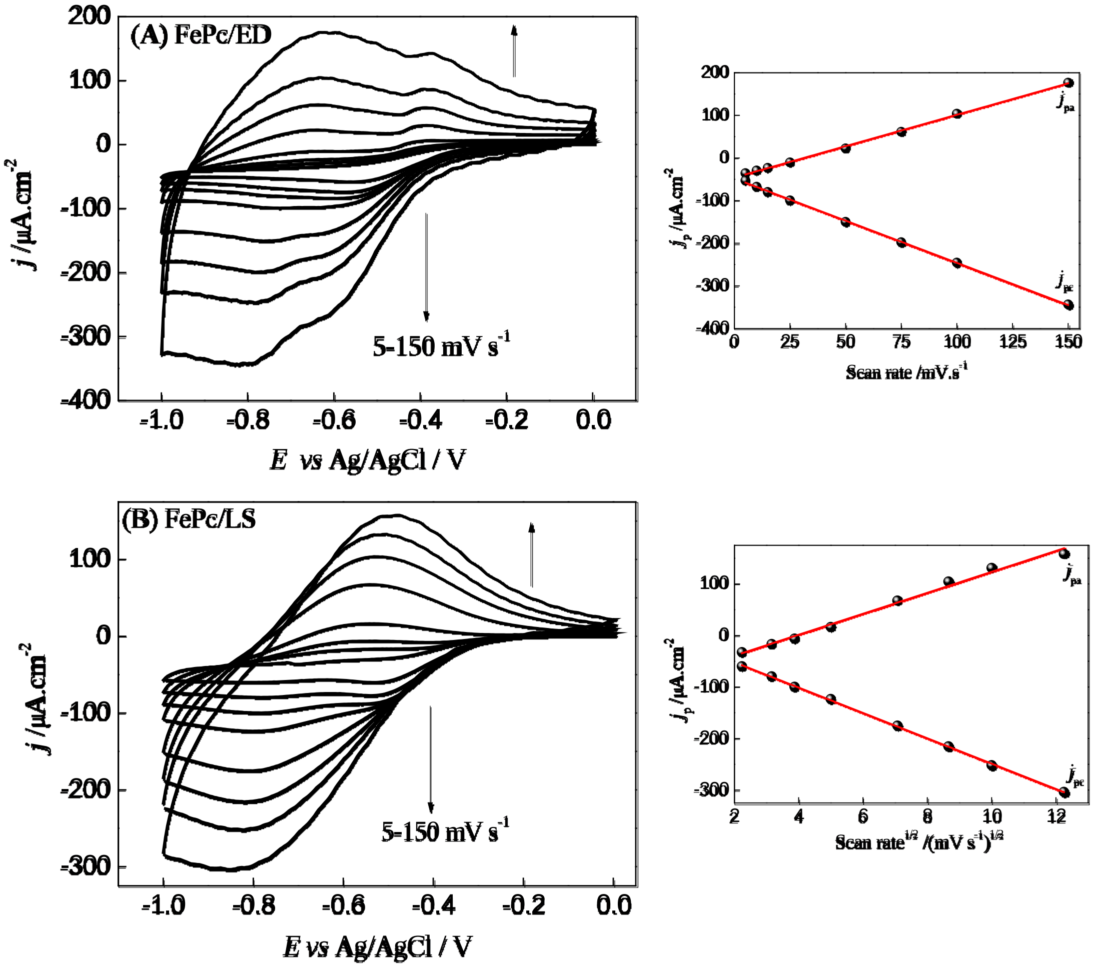

Figure S1. Current density *vs* scan rate (5-150 mV s^{-1}) in 0.1 mol L^{-1} KCl solution for ITO modified electrode with (A) FePc/ED and (B) FePc/LS films. The insets show the increase of peak current of the redox couple assigned to the phthalocyanine ring process.

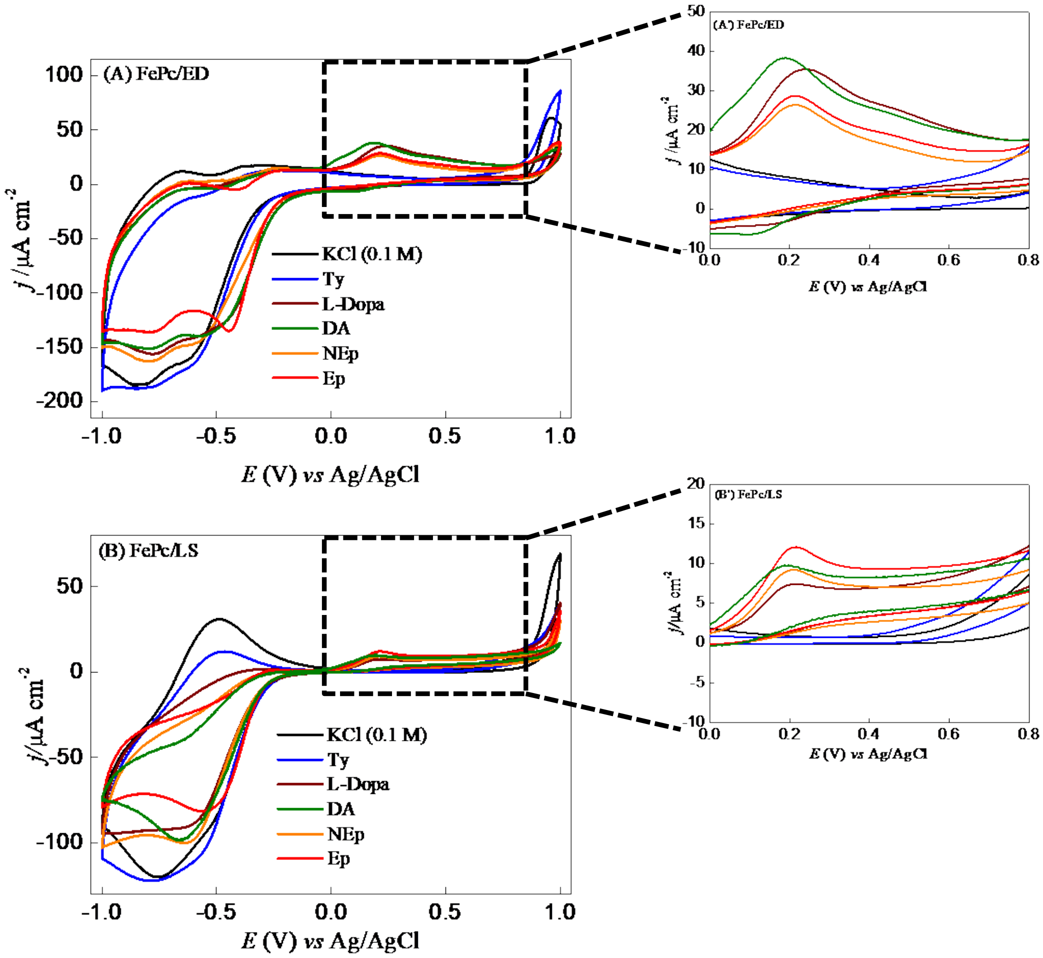

Figure S2. Cyclic voltammograms recorded for ITO electrodes modified with FePc/ED and FePc/LS films immersed in 1.2 x 10^{-4} mol L^{-1} of L-Dopa, NEp, Ep and Ty + 0.1 mol L^{-1} KCl solution. v = 25 mV s^{-1}. Magnifications of the potential range of 0 to 0.8 V are also shown as (A’) and (B’), respectively.

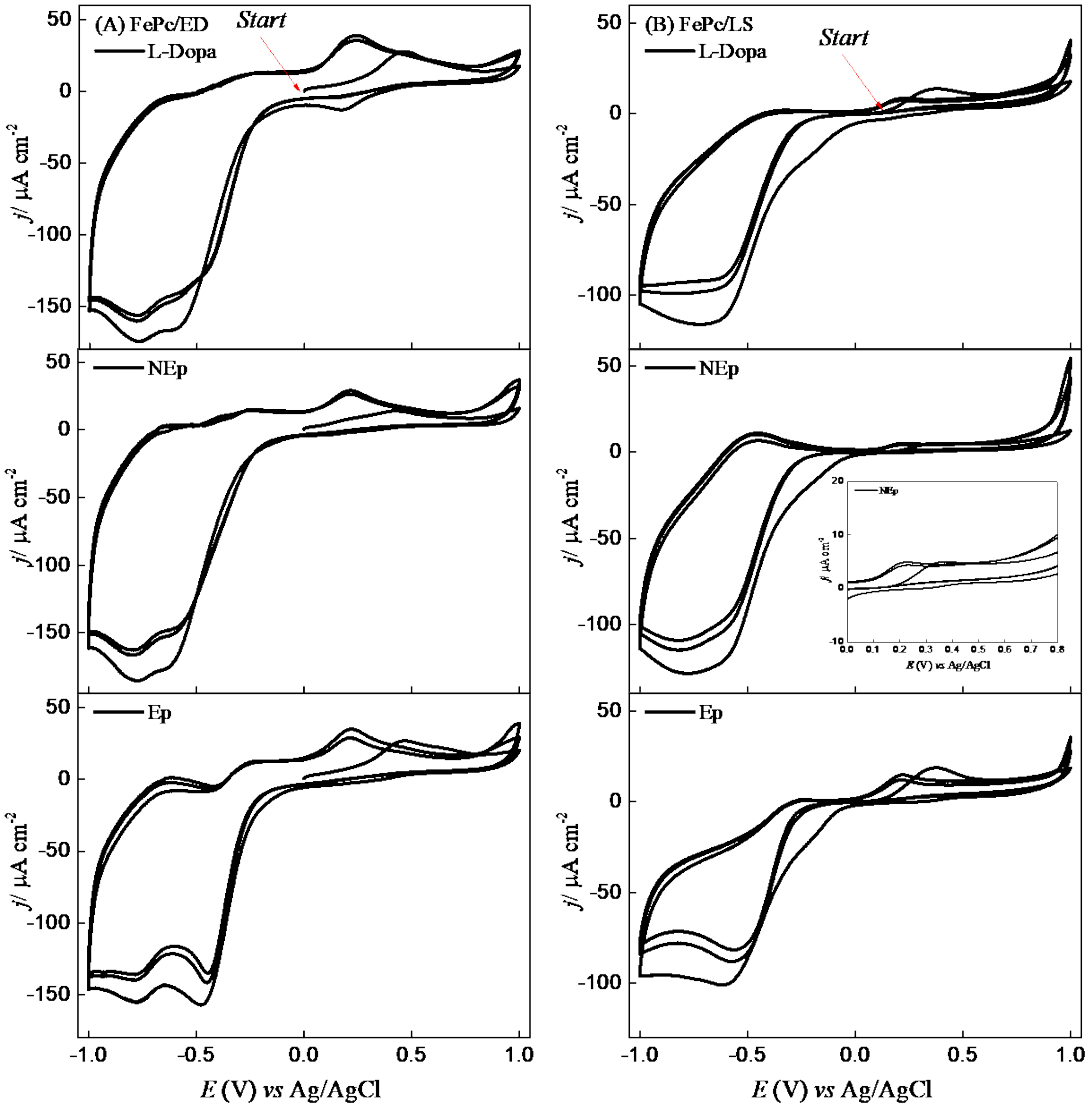

Figure S3. Three potential cycles at ITO electrodes modified with (A) FePc/ED and (B) FePc/LS film immersed in 1.2 x 10^{-4} mol L^{-1} of L-Dopa, NEp or Ep + 0.1 mol L^{-1} KCl solution in the potential range -1.0 to +1.0 V vs Ag/AgCl. The first cycle shows the catecholamine oxidation at a more positive potential than in the second and third cycle. v = 25 mV s^{-1}.

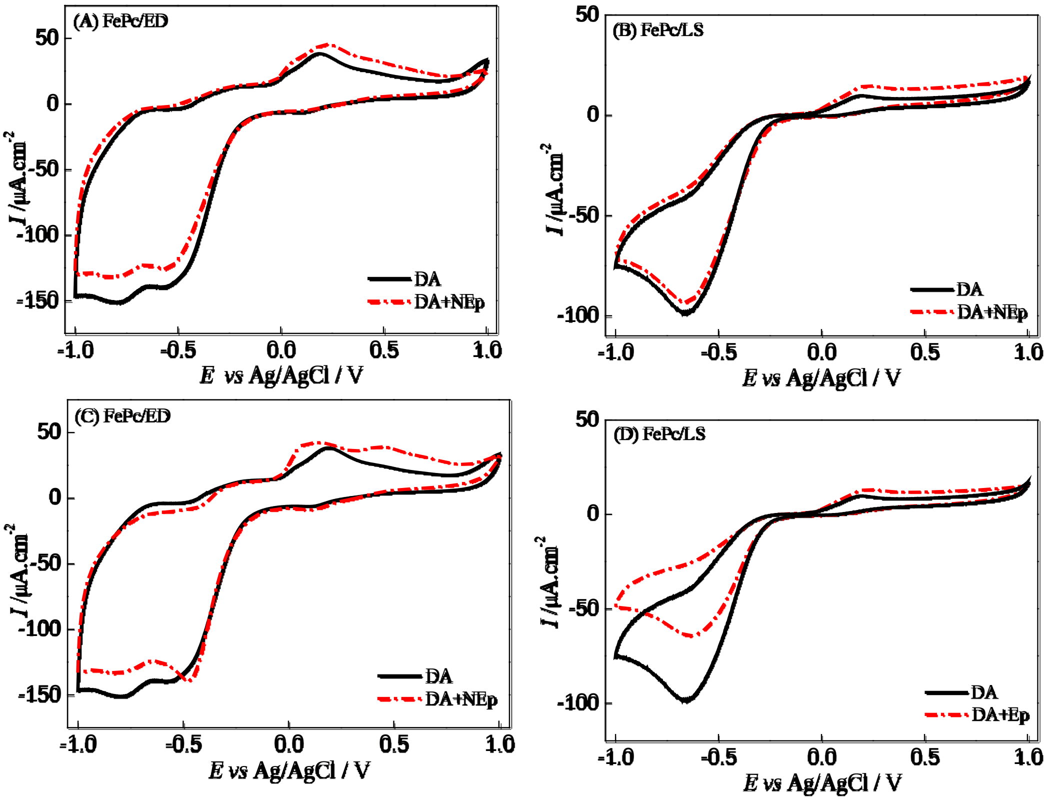

Figure S4. Cyclic voltammograms for ITO electrodes modified with FePc/ED and FePc/LS films immersed in 1.2 x 10^{-4} mol L^{-1} DA (black curve) and in a mixture of 1.2 x 10^{-4} mol L^{-1} of DA and NEp or Ep (red curve), in 0.1 mol L^{-1} KCl electrolyte solution. v = 25 mV s^{-1}.