*ds*DNA Sensing Capabilities of Metallopolymers Electrochemically Deposited from Ruthenium-Pyrrole and -Thiophene Complexes

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In the current work, a study is presented based on the variation of the monomer unit (thiophene or pyrrole) at electrochemically polymerizable ruthenium complexes, evaluating their possible applications in the field of biosensors to detect *ds*DNA. For both complexes ([Ru(p-cymene)(C$_4$H$_4$S)$_2$]$^{2+}$ and [Ru(p-cymene)(C$_5$H$_4$NH)$_2$]$^{2+}$), the metallopolymer is deposited on platinum electrodes displaying voltamperometric responses consistent with expected polymer including the corresponding Ru$^{III \to II}$ redox signa. The subsequent evaluation of these electrodeposits, in the presence and absence of *ds*DNA, demonstrated the essential role that monomer play when an application of these modified electrodes is needed. The use of thiophene as a polymerizable produces a more intense analyte-electrode interaction, with an electrode about 1.7 more sensitive to *ds*DNA compared to that of pyrrole.

1. INTRODUCTION

In recent years the interdisciplinary interest in the use of conducting polymers (CPs) in various areas has grown considerably, due to the intrinsic properties of the matrices obtained with a wide variety of commercial monomers such as thiophene, pyrrole, aniline, quinones, among others. The CPs have defined electronic properties, due to the delocalization of π electrons along the polymer backbone that has carbon as its main atom [1, 2]. It is for this particular reason that their applications vary from chemical and biological sensors to employment in solar cells [3-7]. Polypyrrole and polythiophene are examples of CPs with interesting applications. Polythiophene has been used for designing light emitting diodes [8-11] or solar cells [12-16], among others. Polypyrrole presents very similar characteristics to polythiophene, *e.g.*, both are isovalent -which allows them to show a similar electronic behavior-, and both adopt a stair-like configuration [17]. In this class of polymers, there is greater bonding between neighboring monomers, which favors conduction between chains and, therefore, obtaining more homogeneous and reproducible conductive films. A difference between these homopolymers, is related to the variation of the representative atom of its monomers, such as sulfur and nitrogen. This change should first affect the solubility, as occurs with most organic compounds containing nitrogen [17].

Currently, various disciplines such as inorganic chemistry, engineering, microbiology etc. have incorporated these materials into their research topics. For instance, transition metals could form complexes with these monomeric units and if these complexes were polymerized, one could obtain conducting polymers containing coordinated metal centers along their backbone, also known as conducting metallopolymers [18-20]. These metallopolymers display several applications, especially when supported over a conductive surface as when obtained through the electrochemical polymerization method [21, 22]. Some of the advantages of electrochemical synthesis are the ease, speed, and safety of having a pure polymeric matrix, not contaminated with the precursors that are usually used for chemical polymerizations. Such complexes have proved to be of interest, for example, in asymmetric synthesis [23, 24] and for their nonlinear optical properties [25-27].

At the present work, a ruthenium-thiophene complex -reported some time ago by our group [28, 29]-, and its analogue with pyrrole, are used for solid electrodes modification and evaluated as candidates in the design of double stranded deoxyribonucleic acid (*ds*DNA) biosensors.

2. EXPERIMENTAL

Thiophene (Th), pyrrole (Py), [Rucl$_2$(*p*-cymene)]$_2$, tetrabutylammonium hexafluorophosphate (TBA·PF$_6$), AgOSO$_2$CF$_3$, and high purity dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich. Dichloromethane, diethyl ether and ethanol were obtained from Merck, and all the aqueous solutions were prepared with fresh Milli-Q grade water.

The method to synthesize precursors for [Ru(p-cymene)(C$_4$H$_4$S)$_2$]$^{2+}$, complex(1) [30] and [Ru(p-cymene)(C$_4$H$_4$NH)$_2$]$^{2+}$, complex(2) are the same: the compounds have been prepared by reacting [RuCl$_2$(*p*-cymene)]$_2$ (0.115 g, 0.190 mmol) with AgOSO$_2$CF$_3$ (0.191 g, 0.740 mmol) in CH$_2$Cl$_2$ (18 mL) in the dark for 2 h. The obtained solution is filtered, to separate and extract the AgCl precipitated, which is discarded.

Afterwards, the solution is mixed with an excess of monomeric unit (Th or Py) during 16 h. The amount of each monomer is 1 mL and 0.8 mL of Th and Py, respectively.

Solvent and residual Th or Py removal was accomplished using a syringe, living a brown oil that is extracted with ethanol. The ethanolic solution was filtered through celite and the filtrate treated with an excess of NH_4PF_6 solution. After overnight storage at -20 ℃, a light-yellow solid was collected by filtration. The obtained product was washed twice with 2 mL portions of dichloromethane, and twice with 3 mL portions of diethyl ether, followed by vacuum-drying. The structural characterization of the precursors is carried out in the same way as reported in previous studies [28, 29], verifying the obtainment of the proposed complexes.

All electrochemical experiments were conducted using DMSO as solvent and TBA·PF_6 as supporting electrolyte. A conventional three-electrode system was employed using anchor-type three-compartment electrochemical cells. A platinum disk (0.07 cm^2 geometric area) was used as working electrode, a platinum wire coil of large geometric area as counter electrode and Ag|AgCl in tetramethylammonium chloride solution, to match the potential of a saturated calomel electrode (SCE) as reference electrode.

Cyclic voltammetry (CV) and linear potential sweep measurements were accomplished at room temperature (20 ℃) under high purity argon atmosphere. The metallopolymers were electrochemically synthesized by CV, after having made the optimization of the experimental parameters, such as working potential window, monomer concentration and supporting electrolyte, among others. Thus, in each case the optimal conditions were: working solution $1x10^{-3}$ mol L^{-1} of (1) or (2) + 10^{-2} mol L^{-1} TBAPF$_6$ in DMSO; the appropriate working windows were between -0.8 and 1.35 V for (1) and 0.0 to 1.6 V for (2), at 0.05 V s^{-1} scan rate, performing 5 successive voltammetric cycles, within the mentioned potential windows for each complex. After the CV synthesis step, the respective polymer deposit visually coats the working electrode. Subsequently, the Pt|poly-complex(1) and Pt|poly-complex(2) modified electrodes responses were studied employing a 10^{-2} mol L^{-1} TBAPF$_6$ solution in DMSO using CV and linear potential sweep measurements.

*ds*DNA determination using poly-complexes (1) and (2) was carried out utilizing a 0.15 g L^{-1} fish sperm (Aldrich) working solution, diluted with milli-Q water, in a PBS (phosphate buffer saline) of pH 7.3 containing 0.1 mol L^{-1} sodium chloride (NaCl 99.99% w/w, Merck), 2.6 mmol L^{-1} potassium chloride (KCl 99.5% w/w, Merck), $4x10^{-2}$ mol L^{-1} potassium hydrogen phosphate (K_2HPO_4 99% w/w, Merck) and 10^{-2} mol L^{-1} potassium dihydrogen phosphate (KH_2PO_4 99.5% w/w, Merck) as stock solutions. Its actual concentration ($3.2x10^{-2}$ mol L^{-1}) was determined by UV-Vis spectrometry at 260 nm wavelength.

3. RESULTS AND DISCUSSION

The synthesis of novel complex(**2**) with Py is accomplished analogously to that previously reported for the complex(**1**), Scheme 1. [$RuCl_2$(p-cymene)]$_2$ reacts with $AgOSO_2CF_3$ in dichloromethane, generating *in situ* [Ru (*p*-cymene)] (OSO_2CF_3)$_2$, which then allows obtaining the complex(**2**), by adding Py (Scheme 1). Both solids are translucent yellow and must be stored under

argon atmosphere due to their hygroscopic nature. The reaction yields for complexes (**1**) and (**2**) were 78% and 80%, respectively.
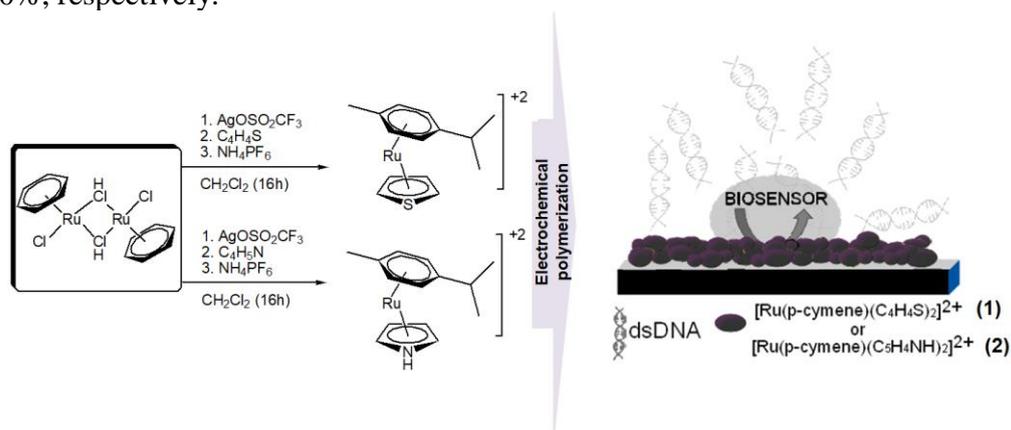
Scheme 1. Synthetic route of complexes (**1**) and (**2**) and application of their polymers on biosensing.

Figure 1 a-b shows the CV profiles recorded during the ruthenium metallopolymers electrosynthesis.
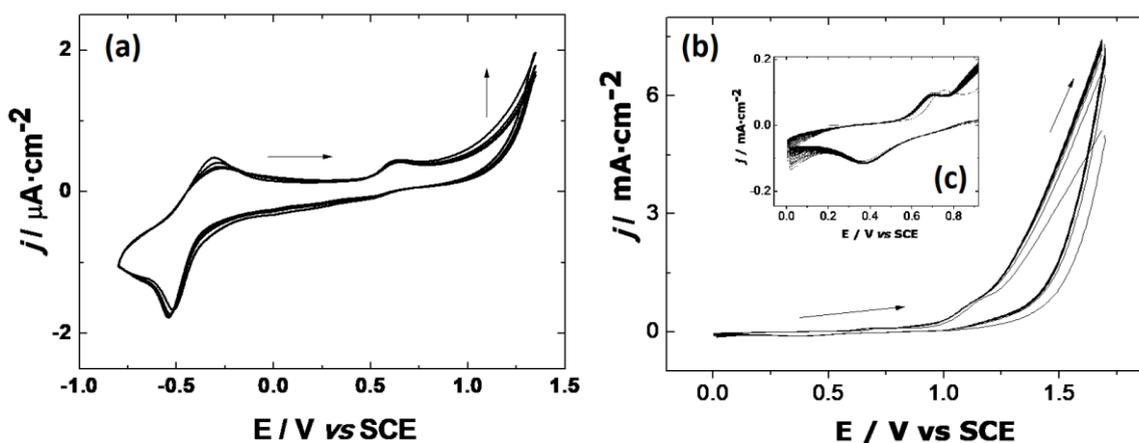
Figure 1. CV profiles during the electro-oxidation of complex(**1**) (a) and of complex(**2**). (b) Insert (c) Ru (III)/(II) redox pair, complex(**2**). In every case (a, b and c), 1×10^{-3} mol L^{-1} complex + 1×10^{-2} mol L^{-1} TBAPF$_6$ in DMSO as solvent. Scan rate: 50 mV s^{-1}.

The response during complex(**1**) electrochemical polymerization using cyclic voltammetry is shown in Fig. 1 a with an intense oxidation is observed after 0.8 V *vs*. SCE which corresponds to monomer oxidation. After consecutive cycles, the current outputs increases with the number of cycles denoting the formation of a conductive deposit over the electrode. Past reports established that thiophene oxidation starts at 1.6 V *vs*. SCE (in CH$_2$Cl$_2$ solution) during cyclic voltammetry experiments [31]. Therefore, the complex structure influences monomer oxidation process surely do to radical-cation higher relocation possibilities, requiring less energy to be oxidized, compared to free thiophene units [4, 31-34]. In addition to current growth after each cycle, indicating formation of polymer deposit, a large reversible reduction process is observed, assigned to Ru$^{III\rightarrow II}$ reduction during deposit formation.

Cyclic voltammogram after complex(**2**) electrochemical polymerization is shown at Fig. 1 b. Complex(**2**) has Py as the polymerizable unit. Similarly to the situation observed for complex(**1**), complex(**2**) displays a slightly lower oxidation potential (around 0.9 V *vs*. SCE) than pyrrole during electrochemical polymerization on anhydrous solvent conditions (1.1 V *vs*. SCE in CH_3CN) [35]; same reasoning with respect to higher radical-cation relocation possibilities found at complex structure explain the potential shift. On the other hand, it is important to mention that the recorded currents, for the same number of cycles, are always greater at complex(**2**) if compared to complex(**1**), Fig. 1a and b. Finally, the $Ru^{III \to II}$ redox pair is observed for both complexes at different potential values during electrochemical polymerization, Fig. 1a and c. It is possible that the different nucleation and growth mechanisms for each complex produce an unique chemical environment that provokes an intense potential shift for the $Ru^{III \to II}$ redox process

The metallopolymers of complexes (**1**) and (**2**), poly-complex(**1**) and poly-complex(**2**), are electrochemically characterized by evaluating the voltammetric response of their deposits made over the electrodes. Essentially, their cyclic voltammetry response is evaluated on a DMSO solution containing supporting electrolyte only, Fig. 2. At the CV profiles, a reversible redox couple is observed at similar potential value for both poly-complexes. This would mean that, at the experimental conditions mentioned, between Th and Py there is no great difference regarding their contribution to the redox processes taking place at the metallopolymer deposits. Nevertheless, poly-complexes (**1**) and (**2**) do show great differences with respect to the shape and intensity of the oxidation and reduction peaks. In the case of the poly-complex(**2**), it is possible that the hydrogen bound to the nitrogen of Py, interacts by hydrogen bridges with neighboring chains. This would produce a more disperse electronic cloud delocalizing the electrons normally exchanged by the redox couple ($Ru^{III \to II}$) for poly-complex(**2**), which finally results in a broad peak, much less defined than in the case of the poly-complex(**1**), where the oxidation and reduction peaks are well defined.
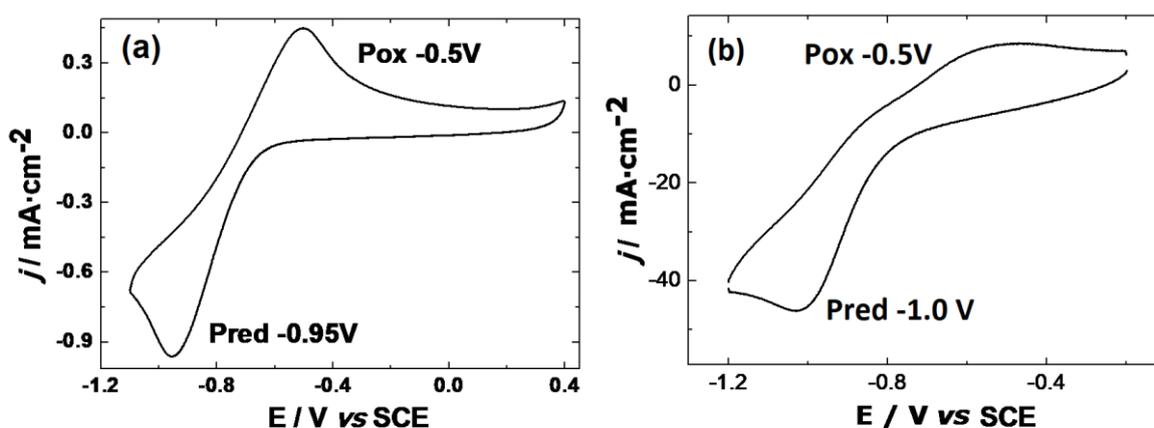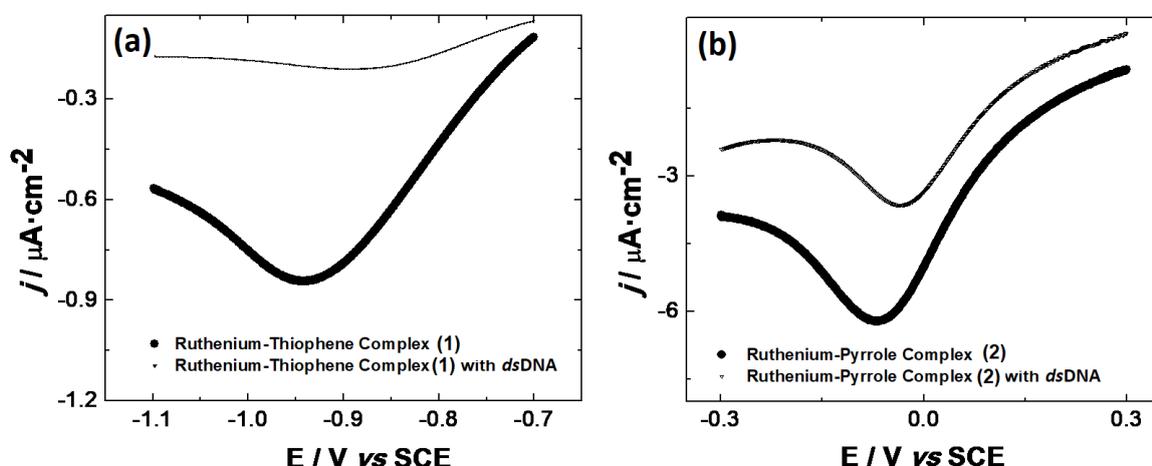

Figure 2. (a) Pt|poly-complex(**1**), and (b) Pt|poly-complex(**2**) responses in 1×10^{-2} mol L^{-1} TBAPF$_6$ in DMSO. Scan rate: 100 mV s^{-1}.

Figure 1 and 2 showed current densities for poly-complex(2) about 500 times greater than that of poly-complex(1). Even though both polymerizations were possible, due to the presence of Th at

poly-complex(1) is necessary to consider aprotic solvent during electrosynthesis. Nevertheless, both complexes (1) and (2) are highly soluble on most aprotic solvents employed for electrochemical preparation (dichloromethane, acetonitrile, dimethylformamide, etc.) which is a problem for oligomer precipitation step at the electrochemical-polymerization mechanism [32]; thus DMSO was the solely choice for synthesizing the respective poly-complexes. There's a risk, however, when selecting DMSO as solvent for the electrochemical polymerization of thiophene-based conducting polymers: DMSO may likely contain trace-amounts of water. The use of hydrated solvent is known to hinder the obtainment of more conductive thiophene-based polymeric deposits; thus, this could explain the lower current outputs observed during electrochemical-synthesis and response-study of poly-complex(1) with respect to its analogue (2), Fig. 1 and 2.

　　　　Figure 3 shows the voltammetric response after linear potential sweep measurements of electrodes modified with the polymers from complexes (**1**) and (**2**) in the presence and absence of *ds*DNA.

Figure 3. Linear potential scan response in the presence and absence of *ds*DNA, of Pt|poly-complex(**1**) (a) and Pt|poly-complex(**2**) (b). Working solution: 0.15 g L^{-1} *ds*DNA in PBS. Scan rate: 100 mV s^{-1}.

　　　　The linear potential scan measurement will become modified as a function of the working solution composition, it is necessary to test new potential windows that will produce a current variation as function *ds*DNA concentration. In this sense, and considering how *ds*DNA behaves as an analyte - presenting large chains that tends to roll into balls in solution-, it is not surprising that potential windows differ between electrodes modified with poly-complexes (**1**) and (**2**).

　　　　To make an effective comparison between both metallopolymers, each curve obtained in the absence and presence of *ds*DNA have been normalized by the area under the curve for the respective voltammogram on Figure 3 (see Table 1 and Fig. 4).

　　　　As can be observed, it would seem that since pyrrole is present as a polymerizable monomer in complex(**2**), its NH group could favor interactions between poly-complex(**2**) chains decreasing available active sites at the metallopolymer. As a consequence, the interaction between poly-

complex(**2**) and the *ds*DNA should be less intense as corroborated by Fig. 2. Moreover, if the difference between the normalized currents is compared, the interaction between *ds*DNA and poly-complex(**1**) electrode is about 1.7 times more intense then that with poly-complex(**2**). Variations of this magnitude have been observed between polythiophene- and polypyrrole-based analogous electrochemical biosensors for different systems. Türkarslan *et al.* (2009) [36] reported a sensitivity of 14.3 µA mM^{-1} cm^{-2} for an amperometric cholesterol biosensor based on cholesterol oxidase immobilized into the matrix of poly(3,4-ethylenedioxythiophene). Later, same year, the authors reported a different study [37] with the same experimental procedure but using poly(3,4-ethylenedioxypyrrole) instead, achieving a sensitivity of 10 µA mM^{-1} cm^{-2} on this case. On this sense, the cholesterol sensor based on the thiophene-analogue was about 1.4 more sensitive towards cholesterol detection than same sensor build with the pyrrole-analogue.
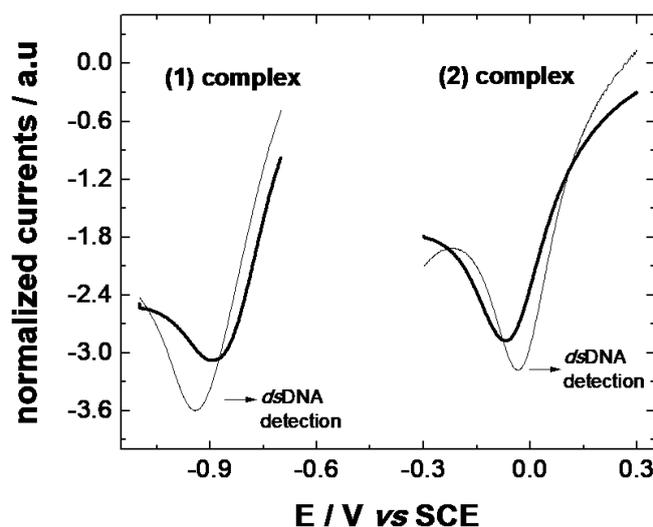

Figure 4. (a) Normalized currents for *ds*DNA detection.

Table 1. Normalized currents for the responses of electrodes modified with poly-complexes (**1**) and (**2**).

	Poly-complex(1)		Poly-complex(2)	
[*ds*DNA] (g/L^{-1})	0	0.15	0	0.15
Normalized current (a.u)	-3.5854	-3.0812	-2.8773	-3.1801
Difference between normalized currents	0.5042		0.3028	

Experience gained with similar systems, evidenced on past reports, permits to correlate that polymeric deposit with low roughness, specially polythiophene deposit with its particular spatial configuration, confers higher degree of order when compared with other conducting polymers [22, 28, 29, 33, 38, 39]. Therefore, unlike polypyrrole, the lower degree of cross-linking and smoother surface of polythiophene deposit may at least explain its best performance for the design *ds*DNA sensor, since

in the presence of bio-analytes displays a potentially higher sensibility (more intense current response) as electrochemical sensor.

Finally, Table 2 presents dsDNA detected concentrations reported by other authors compared to present work. Different concentrations have been reported and, compared to present report, it can be stated that an average performance has been obtained. Thus, considering that solely electrochemical means were employed, Pt|poly-complex(1) reached decent detection levels due to the synergistic effect between Th and Ru core at the metallopolymer. The use of poly-complex(1) for sensors construction is a simple, low cost and repeatable method that will be explored on further research.

Table 2. DNA detected concentration from other reports compared to present work.

Method: material	dsDNA detection (g L^{-1})	Reference
CV: rGO/ss DNA-OMC/Ni-OTC NPs/PGE	1.11×10^{-3}	40
CV: Poly(azomethine-urethane) and zeolite-based composite	1.00	41
CV: Au@Nb2O5	0.02	42
CV: Pt|poly-complex(1)	0.15	This work

4. CONCLUSIONS

It was verified that the chemical synthesis of metal complexes attached to electrochemical-polymerizable monomers, allows generating, by electro-oxidation, metallopolymers deposited directly on a working electrode, exhibiting growth profiles that are consistent with those of homopolymers obtained from thiophene and pyrrole monomers, herein used as ligands in complexes (**1**) and (**2**), respectively.

In addition to the polymerization, in its voltammetric profiles it is possible to visualize the $Ru^{III \rightarrow II}$ couple for both metallopolymers, which accounts corroborating the presence of the coordinated metal centers active sites within the electrodeposited polymer matrix.

Meanwhile, in the current work, it has been corroborated that, in the case of ruthenium complexes usually employed for the detection of *ds*DNA of various chain lengths, the choice of the synthesis route of a suitable monomer seems crucial when thinking about possible applications. In this respect, it is conclusive that the use of thiophene as a polymerizable produces a more intense analyte-electrode interaction, with about 1.7 more sensitive electrode compared to that of pyrrole; such behavior has been observed by other author on similar systems.

Hence, these results point out that electrodes modified with polythiophene metal complexes, would be more suitable for sensing *ds*DNA, due to the greater variation in the sensitivity recorded in the presence and absence of the analyte, which allows forecasting its future employment in the biosensing field.

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