

Self-Assembled Redox Polyelectrolyte-Surfactant Complexes: Nanostructure and Electron Transfer Characteristics of Supramolecular Films with Built-In Electroactive Chemical Functions



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ABSTRACT

The mesostructural and electrochemical characterization of a redox-active polyelectrolyte-surfactant complex formed by polyallylamine tagged with an osmium complex and dodecylsulfate is presented. X-ray reflectivity (XRR), grazing-incidence small-angle X-ray scattering (GISAXS), X-ray photoelectron spectroscopy (XPS), contact angle goniometry (CA) and cyclic voltammetry (CV), including the numerical simulation of the voltammetric response, were employed to analyze the structure, stability and the electrochemical response of these supramolecular films. In contrast to redox-active polyelectrolyte multilayers (PEMs), the self-assembled system presented here shows a mesoscopic order yielding a film of layered structure very stable to an aqueous environment where the hydrophilic moieties (amino and sulfate groups) are not exposed to the solution since a contact angle of 95° is observed upon exposure to water. However, the film shows a self-exchange electron transfer mechanism with an apparent diffusion coefficient of $2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for a film of 300 nm of thickness. This behavior shows that the film exposed to an aqueous solution undergoes a fast electron transfer process to/from the electrode surface and ions to/from the electrolyte solution.

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1. Introduction

Ionic self assembly (ISA) has opened doors to the facile creation of supramolecular materials. This approach offers new strategies for the bottom-up assembly of integrated supramolecular systems displaying concerted functions. This construction strategy was pioneered by Decher assembling layer by layer oppositely charged water-soluble polyelectrolytes generating a polyelectrolyte multilayer system (PEM).[1] The technique has since been used to construct highly ordered three-dimensional, multifunctional, reactive thin films. Polyelectrolyte systems fabricated through PEM are currently incorporating different building blocks sensitive to specific stimuli to obtain responsive films, which have found different application as lens coatings, drug-delivery systems, biosensors, light emitting and nonlinear optical devices, among others.[2]

In particular, electroactive PEMs contain building blocks that can efficiently exchange electrons. They have been applied in fundamental studies,[3–7] sensors,[8,9] microelectronics,[10] photovoltaics,[11–13] biofuel cells[14] and battery design.[15] For all these applications it is necessary to ensure a stable structure that guarantee an efficient charge transport between the redox-sites in the multilayer and the electrode for a certain period of time. The electron transfer mechanism in all the electroactive PEMs investigated up to now can be explained by electron hopping, this transfer mechanism can be described by a diffusive behavior characterized by an apparent electron diffusion coefficient (D_{app}), typically ranging between 10^{-8} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$. The PEMs with higher D_{app} corresponds to systems of linearly grown multilayers where the polyelectrolyte interdiffusion plays an important role in the electron hopping process.[7]

An alternative method for the modification of electrode surfaces can be carried out using polyelectrolyte-surfactant complexes. These complexes combine in unique ways the properties of polyelectrolyte with those of low molecular weight amphiphiles. The polyelectrolyte components can provide, for instance, mechanical strength and thermal stability, while the surfactants retain their

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tendency to assemble in layered structures.[16,17] They can be completely dissolved in organic solvent[18] and to be applied as a paint on practically any surface, yielding an spontaneous self-assembled system.[19]

We have recently presented results regarding the formation of self-assembled system using a polyelectrolyte (polyallylamine, PA) containing a polypyridyl osmium complex (OsPA) and a surfactant (sodium dodecylsulfate, SDS). The osmium modified polyelectrolyte in presence of SDS precipitates, generating a product that is readily soluble in DMF. This organic solution applied on graphite or gold substrates forms an extremely stable and resistant film after solvent evaporation, showing a quasi-reversible electrochemical behavior.[20]

In this work our investigation was aimed at characterizing the mesostructural features and the electron transfer mechanism taking place in this redox-active polyelectrolyte-surfactant complex. Also, new surfaces (glassy carbon, ITO and silicon) were explored to show the universality of the construction process. To this end we drew upon a set of techniques including x-ray reflectivity (XRR), grazing-incidence small-angle X-ray scattering (GISAXS), X-ray photoelectron spectroscopy (XPS), contact angle goniometry (CA) and cyclic voltammetry (CV) including the numerical simulation of the voltammetric response. The use of a surfactant instead of a polyelectrolyte as counter ion in the construction of the self-assembled system with a redox-active polyelectrolyte generates a system with a mesoscopic order randomly oriented on the surface electrode where the electron hopping process is taking place with a D_{app} higher than $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for films of different thickness. The combination of a stable ordered structure with an efficient electron transfer process is a remarkable difference with respect to electroactive PEMs where the interdiffusion of the polyelectrolytes plays a relevant role.[7] Here, the surfactant is able to maintain a tight structure but, at the same time, the redox centers are close enough to efficiently allow the electron transfer process.

2. Experimental

2.1. Reagents and Materials

The synthesis of poly(allylamine) containing a pyridine based osmium complex (OsPA) is described elsewhere,[21] the stoichiometry ratio between of osmium complex and allylamine monomer was: 1:35. All other reagents were analytical grade. Glassy carbon electrodes were from Tokay; ITO electrodes were from Delta technologies and silicon substrates (single side polished, <100>, N-type, P as dopant, resistivity: 560–840 ohm-cm) were supplied by UniversityWafer Inc.

2.2. Polyelectrolyte-surfactant composite material

200 μL of SDS 1% in Milli-Q water were added to a 100 μL of OsPA (0.2 mM). The mixture immediately generated a precipitate (OsPA-DS), which was easily separated by centrifugation. The OsPA-DS complex was analyzed by elemental microanalysis showing a ratio ca. 1:1 between allylamine monomer and dodecylsulfate (N:S ratio).

2.3. Modified electrodes

ITO and glassy carbon were employed as working electrodes. The precipitated complex is dissolved in 250 μL of DMF yielding 3 mM solution in osmium complex. This solution was applied on ITO by spin coating. Glassy carbon electrodes were modified by drop coating.

2.4. Equipment

2.4.1. Electrochemical Measurements

Electrochemical experiments were carried out using a purpose-built potentiostat (TEQ-02) using a three-electrode Teflon electrochemical cell equipped with a platinum mesh counter electrode and an Ag|AgCl reference electrode. Cyclic voltammetry experiments were carried in a 20 mM Tris-HCl buffer (pH = 7.4, 0.1 M KNO_3).

2.4.2. Surface Profilometry

Film thicknesses were determined using a Dektak 150 Stylus Surface Profiler with a stylus of 12.5 μm and an applied force of 29 μN .

2.4.3. Contact Angle Measurements

A KSV Cam200 equipment was used for contact angle measurements. Distilled water was used as liquid probe in all assays.

2.4.4. X-ray reflectometry (XRR) and grazing-incidence small-angle X-ray scattering (GISAXS)

XRR and GISAXS measurements were performed at the D10A-XRD2 line of Laboratório Nacional de Luz Síncrotron (LNLS, Campinas, Brazil). A monochromatic beam of 7709 eV ($\lambda = 1.608 \text{ \AA}$) was used to perform both, XRR and GISAXS, experiments. XPS measurements were performed at D04A-SXS beamline of LNLS, using photon incident energy $I = 1840 \text{ eV}$ with a 45° detection angle. Quoted binding energies were referenced to the adventitious C 1s emission at 285 eV. Si (100) wafers were used as support substrates and were pretreated before coating. They were rinsed with acetone and dried with argon blowing before coating. Thin polymer films were prepared by spin-coating a 50 μL portion of OsPA-DS dispersion using a commercial spin coater (Laurell WS-400B).

2.5. Numerical model

Finite-element software (Comsol Multiphysics 3.4) was used to simulate the cyclic voltammetry experiments and the concentration profiles. Further details are given in Supplementary information.

3. Results and Discussion

3.1. Mesostructural organization of the polyelectrolyte-surfactant complex

The structure of the film was characterized by specular X-ray reflectivity analysis and grazing incidence small-angle X-ray scattering measurements. They were carried out with synchrotron radiation sources to investigate the mesostructural organization of the OsPA-DS film formed on solid surfaces, Si(100). Fig. 1 shows the X-ray reflectivity data corresponding to the PA-DS thin film as a reference system[19] and the OsPA-DS thin film studied in this work. The presence of sharp Bragg peaks up to the third order indicates highly oriented lamellar structures for both films. From the Bragg peak positions, it can be deduced a lamellar spacing (d) of 3.96 and 4.15 nm for the PA-DS and OsPA-DS systems, respectively. The simplest lamellar nanostructure of a polyelectrolyte-surfactant complex is a microphase-separated model consisting of an ionic phase and a non-ionic phase.[22] The ionic phase contains the polyelectrolyte chains and the ionic head groups of the surfactants, where the non-ionic phase contains the hydrophobic moieties such as alkyl chains (see Fig. 2, left). The repeating unit of the lamellar system presents a thickness values close to those observed in self-assembled systems built by layer by layer deposition; for instance, 5 nm was reported for a layer of poly(vinylsulfonate)-ferrocene

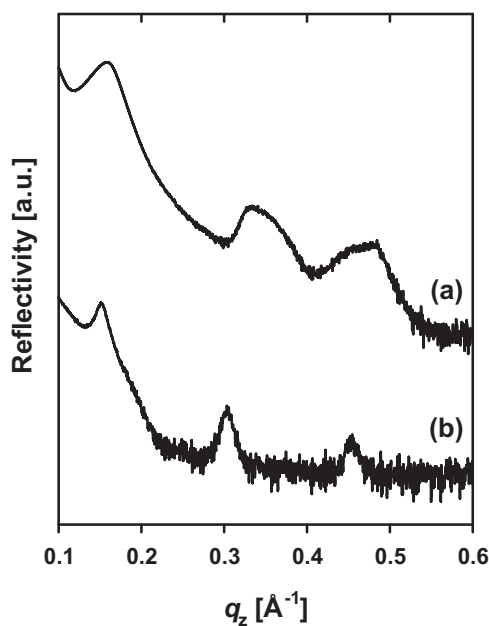


Fig. 1. X-ray reflectivity data for the (a) PA-DS films measured under ambient conditions, (b) OsPA-DS films measured under ambient conditions.

modified polyallylamine[23] and *ca.* 2 nm poly(vinylsulfonate)-osmium modified polyallylamine.[24]

GISAXS with an incident angle of 0.27° was carried out to elucidate the orientation of these lamellar domains with respect to the substrate (Fig. 3). As presented elsewhere,[19] the GISAXS pattern for PA-DS system shows the presence of a very faint circular halo and a very intense bright region in the q_z direction (for $q \rightarrow 0$) (Fig. 3a). This indicates that lamellar structures PA-DS are found predominantly oriented in a direction parallel to the substrate (see Fig. 2, right at the top). The results obtained for OsPA-DS (Fig. 3b) show interesting changes. Unlike PA-DS, films in which the polyelectrolyte has been modified with osmium complexes show that the bright region in the q_z direction becomes smaller, but it is evident the appearance of bright regions (spots) in the q_y direction. These changes in GISAXS patterns suggest that films of OsPA-DS have a fraction of the lamellar domains oriented perpendicular to the substrate (see Fig. 2, right at the bottom). This would indicate that the presence of osmium complexes alters the orientation of its mesostructure in such a way that the connectivity of the redox polyelectrolyte domains with the conducting substrate would be facilitated.

The OsPA-DS film was also analyzed by contact angle measurements. The system exposed to water presents a contact angle of 95° ; this value represents an obvious hydrophobic behavior, similar

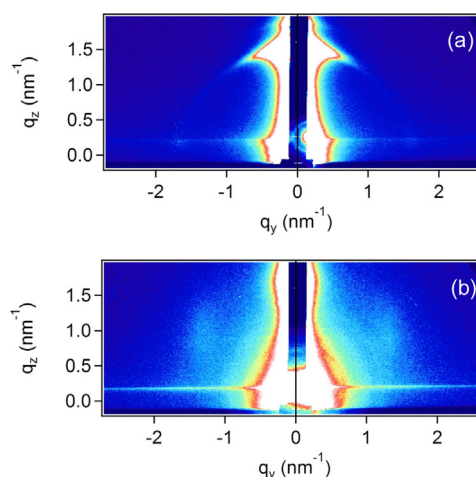


Fig. 3. GISAXS patterns corresponding to (a) PA-DS and (b) OsPA-DS. Films measured at an incident angle of 0.27° under ambient conditions. Films were spin-coated on Si(100) substrates.

to the one presented by the system PA-DS, 86° .[19] In the literature there are several examples of self-assembled systems built by layer by layer deposition containing polyallylamine where the contact angle observed is smaller. For example, a layer by layer system built using OsPA and glucose oxidase as building blocks present a contact angle of 59° when OsPA is the outer layer.[25] Another example is the system built using polyallylamine (PAH) and polyacrylate (PAA) at pH 4.5 the contact angle for water is 45° when polyallylamine is the outermost layer.[26] These values are in contrast with the one presented in this work. It is evident that the interplay between ionic interactions and hydrophobic forces promotes a mesostructural organization of the film that leads to the exposure of hydrophobic domains to the aqueous solution. In fact, X-ray photoelectron spectroscopy (XPS) characterization of the polyelectrolyte-surfactant complex revealed that $\sim 60\%$ of the amino groups in the supramolecular assembly are protonated, $-\text{NH}_3^+$ (Figure S1, supplementary information). The evidence from these experiments (XPS and contact angle) reinforces the idea that charged/polar groups are not directly exposed to the solution, instead they remain buried in the mesostructured film. This is a clear different behavior compared with previously presented results.

3.2. Charge transport through the film

As the electrode modification is carried out by spreading an organic solution containing the polyelectrolyte-surfactant complex, electrodes with different layer thickness can be obtained.

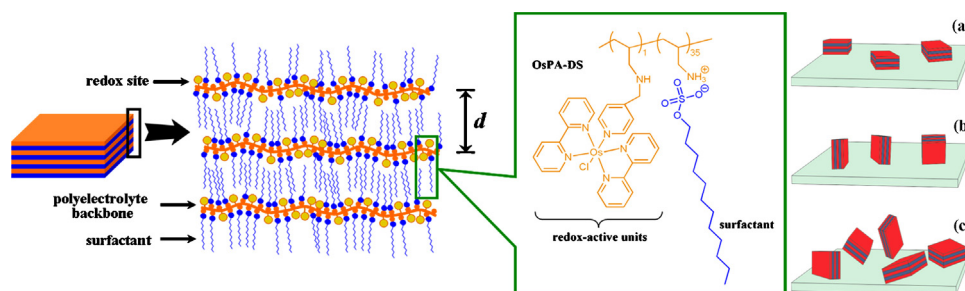


Fig. 2. Left: Schematic of the different layers constituting the lamellar assembly: ionic layers (orange) correspond to the polyelectrolyte and dodecyl sulfate head groups, whereas the alkane layers (blue) correspond to interdigitated hydrophobic tails (dodecyl groups). Right: Schematic depiction of lamellar domains presented in different orientations with respect to the substrate: (a) lamellar structures oriented parallel to the surface; (b) lamellar structures oriented perpendicular to the surface; (c) lamellar structures oriented randomly with respect to the surface.

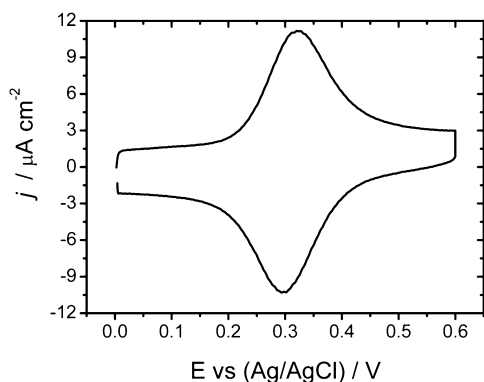


Fig. 4. Cyclic voltammetry of the OsPA-DS film on ITO at 100 mV s^{-1} in 20 mM Tris-HCl buffer, pH 7.4 and 0.1 M KNO_3 . Film thickness: $150 \pm 20 \text{ nm}$.

Films of 150, 300 and 2000 nm were studied and their electrochemical behavior modeled through the numerical simulation of the experimental results. The surfaces used in these experiments were ITO and glassy carbon.

ITO electrodes were modified by spin coating; electrodes with thickness of 150 and 300 nm were obtained. A correlation between the thickness of the film and the current detected during the oxidation of the osmium complexes was observed; a charge increase of $10 \mu\text{C cm}^{-2}$ is observed for an increase of ca. 100 nm in thickness. Considering the magnitude of the charge and the thickness of the film, we estimated a nominal concentration of osmium centers in the supramolecular film of $9 \pm 1 \text{ mM}$.

Fig. 4 displays the cyclic voltammogram of a $150 \pm 20 \text{ nm}$ film of OsPA-DS in which the potential was scanned at 100 mV s^{-1} . The voltammogram presents a quasi-reversible behavior with a peak potential separation of 21 mV and a full width at half maximum (FWHM) of 110 mV, slightly larger than the value expected for an ideal one-electron redox system under finite diffusion conditions (90.6 mV).^[27]

Considering that the stability of the film is in part due to the interactions of sulfate groups in the surfactant with the amino groups in the polyelectrolyte, ionic strength in the bathing solution may have an important effect in the formal potential of the redox species in this highly charged environment; this effect has been widely studied in redox polyelectrolytes^[28–30] and proteins naturally, or by design, containing redox moieties.^[31,32] For the self-assembled system presented in this work, it can be observed that the whole voltammogram shifts to cathodic potentials as the ionic strength is increasing (Figure S2), without changing the peak currents. Taking as reference the anodic peak current potentials it can be determined that a shift of ca. 40 mV is observed per concentration decade, in accordance with previous results observed for redox hydrogels^[28] and layer by layer deposition of the same polyelectrolyte modified with ferrocene moieties, where a shift of 43 mV per decade was observed.^[33] The direction of the potential shift is consistent with the increasing electrostatic interaction with free anions in the bathing electrolyte stabilizing the extra positive charge on the redox moiety due to the oxidation process. This fact reveals that the free ions in solution are able to interact stronger with the redox moiety than the charges already present in the film even though their closeness and tight structure.

The information provided by the cyclic voltammetry experiments of the 150 nm film of OsPA-DS at different scan rates was used to feed a numerical model developed in our group^[20] using a finite-element software in which the redox centers are assumed to be confined within the film to obtain kinetics parameters related to the heterogeneous electron transfer rate between the electrode surface and the redox centers (k_0), and information related to the

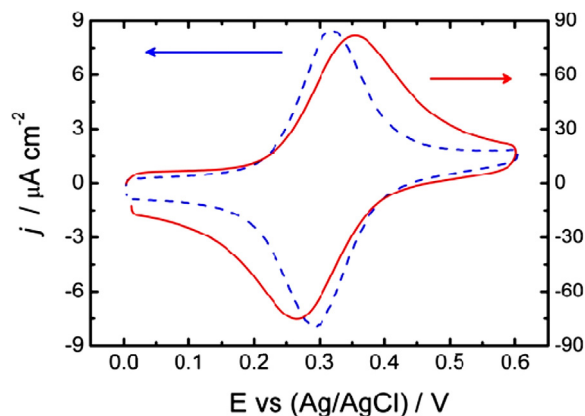


Fig. 5. Cyclic voltammograms of thick OsPA-DS film deposited on ITO electrode. Blue (dashed trace), CV at 25 mV s^{-1} (current density scale on the left side of the plot); Red (solid trace), CV at 500 mV s^{-1} (current density scale on the right side of the plot). Film thickness: $300 \pm 35 \text{ nm}$.

electron self-exchange between redox centers in the film in the form of an apparent diffusion coefficient (D_{app}). To simulate the cyclic voltammograms, it is necessary to know the concentration of redox centers. They were determined calculating the charge from cyclic voltammograms whereas the film thickness was determined by profilometry. Taking these two parameters into account and considering the electrode area, the nominal concentration of redox centers yields a value of $9 \pm 1 \text{ mM}$.

The charge propagation within the film, occur by electron self-exchange or “hopping” between reduced and oxidized forms of the redox centers. This charge transfer process is commonly described by an apparent diffusion coefficient D_{app} .^[34] In a previous work,^[20] we have estimated the value of the diffusion coefficient for a film of similar characteristics as $1.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, using this value and modeling cyclic voltammograms at different scan rates the standard electron transfer rate constant (k_0) was estimated to be $2.0 \times 10^{-4} \text{ cm s}^{-1}$. The k_0 observed for the osmium complex on ITO is comparable to the one obtained by Tagliazucchi and Calvo ($1.5 \times 10^{-4} \text{ cm s}^{-1}$)^[24] for a self-assembled system composed by polyvinylsulfonate and polyallylamine derivatized with the same osmium complex. On the other hand, a systematic work by Forster and Vos on electron hopping in redox hydrogel films,^[35–38] exemplified by poly(4-vinylpyridine) with part of the pyridines coordinated with $[\text{Os}(\text{bpy})_2\text{Cl}]^{+2+}$, also reported D_{app} values in the order of $10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

As the electrode modification is carried out by a spreading a solution, in this case it is easier to build thicker layers respect to the layer by layer deposition method. The effect of the thickness layer and the applied scan rate has an important impact in cyclic voltammograms shape. For thin film and/or slow scan rates, all the redox centers are involved in the electron exchange process and a symmetrical bell shape voltammogram is observed for oxidation and reduction process. For thick films and/or fast scan rates, not all the redox centers are involved in the electron exchange process, a concentration profile through the film is produced and the voltammogram presents a different shape characterized by the potential peak separation between the oxidation and reduction process.

A cyclic voltammogram describing the electrochemical response of an ITO electrode modified with a thicker film ($300 \pm 35 \text{ nm}$) is presented in Fig. 5. It can be observed that at high scan rates (500 mV s^{-1}) the voltammogram adopts the typical shape of a voltammetric response governed by semi-infinite diffusion process, while at slower scan rates (25 mV s^{-1}), the shape of the voltammogram resembles a bell, typical of a thin layer system. In the first case, the diffusion layer is very thin and the film behaves almost as a viscous solution; comparing the

two peak currents, it can be observed an increase of ca. 10 times between the cyclic voltammograms at 25 and 500 mV s⁻¹. This results does not correspond to a linear increase with the scan rate (20 times), neither with the square root (ca. 4.5 times); showing a more complex behavior that can be described by the diffusion in a medium bounded by two parallel planes as it will be described further on.

In the supplementary information, results from the computing simulation show very good agreement with the experimental results involving not only the dependence of the current density in the potential scan rate (Figure S3) but also the intensity, shape and position of the voltammetric peak and it represents the best fit found for the voltammogram (Figure S4). In addition, the simulation is able to estimate the concentration profiles at different potentials showing a mixed behavior between the whole consumption of the redox species throughout the film at slow scan rates, typical of thin layer experiments (Figure S5a); and a concentration gradient close to the electrode surface, at fast scan rates (Figure S5b), as it happens with species in solution. This mixed behavior explains the fact that peak current scales neither linearly nor with the square root of the scan rate as it was shown in Figure S3.

Glassy carbon was another conducting surface where the complex OsPA-DS was tested. In this case the modification was carried by drop coating, producing a thick film with a meniscus shape and an average thickness of $2.0 \pm 0.6 \mu\text{m}$. The modified electrode presents a good stability comparable to those observed for ITO and gold. The response of this modified electrode at 100 mV s⁻¹ presents an efficient current propagation that can be practically regarded as the response of a redox species in a solution (Figure S6). As it is happened in the case shown in Figure S5b, there is not a complete consumption of the osmium present in the modified electrode, here being apparent at a slower scan rate.

4. Conclusions

In this work a comprehensive characterization of a redox polyelectrolyte-surfactant complex is presented. The system is composed by polyallylamine modified with an osmium complex (OsPA) and dodecyl sulfate (DS) yielding a precipitate soluble in DMF. The organic solution behaves as a varnish, able to modify with the same procedure different type of surfaces (graphite,[20] gold,[20] ITO, glassy carbon and silicon) forming a very stable film in all cases. On the four conducting surfaces, the osmium complex presents a fast heterogeneous rate coefficient, suggesting an outer sphere mechanism where reactants, products, and intermediates do not interact strongly with the electrode material.[39]

In contrast to the lamellar order observed for PA-DS complex, GISAXS patterns for OsPA-DS films suggest that a fraction of the lamellar domains are oriented perpendicular to the substrate. This would indicate that the presence of osmium complexes alters the orientation in such a way that the connectivity of the redox polyelectrolyte domains with the conducting substrate would be facilitated; this represents a striking difference with redox-active polyelectrolyte multilayers where interdiffusion of the polyelectrolyte chains plays an important role in electron transport process.[7] Another important difference with PEMs is given by contact angle experiments showing that the hydrophilic moieties present in both species have a strong interaction between them, exposing the hydrophobic regions to the solution. This interaction yields a compact structure, allowing an efficient current propagation throughout relatively thick films with high apparent diffusion coefficients.

Finally, the effect of the ionic strength increase on the film shifting the redox potentials to more cathodic potentials is consistent with the increasing electrostatic interaction with free anions

in the bathing electrolyte stabilizing the extra positive charge on the redox moiety due to the oxidation process. This fact reveals that ions in the electrolyte solution are free to permeate across the film allowing the interaction with the hydrophilic polyelectrolyte domains. This behavior represents an excellent trade-off between the stability of film exposed to an aqueous solution and its ability to transfer electrons to/from the electrode surface and ions to/from the electrolyte solution. In addition, the capability of these films to interact with species in solution render them excellent candidates for the creation of composite films incorporating catalytic elements, for example glucose oxidase for the construction of biosensors.[20]

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2013.11.188>.

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