Metal-ion responsive redox polyelectrolyte multilayers†

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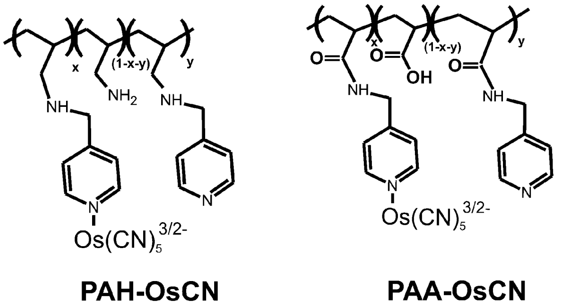
We present polyelectrolyte multilayer modified electrodes exhibiting novel chemically responsive redox behaviour due to the combination of both redox and metal-ion–ligand functionalities on the same sites.

Responsive materials embrace several kinds of bulk and surface systems that can alter their structure, behaviour or physical properties as a response to a change in their chemical or physical environment.[1] Among them, electrodes modified with thin responsive polymers and polyelectrolytes allow stimuli-gated electrochemical behaviour and find applications in sensing,[2] chemical logical gates and transistors[3,4] and switchable energy devices.[5] For example, several kinds of pH-dependent electrochemical and ion gates have been constructed using weak polyelectrolyte multilayers, brushes or hydrogels.[3,6,7] Electrochemical devices sensitive to temperature,[7] cholesterol concentration[2] and the presence of hydrophobic anions[8] have also been reported. While most examples rely on electroactive probes in solution (such as $Fe(CN)_6^{4-/3-}$ or $Ru(NH_3)_6^{2+/3+}$) to transform a chemical or physical input into an electrochemical response, there also exist reports describing integrated surface confined redox systems.[3,4,9–11] The potential applications for chemically gated electrodes are well demonstrated by these previous reports, although the spectrum of available chemical stimuli is still narrow.

In this work, we introduce novel redox polyelectrolyte multilayers that reversibly switch off their electrochemical activity as a response to micromolar concentrations of transition metal ions and analyze the underlying mechanism of this unusual behaviour. The films under study are based on redox polymers composed of osmium pentacyano pyridine complexes tethered to poly(allylamine) (PAH–OsCN) or polyacrylic acid (PAA–OsCN) backbones. The structures of these polyelectrolytes are shown in Scheme 1 and their synthesis and characterization is described in the ESI†.



Scheme 1 Molecular structure of the redox polymers PAH–OsCN (pentacyano osmate modified poly(allyamine)) and PAA–OsCN (pentacyano osmate modified polyacrylic acid).

The cyclic voltammograms for PAH–OsCN/poly(vinyl sulfonate) and PAA–OsCN/poly(allylamine) multilayer films in 0.2 M KNO_3 are depicted in Fig. 1A and B, respectively (solid black lines). Both systems show a well defined redox peak around 0.52 V *vs.* Ag/AgCl; 3 M Cl, corresponding to the Os(II/III) couple.[12] Addition of the electroinactive cation Zn^{2+} to the solution has a dramatic effect on the current potential waves for both electrodes, producing the disappearance of the redox peak (red dashed lines). While the redox activity of the Zn^{2+} treated samples was not recovered by rinsing with water and measuring in a metal-free electrolyte, it is possible to completely restore the redox peak by treating the electrode with a 10 mM solution of the metal chelating agent EDTA for a few minutes (dotted dash blue lines). This observation indicates a strong interaction between the metal ion and the sample. Switching the redox response off/on with Zn^{2+}/EDTA can be repeated several times with little loss of the redox charge, as shown in Fig. 1C for the electrode in Fig 1B.

Fig. 1D shows the current potential waves recorded for the electrode in Fig. 1A and increasing Zn^{2+} concentration in solution. It can be observed that the electrochemical response is affected by even submicromolar concentrations of the metal ion. For instance, the inset shows that a concentration of Zn^{2+} of 0.5 μM decreases the Faradaic current to half its initial value. We found that other transition metal ions such as Cd^{2+}, Ni^{2+} and Cu^{2+} affect the redox response in a similar way to Zn^{2+}, but interestingly, Ca^{2+}, Pb^{2+} and La^{3+} produced no changes in the electrochemical response up to 10 mM concentration (see ESI†). In addition, a film made of poly(vinyl sulfonate) (PVS) and an osmium pyridine–bipyridine derivatized poly(allylamine) (PAH–Os)[13] was not affected by the presence of Zn^{2+} up to a concentration of 10 mM. These results suggest that the effect under study has an origin in the interaction between the transition metal ions and the osmium pentacyano redox couple, which is consistent with the well known ability of these cations to form precipitates with hexacyanometallate anions in solution.[14–16]

The C–N stretching band in the ATR-FTIR spectra of the films provides spectroscopic evidence of the local environment of the redox couple. This band is located at 2035 cm^{-1} for a freshly prepared PAH–OsCN/PVS multilayer (Fig. 2A and

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† Electronic supplementary information (ESI) available: Synthesis and characterization of the redox polyelectrolytes PAH–OsCN and PAA–OsCN, experimental methods and effect of different metal ions on the redox response of PAH–OsCN/PVS films and cyclic voltammograms for a $(PAH–OsCN/PVS)_4PAHOs–CN$ multilayer on HOPG. See DOI: 10.1039/c0cc02738c

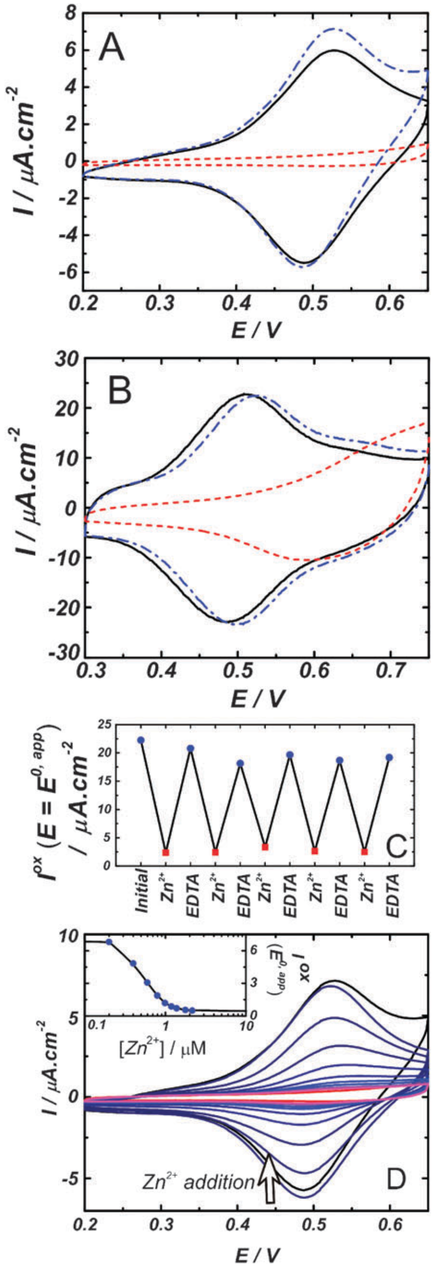

Fig. 1 Cyclic voltammograms for (PAH–OsCN/PVS)$_4$PAH–OsCN (A) and (PAA–OsCN/PAH)$_4$PAA–OsCN (B) in 0.2 M KNO$_3$ before (black solid line) and after (red dashed line) the addition of Zn^{2+} up to a final concentration of 1 mM Zn^{2+}. The electrodes were washed with 10 mM EDTA for 5 minutes and the cyclic voltammetry was recorded in 0.2 M KNO$_3$ (blue dotted dash line). (C) Current of the anodic scan at $E = E^{0,\mathrm{app}}$ for the electrode in B for several Zn^{2+}/EDTA treatments. (D) Cyclic voltammograms for the electrode in A in 0.2 M KNO$_3$ solution for different Zn^{2+} concentration in solution (in the direction of the arrow: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.8, 2.0 and 1000 μM). The inset shows the anodic current at $E = E^{0,\mathrm{app}}$ as a function the Zn^{2+} concentration.

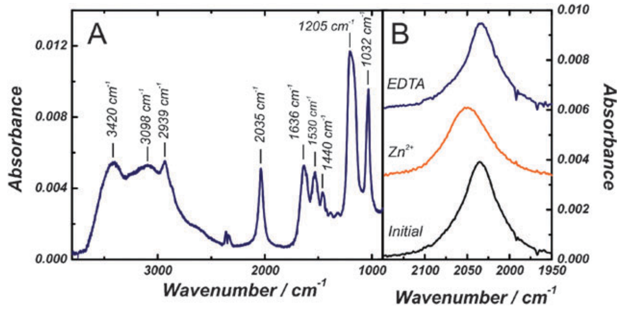

Fig. 2 (A) ATR IR spectrum of a freshly prepared (PAH–OsCN/PVS)$_8$PAHOsCN film. (B) ATR IR spectra in the ν_{CN} region for the film in A (lower spectrum), after immersion in 10 mM Zn^{2+} for 10 min, rinsing with water and blow drying with N$_2$ (middle spectrum) and after treatment with 10 mM EDTA for 10 minutes, rinsing with water and drying with N$_2$ (upper spectra).

upper curve in Fig. 2B, see ref. 12 and 17 for the assignment of the other bands in the spectrum). Treating the film with 10 mM Zn^{2+} produces a 15 cm^{-1} shift of the ν_{CN} band to higher wavenumbers which is ascribed to the formation of an Os–CN–Zn structure based on observations in hexacyanometallate solids and polynuclear complexes.[16,18,19] This effect was suggested to occur due to kinematic coupling between the nitrile bridge and the N-coordinated metal center, which hinders the vibration of the CN bond.[18] The shift of ν_{CN} band is completely offset after dipping the electrode in 10 mM EDTA for 10 minutes (Fig. 2B).

We found that treating PAH–OsCN/PVS samples with other metal ions that switch off the electrochemical response also increases ν_{CN} by 3 cm^{-1} for Ni^{2+}, 5 cm^{-1} for Cd^{2+} and 21 cm^{-1} for Cu^{2+}. On the other hand, no changes in the CN stretching frequency were observed for Ca^{2+}, La^{3+} and Pb^{2+} treated samples. These cations do not affect the electrochemical response and hence do not interact with the Os–CN complex. It is worthwhile to note that the CN stretching IR-peaks indicate that Os complexes are fully reduced for all these samples, since the frequency shift introduced upon oxidation is larger than those observed in this work and it is accompanied by a decrease in the extinction coefficient.[12]

X-Ray photoelectron spectroscopy was used to analyze film stoichiometry. For PAH–OsCN/PVS samples treated with 10 mM solutions of Zn^{2+} and Cu^{2+}, this technique yields metal ion to osmium complex ratios of 0.51 and 1.1, respectively. These values are lower than 1.5 expected for an electrically neutral adduct between M^{2+} and [Os(CN)$_5$pyX]$^{3-}$, probably due to the topological constraints introduced by the polymeric network that hinder the formation of complexes between the metal ions and the pentacyano sites. The pairing of the negatively charged osmium complexes and the positive amino groups in PAH–OsCN can also lead to deficient complexation of the transition metal ions. When the samples were treated with 10 mM Ca^{2+}, XPS did not detect this cation in the film, in agreement with its lack of effect on the redox response and the CN IR-band frequency.

The results presented so far demonstrate the interaction of transition metal ions with the osmium sites in the film, although is not yet clear how this interaction blocks the redox response. A possible mechanism would involve a shift of the redox potential of the [Os(CN)$_5$pyX]$^{3-}$–M^{2+} couple outside the electrochemical window. For instance, cyclic voltammetry for layer by layer films containing Prussian Blue nanocrystals display a Fe(II/III)CN redox peak at 0.85 *vs.* SCE.[20] For

Os(II/III)CN, the redox potentials in osmium purple have been reported around 0.9–1.0 V.[14] In our case, no redox peaks assignable to an Os(II/III)–CN–M^{2+} have been observed in experiments performed on HOPG with a broader electrochemical window (see ESI†). Furthermore, since there is only approximately one Zn^{2+} per two Os sites, one should expect to observe the redox peak of the unbound $[Os(CN)_5pyX]^{3-}$, but the experiment in Fig. 1A shows that this peak almost completely disappears after Zn^{2+} treatment. While these results do not discard a shift in the redox potential, they indicate that this shift is not responsible for switching off the redox activity. We propose an alternative mechanism that hinders the propagation of the electrochemical response into the film upon metal ion binding.

It is known that the mobility of polymer tethered redox groups around their equilibrium positions plays a key role facilitating the electron hopping mechanism between neighboring sites (bound diffusion mechanism).[21] The dependence of the electrochemical response on the mobility of the redox sites is a well established concept in the electrochemical literature. For example, it has been shown that increasing the length of the linker connecting the polymer backbone to the redox couple increases the mobility of the latter, resulting in a great enhancement of charge transport.[22] Both in polyelectrolyte multilayers[10] and in random hydrogels,[23] it has been shown that hydrophobic anions such as perchlorate, can decrease the electron diffusion coefficient. This is due to the formation of ion pairs between anions and the redox complexes and amino groups in the film that limit polymer dynamics. Provided that the transition metal ions can bridge two or more osmium pentacyano sites,[14,16,18,20,24] metal ion binding can drastically decrease site mobility in PAH–OsCN and PAA–OsCN multilayers, hindering the redox process. Since immobilization of a given number of the redox sites is sufficient to suppress the percolation across the entire film, the redox reaction would be blocked even for a Zn/Os ratio smaller than 1, consistent with the experimental evidence.

The blocking effect of the transition metal ions on the electrochemical response of osmium pentacyano based polymers disclosed here for the first time is an interesting concept with a very sharp transition between active and blocked states and can be achieved with micromolar cation concentrations. This behaviour results from the high affinity of the osmium pentacyano groups towards low concentration of transition metal ions, unlike hydrophobic anions that require high millimolar concentrations to affect the electrochemistry of Os pyridine–bipyridine based polymers[10,23] and ferrocene tagged polyelectrolyte brushes.[9] The concept of a chemically switchable redox system arising from the combination of redox and ligand/receptor functionalities in the same group has further important implications for the emerging field of responsive materials. We foresee this concept generalized in the future to other species of interest, bringing novel tailor-made redox systems with chemically gated activity for applications in sensors and switchable electrochemical devices.

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