Supporting Information

Metal-ion Responsive Redox Polyelectrolyte Multilayers

Experimental Section

Chemicals and Solutions. 3-Mercapto-1-propanesulfonic acid sodium salt, MPS (Aldrich); Cysteamine (Aldrich); poly(acrylic acid) sodium salt, PAA (Aldrich, 35% in water Mw 100000); poly(allylamine) chloride salt, PAH (Aldrich Mw 56000) and poly(sodium vinyl-sulfonate), PVS (25 wt. % solution in water, Aldrich) were used as supplied. Other reagents were analytical grade and were used without further purification. Polyelectrolyte solutions were prepared with 18 MΩ.cm Milli-Q (Millipore) deionized water and their pH was adjusted to pH 7 (PAH-OsCN, PVS and PAH) or pH 4 (PAA-OsCN) using either HNO_3 or NaOH 0.1 M. The polyelectrolyte concentrations were 10 mM for PVS and PAH. The redox polymers PAH-OsCN and PAA-OsCN were adsorbed from 2 mM solutions, as determined from the UV-vis spectrum of working solution and the ε_{MLCT} ($[Os(CN_5)py]^{3-}$) = 5460 M^{-1} cm^{-1} [1].

Synthesis of PAH-OsCN. The redox polyelectrolyte PAH-OsCN was prepared as described previously[2] from a pyridine modified poly(allylamine) (PAH-py) (prepared according refs. 2 and 3, see NMR spectrum in Figure 1S) and the complex $K_2[Os(CN)_5NO].H_2O$, prepared and purified according to the literature[1, 4, 5]. The complex-substituted polymer was purified by dialysis against NaCl 0.5 M + HNO_3 1 mM for 2 days and against MilliQ water for 5 days.

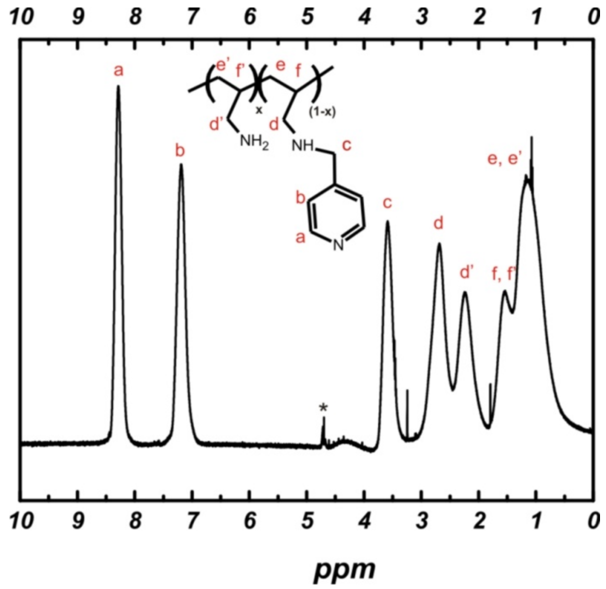

Figure 1S: ^{1}H NMR spectra of PAH-py. * HDO/H_2O (suppressed)

The identity of the product was analyzed by UV-VIS in solution, FTIR in KBr pellet and XPS (NMR was not performed because the freeze dried solid was insoluble in any available deuterated solvent). The FTIR spectrum (Figure 2S-A and 2S-B) shows a very intense band at 2035 cm^{-1} that is absent in the PAH-py spectrum and can be assigned to the C≡N stretching mode in the reduced -$Os(CN)_5$ group. Both the PAH-OsCN and PAH-py shows a small band at 3060 cm^{-1} and several bands in the range 1600-1200 cm^{-1} (i.e. the band at 1414 cm^{-1}) that can be assigned to pyridine aromatic C-H stretching mode and ring stretching vibrations, respectively[6]. The UV-vis spectra of PAH-OsCN (Figure 2S-C) shows the metal to ligand charge transfer (MLCT) band at 324 nm, close to the literature value for the complex $[Os(CN)_5py]^{3-}$, λ_{MLCT} = 318 nm[1]. The XPS spectra (recorded for a $(PAH\text{-}OsCN/PVS)_8PAH\text{-}OsCN$ multilayer, see Figure 3S) shows well defined peaks in the Os 4f and N 1s regions. The N 1s peak can be deconvoluted into three peaks. The highest BE peak (402.3 eV) is assigned to protonated amino groups and pyridine groups[7]. Deprotonation of these groups decreases the BE, giving rise to the peak at 400.4 eV, which can be assigned to the convolution of unprotonated amino and pyridine moieties[7]. Finally the lowest BE peak

(398.3 eV) can be assigned to the CN ligand in the osmium complex[8, 9]. The atomic N(CN)/Os ratio determined from these spectra is 4.4, close to the expected value of 5.

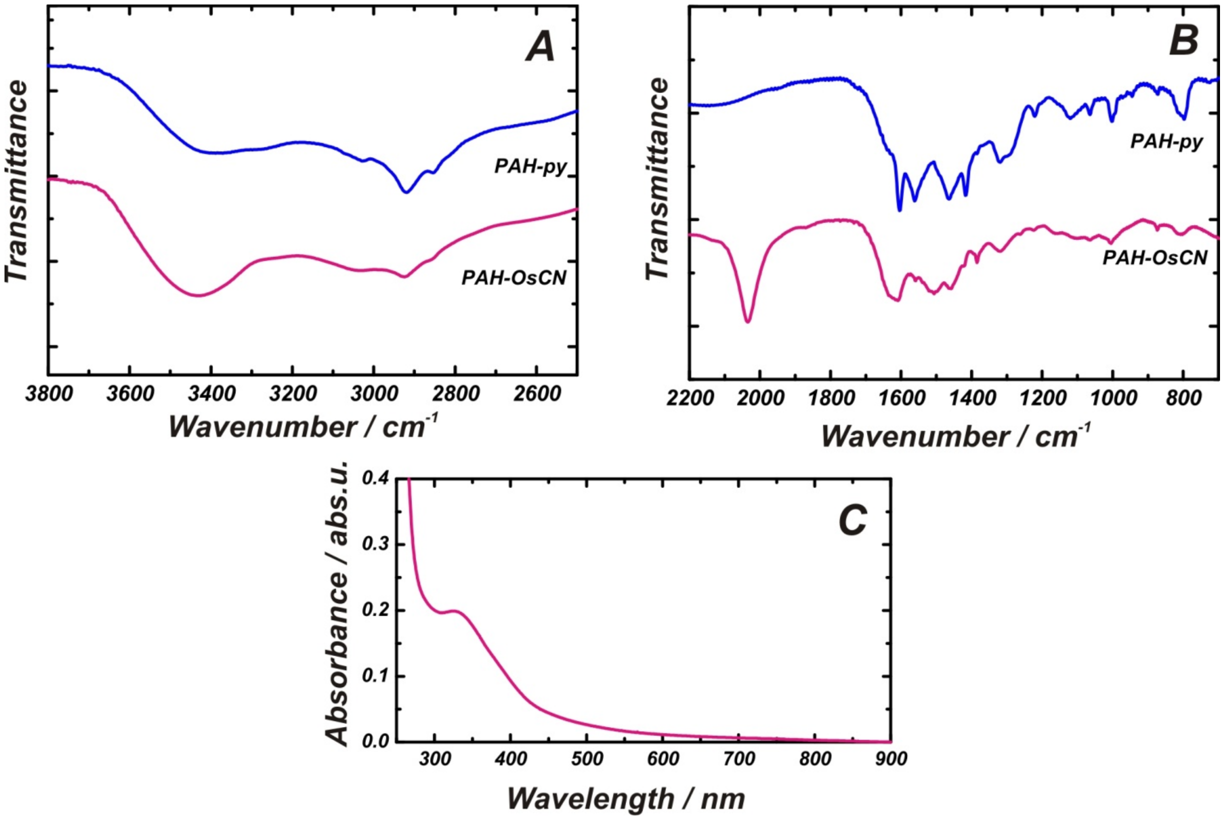

Figure 2S. Transmittance FTIR spectra in KBR pellet for PAH-py and PAH-OsCN in the 3800-2600 cm^{-1} (A) and 2200-700 cm^{-1} (B) regions. C. UV-vis spectra for a PAH-OsCN in solution.

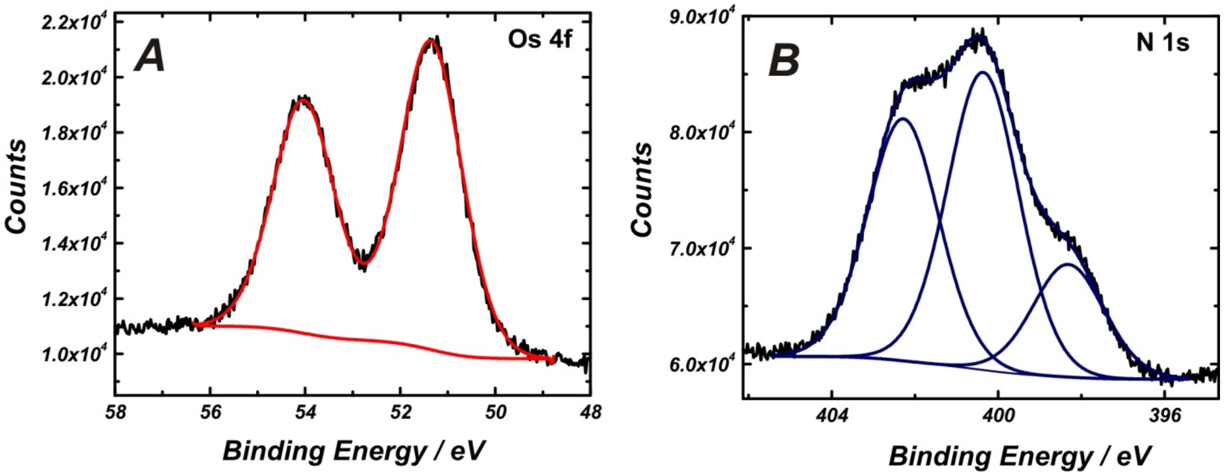

Figure 3S: XPS spectra for a $(PAH\text{-}OsCN/PVS)_8PAHOsCN$ in the Os 4f (A) and N 1s (B) regions.

Synthesis of PAA-OsCN.

The osmium pentacyano modified poly(acrylic acid) was prepared from pyridine modified poly(acrylic acid) (PAA-py) and the complex $K_2[Os(CN)_5NO].H_2O$.

PAA-py was synthesized by mixing 200 mg of PAA sodium salt (2.1 mmol) dissolved in 10 ml of anhydrous N-Methyl-2-pyrrolidone (NMP) with 500 mg of N,N'-dicyclohexylcarbodiimide (DCC) and 300 mg of N-Hydroxysuccinimide (NHS) dissolved in 5 ml of anhidrous NMP. The mixture was heated at 60ºC for 1 hour. After that period, the N,N'-dicyclohexylurea precipitate was filtered and 360 µl of picolylamine (3.3 mmol) were added to the solution. The reaction was left to proceed overnight at 60ºC, the final solution was diluted with water and purified by dialysis against MilliQ water for a week. The final product was analyzed by ^1H NMR (Figure 4S) and FTIR in KBr pellet (Figure 5S). The FTIR spectrum shows a small band at 3060cm^{-1} and several bands in the region 1600-1200 cm^{-1} that correspond to the pyridine groups[6].

PAA-OsCN was prepared by dissolving 40 mg of $K_2[Os(CN)_5NO].H_2O$ and 20 µl of N_2H_4 in 5 ml of methanol:water 1:1. Attack of the NO group by hydrazine after 24 hours at room temperature was confirmed by the disappearance of its characteristic visible absorption band at 420 nm [4]. The solution was mixed with 70 mg of PAA-py dissolved in water and the final pH was set to 6 with acetic acid. The reaction was left to proceed for 3 days at 65ºC under Ar atmosphere and the final product was purified by dialysis against NaCl 0.5 M for 2 days, followed by dialysis against MilliQ water for a week.

The identity and purity of the final product was confirmed by ^1H NMR (Figure 4S). The H_a y H_b peaks in PAA-py spectra split after $Os(CN)_5^{3-}$ coordination to some of the pyridine groups. These observation is consistent with the chemical displacements of aromatic protons in pyridine and $[Fe(CN)_5py]^{3-}$ [10, 11]. Additional spectroscopic evidence for the proposed structure is given by the presence of the CN stretching band around 2035 cm^{-1} in the FTIR absorption spectra in KBr pellet (Figure 5S) and the MLCT band of the osmium complex at 318 nm (λ_{MLCT} = 318 nm for $[Os(CN)_5py]^{3-}$ [1]) in the UV-VIS absorption spectra in water solution.

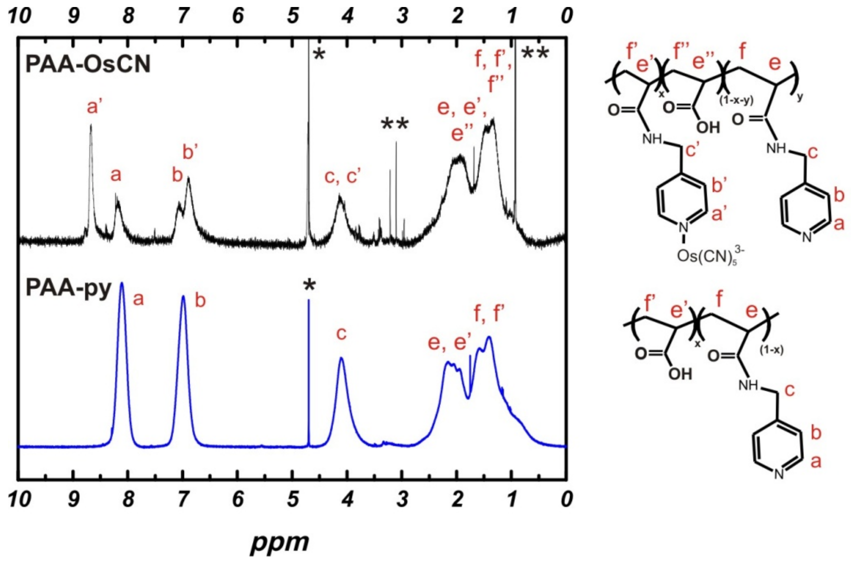

Figure 4S: ^1H NMR spectra for PAA-py and PAA-OsCN. * HDO/H_2O (suppressed), ** unidentified impurity.

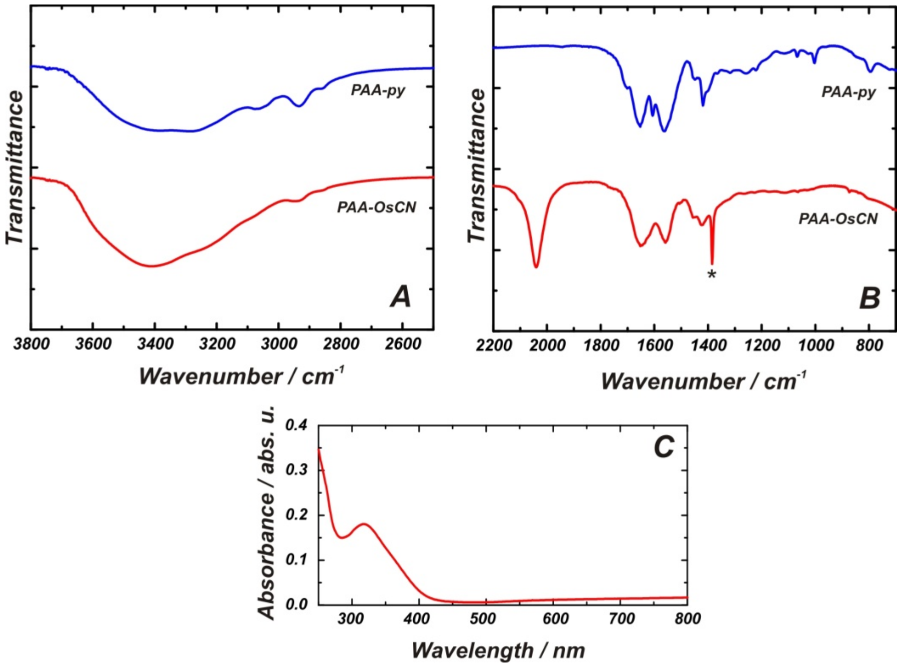

Figure 5S. Transmittance FTIR spectra in KBR pellet for PAA-py and PAA-OsCN in the 3800-2600 cm^{-1} (A) and 2200-700 cm^{-1} (B) regions. * NO_3^- band from HNO_3 used to bring the solution to the final pH (1380 cm^{-1}).C. UV-vis spectra for a PAA-OsCN in solution.

Surface Modification. Silicon (100) substrates coated with 200 nm gold layer on a 20 nm titanium and 20 nm palladium adhesion layer by thermal evaporation (Edwards Auto 306 vacuum coating system) were employed as electrodes and substrates for ATR-FTIR and XPS spectroscopies.

Electrodes were electrochemically cleaned by potential cycling in 2 M sulfuric acid between 0.2 and 1.6 V at 10 V.s^{-1}, followed by one scan at 0.1 V.s^{-1} to check for surface contamination and determine the electrochemically active area from the reduction peak of gold oxide[12]. Clean gold film substrates were primed either with sulfonate or amino groups by immersion in a 50 mM MPS solution in H_2SO_4 10 mM for 30 min or in 0.1 mg/ml cysteamine in ethanol for 2 hours, respectively.

After thiol adsorption and rising with water, the first polyelectrolyte layer was deposited on the thiol-modified Au surface by 15 min dipping in PAH-OsCN or PAA-OsCN solution for Au/MPS and Au/cysteamine, respectively, followed by rinsing with Milli-Q water. The next and subsequent layers were deposited onto the modified surface by alternate immersion in polyelectrolyte solutions for 15 min and rinsing with Milli-Q water until the desired number of layers was achieved. In the case where HOPG was used as a substrate, multilayer built up was performed on the freshly cleaved surface as described above, employing PAH-OsCN in the first adsorption step.

Electrochemical Experiments. Cyclic voltammetry measurements were carried out at room temperature with an Autolab PGSTAT 30 potentiostat (Autolab, Ecochemie, Holland) in a purpose built three electrode Teflon cell, with an electrode exposed area of approximately 0.25 cm^2 delimited by an inert O-ring. A Ag/AgCl; 3 M KCl (0.210 V vs. NHE) was employed as reference electrode and all electrode potentials herein are quoted with respect to it; a platinum gauze auxiliary electrode of large area was used.

Attenuated Total Reflection Infrared Spectroscopy: ATR measurements were performed with a Nicolet Magna 560 FTIR spectrometer equipped with a Spectra-Tech Foundation Thunderdome single reflection ATR Germanium crystal and a MCT-A cryogenic detector. Spectra were acquired with a 2 cm^{-1} spectral resolution integrating 1000 interferogram scans.

X-Ray Photoelectron Spectroscopy. X-ray Photoelectron Spectroscopy measurements (XPS) were performed under UHV conditions (base pressure < 5.10^{-10} mbar) in a SPECS UHV spectrometer system equipped with a 150 mm mean radius hemispherical electron energy analyzer and a nine channeltron detector. XPS spectra were acquired at a constant pass energy of 20 eV using an un-monochromated MgKα (1253.6 eV) source operated at 12.5 kV and 20 mA and a detection angle of 30 degrees with respect to the sample normal. Quoted binding energies are referred to the Au $4f_{7/2}$ emission at 84 eV. Atomic ratios were calculated from the integrated intensities of core levels after instrumental and photoionization cross-section corrections.

Effect of different cations on the electrochemical response of PAH-OsCN/PVS multilayers

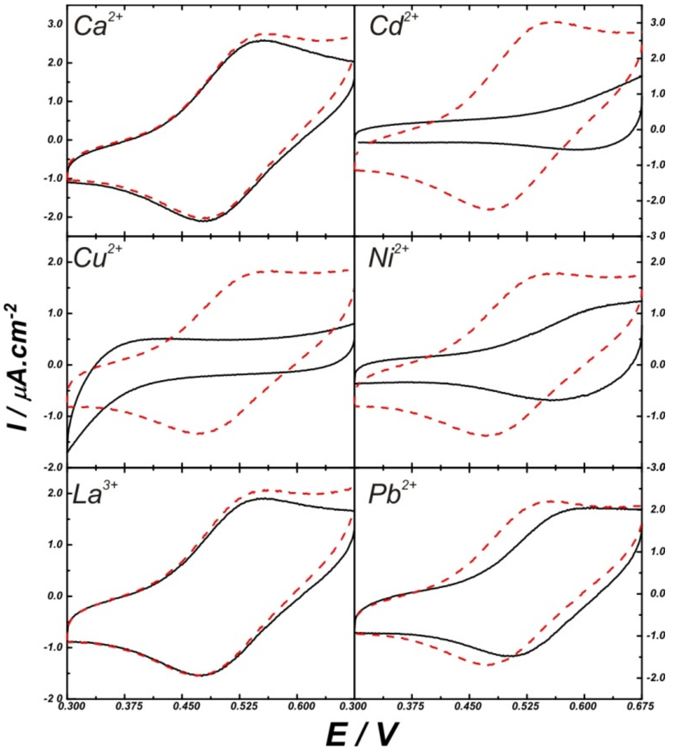

Figure 6S. Effect of different metal ions on the redox response of $(PAH\text{-}OsCN/PVS)_3PAHOs\text{-}CN$ multilayers. Films were immersed for 5 minutes in a 10 mM solution of the metal ion, rinsed with water and tested with CV (black lines). The electrodes were then dipped in EDTA 10 mM for 5 minutes, rinsed and the CV was measured again (red dashed lines). Scan rate: 50 mV.s^{-1}.

Cyclic Voltammetry experiments for HOPG modified electrodes in a broad electrochemical window.

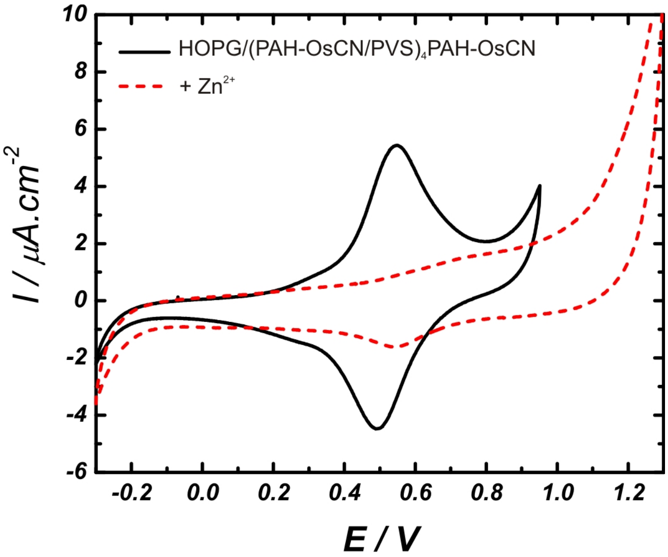

Figure 7S: Cyclic voltammograms for a (PAH-OsCN/PVS)$_4$PAHOs-CN multilayer on HOPG in KNO$_3$ 0.2 M (black line) and KNO$_3$ 0.2 M + Zn^{2+} 1mM (red dashed line). Scan rate: 50 mV.s^{-1}.

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