Donnan Potential in polyelectrolyte multilayer films made from poly-L-glutamic / polyallylamine hydrochloride and stability of hexacyanoferrate retention in the films.
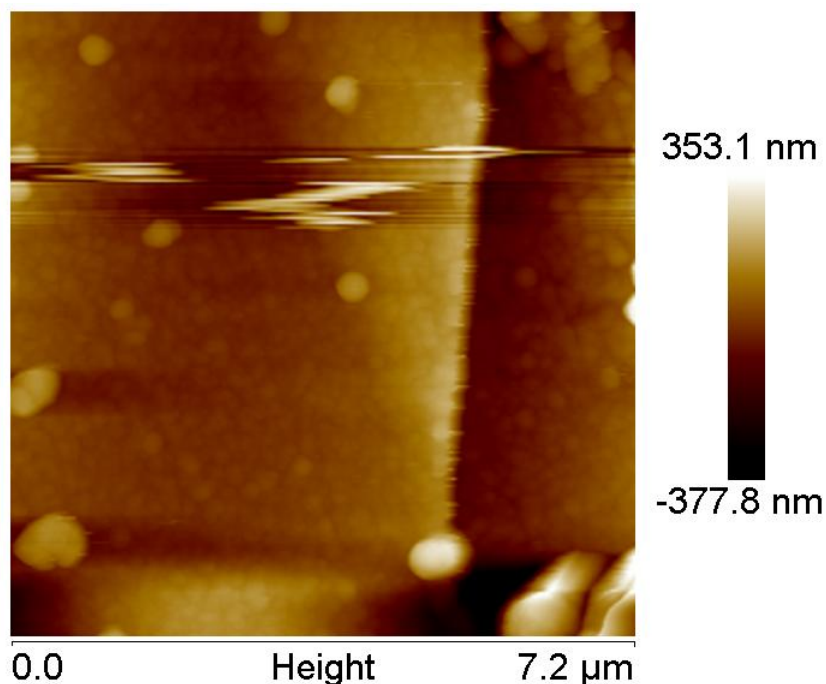
V. BALL

Supporting Information

Figure 1: AFM topography of a scratched region of a PEI-(PGA-PAH)$_{10}$ film put in contact with a 1 mM Fe(CN)$_6$$^{4-}$ containing solution during 25 min.

The surface concentration Γ in redox probes accessible to the electrode can be calculated from CV experiments performed at different scan rates [1]:

$$\Gamma = \frac{4.R.T}{n^2.F^2.A} \cdot \frac{i_p}{v} \qquad (1)$$

Where R, T, n, F and A are the gas constant, the absolute temperature, the number of electrons exchanged in one oxidation/reduction step (here $n = 1$), the Faraday's constant and the effective area of the electrode. Ip/v is the slope of the oxidation current peak versus the scan rate curves. A typical curve is represented in Figure 2 for a 2 mM $Fe(CN)_6^{4-}$ solution put in contact with a PEI-(PGA-PAH)$_{10}$ film during 25 min, the electrode being then immersed in a 0.15 M NaCl solution before performing CV experiments at different scan rates v. For scan rates higher than about 50-100 mV.s^{-1}, the linear dependence of I_p versus v does not hold anymore (Figure 4A of the main text). The surface concentration of electroactive species depends critically on the effective electrode area A. We assume herein that A is equal to the geometric area of the electrode, neglecting its roughness. For an electrode with 2 mm in diameter this leads to 3.14×10^{-6} m². This underestimation of A leads to an overestimation in the value of Γ.

Knowing the surface concentration of electroactive molecules one is able to calculate the volume concentration in electrically addressable redox probe via the film thickness, d:

$$C = \frac{\Gamma}{d} \qquad (2)$$

We take $d = 1$ µm $= 10^{-6}$ m herein which is consistent with the data in Figure 1 of the main text. We also make the assumption that the film does not swell substantially when put in contact with the $Fe(CN)_6^{4-}$ anions which is corroborated by our AFM measurements (Figure 2 of the main article).
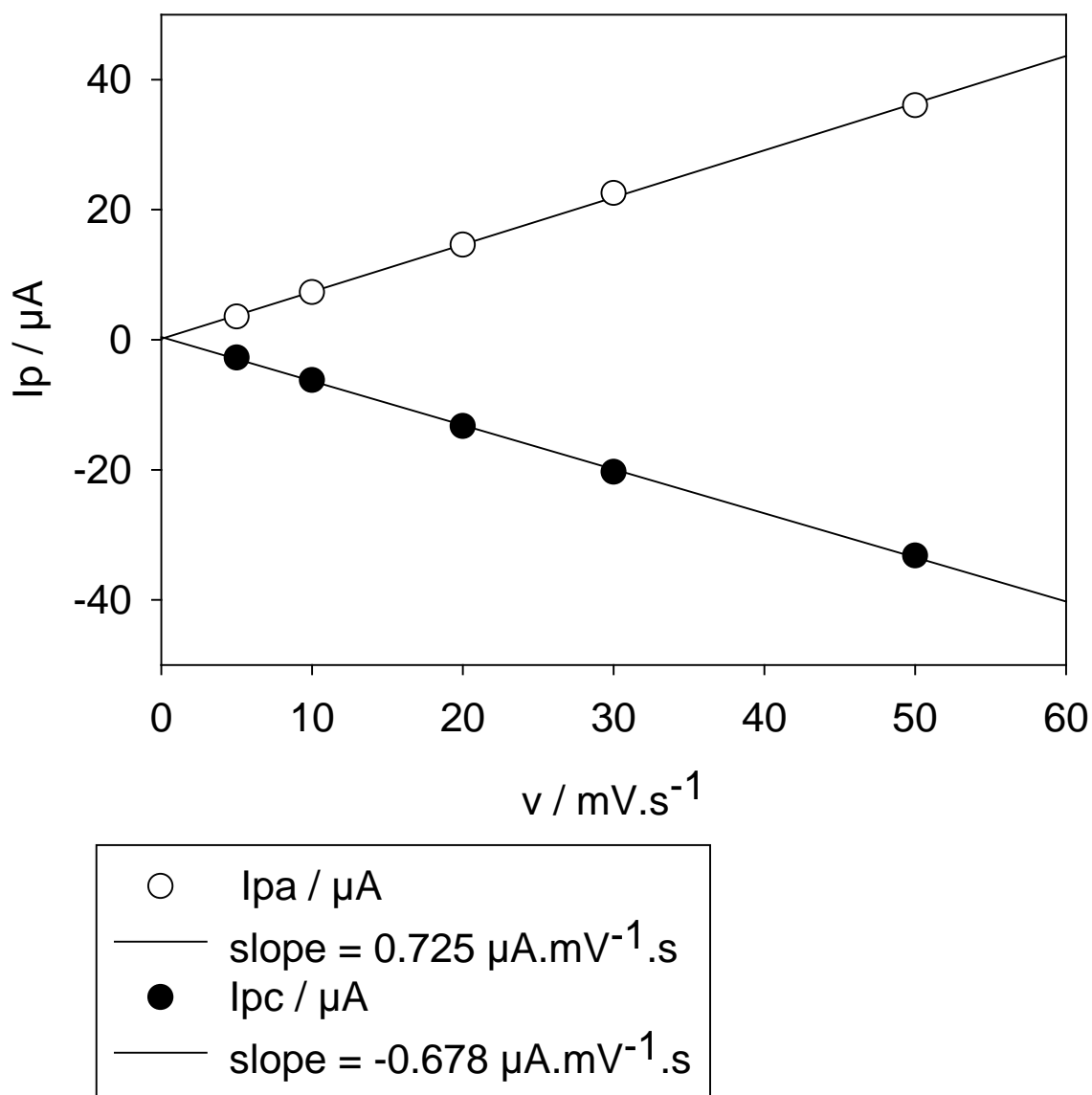
Figure 2: Oxydation (O) and reduction (●) peak currents as a function of the potential scan rate for $Fe(CN)_6^{4-}$ anions immobilized in a PEI-(PGA-PAH)$_{10}$ film. The film was put in the presence of $Fe(CN)_6^{4-}$ anions at 2 mM (in the presence of 0.15 M NaCl) during 25 min, rinsed with 0.15 M before measuring CV curves at different potential scan rates.

Taking all the results from curves as those shown in Figure 2, one obtains the variation of c , the concentration of electrically addressable redox probe in the PEI-(PGA-PAH)$_{10}$ films as a function of the $Fe(CN)_6^{4-}$ concentration in solution, Figure 3.
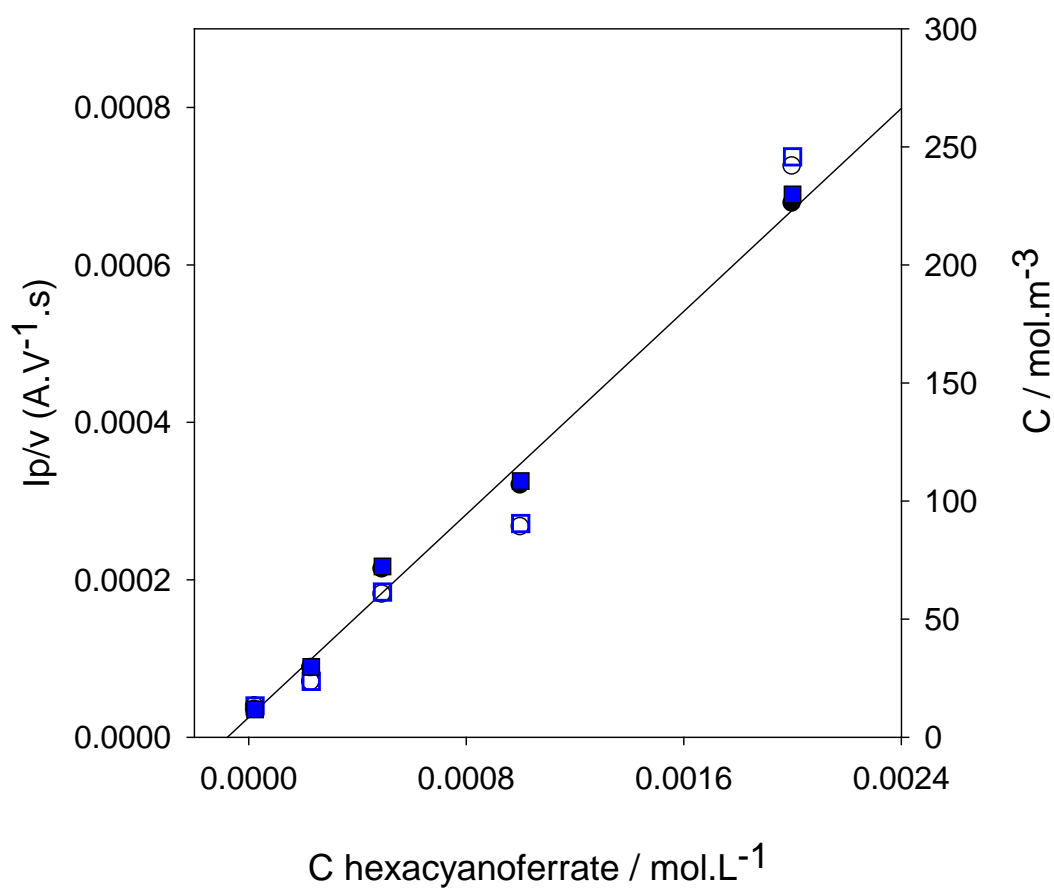
Figure 3: Left hand vertical scale: variation of the I_p/v values obtained from CV experiments, as those displayed in Figure 1, for PEI-(PGA-PAH)$_{10}$ films put in the presence of K$_4$Fe(CN)$_6$ containing solutions during 25 min, before rinsing with 0.15 M NaCl and CV measurements. The volume concentration of the electrically addressable redox probe is plotted on the right hand vertical scale, these data are calculated from the Ip/v values using equations (1) and (2.) The data from the oxidation and reduction currents are represented with □ and ■ respectively. The straight line corresponds to a linear regression to the experimental data.

Note that the concentration in the film reaches values as high as 0.250 mol.L^{-1}, ie 250 mol.m^{-3}, when the concentration of Fe(CN)$_6$$^{4-}$ in the solution was only of 2x 10^{-3} mol.L^{-1} . This result confirms results from previous studies [2] in which it was shown that PEM films made from PGA and PAH are able to entrap high concentrations in negatively charged redox

species. The surprising result obtained here is that the amount of addressable hexacyanoferrate in the film increases almost linearly (Figure 2) with the concentration in solution. One would have expected a "high affinity" type isotherm, ie an almost independent value of C with respect to the bulk concentration, indeed the amount of $Fe(CN)_6^{4-}$ anions in solution is always sufficient to saturate the film at 0.250 $mol.L^{-1}$. The lower value of incorporated $Fe(CN)_6^{4-}$ anions at lower concentrations in solution is not due to a kinetic limitation because the oxidation and reduction currents always reach saturation values after 20-25 min (data not shown). Hence to explain the shape of the binding isotherm displayed in Figure 3, it is assumed that the structure of the PEI-(PGA-PAH)$_{10}$ films changes to incorporate more hexacyanoferrate anions when the concentration of those species increases in solution.

Additional references:

[1] A.P. Brown, F.C. Anson, *Anal. Chem.* **1977**, *49*, 1589-1595.

[2] N. Laugel, F. Boulmedais, A.E. El Haitami, P. Rabu, G. Rogez, J.-C. Voegel, P. Schaaf, V. Ball, *Langmuir* **2009**, *25*, 14030-14036.