

Large distribution in the Donnan potential of hexacyanoferrate anions permeating in and partially dissolving (PAH-HA)_n polyelectrolyte multilayer films

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Supporting Information

Additional Figures

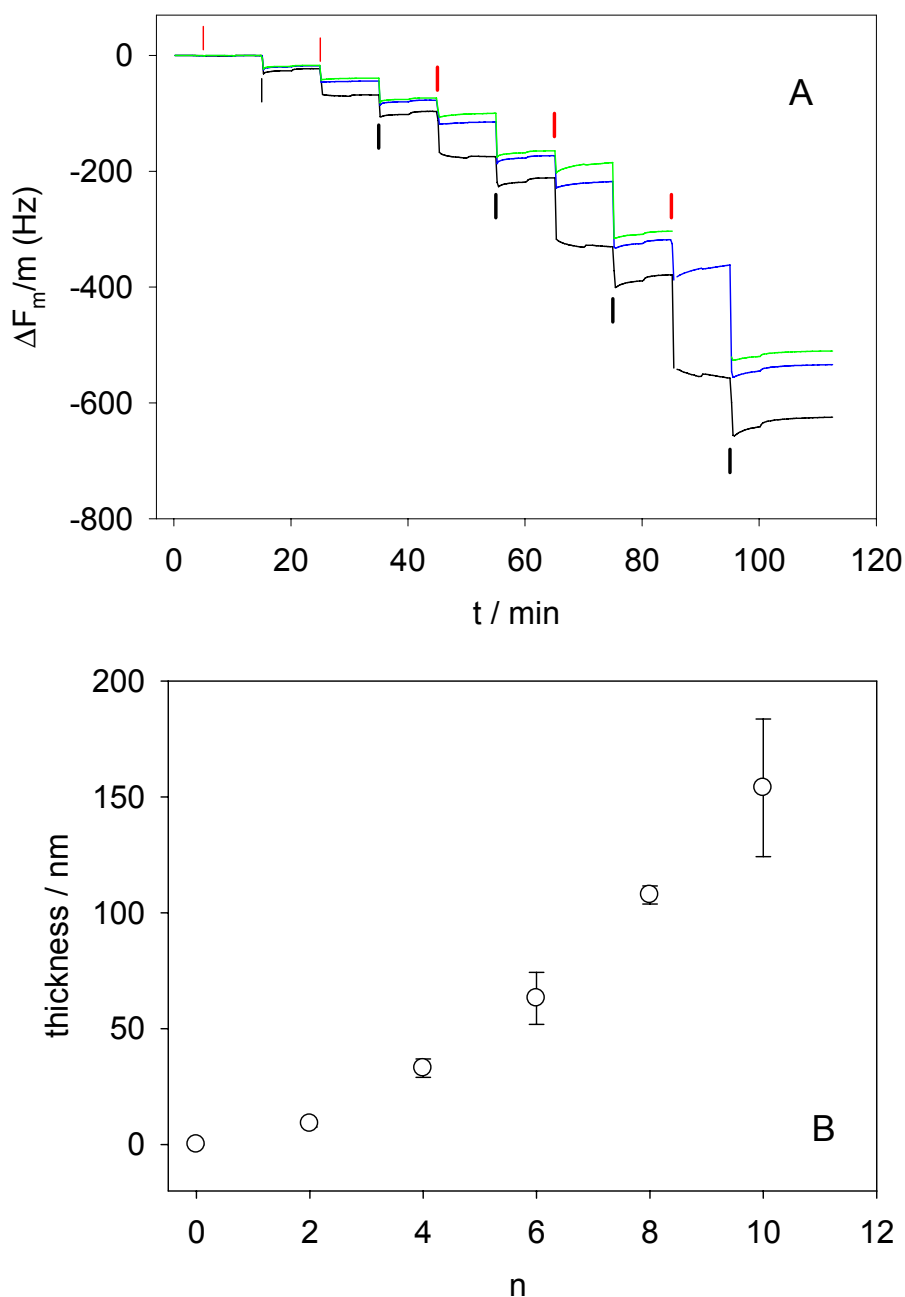


Figure S1: A. Kinetics of frequency changes monitored by means of QCM-D for a (PAH-HA)₅ film deposited in the presence of 0.15 M KCl at different overtones of the quartz crystal : third overtone (—), fifth overtone (—) and seventh overtone (—). The vertical red and black lines correspond to the injection of PAH and HA respectively. The opposite of the

reduced frequency changes, indicative of mass uptake by the quartz crystal, were obtained by measuring the absolute frequency changes and dividing them by the overtone number m .

B. Thickness increase of a $(\text{PAH-HA})_{n=10}$ film deposited in the presence of 0.15 M KCl monitored by means of ellipsometry in the dry state. Each point corresponds to the average over 5 measurements along the main axis of the silicon substrate. The error bars correspond to one standard deviation.

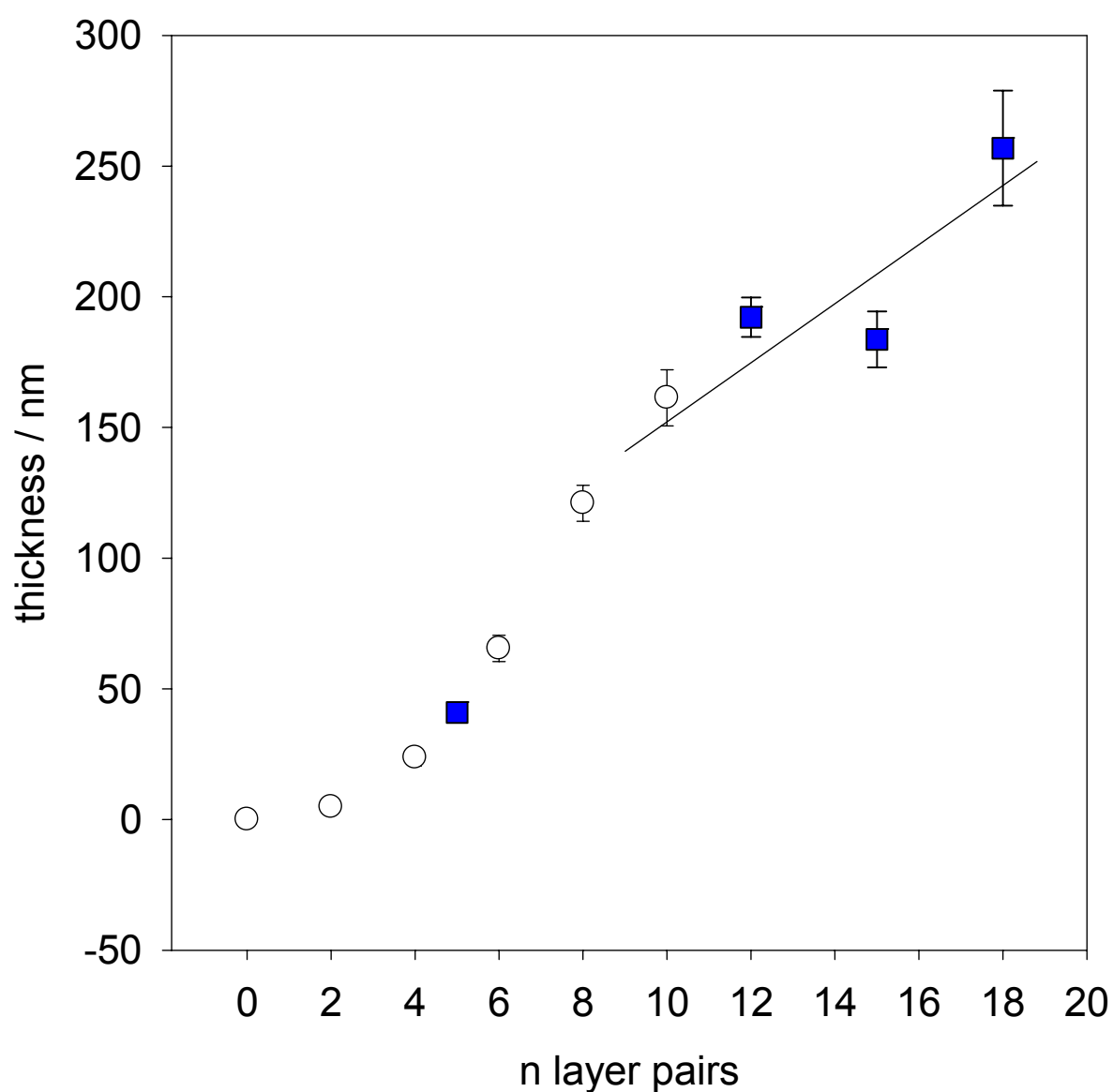


Figure S2: Influence of the drying steps in the deposition of (PAH-HA)_n films on their thickness change: (○): corresponds to the deposition of a (PLL-HA)₁₀ film in which the film was dried every two layer pairs before thickness measurement, rehydration and deposition of new layers. (■): experiments performed on individual films, the drying step being performed only after the deposition of *n* layer pairs.

The line does not correspond to a fit but is aimed to show that a transition from a supralinear to a linear growth regime occurs after the deposition of about 8 layer pairs.

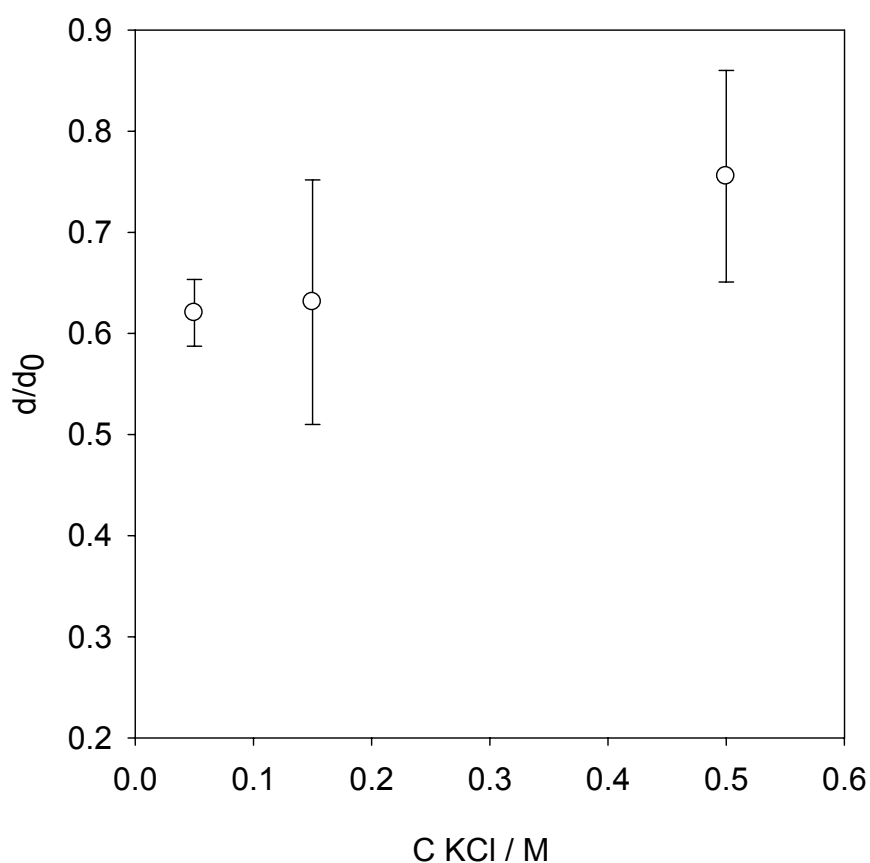


Figure S3: Evolution of the fraction of film thickness remaining on the silicon substrates after having exposed the (PAH-HA)₁₀ films to potassium hexacyanoferrate solutions at 1 mM during 30 min. in the presence of KCl at different concentrations. The film thickness was

measured by means of ellipsometry before (d_0) and after (d) exposure to the hexacyanoferrate containing solution. The error bars are calculated from the standard deviations of the individual thickness values (d_0 and d).

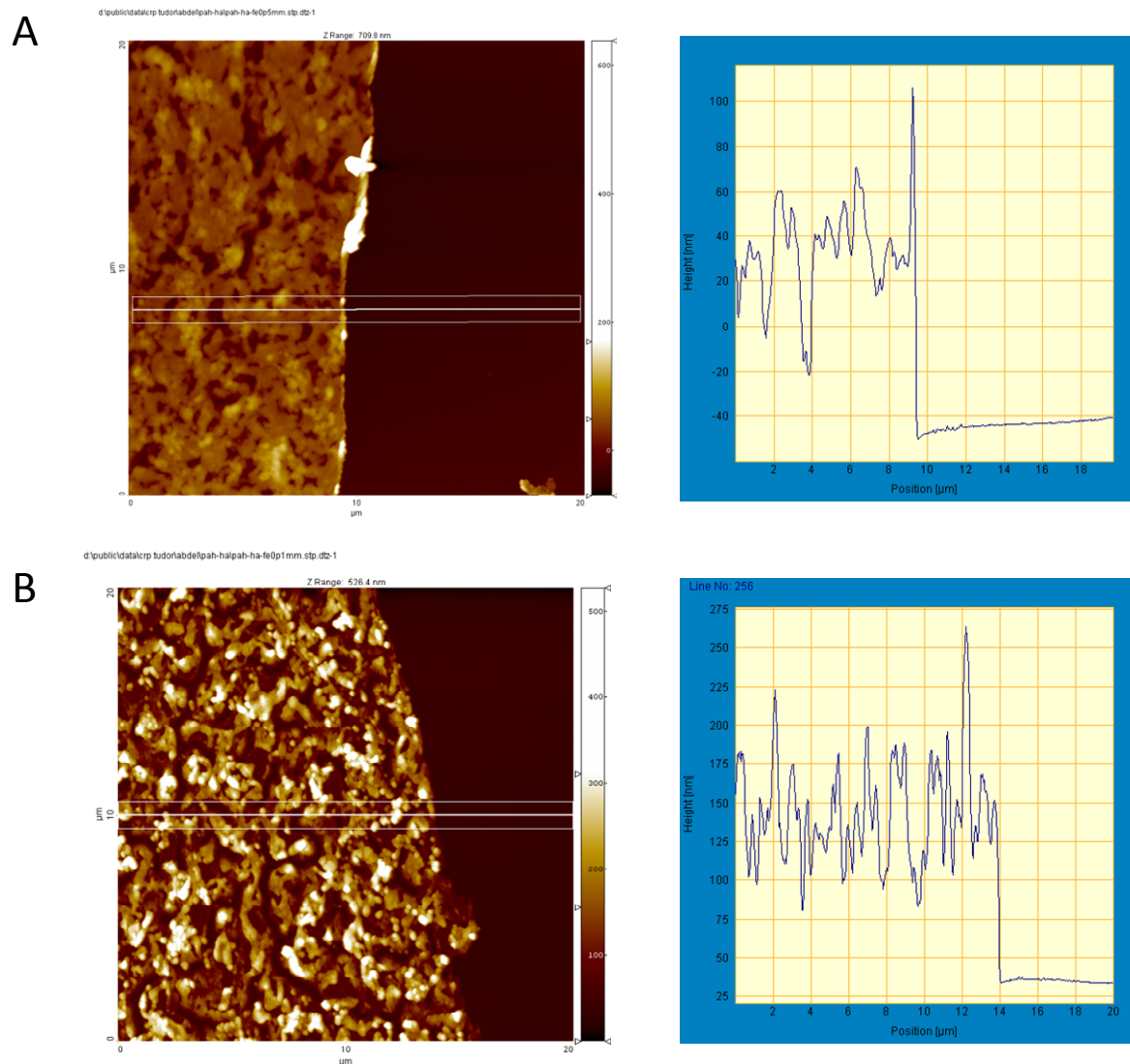


Figure S4: AFM topographies (left) and height scans (right) obtained on a (PAH-HA)₁₀ film put in contact with a 0.5 mM (A) and a 0.1 mM (B) hexacyanoferrate containing KCl solution (at 50 mM) during 30 min. The films were rinsed with KCl solution, distilled water and intensively dried before imaging in the tapping mode. The dashed rectangles on the

topographical images correspond to the region on which the average height scan (right) is given. The films were needle scratched before imaging over a $20\ \mu\text{m} \times 20\ \mu\text{m}$ area. The z scale corresponds to 600nm in A and to 500 nm in B.

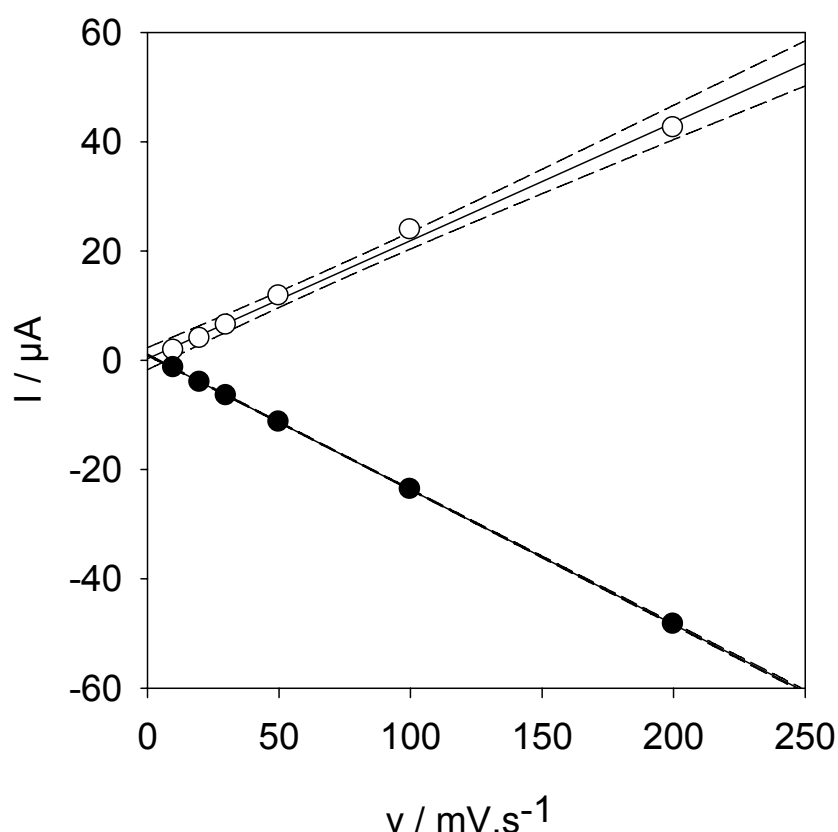


Figure S5: Evolution of the oxidation and reduction currents of hexacyanoferrate anions remaining entrapped in a $(\text{PAH-HA})_{10}$ film after 30 min of loading in the presence of potassium hexacyanoferrate at 1 mM and after 30 min of buffer rinse. The film deposition, redox probe incorporation and release were all performed in the presence of 50 mM KCl. The full lines correspond to linear regressions whereas the short dashed lines correspond to the limits of the 95 % confidence interval.