SUPPORTING INFORMATION

Long-Range Electron Transfer through Ultrathin Polyelectrolyte Complex Films: a Hopping Model

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PSS molar absorptivity

To determine the concentration of the labeled PSS, the molar absorptivity of narrow MWD PSS was measured. The analysis of the absorbances at λ = 225 nm of a series of PSS solutions prepared by the dilution of a 24 x 10^{-5} M stock yielded a molar extinction coefficient of 9,361 M^{-1} cm^{-1} (Figure S1). Using this ε value, the molar concentration of the labeled PSS was determined to be 0.57 mM and this concentration was used to build up the labeled and unlabeled PEMUs.

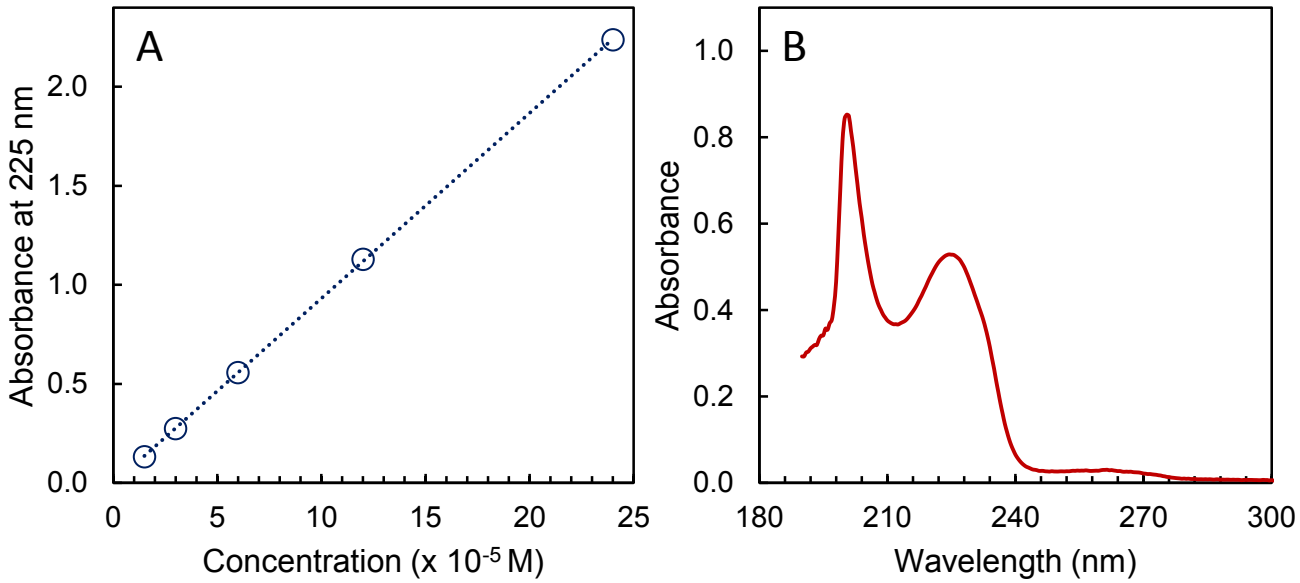

Figure S1. A) The absorbance of narrow MWD PSS at λ = 225 nm as a function of concentration. The extinction coefficient at this wavelength is 9,361 M^{-1} cm^{-1} from the slope of the line. B) Absorbance of labeled PSS solution.

PEMU thickness on Pt

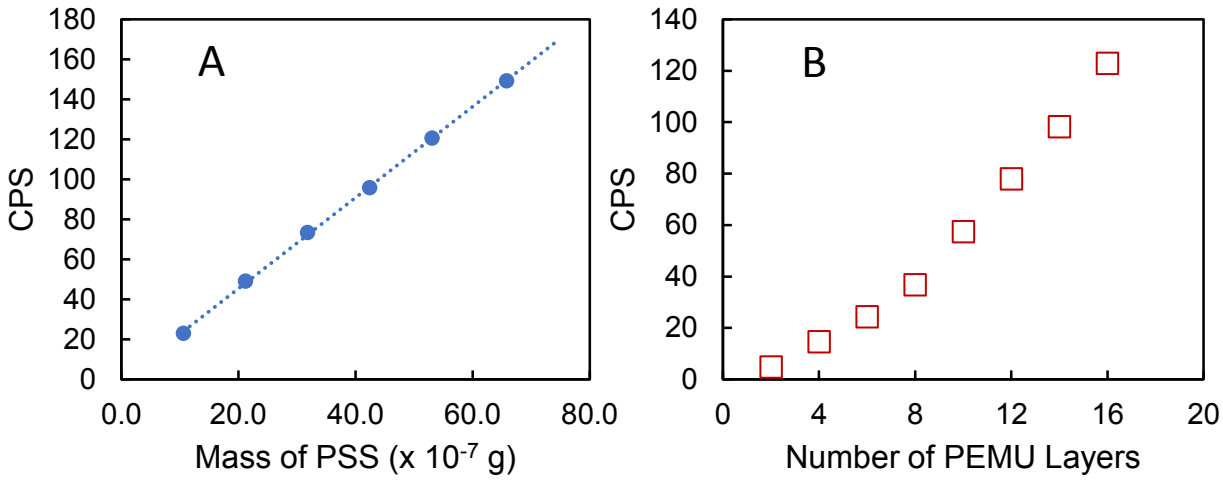

Figure S2. A) Calibration curve showing the counts per second, CPS, as a function of the mass of PSS. B) Raw data for the background corrected CPS vs. number of layers

The thickness d (nm) of each PEMU bilayer was calculated using

$$d = \frac{\frac{M_{PDAD/PSS}}{M_{PSS}} \times m}{A\rho} \times \frac{10^7\ nm}{cm} \qquad \text{[S1]}$$

Where $\frac{M_{PDAD/PSS}}{M_{PSS}}$ is the ratio of molecular weights of the PDADMA/PSS complex to PSS = 1.67, *m* is the mass of the PSS (g), A is the area (cm^2) and *ρ* is the density of the PDADMA/PSS complex (1.26 g cm^{-3}).

Assuming the water content is 40 wt% in a wet PDADMA/PSS film, the wet thickness would be:

$$d_{wet} = \frac{100 \times \rho_{dry}}{60 \times \rho_{wet}} \times d_{dry}$$

$$d_{wet} = \frac{100\ \times 1.26\ g\ mL^{-1}}{60\ \times 1.15\ g\ mL^{-1}} \times d_{dry}$$

$$d_{wet} = 1.8 \times d_{dry} \quad [S2]$$

where ρ_{dry} and ρ_{wet} are the densities (g cm^{-3}) of the dry and wet PDADMA/PSS films respectively and d_{dry} (nm) is the effective dry thickness of the film.

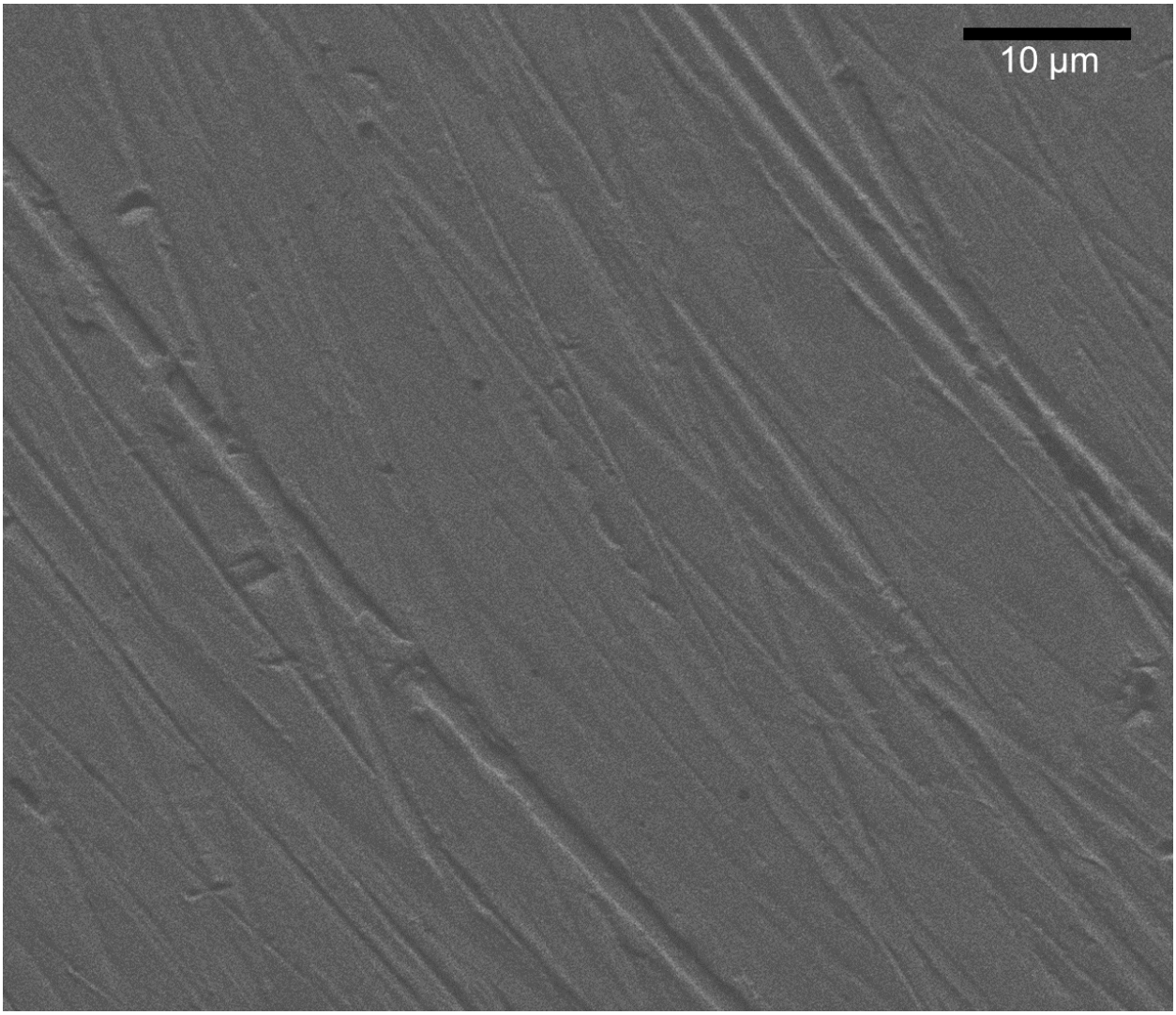

Figure S3. Scanning electron microscopy image of a bare Pt RDE previously polished with 0.3 µm alumina, sonicated for 15 s, rinsed with deionized water, and dried under a stream of N_2.

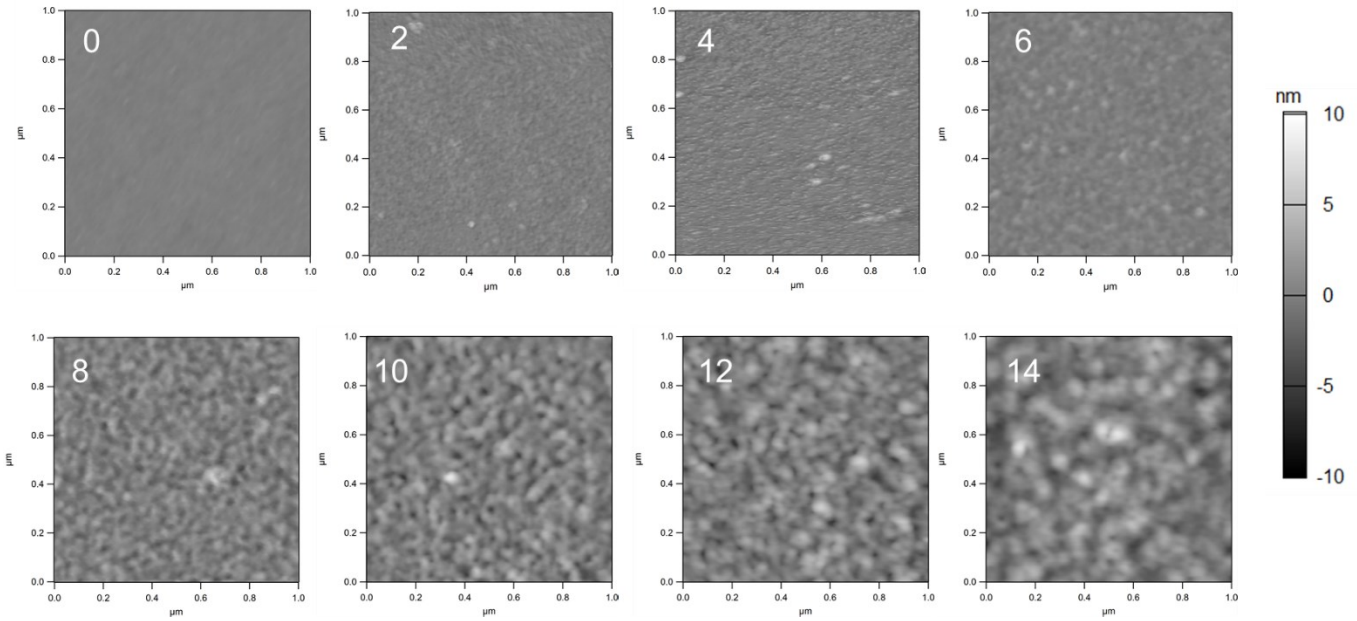

Figure S4. AFM images showing 2D representations of PDADMA/PSS films built on Si wafers in 0.1 M NaCl. Bare silicon, 2,4,6,8,10,12,14 layers. 1 μm x 1 μm scan area.

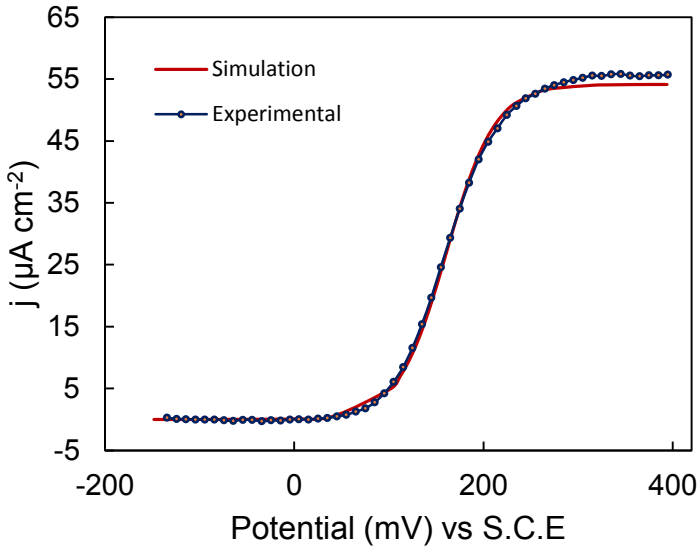

Figure S5. Experimental and simulated voltammograms at the bare electrode. The simulated voltammogram was generated using equation 3 assuming the diffusion coefficients of

ferrocyanide and ferricyanide are the same (main manuscript) with 0.10 mM redox probe, 25 °C temperature, 1000 rpm rotation rate, diffusion coefficient D = 7 x 10^{-6} cm^2 s^{-1}, kinematic viscosity v = 0.0089 cm^2 s^{-1} and electrode area = 0.126 cm^2

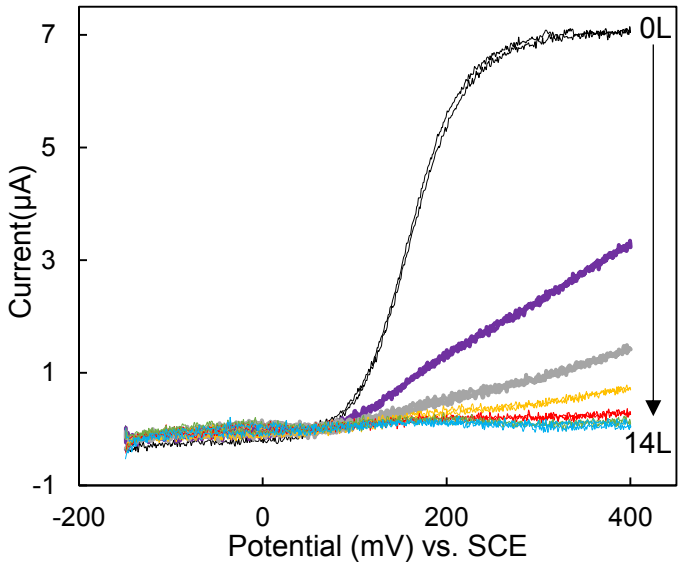

Figure S6. Cyclic voltammograms of 0.10 mM ferrocyanide in 0.1 M NaCl on PDADMA/PSS films at the Pt RDE. 25 °C, 10 mV s^{-1} sweep rate, and 1000 rpm rotation rate. Forward and reverse scans are shown (and almost overlap). The background on bare Pt, corresponding to charging current, was subtracted.

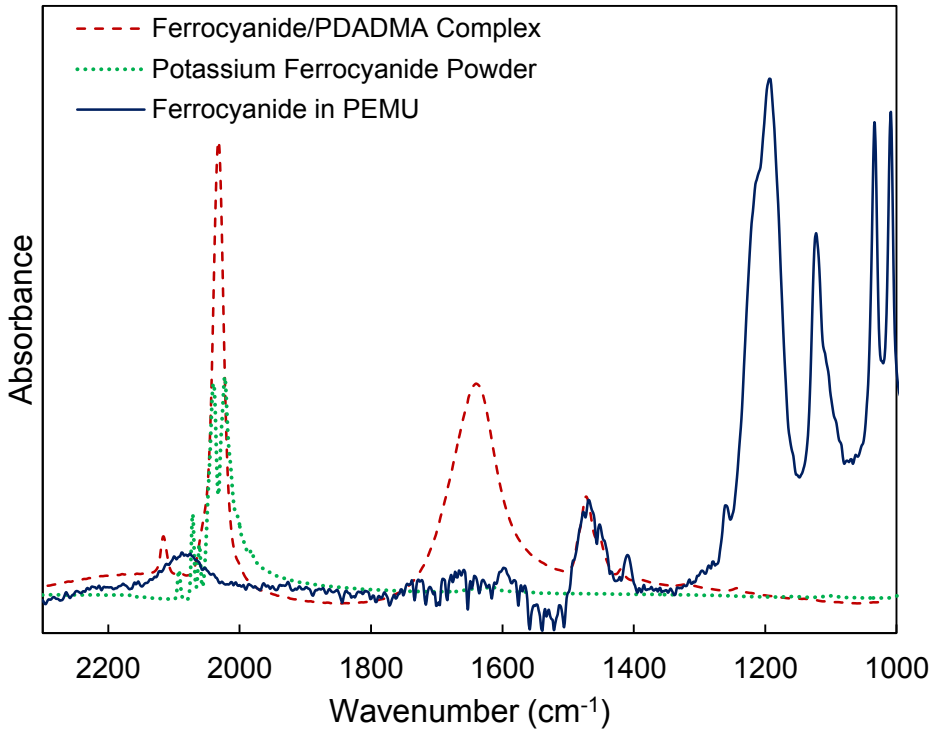

Figure S7. IR spectra normalized to the PDADMA band (1430-1530 cm^{-1}) of ferrocyanide/PDADMA complex as a reference (1:4 molar ratio, dashed red line), potassium ferrocyanide powder (dotted green line) and 32 nm PEMU film in 0.1 mM ferrocyanide in 0.1 M NaCl (solid blue line). Ferrocyanide peak is between 1980 and 2100 cm^{-1}. All samples were measured on double-side-polished Si wafers. Room temperature.

The concentration of ferrocyanide was estimated as follows:

The density of the PEMU is 1.1 g mL^{-1} with a water content of 40 wt% and a polymer content of 60 wt%. Thus, the film contains 660 g L^{-1} of polymer. The molecular weight of the PDADMA:PSS Pol^+Pol^- repeat unit is 310 g mol^{-1}. Thus, the concentration of Pol^+Pol^- is 2.1 M. Comparing the peak areas for ferrocyanide to PDADMA the molar ratio of ferrocyanide to PDADMA (Pol^+) is 0.015 which yields a 0.032 M concentration of ferrocyanide and an average separation of 3.7 nm.

The ferricyanide concentration was determined in a similar manner using the PDADMA/ferrocyanide as a standard and a thicker multilayer. The data have more uncertainty because the ferricyanide is in lower concentration than that of ferrocyanide.

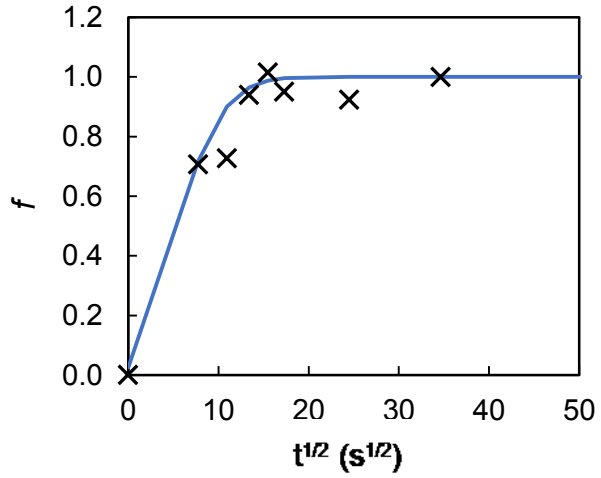

Figure S8. Room temperature doping in a 99 nm PDADMA/PSS PEMU as a function of time from 0.1 mM ferricyanide in 0.1 M NaCl. The solid line is a fit to equation 8 with a D_f of 7 x 10^{-13} cm^2 s^{-1}. The equilibrium concentration of ferricyanide in the PEMU is 0.0024 M. Error in *f* is +/- 15%