Supporting information:

Surface assembly of catechol-functionalized poly(L-lysine)-*graft*-poly(ethylene glycol) copolymer on titanium exploiting combined electrostatically driven self-organization and biomimetic, strong adhesion

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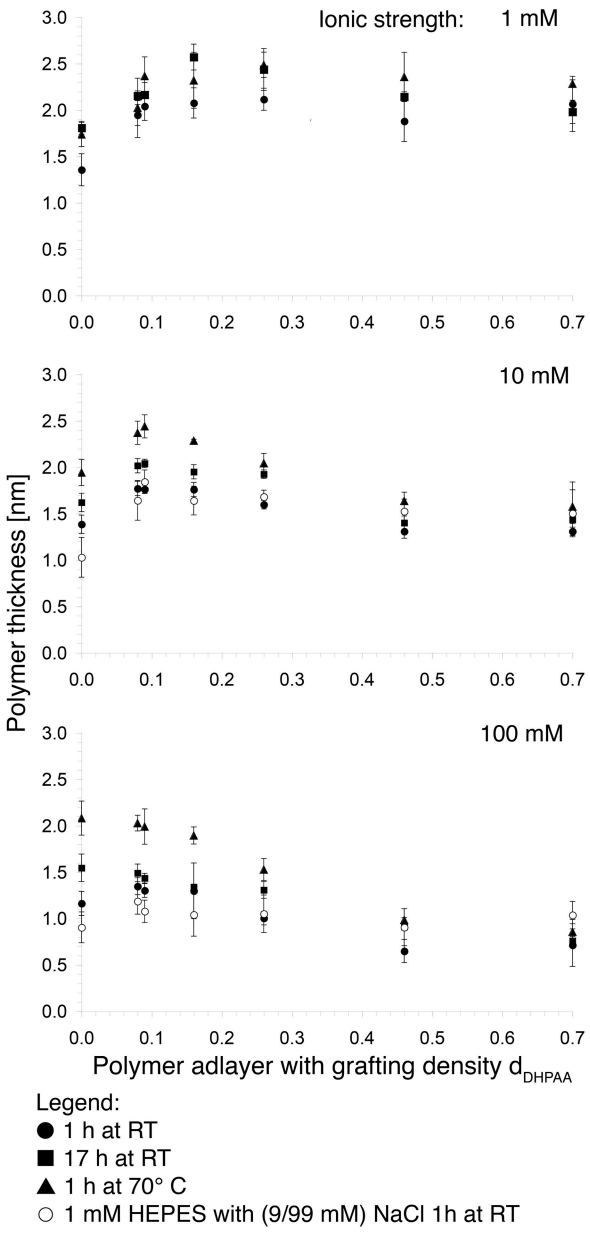

Figure S - 1 Polymer adlayer thickness of six PLL-*g*-(DHPAA; PEG) copolymers with varying concentration of DHPAA grafted to the PLL backbone plus the pure PLL-*g*-PEG (X-axis). The copolymers were adsorbed to TiO_2 coated substrates (22 nm) under different conditions: ionic strength (HEPES buffer (1-100 mM, pH = 7.4) and HEPES buffer (1 mM, 9-99 mM NaCl, pH=7.4)), adsorption time (1 h/ 17 h) and temperature (room temperature (RT)/ 70° C). The dry adlayer thicknesses were measured in air with ellipsometry.

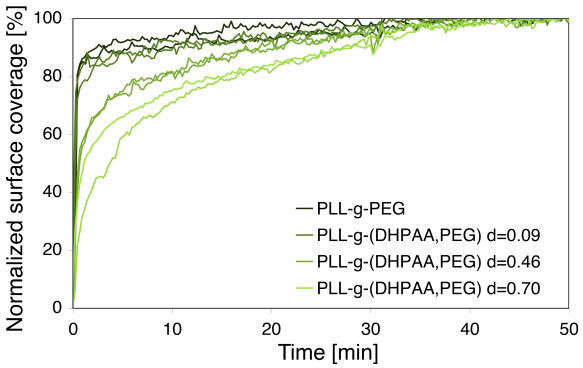

Figure S - 2 Adsorption kinetics of PLL-*g*-PEG and PLL-*g*-(DHPAA; PEG) with d_{DHPAA}= 0.09, 0.46 and 0.70. The increasing mass of the adsorbed polymer as a function of time was measured with optical waveguide lightmode spectroscopy (OWLS) and normalized to 100% = saturation surface coverage. All measurements were performed under flow mode, with a polymer solution concentration of 0.1 mg/mL in HEPES buffer (10 mM, pH=7.4), a flow rate of 30 µL/min, incubation for 30 min and at 25° C. Two measurements per polymer type.

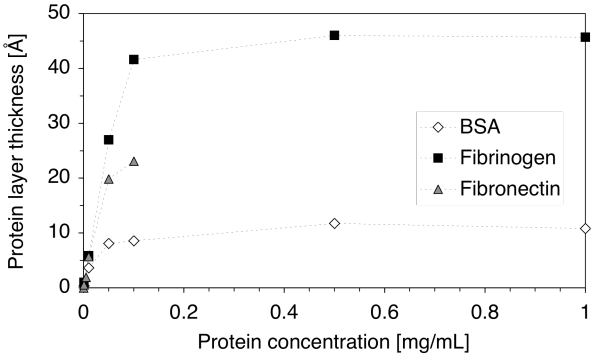

Figure S - 3 Layer thickness of three different proteins (Bovine serum albumin, fibrinogen and fibronectin) adsorbed at different concentrations (X-axis) in HEPES buffer (10 mM, pH=7.4, 150 mM NaCl), at room temperature for 1h on a titania-coated silicon wafer (6 nm). The dry adlayers were measured with ellipsometry.

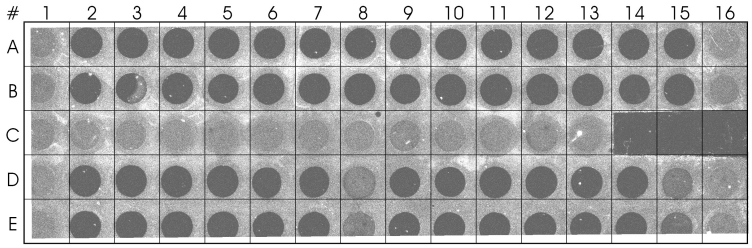

Figure S - 4 Fluorescence image of FITC-Fbg adsorbed on PLL-*g*-(DHPAA; PEG) with increasing DHPAA grafting density (d_{DHPAA}= 0 - 0.70) dissolved in HEPES (0.1 mg/mL, 10 mM, pH = 7.4) and adsorbed on a titanium oxide coated silicon wafer (22 nm). The seven copolymers were adsorbed eight times on spot A2-8, A9-15, B2-8, B9-15, C2-8, C9-15, D2-8, D9-15 with the grafting density d_{DHPAA} decreasing from the left to the right. The polymer adlayers of the D and E row were subsequently treated with 5.3 M NaCl solution for 16 hours. Finally the complete slide was incubated in a 0.1 mg/mL FITC-Fbg dissolved in HEPES (10 mM, pH =7.4, 150 mM) for 1 hour at room temperature. The image was taken with a microarray scanner (Tecan LS).

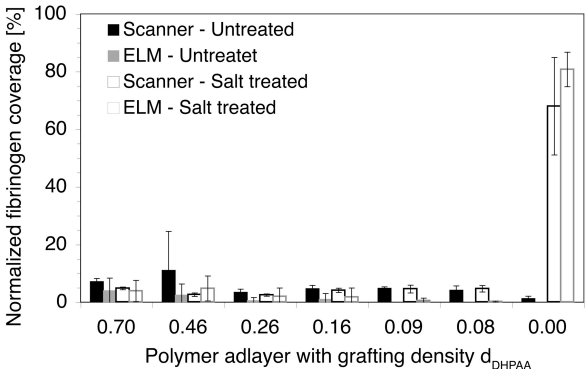

Figure S - 5 FITC-Fbg was incubated on PLL-*g*-(DHPAA; PEG)-coated TiO_2 substrates with d_{DHPAA} = 0-0.70. The polymers were adsorbed (0.1 mg/mL) from HEPES buffer (10 mM, pH= 7.4). The polymer adsorption was repeated eight times, and four adlayers were subsequently incubated with 5.3 M NaCl for 16 h. The FITC intensities were then measured with the microarray scanner (Fig. S-3) and the adlayer thicknesses with ellipsometry. Both values, absorbance and thickness in nm of Fbg, were normalized against full substrate coverage (=100%) and plotted against d_{DHPAA}.

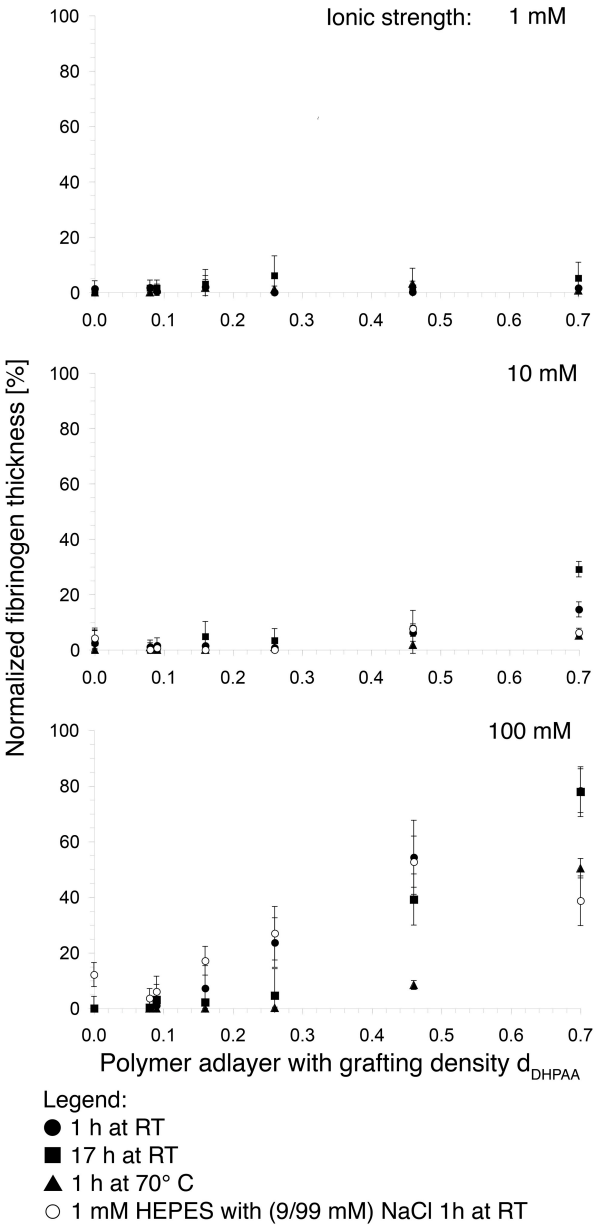

Figure S-6 Fibrinogen adlayer thickness adsorbed on a TiO_2-coated silicon wafer, which was previously coated with PLL-*g*-(DHPAA; PEG) copolymers with varying DHPAA grafting density d_{DHPAA} and under different assembly conditions, such as time, temperature, ionic strength and type of ions. The substrate was incubated in 0.1 mg/mL FITC-Fbg solution (HEPES 10 mM, pH=7.4, 150 mM NaCl) for 1 h at room temperature (RT). The correlating polymer adlayer thicknesses are shown in Fig. S-1.

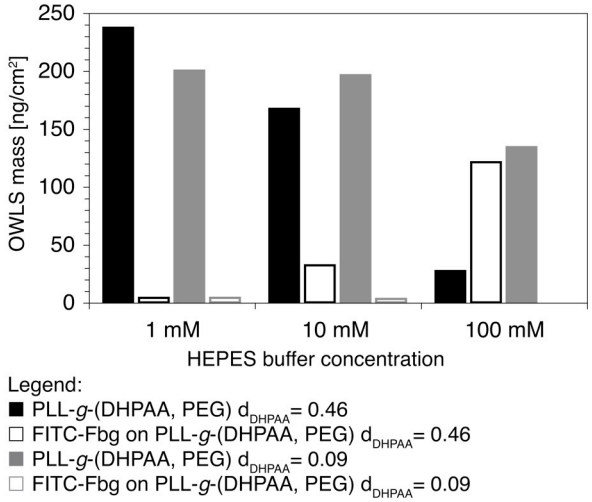

Figure S-7 OWLS measurement of A) adsorption of PLL-*g*-(DHPAA; PEG) at 0.1 mg/ml concentration with d_{DHPAA}= 0.09 and 0.46, dissolved in HEPES buffer with different ionic strength (1, 10 and 100 mM, pH=7.4) for 0.5 h at 25° C (filled bars) and B) subsequent adsorption of FITC-Fbg (0.1mg/mL, HEPES, 10 mM, pH=7.4, 150 mM NaCl) for 0.5 h at 25° C on the polymer-coated substrates (empty bars). TiO_2-coated waveguides were used for all measurements.

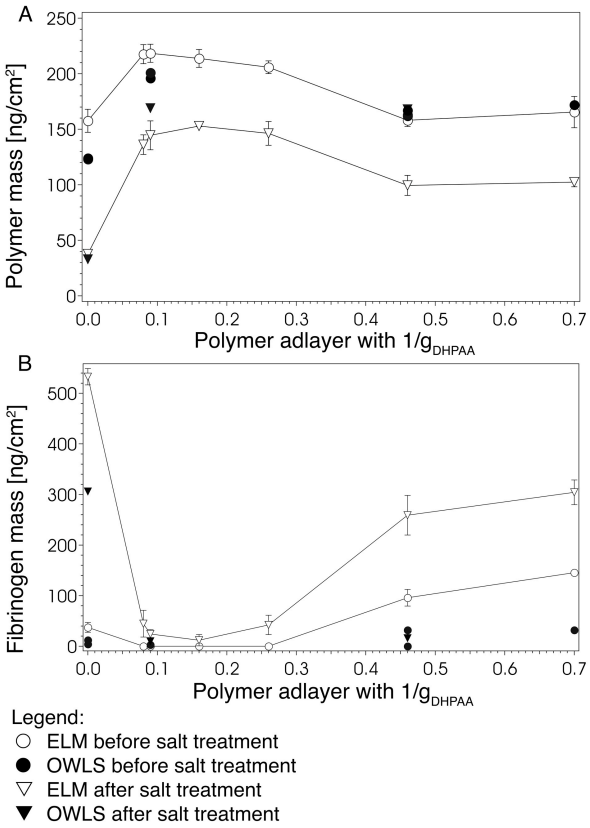

Figure S-8 Comparison of the adsorbed polymer (A) and fibrinogen (B) mass calculated from ellipsometry (ELM) data and the mass obtained directly from optical waveguide light spectroscopy (OWLS). A) The seven PLL-*g*-(DHPAA; PEG) (20 000:168:2 000 M_r; 0.70:0.29 d) polymers were adsorbed on TiO_2 from a 0.1 mg/mL solution (in 10 mM HEPES buffer, pH = 7.4) for 1 h at room temperature (ELM) and for 0.5 h at 25° C (OWLS) . Some of the polymer adlayer were then incubated over night at room temperature (ELM) or for 0.5 h at 25° C (OWLS) in 5.3 M sodium chloride solution. B) The non-fouling property of the polymer adlayers was tested with the incubation in a 0.1 mg/mL FITC-Fbg solution (10 mM HEPES buffer, pH = 7.4, 150 mM NaCl) for 1 h at room temperature (ELM) or 0.5 h at 25° C (OWLS).