



Supporting Information

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Mechanically-Induced Generation of Counterions Inside Surface-Grafted Charged Macromolecular Films: Towards Enhanced Mechanotransduction in Artificial Systems

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Experimental Details

Synthesis of Polyelectrolyte Brushes

Polyelectrolyte brushes were grown on glass using 2-bromo-2-methyl-propionic acid 3-trichlorosilanyl-propyl ester to prepare the initiator-modified substrates. Patterned gold samples were prepared by microcontact printing (μ CP) of a thiol initiator (ω -mercaptoundecylbromobutyrate) onto clean gold substrates. The polymerization solution was prepared as follows: commercially-available (Aldrich) METAC (10 mL (75 wt. % solution in water), 40 mmol) was dissolved in water (2 cm³) and MeOH (8 cm³) at 20 °C and degassed by passing a continuous stream of dry N₂ through the solution whilst being stirred (15 minutes). To this solution was added 2,2'-dipyridyl (416 mg, 2.7 mmol), Cu^ICl (105 mg, 1.1 mmol) and Cu^{II}Cl₂ (14 mg, 0.11 mmol). The mixture was then further stirred and degassed with a stream of dry N₂ (15 minutes). Initiator coated samples (~1 cm² each) were sealed in Schlenk tubes, degassed (4 x high-vacuum pump / N₂ refill cycles) and left at 20 °C under N₂. The polymerization solution was then syringed into each Schlenk tube, adding enough solution to submerge each sample completely. After various polymerization times the samples were removed, washed with water, then methanol, and dried under a stream of N₂.

Dye Uptake

The BTB dye (from Aldrich) uptake was carried out as follows: PMETAC brushes were washed with Milli Q water to remove any excess salts and placed in a 0.6 mM BTB aqueous solution. The samples were again washed with Milli Q water and stored in an atmosphere of controlled high humidity. This was accomplished by placing the glass slides in a dessicator containing a vial with water. The mechanical compression

was carried out by sandwiching the brush-coated glass slides between two pieces of flat cured PDMS (Sylgard 184). The addition of a few drops of water avoids direct contact between the PDMS and the sample. Once the assembly was placed in an IR cell, the screws were tightened.

Characterization Techniques

The spectra taken using a Cary 4000 UV–Vis spectrometer. AFM experiments were carried out in a liquid cell using a MacMode PicoSPM magnetically driven dynamic force microscope (Molecular Imaging). Images were taken using commercially available type II MAClevers with a nominal force constant of 2.8 N.m^{-1} .