Supplementary Material (ESI) for Chemical Communications

Electrochemical Control of Surface Properties Using a Quinone-Functionalized Monolayer: Effects of Donor-Acceptor Complexes

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Supplementary Material

Experimental Section

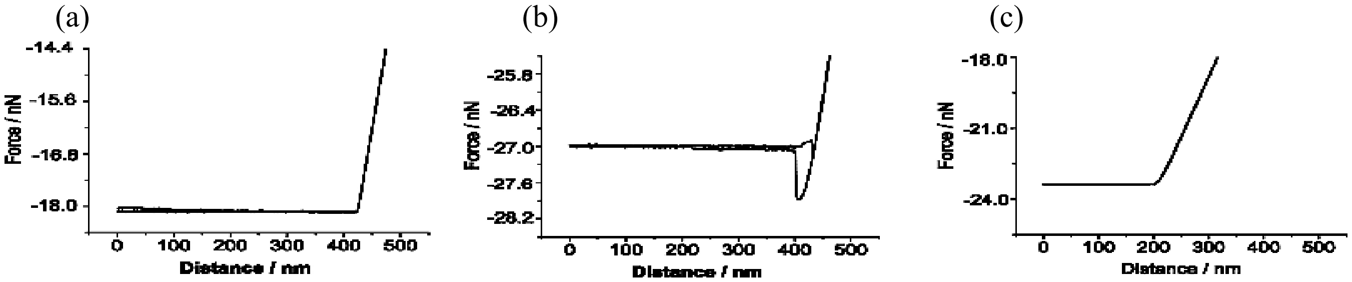
All chemicals were purchased from Aldrich and used without further purification. Ultrapure water from a NANOpure Diamond (Barnstead) source was used throughout all the experiments.

Modification of the Electrodes. A Au-coated (50 nm Au layer) glass plate (22 x 22 mm^2) (Analytical μ-Systems, Germany) was flame annealed for 5 min in a *n*-butane flame and cooled for 10 min under Ar gas. Cystamine was self-assembled onto the Au-coated electrode to yield the amine-functionalized Au surface as previously described.[7] The resulting surface was reacted with an 1.0 mM ethanolic solution of 1,4-benzoquinone at 40 °C for 30 min. Following washing with ethanol and H_2O, the surface was immersed in a 1 mM solution of 1-thiobutane for 30 min.

Electrochemical Surface Characterization and Contact Angle Measurements. The cyclic voltammetry under constant potential applied on the modified electrode were performed on an Autolab electrochemical analyzer (EcoChemie, The Netherlands) connected to a PC (GPES version 4.9 software) in buffer (10 mM phosphate buffer, 100 mM $NaClO_4$) with a graphite counter-electrode and a SCE reference electrode. In situ electrochemical measurements coupled with static contact-angle measurements were performed on the modified Au-glass plates with the Autolab potentiostat with a CAM 2000 Optical-Angle Analyzer (KSV Instruments, Finland). A approximately 20 µL droplet of the buffer solution (10 mM phosphate buffer, 100 mM $NaClO_4$) with a diameter of roughly 0.5 cm was deposited on the surface from a syringe. In the case of electrochemical switching, the counter electrode wire (Pt, diameter = 0.1 mm) and the quasi-reference electrode (Ag, diameter = 0.1 mm) were introduced into the droplet. The images of the droplets were recorded, and each contact-angle measurement was repeated at least 3 times before the value was reported as the average. In the case of chemical switching, measurements of the contact angle were taken with the reductant (ascorbic acid, 10 mM) or the oxidant ($KMnO_4$, 10 mM) directly in the buffer.

AFM Force Measurements. Force measurements were carried out at room temperature using a Multimode scanning probe microscope with a Nanoscope 3A controller and a Pico Force module (Digital Instruments / Veeco Probes / Santa Barbara, CA). The spring constants of the cantilevers (Mikromasch, Germany) were determined in air using the thermal noise method to give an average spring constant of 0.06 $N \cdot m^{-1}$. All experiments were conducted in buffer (10 mM phosphate buffer, 100 mM $NaClO_4$) in a fluid cell. To measure the force interactions, the probe tip was lowered to the surface and immediately retracted at a rate of 0.5 $\mu m \cdot s^{-1}$, and data points were analyzed with their associated spring constants. Histograms were prepared using ORIGINPRO software (OriginLab, Northampton, MA). Different bin sizes did not affect the conclusions drawn from the data. Peaks were fitted using a Lorentzian function that best fit our data with a Levenberg-Marquardt fitting algorithm. Each histogram was the result of at least 300 separate force measurements.

Force Curves



Representative force curves of a viologen tip with the initial surface (a), following reduction with ascorbic acid (b), and following oxidation with $KMNO_4$.