

Covalent Gluing and Post-Gluing of Langmuir-Blodgett Monolayers At Hydrocarbon Surfaces

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Supporting Information

Materials. Calix[6]arene **2** was synthesized using procedures similar to those previously described.²² Poly(allylamine) (Mw=65,000) (PAA, Aldrich) was obtained as a 20% aqueous solution and used directly. *n*-Octadecyltrichlorosilane (OTS) was also purchased from Aldrich, and used as obtained. House-deionized water was purified using a Millipore Milli-Q-filtering system containing one carbon and two ion-exchange stages.

Fluorescent Labeling of Poly(allylamine). To 0.500 g of a 20% aqueous solution of poly(allylamine) (1.54 mmol NH₂ groups), which was first diluted by addition of 4.50 mL of a 5% aqueous NaHCO₃ solution, was added dropwise 0.500 mL of a DMF solution containing 5.0 mg (14 μ mol) of 6-carboxyrhodamine succinimidyl ester. The reaction mixture was stirred in a closed flask for 3 h at room temperature. Extensive dialysis, using dialysis bag (MWCO 500 Da), against 4 \times 1000 mL of H₂O for a total of 48 h resulted in water-soluble product, which did not contain low molecular weight impurities, as evidenced by thin layer chromatography.

Water Contact Angle and Ellipsometric Measurements. Water contact angles were measured using a Rame-Hart NRL model 100 goniometer. A minimum of six measurements were made for three independent drops that were placed at different locations along the substrate. Ellipsometric measurements were made using an automatic null ellipsometer (Rudolph Auto-EL III), equipped with a helium-neon laser (λ = 632.8 nm) that was set at an incident angle of 70°. Measurements were taken at four locations on the surface of each sample and the mean and the standard deviations were calculated.

Film thicknesses were determined using the manufacturer's program, assuming a refractive index for OTS and the LB monolayer of 1.41.

Atomic Force Microscopy. All AFM measurements were made using a tapping mode atomic force microscopy (Nano III, Multimode SPM, Veeco, Santa Barbara, CA). A minimum of three different locations along the surface were examined. For each location 1, 2 and 5 μm -size images were obtained.

X-ray Photoelectron Spectroscopy. All XPS measurements were recorded using a Scienta ESCA-300 spectrometer (Scienta Instruments AB, Uppsala, Sweden), with a take-off angle of 45° .

Attenuated Total Reflectance Absorption (ATR IR) Spectroscopy. ATR-IR spectra in the 1500-3500 cm^{-1} region were collected with a Mattson Polaris spectrometer, which was equipped with a chamber that maintained a dry nitrogen environment. The samples for ATR-IR measurement were prepared by depositing LB films onto SPT ATR silicon crystals (50 x 20 x 2 mm, Harrick Scientific, Pleasantville, NY). Prior to LB deposition, the surface of silicon crystal was cleaned and treated with OTS, using procedures that were similar to those used for modifying silicon wafers and glass coverslips.

Substrate preparation. The silicon wafers that were used in this work were obtained from WaferNet, Inc. (San Jose, CA). Typically, these wafers were cut into 15 x 25 mm pieces and were treated in concentrated H_2SO_4 and 30% H_2O_2 (70/30, v/v) at 70°C for 4 h. The wafers were then rinsed with distilled water, and dried under a stream of nitrogen, before being immersed in a 10 mM anhydrous hexane solution of *n*-octadecyltrichlorosilane (OTS) for 30 minutes at room temperature. The wafers were then rinsed with hexane and chloroform. The advancing contact angle for water, measured at five different locations, was $104^\circ \pm 2^\circ$. Examination of the surface by AFM indicated a mean roughness of 0.28 nm on a 1 μm scale. Similar procedures were used to modify the microscope cover glasses (22 x 22 cm, Fisher) that were used for confocal microscopy.

Monolayer Formation, Surface Pressure-Area Isotherm Measurements and Langmuir-Blodgett Transfers. All monolayer experiments and LB transfers were carried out using a Nima 612D film balance equipped with a LB dipper (Nima Technologies, Coventry England), operating at 25°C .

Typically, 50 μL of **2** (1 mg/mL of chloroform) was spread onto an aqueous subphase (pH 6.5) that was maintained at 25°C. After allowing the solvent to evaporate for 30 min, the film was compressed at a speed of 25 cm^2/min to 20 dyn/cm, and its surface pressure-area isotherm recorded. The monolayer was then transferred to the hydrophobic substrate (OTS-modified silicon wafer or glass coverslip by a single down-trip, at constant surface pressure. The dipping speed that was used was 2 mm/min. After allowing the substrate to remain in the subphase for 60 min, the compressing barrier of film balance was expanded to a maximum area, which reduced the surface pressure of film on the water surface to 0 dyn/cm. The substrate was then pulled out of subphase (vertical up-trip) using speed of 50 mm/min. The monolayer was then compressed again and the isotherm recorded.

Similar experiments were carried out over an aqueous subphase containing 0.5 mM poly(allylamine) (PAA) (repeat unit concentration). In this case, the pH of the subphase was adjusted by addition of 1 M NaOH or 1 M HCl.

Surface Viscosity. A home-built canal viscometer (192 mm \times 40 mm solid Teflon block, having a centrally located 6.0 mm slit) was placed in front of the compressing barrier and monolayers were compressed to a surface pressure of 20 dyn/cm. After the resulting monolayer was allowed to equilibrate at this pressure for 60 min, the film was expanded using a maximum speed of 120 cm^2/min , leaving the canal viscometer at its original position. The resulting surface pressure was then recorded as a function of time. The rate of surface pressure decrease was used as a measure of the relative surface viscosity of the monolayer.

Gluing LB Monolayers Within the Subphase. A single monolayer of **2** on a pure water subphase (pH 6.5) was transferred onto an OTS modified silicon wafer (or glass coverslip) by a single down-trip with dipping speed of 2mm/min at surface pressure 20 dyn/cm. Then the pH of the subphase was then raised by injecting 2 mL of 1 M NaOH at six different locations that were evenly distributed throughout the trough. The pH of subphase was determined after each experiments was completed. After allowing the substrate to remain in the subphase for 60 min, the compressing barrier of film balance was

expanded to a maximum area, which reduced the surface pressure of film on the water surface to 0 dyn/cm. The substrate was then pulled out of subphase (vertical up-trip) using speed of 50 mm/min.

Post-Gluing. A single monolayer of **2** on a pure water subphase was transferred onto an OTS modified silicon wafer (or glass coverslip) by a single down-trip with dipping speed of 2 mm/min at a surface pressure of 20 dyn/cm. The compressing barrier of the film balance was then expanded to a maximum area, which reduced the surface pressure of film on the water surface to 0 dyn/cm. The substrate was then pulled out of subphase (vertical up-trip) using speed of 50 mm/min. The resulting LB monolayer of **2** was then immediately (< 10 min) dipped into a 0.5 mM PAA solution (pH=11) and incubated for 60 min.

Before characterization, all glued and post-glued LB monolayers were washed with pure water (i.e., submerged in water) three times (10 min for each washing cycle). Unglued monolayers that was transferred from a pure water surface, and also those PAA subphases with $\text{pH} \leq 9$ were tested without washing.

Confocal Microscopy and Stability Towards Aqueous NaCl. A Zeiss LSM510 META confocal microscope was used for all fluorescence images that were recorded, using OTS-treated microscopy coverslips as substrates. A fluorescent analog of **2-10** [i.e., **2-10(F)**] was prepared using PAA that was labeled by 6-carboxyrhodamine, and experimental procedures that were similar to those used for the preparation of **2-10**. An ionically cross-linked analog **1/PSS(F)** was prepared from first depositing a glued LB monolayer derived from **1** and poly(styrene sulfonate) onto a OTS-silylated glass coverslip using experimental procedures that were similar to those previously described.⁷ This coverslip was then immersed in a 0.5 mM aqueous solution of PAA that was labeled by 6-carboxyrhodamine (pH 6) for 20 min at room temperature, and washed with pure water (i.e., submerged in water) three times (10 min for each washing cycle).

Half of each of these coverslips [i.e., **2-10**(F) and **1/PSS**(F)] was immersed in a stirred 1 M aqueous NaCl solution for 2 h at room temperature, using a Teflon-coated stir bar. The entire coverslips was then immersed in pure water for 30 min, followed by air-drying.

Reduction of 2-10 with NaBH₄. A sample of **2-10** was immersed in a 50 mM aqueous NaBH₄ solution for 2 h. The sample was then washed in pure water two times (for 10 min each time). Examination by XPS showed a significant increase in the amount of the amine component, relative to untreated **2-10** (Figure S1).

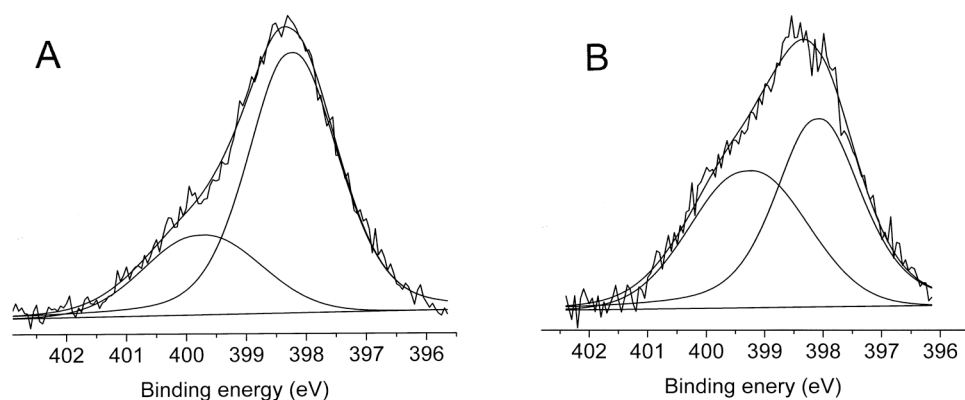


Figure S1. Deconvolution of N1s region of XPS spectra into imine (398.15 eV) and amine (399.4 eV) nitrogen: (A) **2-10** (B) sample **2-10** after exposure to 50 mM NaBH₄.