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8 Introduction of Thiol Moieties, including their
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12 Thiol-ene Reactions and Air Oxidation, onto
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17 Polyelectrolyte Multilayer Substrates
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ABSTRACT

We describe the derivatization of uncross-linked and cross-linked layer-by-layer (LbL) assemblies of polyelectrolytes (polyallylamine hydrochloride and polyacrylic acid) with sulfhydryl groups via Traut's reagent (2-iminothiolane). This thiolation was optimized with regards to temperature, concentration, and pH. The stability of the resulting –SH groups in the air was determined by X-ray photoelectron spectroscopy (XPS). This air oxidation has obvious implications for the use of thiol-ene reactions in materials chemistry, and there appears to be little on this topic in the literature. Three main S 2s signals were observed by XPS: at 231.5 eV (oxidized sulfur), 227.6 eV (thiol groups), and 225.4 eV (thiolate groups). Due to their rapid oxidation, we recommend that thiolated surfaces be used immediately after they are prepared. As driven by 254 nm UV light, thiol groups on polyelectrolyte multilayers react with 1,2-polybutadiene (PBd), and residual carbon-carbon double bonds on adsorbed PBd similarly react with another thiol. In the case of a fluorinated thiol, surfaces with high water contact angles (ca. 120°) are obtained. Modest exposures to light result in derivatization, while longer exposures damage the assemblies. Polyelectrolyte-thiol-PBd-thiol assemblies delaminate from their substrates when immersed for long periods of time in water. Surface silanization with an amino silane prevents this delamination and leads to stable assemblies. These assemblies withstand various stability tests. Techniques used to analyze the materials in this study include XPS, spectroscopic ellipsometry (SE), atomic force microscopy (AFM), and contact angle goniometry.

INTRODUCTION

Surface modification continues to be a very active area of research in modern science because of the many potential applications of functionalized surfaces in biosensors, fuel cells, photovoltaics, bioconjugate chemistry, molecular electronics, adhesion, microfluidics, etc.¹ Some of the basic building blocks of such advanced materials are self-assembled monolayers on gold,²⁻³ organosilane monolayers on hydroxylated surfaces,⁴⁻⁸ alkene and alkyne monolayers on hydrogen-terminated, nanoparticulate, and scribed silicon,⁹⁻¹⁵ phosphonates on alumina, zirconia, and related substrates,¹⁶⁻²⁰ the many reactions of bioconjugate chemistry,²¹ the layer-by-layer assembly of polyelectrolytes and other charged species,²²⁻²⁵ thiol-ene chemistry,²⁶⁻³⁰ and carbon nanotubes.³¹⁻³³ Complex molecular assemblies on surfaces may be prepared using combinations of different chemistries that are compatible with a specific substrate and each other.

Recent developments in thiol-ene chemistry have created a powerful set of tools for materials development, surface modification, and nanotechnology.³⁴⁻³⁵ This chemistry is based on the facile reaction between carbon-carbon double bonds and sulfhydryls (-SH groups). The resulting C-S linkages show good robustness. In the past few years we have employed this chemistry in two ways. First, taking advantage of the well-known reaction between surface Si-H groups and carbon-carbon double bonds, which is obviously analogous to thiol-ene chemistry, we derivatized hydrogen-terminated silicon with 1,2-polybutadiene (PBd).³⁰ The residual, unreacted carbon-carbon double bonds on this surface were then reacted with various thiols. Second, we created thiol monolayers on gold from an α,ω - dithiol.²⁶ The resulting, pendant thiol groups were reacted with PBd and then derivatized with other thiols. This approach yielded a much more stable assembly compared to a traditional monolayer on gold.

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4 In this contribution we continue to explore these reactions and possibilities. In particular, we
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6 create uncross-linked and thermally cross-linked layer-by-layer (LbL) assemblies of
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8 polyelectrolytes, polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA), and then
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10 derivatize them with sulfhydryl groups using 2-iminothiolane (Traut's reagent) (see Figure 1).
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12 Bruening et al. and Rubner et al. have previously studied the thermal cross-linking of
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14 polyelectrolytes, which increases the stability of the films.³⁶⁻³⁹ We then determine, by X-ray
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16 photoelectron spectroscopy (XPS), the stability of the resulting -SH groups in the air. These
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18 results are particularly relevant to the application of the thiol-ene reaction to materials chemistry
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20 because there appears to be little in the literature on this topic. We then confirm that, as driven by
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22 UV light, surface -SH groups on polyelectrolyte multilayers react with PBd, and that residual
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24 carbon-carbon double bonds on the PBd will react with another thiol. Interestingly, modest
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26 exposure to the light results in derivatization, while longer exposures result in damage to the
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28 assemblies. Finally, we observe that polyelectrolyte-thiol-PBd-thiol assemblies delaminate from
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30 their substrates when immersed in water for significant periods of time. Deposition of an amino
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32 silane onto the silicon prior to the LbL of the polyelectrolytes results in robust assemblies. The
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34 assemblies are also stable against swabbing and the Scotch tape test. Techniques used to confirm
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36 and analyze film growth and composition herein include: XPS, time-of-flight secondary ion mass
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38 spectrometry (ToF-SIMS), spectroscopic ellipsometry (SE), atomic force microscopy (AFM),
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40 and contact angle goniometry.
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Figure 1. Creation of complex molecular assemblies. (a) Functionalization of silicon wafers (Si/SiO₂) with alternating layers of PAH and PAA, ending with PAH, followed by reactions with Traut's reagent, PBd, and PDT. (b) Deposition of APTES onto Si/SiO₂ followed by deposition of PAH and PAA.

EXPERIMENTAL SECTION

Materials. Polyallylamine hydrochloride (PAH) ($M_w \sim 58 \text{ kg mol}^{-1}$), poly(acrylic acid) (PAA) ($M_w \sim 10 \text{ kg mol}^{-1}$), 1,2-polybutadiene (PBd) (approx. 90% 1,2-vinyl), triethanolamine hydrochloride (TEA, $\geq 99.0\%$) and 1H,1H,2H,2H-perfluorodecanethiol (PDT, 99.0%) were purchased from Sigma-Aldrich (St. Louis, MO). Traut's reagent was from ProteoChem (Denver, CO). Ethanol (200 proof) was from Decon Laboratories (King of Prussia, PA). Stabilized THF was from Mallinckrodt, Phillipsburg, NJ. Water (resistivity $18 \text{ M}\Omega\text{-cm}$) for making solutions and rinsing surfaces was from a Milli-Q water system by Millipore (Billerica, MA). Silicon wafers (Si/SiO₂) with (100) crystallographic orientation and native oxide were obtained from University Wafers (Boston, MA).

Electrostatic Layer-by-Layer (LbL) Assembly of PAH and PAA. Aqueous solutions of polyallylamine hydrochloride (PAH) (0.02 M) and poly(acrylic acid) (PAA) (0.01 M) were prepared in high purity water. The pH values of these PAH and PAA solutions were adjusted using dilute NaOH to ~ 5 and ~ 5.7 or to ~ 8 and 8.7 , respectively. Shards of Si(100), ca. $1.5 \times 1.5 \text{ cm}^2$, were cleaned either for 1 min with an air plasma cleaner (Model PDC-32G from Harrick Plasma, Ithaca, NY) or in piranha solution ($\text{H}_2\text{O}_2\text{:H}_2\text{SO}_4$, 30:70) to remove organic contamination. Clean silicon shards were then immersed sequentially in a solution of PAH, ultrapure water, a solution of PAA, and again in ultrapure water. All immersion times were 5 min. Between each immersion, silicon shards were rinsed with copious amounts of Millipore water and dried with a stream of nitrogen (N_2). This LbL deposition of the polyelectrolytes was repeated until the desired thickness of an assembly was obtained. These films were prepared by three different laboratory workers, and from solutions prepared on different days. Fresh polyelectrolyte solutions were not prepared if relatively new solutions (1 to 15 days old) were

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4 available. Increases in thickness were monitored by spectroscopic ellipsometry (SE) after the
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6 majority of the deposition steps for more than 100 individual samples. The samples were also
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8 analyzed by XPS and AFM.
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11 **Thermal Cross-linking.** LbL assemblies were placed individually in a glass tube (25 mm
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13 inner diameter), and the center portion of it was wrapped with heating tape. A thermocouple was
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15 inserted into the tube to provide feedback for maintaining its temperature. An inert atmosphere
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17 was then created in the tube by flowing N₂ gas through it. In this manner, electrostatic LbL
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19 assemblies were heated at 150 °C, 200 °C, and 250 °C for 1 – 3 hrs. The samples were then
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21 characterized by SE, XPS, and contact angle goniometry.
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25 **Conversion of Amines to Thiols.** Amine groups were converted into thiols in an aqueous
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27 solution at ca. pH 5 of 0.1, 0.01, or 0.001 M Traut's reagent. The pH of the ultrapure (Millipore)
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29 water used to make the solutions was ca. 5, so no effort was made to adjust the pH of these
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31 solutions after addition of Traut's reagent. For the pH 8 reactions, triethanolamine (TEA), 3.73 g,
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33 was dissolved in 25 mL of high purity water and the pH of this solution was adjusted to ca. 8.0
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35 using conc. HCl. Traut's reagent was then added to this pH 8 solution to prepare 0.1, 0.01, or
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37 0.001 M solutions of this reagent. All solutions were made fresh, immediately before they were
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39 used. Cross-linked and uncross-linked PAH-terminated LbL assemblies were immersed in 1.5
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41 mL of one of these solutions for 30 min, after which they were rinsed with copious amounts of
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43 high purity water and dried under a stream of N₂ gas. The resulting samples were characterized
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45 by XPS, ToF-SIMS, contact angle goniometry, and SE.
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53 **Thiol-ene chemistry.** A UV lamp (254 nm, 18 Watt) was mounted inside a polyethylene glove
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55 bag that was continuously purged with N₂. Thiol-terminated LbL assemblies were immersed in
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57 solutions of 12.5 – 50% w/v PBd in THF in Teflon containers and exposed to UV light for 5 – 11
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4 h. Samples were then rinsed with THF, sonicated in THF for 5 min, rinsed with THF again, and
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6 dried with a stream of nitrogen. The PBd-terminated samples created in this way were immersed
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8 in neat PDT in Teflon containers and again exposed to UV light for 4 – 12 h in an N₂ purged
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10 glove bag. The resulting samples were characterized by SE and contact angle goniometry.
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14 **APTES Deposition.** Air plasma cleaned silicon substrates were placed in 2% solutions of 3-
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16 aminopropyltriethoxysilane (APTES) in toluene for 15 min at 100 °C, after which the surfaces
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18 were rinsed thoroughly with toluene.
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21 **Sample Characterization.** Sessile water contact angles were measured with 20 µL water
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23 droplets using a contact angle goniometer (model 100-00, Ramé-Hart Inc., Netcong, NJ). Film
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25 thicknesses were measured by spectroscopic ellipsometry (SE) at 70° over a wavelength range of
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27 ca. 200 – 1000 nm (M-2000D, J. A. Woollam Co., Lincoln, NE). The substrates were modeled
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29 using the optical constants of silicon in the instrument software, and the native oxide and
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31 polyelectrolyte multilayers were modeled using the optical constants of SiO₂, also from the
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33 instrument software. X-ray photoelectron spectroscopy (XPS) was performed with an SSX-100
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35 ESCA spectrometer from Surface Science equipped with a hemispherical analyzer and a
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37 monochromatic Al Kα (1486.6 eV) source. Sample roughnesses were determined using a Veeco
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39 Dimension V AFM (Digital Instruments Inc., Santa Barbara, CA). ToF-SIMS was performed
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41 with a ToF-SIMS IV instrument (ION-TOF, Münster, Germany) with a gallium, Ga⁺, liquid
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43 metal ion source.
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RESULTS AND DISCUSSION

LbL Films of PAH and PAA.

The LbL deposition of PAH and PAA was explored with solutions of these polyelectrolytes at ca. pH 5.0 and 5.7, respectively.^{36, 40} A series of assemblies was also prepared at ca. pH 8.0 (PAH solution) and 8.7 (PAA solution). Details regarding their growth, thermal cross-linking, and stability is given in the Supporting Information.

Thiol Termination of PAH-Terminated PAH/PAA LbL Assemblies. PAH-terminated LbL assemblies of PAH and PAA ought to possess unreacted amine groups at their surfaces, i.e., this should certainly be the case for uncross-linked assemblies, but even cross-linked assemblies should possess some free amine groups. Traut's reagent (2-iminothiolane) is a well-known, cyclic reagent that is frequently used in bioconjugate chemistry.⁴¹ It works through a ring opening mechanism to convert amine groups into thiol (-SH) moieties. We followed the reaction between Traut's reagent and PAH-terminated LbL assemblies via XPS and SE as a function of the solution pH (5 or 8), reaction temperature (0 or 20 °C), concentration of Traut's reagent (0.001, 0.01, or 0.1 M), and degree of thermal cross-linking of the LbL assembly (cross-linked or not). The exposure time to Traut's reagent was 30 min in all cases.

Traut's reagent reacts well with primary amines at pH 7 – 9.⁴²⁻⁴³ However, this reaction may occur with the primary amines of PAH at even lower pH values, i.e., there may still be free amine groups on the polyelectrolyte below pH 7 because neighboring, positively charged amino groups on PAH may interact and perturb (lower) each other's pK_a values.⁴⁴ Accordingly, the reaction between Traut's reagent and PAH-terminated, uncross-linked PAH/PAA assemblies was attempted at pH 5. Figure 2 indicates that some reaction does take place under these conditions, as measured by XPS S 2s/N 1s ratios and changes in film thickness, which correlate reasonably

well with each other. However, Figure 2 also shows that the reactions run more efficiently at pH 8, even when the concentration of Traut's reagent is quite low.

Figure 2. Thickness changes by ellipsometry (circles) and S 2s/N 1s ratios (triangles) for PAH-terminated PAH/PAA assemblies treated with Traut's reagent under different conditions, as indicated in the figure. All LbL assemblies were uncross-linked, except as indicated above. All reaction times were 30 min. Error bars are standard deviations of the measurements.

The reaction of Traut's reagent with a cross-linked PAH-terminated PAH/PAA assembly was also studied (Figure 2). Here, some reaction appears to take place, but to a lesser degree than for the uncross-linked films. Cross-linking is expected to decrease the number of amine groups available at the surfaces, and also decrease the ability of Traut's reagent to diffuse within the PAH/PAA assemblies, i.e., these results constitute a chemical test that is consistent with the thermal cross-linking of PAH/PAA assemblies. Finally, Figure 2 shows that the reaction between Traut's reagent and the PAH-terminated surfaces is more efficient at higher concentrations of Traut's reagent and with increased reaction temperature. Both of these results are consistent with the general theory of chemical reactivity. As a control, uncross-linked PAH/PAA samples were

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4 exposed to a blank solution (no Traut's reagent) at pH 8 and 20 °C. Here, SE showed a
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6 negligible change in film thickness (0.36 Å), and XPS showed an insignificant S 2s/N 1s ratio of
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8 0.034. The best conditions found for the Traut's reagent/PAH reaction are pH 8, 20 °C, and 0.1
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10 M, i.e., the highest pH, temperature, and concentration studied.
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14 **Analysis and Prevention of Thiol Group Oxidation.** Thiol groups are prone to oxidation so
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16 it is important to ensure that they have not oxidized prior to attempting thiol-ene chemistry.^{21, 26-}
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18 ^{27, 45} This topic is considered important in bioconjugate chemistry,²¹ and there has been some
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20 mention of it with regards to surfaces. For example, Halliwell and Cass⁴⁶ studied mercaptosilane-
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22 terminated surfaces. They noted the possibility of thiol oxidation, and cited a private
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24 communication that suggested that oxidation of thiol groups on surfaces takes place rapidly
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26 above 115 °C, and that this process can be followed by XPS. Fierro and coworkers modified
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28 silica with a mercaptosilane and oxidized the resulting thiol groups using hydrogen peroxide.
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30 However, beyond these studies, there do not appear to have been very many mentions of this
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32 topic in the literature, and we are not aware of any oxidation studies on thiol-terminated surfaces
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34 prepared with Traut's reagent. That is, we have been unable to find any work related to the very
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36 important issue of the oxidation of thiol-terminated surfaces in the air.
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43 To understand their stability against oxidation, PAH/PAA LbL assemblies treated with Traut's
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45 reagent (at pH 8, 20 °C, and 0.1 M) were exposed to the air and room light, i.e., typical
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47 laboratory conditions, for 24 or 48 h, and then analyzed by XPS. Changes in the S 2s/N 1s ratio
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49 were used to determine any loss of sulfur from the surfaces, and peak fitting of the S 2s envelope
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51 was used to assay any changes in the oxidation state of sulfur. The S 2s peak was used in this
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53 analysis instead of the more intense S 2p peak (i) to avoid any possible overlap of the S 2p (160-
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169 eV) region with the Si 2s (155-165 eV) signal from the substrate,⁴⁷ and (ii) because it appears as a simpler, single peak, and not a spin-orbit doublet.

After exposure to the air, both a loss of sulfur from the surfaces and a change in the chemical state of the remaining sulfur were observed. Based on decreasing S 2s/N 1s ratios, 15% of the sulfur was lost after the first exposure to air, and 36% after the second. To assay the chemical state of sulfur in/on the assemblies after these stability tests, the XPS S 2s signals from the surfaces were fit to three 80:20 Gaussian-Lorentzians of equal width with positions that were allowed to vary in an unconstrained manner (see Figure 3). The result of this exercise was three peaks at nearly the same binding energy (231.5 ± 0.2 eV) that were assigned to oxidized sulfur, three peaks at nearly the same binding energy that were assigned to thiol groups (227.6 ± 0.1 eV), and three peaks at nearly the same binding energy that were assigned to thiolate groups (225.4 ± 0.4 eV).⁴⁷ The standard deviation for the thiolate measurement is larger because of the uncertainty associated with the position of the very small thiolate signal in the 48 h sample in Figure 3C (the peak positions of the thiolate signals in Figures 3A and 5B were both 225.7 eV). Based on the peak areas from this fitting exercise, the fraction of thiolate groups on the surfaces decreased from 26% to 7% after 24 h of exposure to the laboratory environment and finally to 3% after 48 h of exposure. The fraction of thiol groups at the surfaces also decreased: from 55% to 43% after 24 h and finally to 36% after 48 h of air exposure. Finally, the fraction of sulfur in an oxidized state increased from 19% initially to 50% after 24 h, and finally to 61% after 48 h. These results indicate that thiolate groups on our PAA/PAH assemblies are more prone to oxidation than thiols, but that the thiols also oxidize to a significant extent. Thus, to avoid degradation of the reduced sulfur species (thiols and thiolates) at our surfaces, PAA/PAH assemblies treated with Traut's reagent were used immediately after their preparation. It was also

shown that the thiol content of the surfaces could be increased by rinsing with dilute acetic acid (see Supporting Information). However, this step was not used before execution of our thiol-ene chemistry (see next section).

Figure 3. XPS S 2s narrow scans of thiol-terminated samples before and after 24 h and 48 h exposures to air and light. The S 2s peak is fitted with three 80:20 Gaussian:Lorentzian peaks of equal width. The peaks are designated as oxidized sulfur, thiol, or thiolate.

Thiol-ene Attachment of 1,2-Polybutadiene to Thiol Terminated Assemblies. Cross-linked LbL assemblies terminated with thiol groups from Traut's reagent were reacted with different concentrations of PBd in THF (12.5 – 25% w/v) for different amounts of time (~6 to ~11 h). These experiments were performed under irradiation of 254 nm UV light in an inert (N_2) atmosphere. The chemisorption of PBd was confirmed by sessile water contact angles (20 μ L water drops) and by SE film thickness measurements. Figure 4 reveals that low exposures of UV light and/or low concentrations of PBd lead to rather thin films of adsorbed PBd (< 10 Å) with contact angles below 100° . Higher concentrations (~25%) of the polymer and/or longer exposure times typically produced 5 – 8 nm films with water contact angles above 100° . For comparison, an uncross-linked assembly terminated with thiol groups was also reacted (4 d after its preparation) with a more concentrated solution of PBd in THF (50% w/v), see data points with

the asterisk (*) in Figure 4. This reaction was carried out with 254 nm UV light without a blanket of N₂. Under these conditions, the thiol groups would be expected to oxidize readily. That is, the smaller number of attachment points that are expected here is consistent with the lower film thickness obtained. Nevertheless, attachment of PBd was successful on both cross-linked and uncross-linked films, whether in the air or not, presumably because the polymers are relatively large and do not require a large number of attachment points.

Figure 4. Ellipsometric thicknesses and water contact angles after reaction of a thiol terminated, cross-linked LbL assembly with 1,2-polybutadiene (PBd) under different experimental conditions. The data point marked with “*” are for thiol terminated uncross-linked LbL assemblies reacted in the air instead of in an inert atmosphere.

Thiol-ene Attachment of 1H,1H,2H,2H-Perfluorodecanethiol to PBd Terminated Assemblies. The PBd-terminated assemblies described in the previous section underwent a second thiol-ene reaction with neat PDT. Reaction times were 4, 5, 8, and 12 h under 254 nm UV light and a blanket of N₂. Increases in film thickness of ca. 4 Å and water contact angles of ca. 120° were observed for the 4 – 8 h exposures on cross-linked and uncross-linked LbL assemblies terminated with PBd (see Supporting Information Figure 7). One cross-linked assembly,

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4 however, showed much higher thickness of its PDT layer: 12.75 Å. The high water contact
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6 angles obtained at these moderate UV exposures suggest that a large number of sites (carbon-
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8 carbon double bonds) are still available on adsorbed PBd for binding to another thiol. However,
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10 after 12 h of UV exposure, the film was catastrophically damaged. That is, long exposures of the
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12 films to UV light damage the films, decreasing their thicknesses and leaving them hydrophilic.
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14 Clearly, these results imply that some damage to the assemblies is always taking place. That is,
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16 the ability of PBd and PDT to impart hydrophobicity and stability (vide infra) appear to
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18 outweigh any film damage at lower exposures.
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23 **Stability of Hydrophobic Assemblies, Including Prevention of Film Delamination by**
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25 **Substrate Silanization.** As a stability test, the cross-linked, hydrophobic surfaces prepared with
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27 PBd and PDT described above were floated upside down on the surface of water for an extended
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29 period of time. After ca. 7 days, the hydrophobic layers delaminated from their silicon substrates
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31 to produce free-standing films. These films were transparent and colorless, and delaminated as
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33 single pieces. We hypothesized that delamination was due to a lack of covalent bonds between
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35 the film and the substrate. Accordingly, a thin layer (1 – 2 nm) of a silane coupling agent,⁴⁸ 3-
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37 aminopropyltriethoxysilane (APTES),⁵ was deposited on the substrates. The LbL of PAA and
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39 PAH was then performed as before, followed by depositions of Traut's reagent, PBd, and PDT.
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41 This tethered layer did not delaminate when floated upside down in water for 9 days in water.
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43 The same sample was then floated upside down in an acidic buffer (pH 1.68) for 30 days. No
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45 delamination occurred. Periodically, during this 30-day stability test, the surface was removed,
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47 rinsed, dried, and characterized by SE and wetting. Essentially no change in its thickness
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49 occurred during this time, although its water contact angle decreased modestly from 122° to
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4 112°. However, the original contact angle could be recovered simply by drying the sample for 1
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7 – 2 h at 70 °C.
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9 The stabilities of complete hydrophobic assemblies tethered through APTES were also tested
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11 by swabbing with ethanol and by the Scotch tape test. For the ethanol swabs, a sponge was
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13 dipped in ethanol and then gently rubbed across the surface of the film. In the Scotch tape test, a
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15 piece of Scotch tape was pressed against the sample surface and then pulled off, where this test
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17 was performed multiple times on the same sample. In neither case was any change in water
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19 contact angle or ellipsometric thickness observed.
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24 CONCLUSIONS

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27 A complex molecular assembly was prepared on a silicon surface using a combination of
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29 uncross-linked or thermally cross-linked polyelectrolyte multilayers, bioconjugate chemistry
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31 with Traut's reagent (2-iminothiolane), thiol-ene chemistry with PBd, thiol-ene chemistry with a
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33 fluorinated thioalkane, and silane chemistry. The oxidation of thiols on assemblies exposed to
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35 the air was monitored by XPS, which showed them to be relatively unstable. Thiol-terminated
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37 assemblies were reactive with PBd, and subsequent thiol-ene chemistry on residual double bonds
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39 from the PBd was possible. Assemblies terminated with a fluorinated thiol showed good
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41 hydrophobicities (WCA 120). Hydrophobic assemblies attached through a silane coupling agent
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43 were well adhered to the substrate. Assemblies resisted rubbing with ethanol swabs, and the
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45 Scotch tape test.
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ASSOCIATED CONTENT

Supporting Information Additional data, including plot of thickness vs. layer number for PAH/PAA LbL growth at pH 5 and pH 8, ellipsometric thicknesses of LbL assemblies before and after thermal cross-linking at 250 °C for at least for 2 h, plot of LbL assembly stability as a function of sonication conditions, discussion and plot showing the effects of rinsing/immersing thiol-terminated assemblies in dilute acetic acid, and plot of the increase in thickness and water contact angle for PBd-terminated assemblies after reaction with PDT.

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Author Contributions

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Graphical Abstract