

Tuning Oleophobicity of Silicon Oxide Surfaces with Mixed Monolayers of Aliphatic and Fluorinated Alcohols

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ABSTRACT

We demonstrate the formation of mixed monolayers derived from a microwave assisted reaction of alcohols with silicon oxide surfaces in order to tune their surface oleophobicity. This simple, rapid method provides an opportunity to precisely tune the constituents of the monolayers. As a demonstration, we sought fluorinated alcohols and aliphatic alcohols as reagents to form monolayers from two distinct constituents for tuning the surface oleophobicity. The first aspect of this study sought to identify a fluorinated alcohol that formed monolayers with a relatively high surface coverage. It was determined that *1H,1H,2H,2H*-perfluoro-1-octanol yielded high quality

monolayers with a water contact angle (WCA) value of $\sim 110^\circ$, and contact angle values of $\sim 80^\circ$ with toluene and hexadecane exhibiting both an excellent hydrophobicity and oleophobicity. Tuning of the oleophobicity of the modified silicon oxide surfaces was achieved by controlling the molar ratio of *1H,1H,2H,2H*-perfluoro-1-octanol within the reaction mixtures. Surface oleophobicity progressively decreased with a decrease in the fluorinated alcohol content while the monolayers maintained their hydrophobicity with WCA values of $\sim 110^\circ$. The simple and reliable approach to preparing monolayers of a tuned composition that is described in this article can be utilized to control the fluorocarbon content of the hydrophobic monolayers on silicon oxide surfaces.

INTRODUCTION

Silicon oxide surfaces with a fine tuned oleophobicity were prepared using microwave assisted reactions with mixtures of fluorinated and aliphatic alcohols. Fluorinated or partially fluorinated surfaces have been previously investigated for their ability to tailor the physical properties of surfaces, such as friction and wettability, electronic properties, or resistance to biomolecules,¹⁻³ for usage in applications that include anti-wetting,⁴ oil-water separation,⁵ electronic devices,⁶⁻⁹ and biomaterials.¹⁰⁻¹² In particular, silicon oxide surfaces modified with fluorocarbon or hydrocarbon chains have been widely pursued in fields requiring a fine control over interface wetting,¹³⁻¹⁵ electronics,⁶⁻⁹ and separation science.¹⁶⁻²¹ In order to functionalize silicon oxides with fluorocarbons or hydrocarbons, silane based compounds have been widely utilized to modify the properties these surfaces through the formation of molecular-scale coatings, commonly referred to as self-assembled monolayers (SAMs).^{3, 22-24} Challenges in the formation of silane based

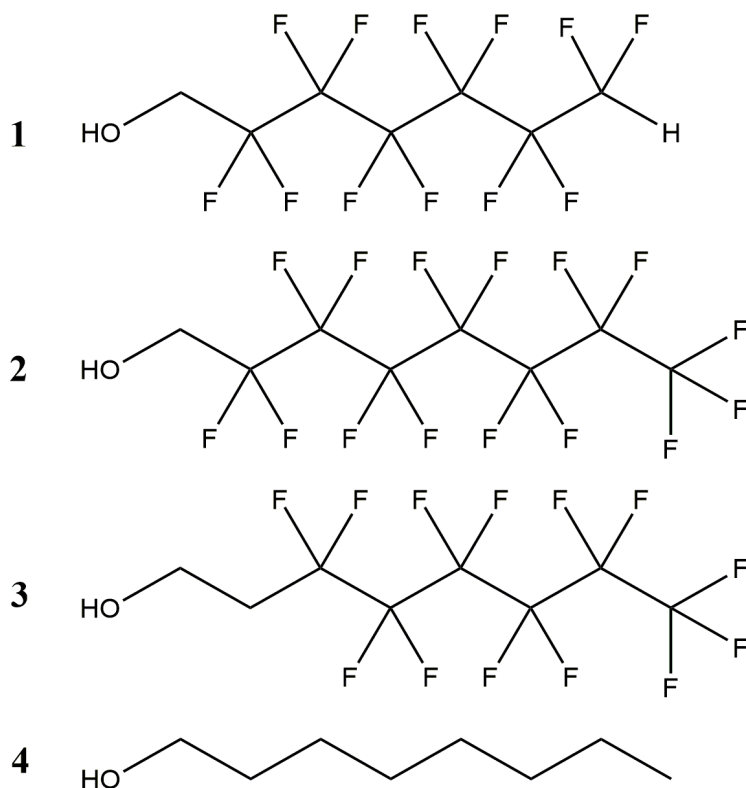
monolayers include the reactivity of silanes with water, their sensitivity to intermolecular polymerization, and tendency to form multilayers.²⁵⁻²⁷ These challenges ultimately limit the control over composition of the monolayers, especially when mixed monolayers are required for tailoring the properties of surfaces. In contrast, alcohol based reagents forego many of these challenges due to their minimal reactivity with water. Such advantages enable a simple experimental setup under ambient laboratory conditions while also tuning the oleophobicity and hydrophobicity of silicon oxides through precisely controlling the composition of the reactants.

Previously, the surface modification of silicon oxide surfaces with various alcohol compounds has been achieved through a microwave assisted condensation reaction.²⁸ Microwaves effectively deliver thermal energy to drive the condensation reaction of alcohols with surface bound silanol groups. Formation of monolayers can be accelerated through microwave induced heating of doped silicon substrates, as well as heating via surface adsorbed water molecules. High temperatures created at the interface accelerates the condensation of alcohol and desorption of water molecules at the silicon oxide surfaces.²⁸ Microwave radiation techniques can also provide good control over the temperatures of solutions in pressurized reaction vessels.²⁹ Here, we utilize these heating techniques to tune the oleophobicity and hydrophobicity of silicon oxide surfaces. These properties were controlled by tuning the molar ratio of fluorinated and aliphatic alcohols used as reagents in these reactions. First, we investigated the reactivity, surface properties, and elemental composition of monolayers formed with three different fluorinated alcohol compounds. Their characterization was largely performed using contact angle measurements and XPS analyses. Monolayers with a fluorocarbon backbone should be easily discernable using these techniques due to its ability to alter the surface wetting properties of the silicon oxide surfaces,²⁻³ while also possessing a unique spectroscopic signature.³⁰ We evaluated each of these three compounds for their ability to

effectively modify the surface properties of silicon oxide substrates. Next, surface oleophobicity was tuned by systematically controlling the molar ratio of fluorinated and aliphatic alcohols within the reaction medium. This approach enabled us to tune the composition of monolayers on silicon oxide surfaces (e.g., fluorinated backbones relative to their hydrocarbon content) in order to finely adjust their resulting surface properties.

A series of three compounds, each with a unique fluorinated, linear backbone and an alcohol head group, were chosen for evaluating their ability to modify silicon oxide surfaces through microwave assisted reactions. The compounds chosen for this study were *1H,1H,7H*-perfluoro-1-heptanol ($\text{H}(\text{CF}_2)_6(\text{CH}_2)\text{OH}$, compound **1**), *1H,1H*-perfluoro-1-octanol ($\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)\text{OH}$, compound **2**), and *1H,1H,2H,2H*-perfluoro-1-octanol ($\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{OH}$, compound **3**). A fourth compound used for comparison was 1-octanol ($\text{CH}_3(\text{CH}_2)_7\text{OH}$, compound **4**). The molecular structures of these four compounds are shown in Chart 1. Each compound has distinguishable traits. Compound **1** possesses a terminal CHF_2 moiety, unlike compounds **2** and **3** that each possess a terminal CF_3 . Differences in the terminal group could affect the overall surface properties of the resulting monolayers due to deviations in their packing density and chemical properties, which is analogous to monolayers of linear chain thiols on gold surfaces.³¹⁻³³ Another difference in the molecular structure of compounds **1** to **3** is in the length of hydrocarbon spacer in between the fluorocarbon chain and the hydroxyl group. Both compounds **1** and **2** have a methylene group between the hydroxyl head group and the fluorocarbon chain, while compound **3** has a bridging ethylene group. The length of bridging hydrocarbon chain between hydroxyl group and fluorocarbon chain may influence the overall packing density of the resulting monolayers, which could ultimately impact their ability to control the wettability of the modified surfaces.³⁴⁻³⁵ In this study, we sought to find a fluorinated alcohol compound capable of forming

Chart 1. Structures of alcohol containing compounds evaluated for their ability to react with and modify the properties of silicon oxide surfaces.



monolayers with a high packing density and a maximum hydrophobicity and oleophobicity. The compounds of interest for this study (compounds **1** to **3**) were chosen because of the similarities in their molecular chain lengths and fluorocarbon contents. Compound **4** was also studied as a reference compound containing only a hydrocarbon backbone with a similar molecular chain length to the other reagents. All four compounds also possess low melting points and are liquids at room temperature with the exception of compound **2**, which was heated to $\sim 50^{\circ}\text{C}$ prior to further use. Reactions were initially carried out using only neat solutions of each reactant; no solvents were used to dilute any of these reactants. Variations in the composition of each reactant was the primary variable in the initial study. This study sought to determine the effectiveness of each reactant to tune the surface properties of silicon oxides. Other parameters, such as microwave

reaction time and temperature, were kept constant for this study. In the second part of the study, formation of mixed monolayers was sought in order to tune the oleophobicity of silicon oxide surfaces. This reaction was achieved through microwave processing of the substrates while immersed in a mixture of fluorocarbon alcohols and aliphatic alcohols. Oleophobicity, hydrophobicity, surface composition, and surface adhesion properties of the modified substrates were evaluated using contact angle measurements, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

EXPERIMENTAL SECTION

Reagents and Materials. All reagents were used as received, which included *1H,1H,7H*-dedecafluoro-1-heptanol [$\text{H}(\text{CF}_2)_6(\text{CH}_2)\text{OH}$, Alfa Aesar, 97%, CAS no. 335-99-9], *1H,1H*-perfluoro-1-octanol [$\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)\text{OH}$, Alfa Aesar, 97%, CAS no. 307-30-2], *1H,1H,2H,2H*-perfluoro-1-octanol [$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{OH}$, Sigma-Aldrich, 97%, CAS no. 647-42-7], 1-octanol [$\text{CH}_3(\text{CH}_2)_7\text{OH}$, Sigma-Aldrich, ACS reagent grade, 99%, CAS no. 111-87-5], octyldimethylchlorosilane (Sigma-Aldrich, 97%, CAS no. 18162-84-0), toluene (Fisher Scientific, Laboratory grade, 99.5%, CAS no. 108-88-3), hexadecane (Sigma-Aldrich, 99%, CAS no. 544-76-3), sulfuric acid (Caledon, ACS reagent grade, CAS no. 7664-93-9), hydrogen peroxide (ACP, ACS reagent grade, CAS no. 7722-84-1), anhydrous ethyl alcohol (Commercial Alcohols, P016EAAN, CAS no. 64-17-5), acetone (Fisher Scientific, reagent grade, CAS no. 67-64-1), and isopropanol (Fisher Scientific, reagent grade, CAS no. 67-63-0). Four inch, p-type, test grade, single-side polished, $\langle 1\ 0\ 0 \rangle$ silicon wafers were purchased from the Nanofabrication Facility in 4D LABS at Simon Fraser University.

Preparation of Silicon Substrates. Preparation of the silicon substrates is described elsewhere in further detail.²⁸ Briefly, a 7:2 (v/v) mixture of concentrated sulfuric acid and 30% (v/v) hydrogen peroxide was used to prepare a piranha cleaning solution. *CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care.* The silicon substrates were diced into 1 cm by 1 cm squares and immersed in the piranha solution for 1 h. The substrates were then rinsed with copious amounts of 18 M Ω ·cm deionized (DI) water (Barnsted NANOpure DIamond water filtration system), followed by drying under a stream of nitrogen gas filtered with a PTFE membrane containing <0.2 micron pores.

Microwave Assisted Reactions. The procedure for the microwave assisted surface modification of silicon oxides with 1-octanol was described previously.²⁸ Briefly, 2 mL of a reactant or a mixture of reactants were placed with a cleaned substrate into a 10 mL glass test tube (Part no. 908035, CEM). Separate tubes were used for each distinct reaction. Each sample was exposed to microwave radiation using a CEM Discover microwave reactor for 30 min at a set point temperature of 130°C. All samples were cooled after the reaction for 5 min before handling. After removing each substrate from its glass reaction vessel, the substrates were individually washed with a series of solvents, such as acetone and isopropanol. Each washed substrate was dried under a stream of filtered N₂ gas. To remove physically adsorbed molecules and contaminants, the substrates were sonicated in anhydrous ethyl alcohol for ~2 min, rinsed with DI water, and dried under a stream of filtered N₂ gas.

Preparation of Mixed Monolayers. Mixtures containing different ratios of 1H,1H,2H,2H-perfluoro-1-octanol and 1-octanol were prepared with specific mole ratios of each reagent. The amount of each reactant required to create these mixtures were calculated from the molar masses of each compound. These solutions were vortexed vigorously to ensure homogeneous mixing.

Approximately 2 mL of each mixture were loaded into separate 10 mL glass test tubes along with clean silicon substrates for microwave processing as described above.

Contact Angle (CA) Measurements. Contact angle measurements were performed to evaluate surface coverage of the monolayers and the effectiveness of tailoring the wettability of the modified surfaces. In particular, hydrophobicity and oleophobicity of the substrates were evaluated by CA measurements using droplets of DI water, toluene, or hexadecane. These measurements were obtained for 2 μ L droplets of each solvent dispensed onto distinct regions of each substrate. The CA was measured as the angle between the air-liquid interface of each droplet and the interface of each liquid and the substrates. Five advancing contact angle measurements were obtained for each sample by adding 2 μ L per consecutive measurement. The average and standard deviation was determined by calculating the average and the standard deviation of these five advancing contact angle measurements.

X-ray Photoelectron Spectroscopy (XPS). Chemical composition of modified silicon oxide surfaces were investigated by XPS. These studies were conducted using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source ($AlK\alpha$ of 1486.7 eV) operating at 150 W at a 90° take-off angle. Survey scans (0 to 1200 eV) were acquired using a pass energy of 160 eV, a dwell time of 100 ms, and 1 sweep. High resolution scans were obtained using a pass energy of 20 eV, a dwell time of 500 ms, and 15 sweeps. An area of 700 μ m by 300 μ m was analyzed for each measurement. The XPS peak analyses and quantification of the peak areas were performed using Vision Processing.

Adhesion Force Measurements. In order to characterize the adhesion force of the samples, force spectroscopy measurements were acquired using an MFP 3D AFM (Asylum Research) using

silicon nitride (Si_3N_4) cantilevers from BudgetSensors (Contact-G, resonant frequency of 13 kHz, force constant 0.2 N/m). Some cantilevers were coated with octyldimethylchlorosilane by vapor deposition at room temperature in a vacuum desiccator over a period of 17 h. The force measurements were acquired from scan areas of 5 μm by 5 μm with a resolution of 32 by 32. The adhesion forces were obtained using Igor Pro 6.22.

RESULTS AND DISCUSSION

The goals of this work include demonstrating the utility of microwave reactions for attaching monolayers of fluorinated alcohols to the surfaces of silicon oxides and further tuning their oleophobicity. Before systematically tuning its oleophobicity, it was essential to first assess the surface properties of the silicon oxide surfaces reacted with different types of fluorinated alcohols. A series of fluorinated alcohols were selected for these microwave assisted reactions, and the modified surfaces investigated for changes in their hydrophobicity and oleophobicity. The structures of the fluorinated alcohols chosen for this study are depicted in Chart 1. Compound **4**, 1-octanol, was chosen as a reference compound for its similar chain length to these reactants and for its known properties when reacting with silicon oxides through microwave assisted reactions.²⁸ Piranha cleaned silicon substrates were immersed in neat solutions of each compound (**1** to **4**) and subsequently heated in a microwave reactor (i.e. performing separate reactions between the silicon oxide surfaces and each of the compounds).

Experimental conditions were tuned as required for the formation of monolayers from each compound. The reaction temperature was set to 130°C, and the reaction time was set to 30 min. In previous work, 1-octanol was exposed to microwave radiation at 180°C, as this temperature yielded the most uniform monolayers with relatively high water contact angle (WCA) values.²⁸ In

the studies described herein, thermal degradation of the fluorinated alcohols was an important limiting factor for the reaction temperature (see Supporting Information). It was determined that thermal degradation of compounds **1** to **3** was minimal at a reaction temperature of 130°C. The duration of each microwave reaction was set to 30 min to ensure the reactions reached completion. Polished silicon substrates covered with a native silicon oxide layer were chosen as the test substrates, which were diced into smaller sections (~1 cm²) and piranha cleaned prior to use in these studies.

Correlation between Molecular Structure of Reactants and Quality of Monolayers. The hydrophobicity of the silicon oxide surfaces after each microwave triggered reaction was investigated through water contact angle (WCA) measurements (Figure 1). The WCA values

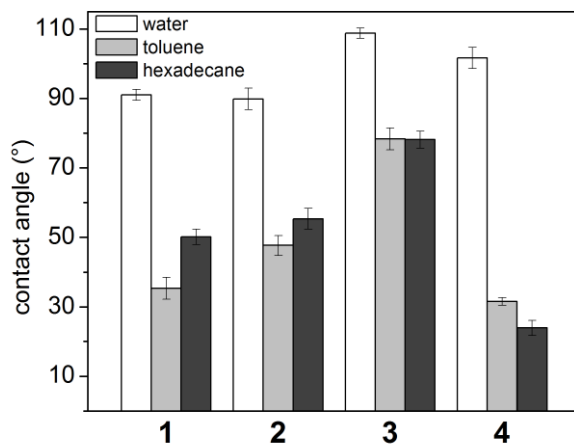


Figure 1. Contact angle measurements for silicon substrates modified using a microwave assisted reaction with compounds **1**, **2**, **3**, or **4**. These measurements were performed with water (white), toluene (light grey), and hexadecane (dark grey). The average of five advancing contact angle measurements are plotted along with error bars indicating one standard deviation.

provided insight into the uniformity and surface coverage of the monolayers formed on the silicon oxide surfaces. Clean silicon substrates with a native oxide film have WCA values of $\sim 20^\circ$, which is attributed to the hydrophilic silanol groups on these surfaces. The WCA values for surfaces reacted with either compound **1** or **2** were 91° and 90° , respectively (Figure 1). These results indicated that the silicon oxide surfaces were rendered hydrophobic when reacted with compound **1** or **2**. However, the WCA values for these modified surfaces were not as high as those reported in the literature for various types monolayers prepared from alkyl chains on oxide surfaces³ or alkanethiols on gold surfaces,³⁶ with the reported WCA values ranging from 105° to 110° . Water contact angles of 109° and 102° were achieved for the silicon oxide substrates following their microwave assisted reaction with compound **3** or **4**, respectively (Figure 1). These results indicated that hydrophobic surfaces were achieved using either compound **3** or **4**. The results also suggest that surface coverage and uniformity of the monolayers derived from reactions with compound **3** were the best among the fluorinated compounds evaluated in this study. This outcome could be attributed to differences in the degree of steric hindrance at the reaction site while the monolayers are being formed from compounds **1** to **3**. Compounds **1** and **2** both have a methylene spacer between the hydroxyl head group and their fluorocarbon chain. The closer proximity of the bulkier fluorocarbon chain to the reacting silanol groups on the surfaces could compromise the reaction by steric hindrance. On the other hand, the ethylene linker in compound **3** could provide a higher degree of freedom of motion for the alcohol head group relative to the other two compounds. It was anticipated that compound **3** would also be better able to reorient itself when immobilized at the interface to minimize steric hindrance within the monolayers.

To further characterize the properties of surfaces modified with compounds **1** to **4**, contact angle measurements were also performed using toluene and hexadecane. There was a clear difference in

the oleophobicity of the substrates when reacted with fluorinated compounds (**1** to **3**) and a non-fluorinated compound (**4**) (Figure 1). The contact angles of toluene and hexadecane were 31° and 23°, respectively, for substrates reacted with compound **4**. These results indicated that the modified surfaces were oleophilic. These values were lower than those obtained from monolayers of undecanethiol on gold surfaces, which yielded a contact angle value of ~50° with hexadecane.⁴ The discrepancy between the results for the monolayers of alkanethiols and those reported herein could be attributed to a limited van der Waal interactions within monolayers prepared from compound **4** due its shorter hydrocarbon chain length. The contact angle values were 35, 48, and 78° for toluene, and 50, 55, and 78° for hexadecane, for substrates reacted with compounds **1**, **2**, or **3**, respectively. These results suggest an increase in the oleophobicity of those surfaces reacted with each of the fluorinated alcohols in comparison to those modified with compound **4**. These values also indicate that the oleophobicity of these surfaces could vary significantly depending on the molecular structure of the fluorinated alcohol. The substrates that exhibited the highest degree of oleophobicity were those that were reacted with compound **3**. Furthermore, this wettability result agrees well with the properties observed for thiol containing fluorocarbon analogues on gold surfaces reported in the literature, with reported contact angles for hexadecane plateauing at a slightly lower value than 80°. ^{4, 34} The substrates reacted with compound **2** yielded lower toluene and hexadecane contact angles than those reacted with compound **3**. Discrepancies between the monolayers formed using either compound **2** or **3** could be attributed to differences in their overall surface coverage. Hydrocarbon chains between the fluorocarbon and hydroxyl group could aid in packing of monolayers by adjusting the molecular tilt to maximize the intermolecular van der Waals interactions.³⁴ A short hydrocarbon chain spacer could compromise these intermolecular interactions and result in a lower surface coverage within the monolayers. Substrates reacted with

compound **1** exhibited the lowest degree of oleophobicity. This result could be attributed, in part, to a decrease in the overall surface coverage of these monolayers. This surface coverage could be compromised by the molecular structure of compound **1**, including its relatively short alkyl spacer between the alcohol head group and the fluorocarbon chain. These results are consistent with reports indicating the formation of disordered monolayers for thiol analogues to compound **1** on gold surfaces.^{2,32} In addition, the partially fluorinated character or hydrogen content of the terminal carbon (CHF_2) for compound **1** could also alter the overall oleophobicity of the resulting monolayers.³¹ Further analyses were required to verify the chemical composition of each of the monolayers when coated onto the silicon oxide surfaces.

Composition of the modified silicon oxide surfaces was analyzed by XPS. All surfaces exhibited a strong fluorine signal (F_{1s}), with the exception of compound **4**, due to the high number of fluorine atoms in the fluorocarbon chains of compounds **1** to **3** (Figure 2A). These results further confirmed that the surfaces were modified with the fluorocarbon containing reactants. Analysis of the high resolution C_{1s} spectra for substrates modified by each compound provided further confirmation of the molecular structure within the resulting monolayers. For instance, surfaces reacted with compound **1** exhibited a single fluorocarbon peak (CF_2) and two additional peaks associated with C-O and a hydrocarbon (CH_2). Substrates modified with compound **2** or **3** exhibited two fluorocarbon peaks (CF_2 and CF_3), the C-O peak, and one hydrocarbon peak (CH_2). The lack of the trifluorocarbon (CF_3) peak for the substrates reacted with compound **1** confirmed the molecular structure of compound **1** within the resulting monolayers, which did not possess a terminal CF_3 . The CF_3 to CF_2 peak ratio was slightly higher for the substrates reacted with compound **3** because compound **2** contained a chain of seven difluorocarbons (CF_2) and a terminal CF_3 , while compound **3** had a chain of only six CF_2 and one CF_3 per molecule.

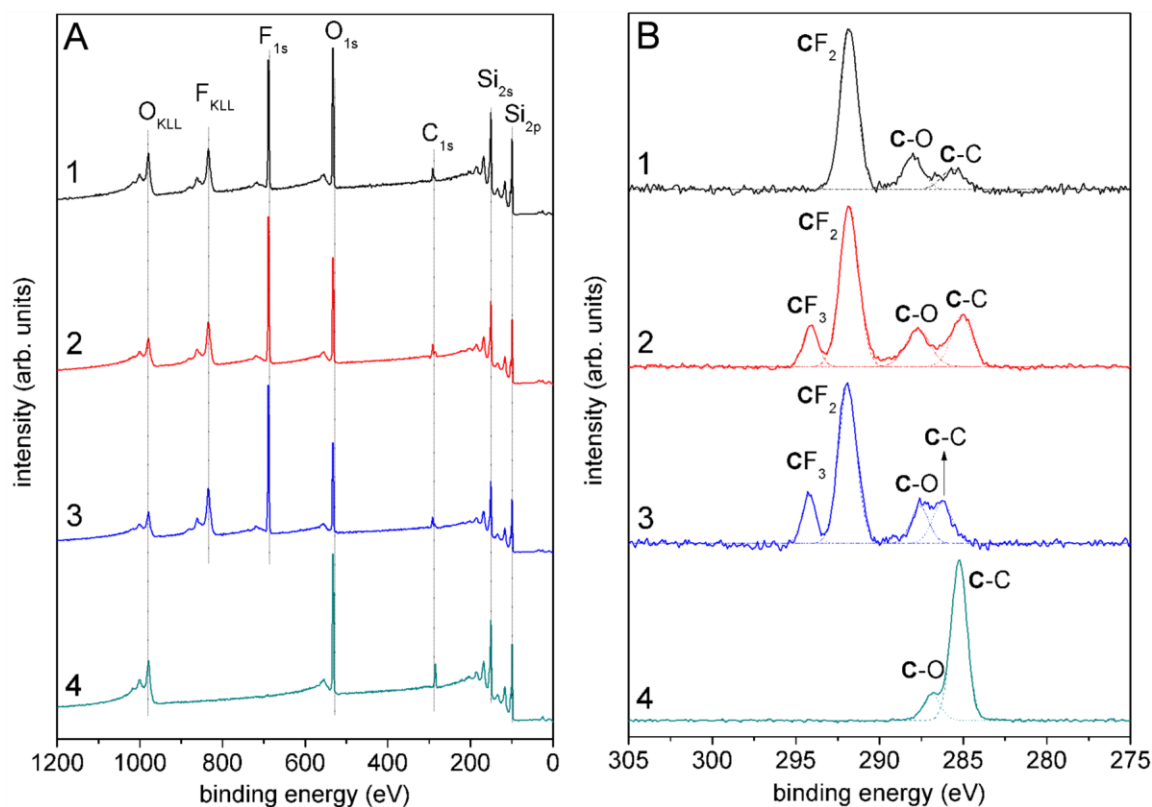


Figure 2. X-ray photoelectron spectroscopy (XPS) of silicon substrates after a microwave assisted reaction with compounds **1**, **2**, **3**, or **4**. Data for each reaction include (A) survey scans and (B) high resolution C_{1s} scans.

An interesting observation is made in the shift in the relative positions of the hydrocarbon peaks in association with the fluorinated alcohols as observed by XPS relative to the peak position for compound **4**. Monolayers formed with compound **4** (aliphatic alcohol) exhibited peak positions for C-C at 285.2 eV. The C-C peak position reported herein is shifted slightly in comparison to literature reported values.^{31,35} This shift in peak position is attributed to discrepancies in the ability to distribute surface charges for the monolayers on thin silicon oxides in comparison to monolayers on gold films.³⁷ The C-C peak position for monolayers prepared from compound **3** was 286.2 eV, indicating a higher relative binding energy for the C-C bond. Contributions from differences in

chain lengths between each of the fluorocarbon and hydrocarbon chains should be minimal because all four compounds have a similar molecular length and, furthermore, attenuation lengths of photoelectrons in the fluorocarbon films have been reported to be similar to those in hydrocarbon films.³⁸ This argument is further supported by the observation that the CF₂ peak position remained centered at 291.8 eV for substrates coated with compounds **1** to **3**. The shift in binding energy of the C-C peak for compound **3** could be attributed to contributions from the terminal fluorocarbon chain that possess stronger electronegativity in comparison to the hydrocarbon spacer. The C-C peaks observed for monolayers formed with compound **1** or **2** did not show any significant shift as these peaks are attributed to miscellaneous contamination present on their surfaces. These monolayers, however, displayed a shift in the peaks attributed to the C-O peaks. The C-O peak positions for monolayers formed with compounds **1**, **2**, **3** or **4** were 288.0, 287.8, 287.6, and 286.9 eV, respectively. This shift in C-O peak position is attributed to the stronger electronegativity of the fluorocarbon chain in comparison to the hydrocarbon chain. The magnitude of the shift observed for the C-O peak position of monolayers prepared from compound **3** is less significant than that observed for the substrates reacted with compound **1** or **2**. This difference in the observed shift in binding energy of the C-O species is attributed to the location of fluorocarbon chain in compound **3** being further away from the C-O bond within the head group of the monolayers.

Quantitative XPS analysis was performed to evaluate the relative packing density of the monolayers formed using the fluorinated alcohols. In particular, peak area ratios of the F_{1s} signal relative to the Si_{2p} signal were analyzed for each of the monolayers prepared from the respective fluorinated alcohols (Table 1). A comparison was sought to provide insight into the relative surface composition of each of these monolayers.³² Relative packing densities were estimated by

Table 1. Quantitative analysis of the XPS survey scans obtained from substrates reacted with compounds **1**, **2**, or **3**.

samples	F_{1s} XPS area	Si_{2p} XPS area	peak area ratio	no. of F atoms	peak area ratio / no. of F	% relative packing density
compound 1	397315	230208	1.73	12	0.144	67
compound 2	902928	427618	2.11	15	0.141	66
compound 3	597861	215782	2.77	13	0.213	100

comparing these XPS peak area ratios to the predicted fluorine content for each of these monolayers using the stoichiometric ratio of fluorine atoms within the respective compounds. The highest relative packing density was obtained for substrates coated with compound **3**. The relative packing density of compounds **1** and **2**, normalized to the density achieved with compound **3**, was 67% and 66%, respectively. These results suggest that the overall packing density of monolayers formed with compounds **1** and **2** were significantly lower than those formed using compound **3**. Furthermore, correlations between the XPS analyses and the results of the wettability studies indicated that the degree of hydrophobicity and oleophobicity of monolayers is proportional to their packing density on the silicon oxide films. Similar correlations have been drawn between wetting properties and the packing densities of monolayers on gold surfaces prepared from thiols with fluorocarbon or hydrocarbon backbones as evaluated by XPS.^{33, 39} In summary, quantitative XPS analyses suggests that the monolayers formed using compound **3** have a substantially higher relative packing density than those prepared with compounds **1** or **2**.

Overall, the contact angle and XPS analyses matched well to the anticipated properties and compositions of monolayers prepared from compounds **1** to **4** on silicon oxide surfaces. Among

the three fluorinated alcohol compounds, monolayers formed with compound **3** exhibited the best ability to create surfaces that were both hydrophobic and oleophobic. Compound **3** was chosen to perform a detailed investigation into monolayers on silicon oxide surfaces containing a mixture of fluorocarbon and hydrocarbon chains to maintain a hydrophobic state while also being able to control and tune their oleophobicity.

Tuning Oleophobicity through Formation of Mixed Monolayers Prepared from Alcohol Based Reagents. We have successfully prepared a series of silicon oxide surfaces modified with either fluorinated or hydrocarbon based alcohols to alter the properties of these surfaces. Compound **3** was identified as an effective reactant to form uniform, fluorinated monolayers on silicon oxide surfaces. We sought to further tune the properties of these monolayers by controlling the molar ratio of compounds **3** and **4** within the reaction mixture. The oleophobicity of the resulting surfaces were evaluated after reacting with mixtures of compounds **3** and **4**. These reaction mixtures were prepared as a molar ratio of compound **3** to compound **4** with specific ratios of 4:1, 3:1, 2:1, 1:1, and 1:2.

Previous studies have demonstrated that phase separation can be observed in mixed monolayers prepared from different chemical constituents.⁴⁰⁻⁴⁵ It was necessary to determine whether this phenomenon was also observed in the monolayers prepared from a mixture of compounds **3** and **4**. Atomic force microscopy (AFM), lateral force microscopy (LFM), and Kelvin probe force microscopy (KPFM) measurements were obtained from substrates coated with the mixed monolayers, but no distinct phase separation was observed from these measurements (Figure S3). Phase separation observed in previous reports for mixed monolayers was driven by the intermolecular interactions between the adsorbed molecular species. The degree of intermolecular interaction and phase separation observed for monolayers prepared from mixtures of distinct

chemical species can be influenced by a number of factors, which include the processing techniques, polarity of solvent(s), reaction mechanism, degrees of freedom (e.g., tilt) of the molecular species within the monolayers, concentrations of each reagent, and temperature of the system.^{40, 44-46} The absence in phase separation observed in our system of study could be attributed to relatively high processing temperatures, the degrees of freedom of the molecular species within the monolayers, and the polarity of solutions used to prepare the monolayers. High temperatures can disrupt molecular structures formed as the result of the separation of distinct chemical species, such as micelles or emulsions formed as a suspension, that are otherwise held together by relatively weak intermolecular interactions. In addition, the alcohol based reagents become immobilized on the surfaces through the formation of covalent bonds, which hinders their rearrangement on these surfaces. In contrast, thiol analogues on gold form dative covalent bonds and can exhibit desorption and lateral migration of species within the monolayers at elevated temperatures.⁴⁶⁻⁴⁷ The solvents used in the preparation of monolayers from alcohol based reagents were the reagents themselves. This approach is distinct from the methods commonly used to prepare monolayers from thiol based species on gold surfaces, which are typically performed using polar solvents such as ethanol. No phase separation was observed within the monolayers prepared from the mixtures of alcohol based reagents, indicating that the fluorocarbon and hydrocarbon species (compounds **3** and **4**, respectively) formed intermixed coatings over the surfaces of the substrates.

Silicon oxide surfaces coated with a series of distinct mixtures of compounds **3** and **4** were evaluated by contact angle measurements. Hydrophobicity of these surfaces was evaluated through WCA measurements (Figure 3). Their hydrophobicity remained consistent across the series of samples with a WCA of $\sim 110^\circ$ regardless of the composition of the reaction mixture. This observation suggests that the uniformity of each of these monolayers was relatively consistent

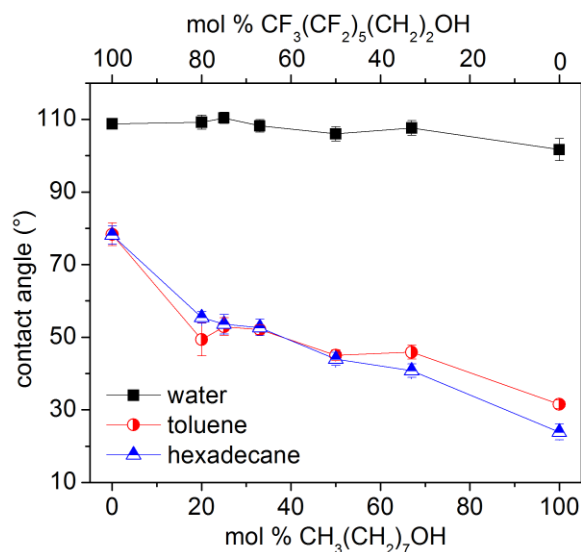


Figure 3. Contact angle measurements (water, toluene, and hexadecane) for silicon substrates after microwave assisted reactions in the presence of mixtures of reactants **3** [$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{OH}$] and **4** [$\text{CH}_3(\text{CH}_2)_7\text{OH}$] at the specified molar ratios.

regardless of the molar ratio of the fluorinated and hydrocarbon based alcohols in solution. Contact angle measurements were also performed using toluene and hexadecane to assess the oleophobicity of these surfaces (Figure 3). Their oleophobicity progressively decreased as the molar ratio of fluorinated alcohols within the reaction mixture also decreased. The relatively small hysteresis values from each of these contact angle measurements (see Supporting Information) further demonstrated the uniform composition of these monolayers prepared from a mixture of fluorocarbon and hydrocarbon reagents. The smaller quantity of fluorinated alcohols within the reaction mixture would, ideally, correspond to the formation of monolayers containing less fluorocarbons and more hydrocarbons. As the proportion of hydrocarbon based alcohols within the mixed monolayers increases, the surfaces should become increasingly oleophilic. The oleophobicity of silicon oxide surfaces was tuned by controlling the molar ratio of fluorinated and hydrocarbon based alcohols in the reaction mixture, suggesting that the composition within the

monolayers closely followed the composition of the mixture in solution. Further studies were, however, required to assess the surface properties and composition of the modified substrates.

Adhesion properties for substrates covered with these mixed monolayers were assessed by AFM (Figure 4). Two types of AFM tips were used in this study, which were silicon nitride (Si_3N_4) tips either with or without a coating of octyldimethylchlorosilane (C8-silane). The interactions between the monolayers on the silicon oxide surfaces and the native Si_3N_4 tips exhibited an interesting correlation between the magnitude of the measured adhesion forces and the composition of the monolayers. Monolayers of either 1-octanol or *1H,1H,2H,2H*-perfluoro-1-octanol exhibited relatively low adhesion forces with average values of 8.5 and 8.8 nN, respectively, in comparison to the monolayers prepared from both components. The substrates with mixed monolayers exhibited adhesion forces up to 15.1 nN. The trends observed in this study suggests that a change in the composition of the monolayers is closely associated with changes to the molecular-scale interactions between the contacting surfaces. This result suggests that the diverse contributions to adhesion are benefiting from the molecular-scale changes in steric strain and nearest neighbor interactions within the mixed monolayers, which is in agreement with previous studies on mixed monolayers prepared from thiols on gold.³²⁻³³ The adhesion forces measured with the C8-silane coated tips, however, progressively increased with an increasing content of 1-octanol in the monolayers. This interaction is likely dominated by the stronger van der Waals interactions between the hydrocarbon chains on the tip and those within the monolayers on the silicon oxide, which is in contrast to the weaker interactions between the fluorocarbons and hydrocarbons. This observed trend corresponds with observations from the studies on the wetting properties of the mixed monolayers; contact angles for the non-polar solvents increased as the fluorocarbon content increased within the mixed monolayers. In conclusion, the adhesion forces

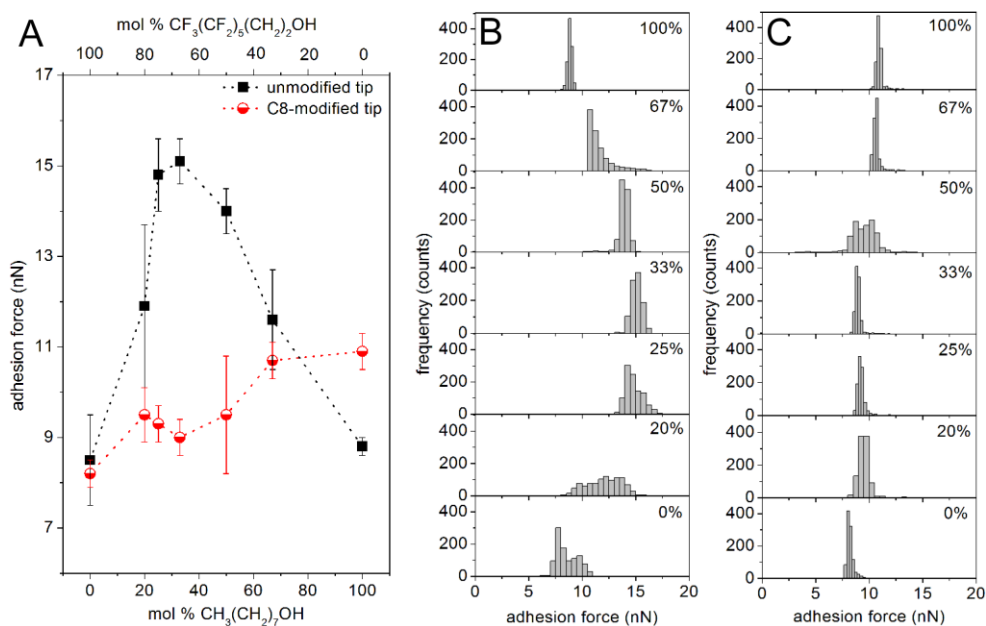


Figure 4. (A) Average adhesion force measurements for substrates coated with different molar ratios of *1H,1H,2H,2H*-perfluoro-1-octanol and 1-octanol. Histograms depict the results of the force spectroscopy measurements performed using either (B) an unmodified silicon nitride (Si_3N_4) tip or (C) a Si_3N_4 tip modified with octyldimethylchlorosilane (C8-silane). The corresponding mole fraction of 1-octanol in the reaction mixture is displayed in the upper right corner of each histogram.

between a Si_3N_4 tip and the single component monolayers were lower than those observed for the mixed monolayers. Furthermore, the adhesion forces between the mixed monolayers and an alkylsilane modified AFM tip progressively decreased with an increase in the fluorocarbon content of the monolayers. Quantitative spectroscopic information on these mixed monolayers was necessary to gain further insights into how the observed properties correlated with specific changes in the surface composition.

The composition of surfaces capped with mixed monolayers were analyzed by XPS. In particular, high resolution C_{1s} scans were quantitatively analyzed by comparing the peak areas associated with the hydrocarbon and fluorocarbon content of the modified surfaces. These peaks were well separated in the high resolution C_{1s} spectra. Relative hydrocarbon and fluorocarbon content of the mixed monolayers were estimated by analyzing the ratio of the respective XPS peak areas. Composition observed for these monolayers on silicon oxide surfaces deviated from the linear changes in molecular composition of the reaction mixtures (Figure 5). There are two distinct trends observed in the composition of the mixed monolayers. Both trends are approximately linear, but with a distinct change in slope or rate of change in composition between the two regions. The first region corresponds to reaction mixtures containing 0 to 25 mol% of 1-octanol containing

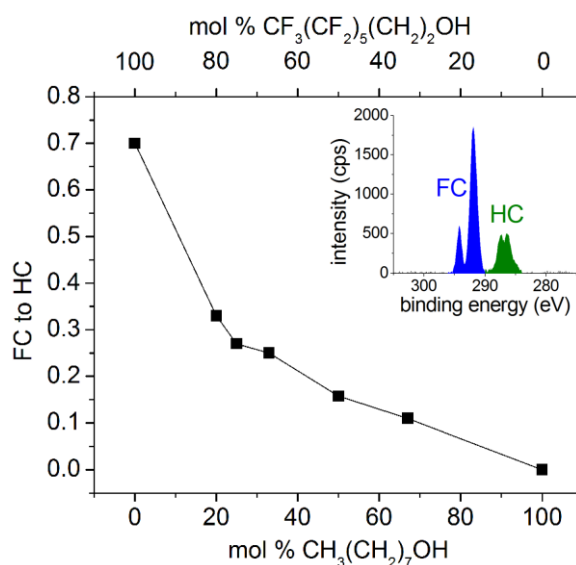


Figure 5. X-ray photoelectron spectroscopy (XPS) analyses of peak area ratios of fluorocarbon (FC) to hydrocarbon (HC) content for silicon substrates after a series of microwave assisted reactions with mixtures of compounds **3** [$CF_3(CF_2)_5(CH_2)_2OH$] and **4** [$CH_3(CH_2)_7OH$] at the specified molar ratios. Inset plots indicate the peaks analyzed in each of these studies.

reaction mixture, and the second region is for reaction mixtures containing 33 to 60 mol% of 1-octanol. Similar trends were observed in the adhesion force measurements, where the average adhesion forces reached a maximum value for monolayers prepared from a reaction mixture containing either 25 or 33 mol% of 1-octanol (Figures 4A and 4B). Deviation between the composition within a solution and that within the resulting monolayers have been reported for mixtures of fluorinated and aliphatic thiol based monolayers on gold surfaces.^{2, 48-49} Additional literature previously reported that the composition of mixed monolayers prepared from fluorocarbon and hydrocarbon based thiols exhibited a linear correlation to the composition of the solution. These studies include mixtures of linear chain, mono-reactive species, such as n-decanethiol and 10-heptadecafluoro-1-decanethiol used to prepare monolayers on silver,⁵⁰ and mixtures of bidentate adsorbates, such as (5-(9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16-heptadecafluorohexadecyloxy)-1,3-phenylene)dimethanethiol (PF PDT) and (5-(hexadecyloxy)-1,3-phenylene)dimethanethiol (HDPDT) used to prepare monolayers on gold surfaces.⁴⁸ The deviation observed in the surface composition of the mixed fluorocarbon and hydrocarbon monolayers derived from alcohol compounds can be attributed to distinct differences between these reagents. One aspect is the discrepancy in the van der Waals diameter of the fluorocarbons and hydrocarbons in the monolayers. The molecular volume of fluorinated species is larger than that of the corresponding hydrocarbon species.^{49, 51-53} This difference in molecular volume can decrease the overall packing density of fluorinated species in monolayers in contrast to hydrocarbon species. The result is a lower fluorocarbon content than anticipated in the resulting mixed monolayers assuming a relative surface area for each species that is proportional to their molar ratio in the reaction mixture. Experimental studies have shown that, although such differences in molecular volume should drive a preferential increase in hydrocarbon content over

that of fluorocarbons in monolayers, the surface composition of fluorocarbon species is often higher than theoretically predicted.⁴⁹⁻⁵⁰ The lower fluorocarbon content could also be attributed to another important factor, which is the increase in polarity of solvents used to prepare many monolayers and its influence on the entropy of mixing.⁵⁴ Surface composition of mixed monolayers can deviate from the solution composition due to interactions of the reactants with the polar solvents.^{42, 54} In contrast, our mixed monolayers utilized solutions prepared from mixtures of relatively nonpolar alcohol based reactants. The interactions of these reactants with a polar solvent were minimized in our studies by using mixtures of two nonpolar alcohols with similar chain lengths. The preferential adsorption of hydrocarbon based alcohols in contrast to the fluorinated alcohols could be attributed to stronger intermolecular interactions (e.g., van der Waals) between the aliphatic alcohols than between the fluorinated alcohols.² These stronger intermolecular interactions between the aliphatic alcohols could accelerate their transport to and, therefore, reaction with the surfaces. Steric hindrance arising from differences in the molecular tilt angle between the fluorocarbon and hydrocarbon species could, in contrast, suppress the reaction between the fluorinated alcohols and the silicon oxide surfaces. The condensation of the alcohol based reagents with the silanol groups on the oxide surfaces result in the immobilization of these reagents. The preferential immobilization of aliphatic alcohols could lead to a further deviation of the surface composition from that in solution as a result of the intermolecular interactions between the species in solution and that bound to the silicon oxide surfaces. To summarize, the oleophobicity of the silicon oxide surfaces progressively decreased with a decrease in the molar ratio of fluorinated alcohol in the reaction mixture, but the fluorocarbon content of the resulting mixed monolayers deviated from the molar ratio of reagents in solution. Monolayers on silicon oxides containing a mixture of fluorocarbon and hydrocarbon based alcohols were derived from a

one pot microwave assisted reaction, which demonstrates the utility of this process to prepare monolayers with a customized composition

CONCLUSIONS

In summary, we systematically investigated the microwave reaction of fluorinated alcohols with silicon oxide surfaces to control surface hydrophobicity and oleophobicity. These modifications were accomplished under ambient laboratory conditions (e.g., without the need of a dry box or vacuum conditions). These processes utilized microwave assisted reactions of neat solutions of fluorinated or aliphatic alcohols, as well as mixtures of these reagents. Monolayers were initially prepared from a series of different fluorinated alcohols, which were evaluated by contact angle measurements. It was determined that the highest quality monolayers of the fluorinated alcohols were those prepared using compound **3** (*1H,1H,2H,2H*-perfluoro-1-octanol). The contact angle values for monolayers prepared from compound **3** were 109°, 78°, and 78° with hysteresis values of 1° or less for water, toluene, and hexadecane, respectively. X-ray photoelectron spectroscopy (XPS) results confirmed the presence of fluorinated species within these monolayers as evidenced by the strong F_{1s} signal and the fluorocarbon content observed in the high resolution C_{1s} scans. These results demonstrated that a microwave assisted condensation reaction with a neat solution of fluorinated alcohols could yield fluorinated monolayers on silicon oxide surfaces. The process demonstrated in this article is a simple method to form monolayers of a fluorinated species, but can also be extended to preparing mixed monolayers. The compositions of mixed monolayers can be controlled by altering the molar ratio of fluorocarbon and hydrocarbon based alcohols in the reaction mixture to tune the fluorocarbon content of these surface modifications. The oleophobicity of the surfaces progressively decreased as the molar ratio of fluorinated alcohols in the reaction mixture also decreased, while the monolayers maintained their hydrophobic properties, as

demonstrated by contact angle measurements. Adhesion force measurements of this series of mixed monolayers were assessed using either native Si₃N₄ AFM tips or the same tips after modification with octyldimethylchlorosilane. The observed trends in the adhesion forces correlated with the wetting properties of the mixed monolayers. The fluorinated composition of these mixed monolayers was analyzed by high resolution XPS C_{1s} scans. These results indicate a distinct difference from mixed monolayers prepared in a relatively polar solvent. Overall, the results of these studies indicate that the ratio of fluorocarbon and hydrocarbon based alcohols within mixed monolayers on silicon oxide surfaces can be tuned using a one pot reaction.

ASSOCIATED CONTENT

Supporting Information. Additional data available includes: i) insight into thermal degradation and optimization of the reaction temperature; ii) tabulated advancing and receding contact angle measurements and associated hysteresis for each type of silicon oxide substrate modified with 1-octanol; iii) tabulated peak positions of XPS for Figure 2B; iv) histograms of adhesion force measurements on piranha cleaned silicon substrate; v) contact mode AFM, KPFM, LFM images for a silicon substrate coated with mixed monolayers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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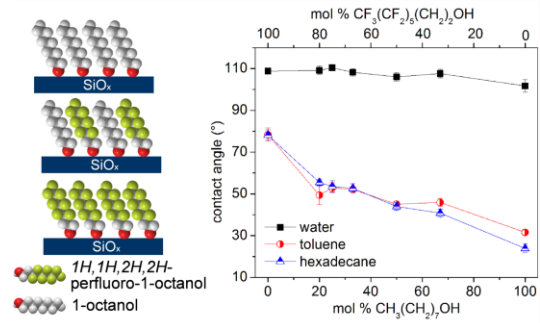


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