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Molecular Packing of Semifluorinated Alkanethiol Self-Assembled Monolayers on Gold: Influence of Alkyl **Spacer Length**

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The structures of semifluorinated alkanethiol self-assembled monolayers (SAMs) generated by the adsorption of $CF_3(CF_2)_9(CH_2)_nSH$ (F10H*n*SH, n = 2, 6, 11, 17, 33) onto gold were investigated with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and surface plasmon resonance spectroscopy. Images obtained by AFM of the F10H2SH SAM showed a remarkably ordered 2D hexagonal lattice with a lattice constant, $a = 5.9 \pm 0.1$ Å, on Au(111)/mica. As the total number of carbon atoms in the alkyl spacer groups (n) was increased, the fluorocarbon adlayer structure appeared more disordered in the AFM images; however, the thicknesses of the fluorocarbon layers estimated from the C 1s (CF₃), C 1s (CF₂), and F 1s XPS signal intensities were indistinguishable in all of the SAMs. In contrast, the C 1s (CH₂) signals revealed that the tilt angles of the alkyl spacer groups depended strongly on n. We utilized a contrast variation SPR technique with various contacting media for an independent determination of the refractive indices and the film thicknesses of the semifluorinated SAMs. The obtained data were consistent with our AFM and XPS results, which show that the longer alkyl chains pack more densely than the shorter ones in these SAMs.

1. Introduction

Self-assembled monolayers (SAMs) of normal alkanethiols on Au(111) have been studied extensively during the past decade, and as an outcome, the fundamental characteristics of these organic thin films are becoming better understood.¹ Recently, SAMs on gold terminated with a variety of functional groups such as fluorocarbon,2-11

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OH, COOH, $\rm NH_2,^{12-14}$ poly(ethylene glycol) (PEG),^{15} and dye moieties^{16-20} have been studied with the goal of

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evaluating the influence of terminal groups on the structure of the SAMs. These molecules often exhibit unique film structures and growth processes on metal surfaces due to a differing balance between vertical (sulfur-gold) and lateral (tail-tail) interactions from that of normal alkanethiol-based SAMs. Studies of these processes are useful to understand the fundamental mechanisms by which SAMs are formed.^{21,22}

Semifluorinated alkanethiol and disulfide SAMs represent one of most studied examples of functionalized SAMs²⁻¹¹ because of their potential to produce extremely low energy and highly hydrophobic (low wetting) surface coatings. $^{3,8-11,21-23}$ Fluorinated SAMs are also of interest for conformational studies related to the helical structure of fluorocarbon chains.^{2,4,5} The molecular packing of CF₃-(CF₂)₇(CH₂)₂SH on Au(111) has been studied with various surface characterization techniques by independent research groups,²⁻⁵ and similar structural models have been proposed. The rigid helical fluorocarbon tails are densely packed in the SAMs, forming a hexagonal lattice with a nearest-neighbor distance of \sim 5.8 Å, in which the rodlike fluorocarbon chains are expected to be aligned nearly normal to the surface.²⁻⁵ Even if ester or amide linkages are incorporated between the fluorocarbon and hydrocarbon portions of the chains, similar lattice structures were reported when ethylene (-CH₂CH₂-) moieties served as the spacer groups.^{7–9}

The length of the alkyl spacer groups is known to influence the molecular assembly of surfactants,²⁴ especially in cases where the molecules possess bulky headgroups. However, no systematic study of the spacer-length dependence has been performed with fluorinated SAM systems. With the exception of our recent report,²⁵ we found only one study of semifluorinated SAMs possessing long alkyl spacer groups.⁵ In the present investigation, we undertake a detailed analysis of SAM structures by utilizing a series of semifluorinated thiols having different alkyl spacer lengths (i.e., $CF_3(CF_2)_9(CH_2)_nSH$, where n =2, 6, 11, 17, and 33) and explore the influence of the spacer length on the molecular packing and orientation of the films on gold.

In the work reported here, we utilize a high-resolution atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS) to characterize the SAM structures. High-resolution AFM images are used to probe the molecular ordering of the perfluorocarbon adlayers as a function of alkyl spacer length. The obtained AFM images are compared with our recent analyses by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS).²⁵ The XPS peak intensities of C 1s (CF₃), C 1s (CF₂), C 1s (CH₂), and F 1s are also compared among the SAMs to evaluate the molecular packing of both the fluorocarbon and the hydrocarbon layers.

Furthermore, we utilize a contrast variation technique with surface plasmon resonance spectroscopy (SPR),²⁶ in which various contacting media were used for independent determination of the refractive indices and the film thicknesses of the semifluorinated SAMs. If the refractive index of a SAM is identical to that of the medium contacting

the SAM, no shift of the plasmon peak is expected regardless of the thickness of the SAM. By use of this "optical contrast match", we first determine the refractive index of the SAM (*n*) in a particular solvent, and then estimate the thickness (d) from SPR measurements in air and in a variety of other solvents. While Bruijn and coworkers have described the concept of contrast variation SPR,²⁷ unequivocal experimental verification was lacking with their systems. It is possible that artifacts were introduced because the sputtered PTFE surfaces employed in their studies were either inhomogeneous or reactive toward aqueous phosphate buffer. In the present study, we demonstrate that contrast variation SPR can be used not only to determine the refractive indices of SAMs but also to provide enhanced precision in the estimation of film thicknesses. Specifically, we characterize a series of semifluorinated SAMs using contrast variation SPR in which pure organic solvents are used as the contacting media. From these studies and complementary analyses by AFM and XPS, we propose a molecular packing model for the semifluorinated SAMs.

2. Experimental Section

2.1. Au(111)/Mica Substrate and Monolayer Preparation. Au(111)/mica substrates were prepared by the epitaxial growth of 100-150 nm gold films onto freshly cleaved mica sheets in a vacuum chamber (BIEMTRON Co. Ltd., Ibaraki, Japan). Gold was thermally deposited on mica surfaces prebaked at 550 °C for 3 h. Depositions were carried out at a rate of 1 Å/s and a substrate temperature of 350 °C under a vacuum pressure of 10⁻⁷-10⁻⁸ Torr. After deposition, the substrates were annealed at 550 °C for \sim 3 h. This procedure produced an atomically flat Au(111) surface with single-crystal grains measuring 500-1000 nm in diameter.¹⁶ The Au(111) surfaces were removed from the vacuum chamber before use and immersed into freshly prepared thiol solutions within 10 min after exposure to air. The synthesis of the partially fluorinated alkanethiols $(CF_3(CF_2)_9(CH_2)_nSH)$, F10H*n*SH, n = 2, 6, 11, 17, 33) is described elsewhere.^{28,29} We prepared an "equilibrium" surface for AFM and XPS measurements by exposing the gold substrate to a 1 mM solution for over 24 h at room temperature. This condition generates a densely packed SAM on Au(111), which was confirmed by kinetics measurements with SPR. At the designated times, the substrates were quickly removed from the solutions and immediately rinsed with absolute CH₂Cl₂ and dried in a stream of N₂. AFM and XPS measurements were performed within 1 day after preparation of the SAMs.

2.2. AFM Imaging and X-ray Photoelectron Spectroscopy (XPS). The AFM system used in this study was a commercially available NanoScope III (Digital Instruments, Inc. Santa Barbara, CA). The measurements were performed in contact mode (30 µm scanner) in air at room temperature. A Si_3N_4 cantilever with a spring constant of 0.12 N/m was used for large-sized scans (scanning rate = 3-10 Hz), while a cantilever with a spring constant of 0.38 N/m was used for molecular resolution imaging (scanning rate = 10-30 Hz). All images (400 \times 400 pixels) were collected in the "height mode", while maintaining a constant force. The applied force was minimized during the AFM imaging by adjusting the "set point voltage" to the lower limit; the images were not significantly affected unless the applied force was more than 50 nN.

XPS measurements were carried out using an ESCALAB 220iXL system (VG Scientific, Inc.) with an Al Ka X-ray source (1486.6 eV). The pass energy of the analyzer was set at 20 eV. Fitting of XPS peaks was performed using the spectra processing

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program in the XPS software. The energy resolution of this system is less than 0.6 eV, estimated by the Ag $3d_{5/2}$ peak width under our measurement conditions.

2.3. Surface Plasmon Resonance Spectroscopy (SPR).²⁶ The SPR setup was based on the configuration introduced by Kretschmann and Raether.³⁰ The details of the experimental setup have been described elsewhere.³¹ In the present study, we used high refractive index glass (LaSFN9, n = 1.845) slides and a 45° prism. A p-polarized HeNe laser ($\lambda = 632.8$ nm) was used as the light source, which was mechanically chopped in conjunction with a lock-in amplifier before entry into the prism. The intensity of the beam reflected at the gold interface was detected by a photodiode detector and recorded as a function of the incidence angle for "angular-scan" measurements, or as a function of time at a fixed angle of incidence for "kinetics-scan" measurements. All sample cells and the tubes were made of Teflon, which is resistant to most organic solvents.

The gold (~50 nm) was deposited on glass plates by thermal evaporation in a vacuum chamber (AUTO 306, Edwards, $\sim 1 \times$ 10^{-6} mbar). The thickness and the complex refractive index of the gold layer were determined by curve fitting of the SPR data (angular scan) in absolute CH₂Cl₂.^{30,32} SAM formation was initiated by injection of the thiol solution (0.1 mM CH₂Cl₂ solution) into the cell, and the adsorption process was monitored via the change of reflectivity during the kinetics-scan measurement (incidence angle 66°). It was confirmed that the reflectivity changed monotonically during the SAM adsorption and reached a constant value within 10 min after injection for all of the fluorinated SAMs. The adsorption was continued for at least 12 h, after which the surface was rinsed with absolute CH₂Cl₂. The SPR measurements were carried out in various solvents for independent determination of the thicknesses and the refractive indices of the SAMs. During this process, one solvent was successively replaced by another miscible solvent, and the measurements with CH_2Cl_2 were performed several times in between to confirm that no damage or contamination to the SAM surfaces occurred during exposure to the different solvents: CH2- $Cl_2 (1st) \rightarrow CHCl_3 \rightarrow CH_2Cl_2 (2nd) \rightarrow acetone \rightarrow hexane \rightarrow THF$ $\rightarrow CH_2Cl_2 (3rd) \rightarrow air (1st) \rightarrow perfluorohexane \rightarrow air (2nd) \rightarrow$ methanol \rightarrow water. The shift of the SPR peak upon SAM formation (i.e., the difference of the SPR minimum position before and after SAM adsorption) was determined experimentally in CH₂Cl₂, while those in other solvents were estimated by making use of the bare gold data reconstructed with the optical constants of glass, gold, and solvent by Fresnel's equation.^{30,32} Here, we used the thickness and complex refractive index values of gold obtained in absolute CH₂Cl₂. The refractive index of each solvent was obtained from the critical angle for total internal reflection (θ_c) in the SPR curve with SAMs for each measurements.

3. Results and Discussion

3.1. AFM Imaging. Figure 1 shows high-resolution AFM images of the semifluorinated alkanethiol SAMs, which were prepared by immersion in 1 mM solutions of the respective thiols for 24 h. The F10H2SH SAMs (Figure 3a) exhibited a remarkably ordered regular lattice (hexagonal lattice with a lattice constant, $a = 5.9 \pm 0.1$ Å) that was negligibly larger than related semifluorinated alkanethiol SAMs having the same ethylene spacer (i.e., CF₃(CF₂)₇(CH₂)₂SH).^{2–5} Although some defect sites (e.g., discontinuous lattices divided into two parallel lattice lines) were found, we typically observed continuous single crystalline domains that extended over 50 nm. Compared with normal alkanethiol SAMs on the same type of Au(111) substrate,³³ the lattice of the F10H2SH SAM was

more regular and stable. For example, the film remained undamaged by scanning, even in air, at the applied loads employed here.

As the alkyl spacer length (*n*) increased, the disorder in the AFM images increased as shown in panels b-e in Figure 1. The F10H6SH and F10H11SH SAMs formed regular hexagonal lattices across the entire surface as with the F10H2SH SAM (i.e., a regular lattice as shown Figure 1b and Figure 1c could be observed wherever scanning was performed); however, the images also included more disordered phases (i.e., phases with no regular lattice structures and/or with more domain boundaries). For the case of the F10H17SH SAM, portions of the surfaces were totally disordered (i.e., there were no clear lattice structures in the frame), and Figure 1d is one of the few ordered surfaces we were able to find. However, the lattice constants estimated from the 2D Fourier transformed (FT) images of Figure 1b-d are basically the same as those of the F10H2SH SAM (hexagonal lattice with a lattice constant, a = 5.9 Å), although it is difficult to identify all six spots clearly in the FT images as was possible with the F10H2SH SAM. When n increases to 33 (i.e., the F10H33SH SAM), regular hexagonal structures were not observed. A striped pattern as shown in Figure 3e was the only structure we found; however, the distance between the stripes was also approximately 5.9 Å, and we presumed that the magnitude of the distance originated from the characteristic molecular packing of the fluorocarbon chains observed for the other SAMs.

The observed molecular distance, 5.9 Å, is reasonably attributed to the large van der Waals diameter of perfluorocarbon chains (5.67 Å),34 which gives rise to $p(2 \times 2)$ or $c(7 \times 7)$ structures on gold as densely packed commensurate adlayers.²⁻⁵ From this value, the tilt angle of the fluorocarbon chain (α) is estimated to be 16.4°, which indicates that the fluorocarbon chains are aligned nearly perpendicular to the gold plane in the ordered phases. Since lattices no larger than 5.9 Å could be found for these semifluorinated SAMs, it is possible that fluorocarbon chains are unable to form other stable 2D crystalline structures. Furthermore, to rationalize the disordered fluorocarbon adlayers observed in the SAMs with long alkyl chains, we have a picture of molecular assembly dominated by the attraction between alkyl chains. When the length of the alkyl chains increases, the van der Waals attraction between the alkyl chains becomes larger than that between the fluorocarbon chains. Because of the different diameters of fluorocarbon chains (5.67 Å) and alkyl chains (4.24 Å), the alkyl chains in semifluorinated SAMs must tilt to achieve optimal van der Waals packing, even when the fluorocarbon chains are densely packed with a molecular spacing of 5.9 Å. If, however, the underlying alkyl chains are tilted, the fluorocarbon adlayer must possess domain boundaries and defects due to anisotropic features of the films, which can plausibly give rise to the disordered adlayer images observed in the SAMs with long alkyl chains. In the other words, the fact that the fluorocarbon adlayers appear more disordered does not necessarily mean that the underlying alkyl chains are also disordered (see, for example, our previous PM-IRRAS studies).²⁵ Furthermore, the semifluorinated alkanethiol SAMs with long alkyl chains are more thermally stable than those with short alkyl chains, regardless of the apparent disordered adlayer structures in the former.²⁵ Consequently, our proposal that molecular packing is favorable for alkyl chains but unfavorable for helical

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F10H33SH on Au(111)

Figure 1. AFM images and the corresponding 2D Fourier transforms of semifluorinated alkanethiol SAMs on Au(111) (10×10 nm², unfiltered image): (a) F10H2SH; (b) F10H6SH; (c) F10H11SH; (d) F10H17SH; (e) F10H33SH.

fluorocarbon chains is plausible for semifluorinated SAMs with long alkyl spacer groups.

3.2. Peak Position Analysis with XPS Signals. The XPS spectra of C 1s, S 2p, and F 1s for the F10H2SH, F10H11SH, and F10H33SH SAMs are shown in Figures 2-4 (note: the peak positions (λ_{max}) and peak intensities for Au, C, S, and F in all of the semifluorinated alkanethiol SAMs are provided as Supporting Information). The C1s spectra are composed of three peaks, which are assigned to carbon atoms in the CF_3 , CF_2 , and CH_2 groups, respectively. When *n* becomes longer, all C 1s peaks are shifted to higher binding energy (e.g., F10H2SH, C 1s $(CF_3) = 293.1 \text{ eV}, C 1s (CF_2) = 290.8 \text{ eV}, C 1s (CH_2) =$ 284.4 eV \rightarrow F10H33SH, C 1s (CF₃) = 293.5 eV, C 1s (CF₂) $= 291.3 \text{ eV}, \text{ C} 1 \text{ s} (\text{CH}_2) = 284.7 \text{ eV}$). This shift in binding energy with increasing molecular length has also been observed in normal alkanethiol SAMs,³⁵⁻³⁷ where the surface charge generated by the X-ray induced secondary

electrons cannot be discharged completely (especially on densely packed SAMs with longer chains) and consequently gives rise to the shift of the XPS peaks to higher binding energies. Our results suggest that the total film thickness of the semifluorinated SAMs, considering the film density, increases monotonically as the alkyl spacer length increases. A more detailed discussion of the film thickness of the SAMs appears below.

The S 2p peaks appeared as doublets at 163.2 eV $(2p_{1/2})$ and 162 eV (2p_{3/2}) for all SAMs.³⁸ In previous reports, these peaks have been assigned as sulfur atoms "bound" to gold.^{39,40} Consequently, the results presented here can

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Figure 2. XPS spectra of the C 1s regions for (a) F10H2SH, (b) F10H11SH, and (c) F10H33SH SAMs on Au(111).



Figure 3. XPS spectra of the S 2p regions for (a) F10H2SH, (b) F10H11SH, and (c) F10H33SH SAMs on Au(111).



Figure 4. XPS spectra of the F 1s regions for (a) F10H2SH, (b) F10H11SH, and (c) F10H33SH SAMs on Au(111).

be interpreted to indicate that the thiol groups in semifluorinated alkanethiol SAMs are chemisorbed on Au(111) independently of the alkyl spacer length. Recently, Schoenfisch and Pemberton investigated the stability of alkanethiol SAMs on Au and Ag surfaces in air,⁴¹ and they observed rapid oxidation of the sulfur atoms in the monolayer. However, we detected no oxygen peaks nor any oxidized carbon or sulfur peaks for any of the SAMs examined here.

3.3. Quantitative Analysis of XPS Signal Intensity. The absolute intensities of the Au $4f_{7/2}$ peaks of the semifluorinated alkanethiol SAMs are plotted in Figure 5a as a function of the total number of carbon atoms per adsorbate (F10H*n*SH, total carbon number = 10 + *n*). The Au $4f_{7/2}$ peak intensity decreases monotonically with the total number of carbon atoms in a manner similar to that reported previously for alkanethiol or other ω -terminated alkanethiol SAMs.^{22,42} The Au $4f_{7/2}$ XPS intensity can be described as shown in eq 1 with regard to the attenuation length for photoelectrons⁴²

$$N(Au) \propto \exp(-d/(\lambda \sin \theta))$$
 (1)

where N(Au) is the total intensity of Au $4f_{7/2}$ photoelectrons attenuated by SAM layers, d is the effective thickness of the SAM layers, λ is the attenuation length, and θ is the angle of the analyzer with respect to the sample surface (i.e., the takeoff angle). Since the takeoff angle of our XPS setup is 90°, the intensity of the Au $4f_{7/2}$ peak in our system can be written as in eq 2 in logarithmic form

$$\ln N(\mathrm{Au}) \propto -\mathbf{d}/(\lambda \sin(90^\circ)) + C = -\mathbf{d}/\lambda + C \quad (2)$$

where *C* is a constant. Thus, the attenuation length can be estimated from the slope of the semilogarithmic plot of the XPS intensity vs the film thickness d. We calculate the film thickness **d** from the total number of carbon atoms per adsorbate by assuming the same structure as normal alkanethiol SAMs, where the thickness (in Å) is given by $1.27 n \cos(30^\circ)$.⁴² The use of this model yields the values d = 13.2 Å (F10H2SH), 17.6 Å (F10H6SH), 23.1 Å (F10H11SH), 29.7 Å (F10H17SH), and 47.3 Å (F10H33SH). Given that the fluorocarbon chains examined here are too long (i.e., F10) to be treated as simple ω -terminal groups²² and the fact that fluorocarbon chains are known to possess helical chain conformations rather than the transextended conformations characteristic of hydrocarbon chains,³⁴ our model calculation is probably inaccurate for semifluorinated thiol SAMs. Nevertheless, this approach permits us some standard of comparison with normal alkanethiol SAMs.

The XPS intensities of the Au $4f_{7/2}$ peaks are replotted in semilogarithmic fashion in Figure 5b against the calculated film thickness values. The best fit by linear regression gives a slope of -0.0219 (R = 0.988) from this plot, and the attenuation length is estimated as $\lambda = 45.7$ Å. This attenuation length is significantly larger than that of alkanethiol SAMs ($\lambda = 42 \pm 1.4$ Å at a kinetic energy of 1402 eV Au $4f_{7/2}$ by Bain et al.,⁴² and $\lambda = 32$ Å at a kinetic energy of 1402 eV Au $4f_{7/2}$ by Harder et al.).^{15,43} Thus, the total film thickness of our semifluorinated alkanethiol SAMs increases monotonically with the number of carbon atoms; however, the observed increase in the film thickness per CH₂ group is apparently less than that of analogous normal alkanethiol SAMs. This result is consistent with a model in which the alkyl chains

⁽³⁸⁾ F10H11SH and F10H17SH SAMs exhibited a small shoulder at 164 and 161.1 eV, suggesting the existence of different sulfur species (e.g., sulfur at 164 eV can be assigned as "unbound" sulfur)³⁹ on the surface. These peaks were, however, negligibly small.

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⁽⁴²⁾ Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 1670. (43) Since the attenuation length varies with the takeoff angle (θ) , the data in ref 15 ($\theta = 90^{\circ}$) are more reliable for our studies. Following the equation, $\lambda = kE$ (in ref 42), the attenuation length of 26 Å for Au 4d_{5/2} corresponds to the value of 32 Å for Au 4d_{7/2}.



Figure 5. Semilogarithmic plot of the Au $4f_{7/2}$ XPS intensity vs (a) the total number of carbon atoms per adsorbate, and (b) the effective film thickness of the semifluorinated alkanethiol SAMs (F10HnSH). The effective film thicknesses *d* are estimated from the total number of carbon atoms assuming the same chain tilts are the same as normal alkanethiol SAMs. The dashed line was calculated by linear regression.



Figure 6. XPS signal intensities of C 1s (CF₃), C 1s (CF₂), and F 1s vs the carbon number of the alkyl spacer group (*n*).

in semifluorinated SAMs are less densely packed than those in normal alkanethiol SAMs.

In Figure 6, the XPS intensities of the C 1s (CF₃), C 1s (CF₂), and that of F 1s are plotted against the carbon number of the alkyl spacer group (*n*). For C 1s (CF₃), C 1s (CF₂), and F 1s, the intensities of the XPS signals are invariant with *n*, suggesting that the "effective" film thicknesses (i.e., the film thickness and/or packing density) of the fluorocarbon layers are similar in all of the semifluorinated alkanethiol SAMs, independent of the alkyl spacer length. The observed invariance with *n* suggests that the number of adsorbed molecules (i.e., the surface density of fluorocarbon chains) is similar in all of the SAMs and is presumably governed by the size of bulky fluorocarbon chains (5.67 Å in diameter),³⁴ despite the

fact that the various SAMs exhibit different adlayer structures by AFM.

On the other hand, the intensities of the XPS signals of C 1s (CH₂) and S 2p changed drastically with the increase in the number of carbon atoms in the alkyl spacer groups (*n*) (Figures 7 and 8). If the effective film thickness of the hydrocarbon layer is proportional to *n*, the C 1s (CH₂) intensity must increase exponentially with increasing *n*, since the thickness of the fluorocarbon adlayers is identical for the escape of photoelectrons in all of these SAMs. However, a clear negative deviation could be detected from the linear regression line in the plot of Figure 7. These data suggest that the effective thickness of the hydrocarbon layer does not increase in proportion to *n* (i.e., the alkyl chains become more tilted as *n* increases),



Figure 7. Semilogarithmic plot of the C 1s (CH_2) intensity vs the carbon number of the alkyl spacer group (*n*). The dashed line was calculated by linear regression using the data obtained only from the SAMs generated from F10H2SH, F10H6SH, and F10H11SH.

which is consistent with our previous PM-IRRAS studies, 25 and the discussion for the attenuation length from Au $4f_{7/2}$ intensities described above, and also our SPR results presented below.

We estimated the attenuation length of the semifluorinated alkanethiol SAMs from the S 2p XPS signals in the same way as for the Au $4f_{7/2}$ signals. Since the sulfur signals are much weaker than the gold signals, large fitting errors are unavoidable. However, it is important to know the influence of the sulfur atoms upon the escape of photoelectrons to enable direct comparison with other monolayer systems, such as carboxylic acids (-COOH) and organosilanes (-Si(OH)₃), which have different headgroups. The attenuation length was estimated as $\lambda = 49.3$ Å from the same model plot from Figure 8 (R = 0.948) at a kinetic energy of 1323.4-1324.6 eV. This value can be converted into an attenuation length of $\lambda = -52.2$ Å at a kinetic energy of 1402 eV, which is significantly larger than that calculated from the Au $4f_{7/2}$ peaks. The different attenuation lengths estimated from the S 2p signals probably arise because the photoelectrons from the sulfur atoms pass through the alkyl spacer and fluorocarbon chains, while those from Au pass through the sulfur layer in addition to the alkyl spacer and fluorocarbon chains (i.e., the S 2p signals are less attenuated).

3.4. Estimation of Refractive Index and Film Thickness with SPR. In Figures 9 and 10, the SPR peak shifts observed upon the formation of F10H2SH and F10H11SH SAMs are plotted against the dielectric constants ϵ ($\epsilon = \mathbf{n}^2$, where \mathbf{n} is the refractive index) of the contacting medium, together with simulation curves assuming that the SAM layers possess specific dielectric constants (ϵ) and film thicknesses (**d**). All of the numerical data are available as Supporting Information. Good agreement between the experimental results and the simulations were confirmed for all of the SAMs as suggested by Figures 9 and 10. Fluorinated surfaces are inert toward most organic solvents, and while only perfluorohexane and CH₂Cl₂ can plausibly absorb into the fluorinated surfaces,³⁴ no clear deviation of the data was detected even with these solvents. We first determined



Figure 8. XPS signal intensities of S 2p (S $2p_{3/2} + S 2p_{1/2}$) vs the carbon number of the alkyl spacer group (*n*).

 ϵ of the SAM layers from the point where the peak shift was equal to zero, and then we estimated *d* from the best fit between all of the data and the simulation profiles. From the scatter of the data points, we can estimate the errors as ± 0.01 for ϵ and $\pm 1.0 - 1.5$ Å for *d*, which correspond to a high precision compared with conventional SPR detection methods.^{26,27} The thusly obtained ϵ and \underline{d} values are listed in Table 1 as a "single-layer model" (an averaged refractive index and thickness corresponding to a single SAM layer) and also are plotted in Figure 11 against the carbon number of the alkyl spacer group (*n*). As shown in Figure 12, not only the value of **d** but also the value of ϵ varies with *n*, suggesting a change of refractive index for SAMs as a function of alkyl spacer length *n*. This analysis indicates that the estimation of the film thickness *d* using a constant value for ϵ is not appropriate for this system. As a test, we recalculated the attenuation lengths of the Au 4f_{7/2} photoelectrons using the obtained SPR film thicknesses (see section of 3.3, Figure 5b). The best fit by linear regression gives a slope of -0.0400 (R = 0.990) and the attenuation length $\lambda =$ 25.0 Å. This attenuation length is unreliably small for an organic material, ^{15,42,43} suggesting that the change of the film density (as indicated by ϵ in the SPR data) is nonnegligible for the XPS analysis as well.

We attempted an alternative analysis with the SPR data based on a "double-layer model". In this model, the fluorocarbon parts and the hydrocarbon parts were treated as separate layers having individual refractive indices and film thicknesses (fluorocarbon layer, n1, d1; hydrocarbon layer, *n2*, *d2*). Using this model, we estimated the refractive index and the thickness of the alkyl spacer groups (*n2*, *d2*), assuming that the respective values for the fluorocarbon layer (**n1**, **d1**) were constant. We used the **n1**, **d1** values calculated from the physical properties of PTFE and the lattice constants in the AFM images as depicted in Figure 12. For case A, the fluorocarbon chains were assumed to be aligned normal to the surface, forming a "thicker" but "less dense" layer. In this model, the thickness **d1** was estimated to be 13 Å with a unit length of 1.3 Å/ $\overline{CF_2}$ from PTFE.³⁴ The refractive index *n1* was calculated using the Clausius–Mossotti relation, $(\epsilon - 1)/\epsilon$

 Table 1. Estimation of Refractive Index and Film Thickness of SAM Layers: Single-Layer Model and Double-Layer Model (Case A)

		F10H2SH	F10H6SH	F10H11SH	F10H17SH
single-layer model	n	1.36 ± 0.01	1.38 ± 0.01	1.40 ± 0.01	1.42 ± 0.01
	d (Å)	19 ± 1	21 ± 1	23 ± 1	27.5 ± 1.5
double-layer model: A	$\overline{\mathrm{C}}\mathrm{F}_2$	n1 = 1.344, d1 = 13 Å			
-	CH ₂ <i>n2</i>	1.39 ± 0.01	1.45 ± 0.01	$-$ 1.50 \pm 0.01	1.49 ± 0.01
	CH2 d2 (Å)	6 ± 1	8 ± 1	10 ± 1	14.5 ± 1.5



Figure 9. SPR peak shifts upon F10H2SH SAM formation in air and in various solvents plotted against the dielectric constant ϵ of the contacting phase. The solid and dashed lines are simulation results obtained by assuming the SAM layers possess the indicated dielectric constants ($\underline{\epsilon}$) and film thicknesses (\underline{d}).

 $(\epsilon + 2) = N\alpha/3\epsilon_0$, in a manner similar to Langmuir films,⁴⁴ where ϵ is the relative dielectric constant ($\epsilon = n^2$), N is the molecular density, a is the molecular polarizability, and ϵ_0 is a constant (=8.854 × 10⁻¹² F m⁻¹). Since $(\epsilon - 1)/(\epsilon +$ 2) is proportional to the molecular density N, the refractive index *n1* can be deduced from the refractive index of PTFE $(\mathbf{n} = 1.376)$ using the ratio of molecular lattice constants (SAMs, 5.9 Å; PTFE, 5.67 Å).³⁴ By this calculation, the refractive index of the fluorocarbon layer in case A was estimated to be n1 = 1.344. For case B, however, the fluorocarbon chains were assumed to form "thinner" but "more dense" layers by tilting. From the molecular lattice constants, the tilt angle was estimated to be 16.4°, and the thickness *d1* was estimated to be $\cos(16.4^\circ) \times 13$ Å = 12.5 Å. The refractive index of PTFE (\mathbf{n} = 1.376) was used as **n1** in case B. However, given that the averaged refractive index of the shortest molecule, F10H2SH (*n* = 1.36 for the "single-layer model") was smaller than that of PTFE (n = 1.376), we concluded that B is an unsuitable model. It is implausible that the remainder of the molecule

(44) Tamada, K.; Minamikawa, H.; Hato, M.; Miyano, K. Langmuir 1996, 12, 1666.



Figure 10. SPR peak shifts upon F10H11SH SAM formation in air and in various solvents plotted against the dielectric constant ϵ of the contacting phase. The solid and dashed lines are simulation results obtained by assuming the SAM layers possess the indicated dielectric constants ($\underline{\epsilon}$) and film thicknesses (\underline{d}).

(hydrocarbon + sulfur) exhibits a refractive index smaller than that of PTFE.

For this reason, we performed further calculations on the double-layer model only for case A. In these calculations, the packing status of the fluorocarbon chains was assumed to be the same for all of the SAMs independent of the carbon number of the alkyl spacer groups *n*, given the invariant XPS data in Figure 6 (i.e., the constancy of the C 1s (CF₂) and C 1s (CF₃) and F 1s XPS peak intensities). The results of the calculations are provided in Table 1. The <u>d2</u> values were obtained simply by taking the difference between the total film thickness and the thickness of the fluorocarbon layer (<u>d2</u> = <u>d</u> - <u>d1</u>), while the <u>m2</u> values were estimated by Fresnel's equation^{30,32} to match the SPR peak shifts with empirically determined <u>m1</u>, <u>d1</u>, and <u>d2</u> values.

While the data should be regarded carefully considering the potential errors associated with the conformational model of the fluorocarbon chains, several important trends are indicated. First, the refractive index of the hydrocarbon layer <u>**n**</u> increases with alkyl spacer length (i.e., the shorter alkyl chains for the F10H2SH and F10H6SH SAMs appear



Figure 11. Dielectric constants (ϵ) and film thickness (d) determined using the SPR contrast variation technique for each of the four semifluorinated SAMs plotted against the alkyl spacer length (n). The lines through the data were calculated by linear regression.



Figure 12. Proposed structural models of the semifluorinated SAMs on gold. In these models, the fluorocarbon and hydrocarbon parts are treated as separated layers having individual refractive indices and film thicknesses (fluorocarbon layer, **n1**, **d1**; hydrocarbon layer, **n2**, **d2**). In case A, the fluorocarbon chains are assumed to be aligned normal to the surface, thereby forming "thicker" but "less dense" layers. In case B, the fluorocarbon chains are assumed to tilt from the surface normal, thereby forming "thinner" but "more dense" layers.

to pack less densely than the longer ones for the F10H11SH and F10H17SH SAMs). Interestingly, the <u>*n2*</u> value of the shorter molecules is close to that of liquid hydrocarbons (e.g., for hexane, n = 1.375), while that of the longer ones is close to the value of solid hydrocarbons (e.g., for polyethylene, n = 1.5). Second, the unit length of the alkyl spacer groups obtained by dividing the <u>*d2*</u> values by the

carbon number *n* follows the trend 3 Å/CH₂ (F10H2SH), 1.3 Å/CH₂ (F10H6SH), 0.9 Å/CH₂ (F10H11SH), and 0.9 Å/CH₂ (F10H17SH). These data provide complementary information regarding the packing status of the alkyl spacer groups as suggested by the <u>*n2*</u> values (i.e., the longer alkyl chains appear to be tilted more to form densely packed layers than the shorter ones).

Before, however, discussing detailed values of the tilt angles, one must be aware that the obtained *d2* value is too large for the ethylene group in the case of F10H2SH, which can be interpreted to indicate that the thickness of thiolate layer (S-Au) is non-negligible for the estimation of SAM thicknesses. This interpretation is consistent with previous reports regarding the ellipsometric thicknesses of alkanethiol SAMs, in which a linear regression line of SAM thickness vs the number of methylene groups in the chain exhibited an intercept significantly greater than zero, which was interpreted to reflect the thickness of the sulfur moiety.^{12,45} In contrast to other studies,^{12,45} our SAM thicknesses are derived completely independent of any assumptions regarding the refractive indices of the layers. Nevertheless, our approach still reveals the influence of the thiolate layers on the estimated thicknesses of SAMs on gold. If we assume a stretched chain (1.27 Å/CH₂) for F10H2SH, the thickness of the thiolate layer can be estimated to be \sim 3.5 Å, which is not substantially different from the expected S-Au layer thickness based on molecular models (Au-S bond length, 2.11 Å; S-C bond length, 1.80 Å).

4. Conclusions

The molecular packing of semifluorinated alkanethiol SAMs was investigated using AFM, XPS, and SPR techniques. In these studies, we found that the alkyl spacer length has a profound influence on the molecular packing of the SAMs. The longer alkyl chains formed densely packed layers due to the strong interaction between the chains, which led to a surface disordering of the fluorocarbon adlayers in the SAMs. The SPR contrast variation technique, which utilized contacting media having a variety of bulk refractive indices, was determined to be useful for accurately measuring the refractive indices and the film thicknesses of semifluorinated SAMs. This technique was used to provide insightful complementary information regarding the structures and physical properties of SAMs on gold.

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Supporting Information Available: Peak positions (λ_{max}) and peak intensities for Au, C, S, and F in the all of the semifluorinated alkanethiol SAMs and SPR peak shifts observed upon the formation of F10H2SH and F10H11SH SAMs. This material is available free of charge via the Internet at http://pubs.acs.org.

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