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The Formation and Stability of Alkylthiol Monolayers on Carbon Substrates

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Abstract

The formation and stability of alkylthiol monolayers on amorphous carbon thin films are investigated. Alkylthiol monolayers were prepared via a two-step, wet chemical process in which the carbon surface was first halogenated and then incubated with (4-(trifluoromethyl)phenyl)methanethiol (4tBM). The 4tBM covalently attaches to the surface in a substitution reaction in which the 4tBM thiol replaces the surface halogen. Studies of the substitution mechanism showed that monolayer formation is affected by the nature of the surface-bound halogen as well as the concentration and nucleophilicity of the 4tBM sulfur atom, consistent with a bimolecular (S_N2) substitution reaction mechanism. The alkylthiol monolayers are stable over a wide range of solvent, pH, and temperature conditions.

1. Introduction

The semiconducting properties of the Group IV elements carbon, silicon, and germanium have made them the materials of choice for microelectronic device fabrication. Historically, silicon has been the principal material employed due to its wide availability, low cost, as well as the stability and uniformity of its native oxide layer, however, carbon- and germanium-based materials have also been utilized.^{1,2} Carbon-based materials such as nanocrystalline diamond and amorphous carbon thin films offer robust chemical and mechanical stability and have tunable electronic properties,³⁻⁵ affording possible next-generation electronic and optical devices. Amorphous carbon films are particularly attractive as they are deposited at room temperature, allowing them to be interfaced with a wide-variety of materials.⁵ In one such example, amorphous carbon thin films were deposited onto surface plasmon active metal (carbon-on-metal) substrates and used in the fabrication and analysis of oligonucleotide arrays.^{6,7} This lamellar carbon-on-metal substrate provides the chemical robustness of carbon while retaining the plasmonic properties of the metal underlayer, affording a means of monitoring the substrate with optical methods such as surface plasmon resonance and polarization modulated Fourier transform infrared reflection-absorption spectroscopy (PM-FTIRAS).^{6,7}

A variety of chemistries have been developed to modify carbon, silicon, and germanium substrates. One approach employs a two-step chemical process in which the substrate is first halogenated and then modified with organic molecules of interest using a Grignard reaction.⁸⁻¹¹ Bansal *et al* first employed this technique to passivate silicon surfaces as a means of eliminating the electrical defects associated with its oxide-containing layer.¹¹ In each reaction the C-X, Si-X, and Ge-X bonds (X = Cl or Br) are replaced with a surface-carbon bond. This means of surface modification, however, is limited to a small number of functional groups as Grignard reagents contain highly reactive nucleophiles.

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Forming monolayers on halogenated carbon substrates with thiol-containing molecules offers a new route of carbon functionalization, utilizing the rich molecule libraries developed for self-assembled monolayers (SAMs) on metal substrates.^{12,13} A similar reaction scheme has also been recently employed by Ardalan *et al*, in which halogenated germanium substrates were modified with 1-octadecanethiol.¹⁰ This work characterizes the formation of alkylthiol monolayers on chlorinated and brominated carbon-on-metal substrates (Scheme 1), with an emphasis on providing mechanistic insight into their formation. The stability of these alkyl thiol monolayers upon prolonged exposure to various chemical environments is also evaluated.

2. Materials and Methods

2.1 Chemicals

All chemicals, unless otherwise noted, used in this work were purchased from Sigma Aldrich and used without further purification. Surfaces were modified with 4-(trifluoromethyl)phenyl)methanethiol (4tBM, Oakwood Products), 4tBM activated with an equivalent of pyridine, sodium 4-(trifluoromethyl)phenyl)methanethiolate (Na4tBM), or 1,2-bis(4 trifluoromethyl)benzyl)disulfane. Figure 1 shows the chemical structures of each of these molecules. Na4tBM molecules were prepared by adding 1.0 mole equivalent of sodium hydride into *tert*-butanol containing 100 mM 4tBM. The 1,2-bis(4-trifluoromethyl)benzyl)disulfane molecules were prepared by adding 1.1 mole equivalents of iodine to benzene containing 100mM 4tBM. The benzene was removed and the molecule resuspended in *tert*-butanol.

2.2 Substrate preparation

The fabrication of the carbon-on-metal substrates used in this work has been previously described in detail.^{6,8} Amorphous carbon thin films (15 nm) were DC-magnetron sputtered (Denton Vacuum) onto commercially prepared gold-coated, glass slides at a base pressure of $\leq 3 \times 10^{-6}$ Torr and an argon pressure of 3 mTorr. The thickness of the carbon films was measured with a calibrated quartz microbalance located in the sputtering chamber. The gold-coated slides (Evaporated Metal Films) were comprised of a 100 nm gold thin film with a 5 nm chromium underlayer.

Prior to use, each carbon-on-metal substrate was hydrogen terminated in a 13.56 MHz inductively coupled hydrogen plasma for 12 minutes (10 mTorr H₂, 15 W, room temperature). The substrates were then placed in anhydrous benzene containing a catalytic amount of benzoyl peroxide and 100 mM PX₅ (X = Cl or Br). The reaction vessels were purged with nitrogen, sealed, and incubated at 80 °C for 1 hour. After the halogenation reaction, each substrate was rinsed with copious amounts of benzene, ethanol, and deionized water and then dried under a stream of nitrogen. Alkyl monolayers were formed on the substrates via incubation at room temperature in varying concentrations (1 – 100 mM) of 4tBM and/or its derivatives in *tert*-butanol. The particular reaction conditions used in each experiment are specifically stated in the Results section of this manuscript. Each substrate was thoroughly rinsed after incubation in the 4tBM solutions with copious amounts of ethanol, benzene, and deionized water and then dried under a stream of nitrogen.

2.3 Substrate Characterization

PM-FTIRRAS¹⁴ measurements were performed on a Bruker PMA50 spectrometer equipped with real-time interferogram sampling electronics (GWC Technologies). Spectra were collected at an 85° angle from surface normal, with 250 scans at 4 cm⁻¹ resolution. All PM-FTIRRAS integration values reported in this work are the average of three measurements made on three separate substrates. The relative extent of 4tBM monolayer formation was

determined by comparing the C–F stretch (integrated peak value) on each surface, which was normalized to the carbonyl stretch on a reference carbon substrate modified with 10-undecenoic acid.¹⁵

X-ray Photoelectron (XP) spectra were collected on a Perkin Elmer PHI5400 ESCA spectrometer with a magnesium K α (1253.6 eV) source 45° from the surface normal at a base pressure of 1×10^{-9} Torr. Survey spectra were collected at 1 eV resolution and high-resolution element spectra were collected at 0.25 eV resolution. The signal from bulk carbon (285.0 eV) was used to align each XP spectrum. Atomic area ratios were determined with CASA XPS software by fitting the raw data to Voigt functions after Shirley baseline correction¹⁶ and applying predetermined atomic sensitivity factors.¹⁷ Reported atomic composition values are the average of three measurements made on three separate substrates. The number of atoms and/or molecules present on the carbon-on-metal substrates was calculated using a density value of 2.2 g/cm³ (appropriate for graphite) and an electron attenuation depth of 2.0 nm.¹⁸

Contact angle images were collected on a Ramé-Hart goniometer (model 200-F1) equipped with *Drop Image Standard* software. Images were analyzed with the NIH imaging package *Image J*. For these measurements, a 1 μ L drop of deionized water was placed on the surface. The contact angle values reported are the average of three measurements taken at different positions on three separate substrates.

3. Results

3.1 Substrate characterization

Alkylthiol monolayers were formed on hydrogen-terminated carbon substrates that were first halogenated. The carbon-on-metal substrates utilized in this work were composed of a 15 nm amorphous carbon thin film deposited on a gold-coated, glass substrate. Each carbon-on-metal substrate was cleaned in an RF-generated hydrogen plasma, to reduce the heterogeneity between substrates. Hydrogen plasma treatment has been shown to decrease the number of nitrogen and oxygen species in the carbon film as well as chemically reduce the surface-bound carbonyl compounds.⁷

Next, each substrate was halogenated in anhydrous benzene containing 100 mM of PX₅ (X = Br or Cl) and a catalytic amount of benzoyl peroxide. This means of halogenating carbon substrates has been reported previously.⁸ XP survey spectra obtained after the halogenation reaction showed an average bromine-to-carbon ratio of 0.0654 ± 0.001 (n=20) and chlorine-to-carbon ratio of 0.116 ± 0.052 (n=10). These ratios can be used to estimate the average number of bromine or chlorine atoms on the surface, assuming that each halogen atom is covalently attached to a single carbon atom. The are approximately 1.44×10^{15} and 2.54×10^{15} atoms/cm² of bromine and chlorine on each surface, which correspond to 0.39 and 0.61 of the theoretical monolayer densities achievable for Van der Waals radii of 185 (Br) and 175 (Cl) nm.¹⁹

The halogenated substrates were then incubated in *tert*-butanol containing a known amount of (4-(trifluoromethyl)phenyl)methanethiol (4tBM), and an alkylthiol monolayer was formed on the surface. Figure 2 shows XP survey spectra of a carbon-on-metal substrate after (a) hydrogen termination, (b) the bromination reaction,²⁰ and (c) a 24h incubation in 100 mM 4tBM. Figure 3 contains an infrared spectrum of a 4tBM monolayer formed after 24 h. Four distinguishing features are observed, which can be attributed to the stretching modes of the aromatic ring (1128 and 1066 cm⁻¹) and to the carbon-fluorine bond (1165 and 1328 cm⁻¹).²¹

High-resolution XP measurements of the C1s region were also obtained before and after monolayer formation (Figure 4). The C1s spectrum of the brominated carbon surface (Figure 4a) contains four components, which can be attributed to carbon-carbon (284.7 and 285.1 eV), carbon-oxygen (285.6 eV), and carbon-bromine (288.9 eV) bonds.^{22,23} An additional component in the C1s spectrum is observed after 4tBM monolayer formation (Figure 4b), corresponding to the presence of carbon-fluorine (293.0 eV) bonds. The average number of 4tBM molecules/cm² was calculated from the C1s high-resolution spectra⁴ of three separate substrates incubated in 100 mM 4tBM for 24 h. An average of $3.51(\pm 0.01) \times 10^{13}$ molecules/cm² was determined for the carbon-on-metal substrates, whose XP survey spectra show a 0.037 ± 0.003 F:C ratio (Table 1). In control experiments, three hydrogen-terminated, carbon-on-metal substrates were incubated in 100 mM 4tBM for 24 h and analyzed with XP survey spectra. Surface fluorine density on these substrates was significantly lower (F:C ratio of 0.006 ± 0.001), demonstrating the requirement of a surface halogen for thiol attachment.

The thermal stability of the 4tBM-modified substrates was examined by heating (200 °C) *in vacuo* for varying lengths of time (20, 40, and 60 minutes). The fluorine and sulfur components, as determined with XP survey spectra, were measured before and after heating (Table 1). No significant decrease in the XP signals were observed. In two control experiments, 4tBM (100 mM) in benzene was placed on hydrogen- or bromine-terminated substrates (three each), the solvent evaporated, and an XP survey spectra obtained before and after heating. The benzene completely evaporated in 10 minutes, under ambient conditions, which is significantly less time than is needed to form a monolayer on the carbon surface (Figures 5 and 6). Less than 2% of the original fluorine signal remained after 60 minutes of heating and there was no detectable sulfur signal, suggesting that the 4tBM molecules are covalently attached to the surface when a monolayer is allowed to form and are not merely adsorbed.

3.2 Monolayer formation

The extent of monolayer formation was studied with both infrared and XP measurements. An initial XP survey spectrum of each brominated substrate was also obtained to compare the bromine-to-carbon ratio before and after monolayer formation. Figure 6a shows a plot displaying the average Br:C ratios over a 72 h period for a series of brominated substrates incubated in *tert*-butanol only and *tert*-butanol containing 100 mM 4tBM. The Br:C ratio remains unchanged for substrates exposed to solvent-only conditions, while there is a general decrease in bromine ($39.6 \pm 2.1\%$) on the surface when exposed to the 4tBM molecules. The increasing F:C and S:C ratios, as a function of incubation time, are plotted in Figure 5b. Figure 6 contains the corresponding PM-FTIRRAS data, monitoring the intensity of the carbon-fluorine stretching mode (1328 cm^{-1}) over the same period of time.

3.2.1 Halogen Effects—To determine the effect of the surface-bound halogen on monolayer formation, chlorine- and bromine-terminated carbon-on-metal substrates were prepared and then incubated (24 h) in either 100 mM 4tBM or 100 mM Na4tBM. The F:C and S:C ratios after monolayer formation are presented in Table 2. Monolayers formed more readily on the brominated carbon surfaces than on their chlorinated analogs, yielding a 2.46 ± 0.53 and 2.36 ± 0.17 times greater F:C ratio for 4tBM and Na4tBM molecules, respectively.

3.2.2 Nucleophile and Radical Effects—The effect of the sulfur atom's nucleophilic strength upon monolayer formation was also studied. Four derivatives of 4tBM, varying in their degree of thiol nucleophilicity, were prepared. These are (a) 4tBM itself, (b) 4tBM activated with one molar equivalent of pyridine, (c) Na4tBM, and (d) 1,2-bis(4-trifluoromethyl)benzyl)disulfane. The increasing order of nucleophilicity is (d), (a), (b), (c).

²⁴ Infrared measurements were used to monitor monolayer formation as a function of time for each molecule. Figure 6 shows that the rate of monolayer formation is strongly correlated with increasing nucleophile strength. For example, the Na4tBM monolayer forms in less than 24 h while the 4tBM molecule monolayer requires 72 h. Neither infrared nor XP measurements detected the presence of the 1,2-bis(4-trifluoromethyl)benzyl)disulfane molecule on the surface after 48h, suggesting that the disulfide sulfur species is not nucleophilic enough for monolayer formation.

To determine if a radical-mediated process was involved in monolayer formation, bromine-terminated carbon substrates were incubated with 100 mM 4tBM for 24 h in the presence of either a radical initiator (benzoyl peroxide) or inhibitor (2,6-di-*tert*-butyl-4-methylphenol, BHT). Two concentrations of radical initiator/inhibitor were used in these experiments (0.01 and 1 μ M) and the results for both concentrations were similar. Monolayer formation was neither enhanced nor hindered in the presence of the (1 μ M) radical inhibitor BHT, as the XP fluorine:carbon and sulfur:carbon ratios were similar to those obtained in the absence of BHT ($0.036(7) \pm 0.004$ and $0.037(2) \pm 0.003$, respectively). Neither fluorine nor sulfur was detected on the substrates incubated in the presence of the radical initiator benzoyl peroxide (1 μ M), however a much higher amount of oxygen was incorporated onto the surface (an oxygen:carbon ratio of 0.240 ± 0.008 as compared to 0.101 ± 0.007 for no radical initiator) suggesting that these reaction conditions favor surface oxidation over alkylthiol monolayer formation.

3.2.3 Concentration Effects—The effect of nucleophile concentration on monolayer formation was also studied by incubating bromine-terminated substrates in 1, 10, or 100 mM of (a) 4tBM, (b) pyridine-activated 4tBM, or (c) Na4tBM molecules. Figure 7 shows the F:C ratios obtained from XP survey spectra after a 24 h incubation period. These data show that the extent of monolayer formation is a function of both concentration and the strength of the thiol nucleophile, the latter is in agreement with the data shown in Figure 6. The effect of concentration on monolayer formation is most evident for the Na4tBM molecules, for which the F:C ratios are 0.028 ± 0.002 , 0.040 ± 0.003 , 0.066 ± 0.004 for 1, 10, and 100 mM, respectively.

3.3 Monolayer stability

An important aspect of functionalized substrates is their stability under ambient conditions, as many applications require surfaces to be further modified on the bench top. The stability of the alkylthiol monolayers formed on the carbon-on-metal substrates was probed with both XP and contact angle measurements. Here, 4tBM monolayers were prepared by incubating brominated carbon-on-metal substrates in 100 mM 4tBM for 24 h. Initial XP and contact measurements of each surface were obtained. The substrates were then incubated at room temperature for 96 h in separate vials in the dark. The hydrophobicity of the substrates was followed over a 96 h incubation period, during which contact angle measurements were obtained every 24 h. A second XP survey spectrum was obtained for each substrate at the end of the 96 h incubation. These two methods of surface analysis were chosen as changes in hydrophobicity correlate with the loss of 4tBM molecules from the surface, which can be determined with XP measurements.

3.3.2 Organic Solvent Environments—The 4tBM substrates were incubated in one of four anhydrous organic solvents (*tert*-butanol, tetrahydrofuran, benzene, and hexanes), representing varying degrees of solvent polarity. The ability to resist monolayer degradation under prolonged incubations in similar conditions is desirable in situations where organic synthesis reactions are performed *in situ* on the surface. Table 3 contains both the contact angle data and XP (F:C ratios from survey scans) measurements obtained at 0 and 96 hours.

Both measurements indicated that the 4tBM monolayers are retained during the incubation period, independent of solvent polarity. The average change in contact angle (-1.227 to $+0.300^\circ$) is well within the standard error associated with these measurements ($\pm 2^\circ$), indicating the hydrophobicity of the monolayer did not change. These data agree with the F:C ratios obtained with survey and C1s survey XP spectra.

3.3.3 Aqueous Solvent Environments—The 4tBM substrates were also incubated in a variety of aqueous environments (deionized water, 1 M MgCl_2 , 0.001 M and 1 M HCl , and 0.001 M and 1 M NaOH), which are common conditions for fabricating biomolecule arrays and/or performing on-surface biological assays. Table 3 contains the measured changes in the contact angle and the atomic composition of the surface obtained after a 96 h incubation period.

The 4tBM monolayers incubated in water and aqueous solution containing a weak acid or weak base retained their hydrophobic character throughout incubation. Here contact angle decreases ranging between 0.853° and 1.962° were observed and a loss of less than of the initial 2.32% of fluorine from each surface. Incubation in high salt (1 M MgCl_2) resulted in a contact angle decrease of 5.151° and a fluorine loss of 5.85%. Significant loss of fluorine and a contact angle decrease of 11.420° and 21.859° was observed for substrates incubated in aqueous solutions containing 1 M HCl and 1 M NaOH , respectively.

4. Discussion

4.1 Monolayer formation

A considerable amount of work has been reported in the literature on the self-assembly of alkylthiol monolayers on gold substrates.^{25,26} The versatility of this chemistry affords one the ability to readily tailor the chemical and physical properties of the gold surface for a multitude of applications and a large number of thiol-containing molecules have been developed, which can be translated to the halogenated carbon-on-metal substrates discussed in this work.

We have shown previously that Grignard reagents can be attached to halogenated carbon-on-metal substrates.⁸ In the present work, the reaction of thiol nucleophiles with these halogenated surfaces is studied with XP and infrared measurements. The formation of the alkylthiol monolayers, 4tBM in particular, on halogenated carbon provides unique chemical signatures that can be monitored and quantified, as evidenced in the XP survey (Figure 2) and C1s high-resolution (Figure 4) spectra. The 4tBM molecule also contains functional groups that are readily monitored with infrared reflection/absorption measurements (Figure 3).

The formation of 4tBM monolayers on halogenated carbon substrates was studied under a variety of reaction conditions, affording insight into its mechanism of formation. The reactivities of chlorine-, bromine-, and hydrogen-terminated substrates were compared. In addition, the effect of thiol nucleophilicity and concentration upon the rate and the degree of surface coverage was examined. The thiols did not react with unmodified carbon substrates, but did react with both chlorine- and bromine-modified surfaces. The rate of reaction with the chlorine-modified surface was substantially lower than that of the bromine-modified surface, as one would expect based upon their relative propensities as leaving groups, indicating that monolayer formation was proceeding via a possible substitution reaction mechanism.

Two possible substitution pathways, resulting in the covalent attachment of a 4tBM molecule to the surface, are (i) the formation of a carbocation and/or radical on the surface,

followed by molecule attachment (Scheme 2a) or (ii) a bimolecular process similar to an S_N2 reaction (Scheme 2b). The first option, resembling a unimolecular substitution reaction, is intuitively easier to conceptualize occurring on a surface than its S_N2 counterpart, largely due to the stereochemical consequences traditionally associated with a bimolecular reaction. Nevertheless, S_N2 -like mechanisms have been proposed on chlorinated silicon substrates and shown to be thermodynamically possible with theoretical calculations.^{27,28} Single-molecule gas phase studies of S_N2 reactions have also led to the proposal of an alternative mechanism pathway, which support the feasibility of a bimolecular substitution occurring on a surface.²⁹

The formation of a carbocation and/or radical on the surface is unlikely, based on the observations made in this work. First, the formation of either would lead to a loss of bromine on the surface when incubated in solvent alone, which is not observed (Figure 5a). The solvent used in these reactions was *tert*-butanol, which contains a nucleophilic tertiary alcohol, and could easily react with a surface-bound carbocation (S_N1 , solvolysis-like reaction) or radical species, forming a surface carbon-oxygen covalent bond. The oxygen-to-carbon ratio also remains constant after prolonged incubation in *tert*-butanol, suggesting that the solvent is not adsorbing to the surface. Studies of monolayer formation in the presence of a radical inhibitor (BHT) and/or a radical initiator (benzoyl peroxide) did not support a radical-based reaction mechanism.

4.2 Monolayer stability

Definitively determining that a sulfur-carbon covalent bond forms between the 4tBM molecule and a carbon surface with the methods commonly utilized in surface science is difficult as there is no unique spectroscopic signature that arises upon bond formation. Accordingly, we undertook an investigation of this issue using more indirect methods and determined the stability of the monolayer to heating and a variety of solvent and pH conditions.

4tBM monolayers were formed on brominated carbon-on-metal substrates and the XP spectra of the surfaces were obtained before and after heating. Less than 2.3% of the bound 4tBM molecules were removed from the surface after heating (60 minutes at 200 °C *in vacuo*). In set of control experiments, a 100 mM solution of 4tBM in benzene was placed on hydrogen-terminated or brominated carbon-on-metal substrates, the solvent was evaporated (approximately 10 minutes at room temperature), and XP spectra of the surfaces were acquired both before and after heating. In both cases, less than 2% of the initial fluorine signal was detected after 60 minutes of heating. The retention of the 4tBM molecules on the 4tBM monolayers indicates they are, in fact, not physisorbed to the surface. Similar stability has been observed for nanocrystalline diamond and amorphous carbon substrates, which have been covalently modified with trifluoroacetic acid protected 10-aminodec-1-ene (TFAAD) molecules.^{4,30}

In a second set of experiments, 4tBM monolayers were formed on brominated carbon-on-metal substrates and their responses to a variety of solvent and pH conditions were followed over a 96h incubation period with contact angle and XP measurements. Monolayers exhibiting a contact angle change of less than $\pm 2^\circ$, within the standard error of the measurements, were deemed unchanged. Contact angle measurements were supplemented with XP survey spectra, comparing the C:F ratio before and after the 96 h incubation period. Substrates incubated in strong acid/base conditions were degraded over time, however those incubated in organic solvents, deionized water, and mild acid/base conditions were unchanged. This information is summarized in Table 3. It should be noted that the S:C ratio was determined for each substrate before and after incubation, and the Δ S:C ratio (%) was

also calculated. The S:C percent change, for each of the incubation conditions, matched that of the F:C percent change, indicating the entire molecule was detaching from the surface.

5. Conclusion

Halogenated carbon substrates can readily be functionalized with alkylthiol monolayers, affording a new means of modifying carbon substrates. The alkylthiol used in this study, 4tBM, provided unique chemical signatures for studying monolayer formation with infrared and XP methods. A series of experiments showed that monolayer formation proceeds via a substitution pathway that strongly resembles an S_N2 reaction. It is shown that nature of the leaving group present on the surface and both the strength and concentration of the thiol nucleophile affect the rate of monolayer formation. The stability of the 4tBM monolayer when heated and/or incubated in organic or aqueous environments for prolonged periods of time support that a sulfur-carbon covalent bond is formed between the 4tBM molecule and the surface.

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Figure 1.

(a) (4-(trifluoromethyl)phenyl)methanethiol (4tBM), (b) 4tBM activated with pyridine, (c) sodium (4-(trifluoromethyl)phenyl)methanethiolate (NatBM), and (d) 1,2-bis(4-(trifluoromethyl)phenyl)disulfane molecules were used in this work.

Figure 2.

XP survey spectra of a carbon-on-metal substrate after (a) hydrogen termination in an RF-generated hydrogen plasma, (b) bromination by incubation of the substrate in 100mM PBr_5 in benzene with a catalytic amount of benzoyl peroxide for 60 minutes at 80 °C, and (c) monolayer formation by incubation in 100 mM 4tBM in *tert*-butanol for 24 hours.

Figure 3. Infrared spectrum of a 4tBM monolayer (100 mM 4tBM, 24 h) formed on a brominated carbon substrate. PM-FTIRRAS was utilized to monitor monolayer formation.

Figure 4.

High-resolution XP spectra of the C1s component of a carbon-on-metal substrate (a) after bromination and (b) 4tBM monolayer formation. Each spectrum contains an inset for the 291 – 295 eV range. This region, corresponding to carbon-fluorine bond, was used to calculate the number of 4tBM molecules attached to the surface.

Figure 5.

The formation of 4tBM monolayers, as a function of time, on brominated carbon-on-metal substrates was monitored with XP survey spectra. (a) Change in bromine:carbon ratio for substrates incubated in *tert*-butanol only (●) and *tert*-butanol containing 100 mM 4tBM (▲). (b) Change in fluorine:carbon (◆) and sulfur:carbon (■) as a function of monolayer formation.

Figure 6.

Integrated C-F signal obtained from infrared measurements of 4tBM (◆), 4tBM activated with pyridine (■), and Na4tBM (▲) molecule monolayers as a function of time. Each point is an average of $n=3$ substrates.

Figure 7.

Fluorine:carbon ratio obtained from XP survey spectra of monolayers formed (24 h incubation) with 1, 10, or 100 mM of 4tBM, pyridine activated 4tBM, or Na4tBM molecules.

Scheme 1.

Preparing alkylthiol monolayers on carbon substrates.

Scheme 2.

Possible substitution reaction pathways of alkylthiol molecules on brominated (X) carbon-on-metal substrates.

Table 1
Elemental Composition of Monolayers after Heating^a

	F:C ratio	S:C ratio
0 minutes	0.037±0.003	0.012±0.003
20 minutes	0.035±0.002	0.012±0.001
40 minutes	0.035±0.007	0.012±0.002
60 minutes	0.034±0.002	0.011±0.004

^aFluorine:carbon and sulfur:carbon ratios are the average XP survey spectral values obtained from three brominated carbon-on-metal substrates upon 4tBM monolayer formation (0 minutes) and after 20, 40, and 60 minutes of heating at 200 °C, *in vacuo*.

Table 2
Elemental Composition of Monolayer Formation^a

	F:C ratio	S:C ratio
Br^b	0.037±0.003	0.011±0.002
Cl^b	0.015±0.003	0.004±0.000
Br^c	0.066±0.004	0.018±0.003
Cl^c	0.028±0.001	0.006±0.001

^aFluorine:carbon and sulfur:carbon ratios are the average obtained from the XP survey spectra of three carbon-on-metal substrates after monolayer formation (100 mM 4tBM^b or 4tBMNa^c in *tert*-butanol for 24h).

Table 3
Changes in monolayer composition, after a 96 h incubation period, monitored with contact angle and XP measurements^a

	Δ Contact Angle (°)	Δ F:C ratio (%)
<i>tert</i> -Butanol	-1.2	-5.67%
<i>n</i> -Hexanes	-0.8	-6.58%
THF	0.8	2.96%
Benzene	0.1	-1.95%
H ₂ O	-0.9	-0.90%
1M MgCl ₂	-5.2	-4.32%
1mM HCl	-1.8	2.34%
1mM NaOH	-2.0	-1.38%
1M HCl	-11.4	-23.40%
1M NaOH	-21.9	-57.52%

^aThe changes in monolayer composition, after a 96 h incubation period, were monitored with both contact angle and XP measurements. Each value is the average of n=3 substrates, and the difference obtained between t = 0 h and t = 96 h. Changes in the F:C ratio were determined from XP survey spectra; percentage values are obtained from the average F:C ratio obtained for all the substrates at t=0h (0.037±0.005).