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Molecularly Ordered Decanethiolate Self-Assembled Monolayers on Au(111) from in Situ Cleaved Decanethioacetate: An NMR and STM Study of the Efficacy of Reagents for Thioacetate Cleavage

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The cleavage of decanethioacetate (C10SAc) has been studied by ^{1}H nuclear magnetic resonance (NMR) spectroscopy and scanning tunneling microscopy (STM) imaging of in situ prepared decanethiolate self-assembled monolayers (SAMs) on Au(111). Solutions of C10SAc (46 mM) and previously reported cleavage reagents (typically 58 mM) in CD_3OD were monitored at 20 °C by NMR spectroscopy. Cleavage by ammonium hydroxide, propylamine, or hydrochloric acid was not complete within 48 h; cleavage by potassium carbonate was complete within 24 h and that by potassium hydroxide or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) within 2 h. Similar cleavage rates were observed for phenylthioacetate. The degree of molecular ordering determined by STM imaging increased with increasing extent of in situ cleavage by these same reagents (2.5 mM C10SAc and 2.5 mM reagent in ethanol for 1 h, then 16 h immersion of Au/mica). Less effective cleavage reagents did not cleave the C10SAc sufficiently to decanethiol (C10SH) and gave mostly disordered SAMs. In contrast, KOH or DBU completely cleaved the C10SAc to C10SH and led to well-ordered SAMs composed of $(\sqrt{3} \times \sqrt{3})$R30° domains that are indistinguishable from SAMs grown from C10SH. Monolayer formation from thioacetates in the absence of cleavage agents is likely due to thiol or disulfide impurity in the thioacetates. Eliminating disulfide by using Bu_3P as a sacrificial reductant also helped to produce good molecular order in the SAM. The methods presented here allow routine growth of molecularly ordered alkanethiolate SAMs from thioacetates using reagents of ordinary purity under ambient, benchtop conditions.

Introduction

Self-assembled monolayers (SAMs) have become an important practical tool in surface science because of their ease of preparation and benchtop-friendly stability.[1] Their surface chemical and physical properties can be tailored by changing the exposed chemical functional groups, which can also be spatially patterned. SAMs can be used as a 2D matrix for supporting and isolating molecules, such as candidate molecules for electronics.[2] The most widely studied system on metallic surfaces is alkanethiol/Au(111), where the monolayer is anchored to the surface by Au−S chemisorption and stabilized by the intermolecular interactions of the rest of the molecule. The chemisorption of organothiols from solution or vapor onto gold is often a successful method to form molecularly ordered organothiolate monolayers. SAMs analogous to those of alkanethiols have also been grown from other derivatized molecules containing a thiol headgroup.[1,3−5] As described in the literature, we have also found that, under ambient, benchtop conditions organothiol samples contained and were prone to form disulfides. Compared to the parent thiol, disulfides typically have lower solubility and vapor pressure, properties that can affect the nature of SAM formation. The presence of disulfides in a nonrigorously purified thiol sample can lead to SAMs with a higher defect density[8] and a reduced degree of molecular order.[9] In the course of this study, we have found that the resulting SAMs formed in the presence of disulfides were often much more disordered than desired for molecularly resolved STM imaging. Our desired outcome was to develop methodology that could achieve high-quality, well-ordered, high-density, crystalline SAMs from organothiols under ambient benchtop conditions, namely, the $(\sqrt{3} \times \sqrt{3})$R30° structure readily prepared from pure decanethiol.

Deprotection of Thiol Derivatives. An approach to obtain thiols for SAM applications that minimizes undesirable disulfide formation is the use of a suitably protected thiol that can be deprotected in situ just before or during SAM formation. Thiocyanates,[10,11] *S*-tritylalkanethiols,[12] and especially acetyl-protected thiols (thioacetates)[3,13−16] have been developed as thiol

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precursors to circumvent disulfide formation while allowing for facile deprotection and monolayer formation. The approach has proved particularly effective for self-assembly of dithiols, where disulfide formation would lead to multilayer formation and, worse, polymerization. Favoring the application of the thioacetates are their convenient preparation from alkyl halides, their effective prevention of oxidative formation of disulfides upon storage, and the ready ability to cleave the thioester to release the thiol.

Deprotection of Thioacetates. Since thioacetates have seen the greatest scope of applications, we have focused our efforts on the use of thioacetate protection and cleavage to address our desire for a simple, reliable method that can be used to produce well-ordered SAMs under ambient conditions with routine benchtop procedures that do not require heroically pure materials. Herein, we highlight pertinent literature examples of in situ deprotection of thioacetates for self-assembly of thiolate monolayers, provide new NMR spectroscopy data for the extent of cleavage of decanethioacetate by various reagents in deuterated methanol or tetrahydrofuran, and show by STM imaging that conditions leading to faster, more complete thioacetate deprotection yield larger fractions of crystalline, molecularly ordered domains in the resultant decanethiolate monolayers formed by in situ deprotection of decanethioacetate.

An initial report on the in situ cleavage of organothioacetates for chemisorption onto gold used aqueous NH_4OH in THF.[3] The characterization of the resulting self-assembled monolayers in this and subsequent reports has relied chiefly on thickness determinations by ellipsometry, X-ray photoelectron spectroscopic (XPS), infrared reflection absorption spectroscopy (IRRAS), near-edge X-ray absorption fine structure (NEXAFS), electrochemistry, contact angle, and/or surface plasmon resonance (SPR) measurements.[1,3] Although these techniques measure bulk properties, such as average effective thickness and molecular tilt (IRRAS and NEXAFS), molecular ordering is not measured but, in the case of IRRAS, can be inferred from comparison to appropriate model systems. An accurate assessment of the molecular order and crystallinity of the SAM requires a direct imaging technique such as STM or a surface diffraction technique such as grazing incident X-ray diffraction (GIXRD) or low-energy atom diffraction (LEAD). One study used STM imaging to characterize SAMs produced by an in situ deprotection of thioacetates, but molecular resolution was not obtained.[7] To our knowledge, no systematic assessment of the molecular order of SAMs formed by cleavage of thioacetates has been undertaken.

Tour et al. reported that, when acetyl-protected arylthiols (0.1 to 41 mM) were initially reacted with NH_4OH in THF before exposing to gold surfaces, the resulting layer thickness was closer to that expected for a full monolayer of standing up molecules, than when no exogenous base was added (ellipsometry and XPS).[3] This result was attributed to a higher concentration of organothiolate being present due to base-catalyzed hydrolysis. Thiolate adsorption to the surface without exogenous base was suggested to possibly occur through initial adsorption of the thioacetates to the gold surface or by limited thioacetate hydrolysis by trace water or enols of the thioesters. NMR measurements were reported to indicate that hydrolysis of the thioacetate in THF-d_8 was complete within 10 min upon exposure to aqueous NH_4OH and that other bases such as *N*,*N*-dipropylamine or 4-*N*,*N*-dimethylaminopyridine (DMAP) were less effective.[3] In that same study, infrared measurements of one of the phenylene ethynylene molecules showed that these rigid-rod molecules were standing up, oriented within 20° of the surface normal, and had infrared intensities consistent with a full monolayer. Furthermore, absence of the carbonyl stretch from the thioacetate implied that deprotection of the molecules incorporated into the SAM was complete. Several other studies on SAM formation cited this initial work as support for in situ cleavage of other arylthioacetates and alkanethioacetates in various solvents through the addition of a wider range of exogenous bases. These conditions include the use of NH_4OH in EtOH, THF, or acetone−MeOH; Cs_2CO_3 in acetone/MeOH or conc. H_2SO_4 in CH_2Cl_2/MeOH;[16] triethylamine or NH_4OH in DMF;[17] NH_4OH or conc. H_2SO_4 in EtOH;[15] NaOH in EtOH;[18] or EtOH/H_2O.[7] Concentrations of the thioacetate compound ranged 0.1−1 mM and concentration of the cleaving agent 0.1 mM to 0.2 M. The cleaving agent to thioacetate mole ratio ranged from nearly unity to over a thousandfold excess.

Direct Use of Thioacetates. It has also been speculated that no cleavage agent is required to form the thiolate SAM, because it seemed that direct deprotection of the thiol could occur at the gold surface[3,14,19−22] SPR, XPS, and TOF-SIMs measurements for thioacetates of alkyl chains and oligo(phenylene ethylnylene)-based α,ω-dithioacetates in EtOH, THF, or 1:1 dichloromethane/EtOH showed that full monolayers can be formed directly from thioacetates.[14] Utilizing surface characterization by XPS and IRRAS, Lee et al. found that SAMs formed from alkanethioacetate are more disordered and less densely packed than the similar alkanethiol-derived SAMs.[21] In followup work, Wöll et al. showed that an ethanolic solution of decanethioacetate carefully purified to be free from thiol formed a molecularly ordered flat-lying decanethiolate monolayer on gold by STM. Only small regions of high-density upright-standing molecules were observed at defect sites and at the boundaries between larger phases of flat-lying molecules.[23] Thus, if direct cleavage occurs, it is not expected to occur at a rate sufficient to allow formation of large regions of dense upright phases. Additionally, XPS and IRRAS studies show that the molecule−gold interface in thioacetate-derived SAMs is predominantly thiolate; thioacetate, if present, is only present as a minority.[14,21] In summary, SAMs derived from thioacetates, of ordinary purity with or without cleavage by exogenous base, have been shown to produce thiolate SAMs with monolayer coverage, but with a large degree of uncertainty regarding long-range crystalline molecular ordering.

Results and Discussion

Given this diverse background for in situ cleavage under various conditions, we initiated an STM study to compare the structure and order of SAMs grown from decanethioacetates with and without the presence of a thioacetyl cleaving agent. As discussed below, we did observe striking differences in the quality of high-density, upright-standing SAMs produced in the presence of various cleaving agents. Although the exact percentages of molecularly ordered SAM regions were not quantified, the SAMs formed in the presence of different thioacetate cleaving agents ranged from almost completely disordered regions to almost

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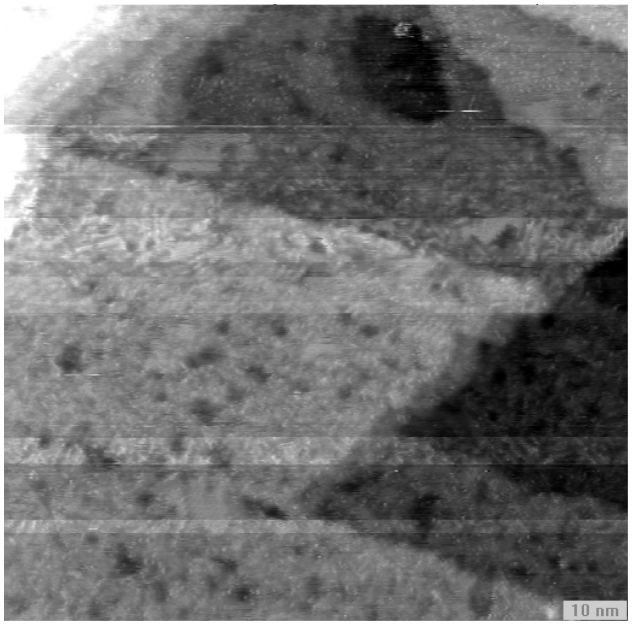

Figure 1. STM image of SAM on Au(111) grown for 16 h from C10SAc. The image is 100 nm × 100 nm. Tunneling conditions are $V_{sample} = -1$ V and $i_{tunnel} = 1$ pA. See text for details.

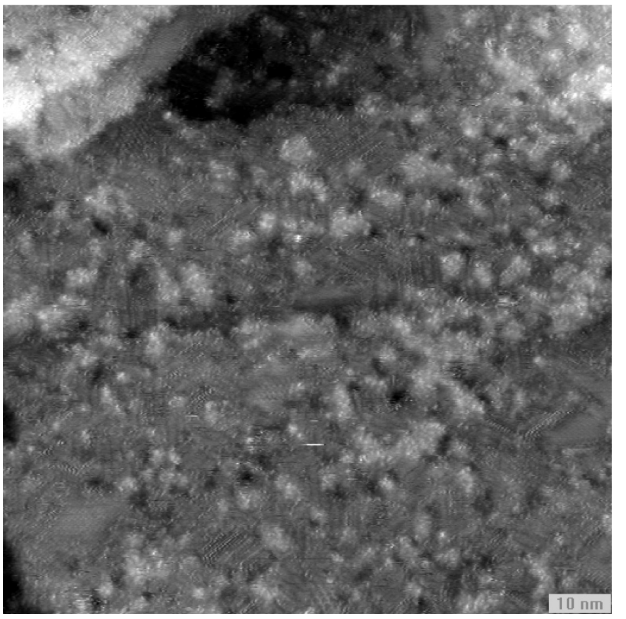

Figure 2. STM image of SAM on Au(111) grown for 16 h from C10SAc, precleaved for 1 h in NH_4OH. The image is 100 nm × 100 nm. Tunneling conditions are $V_{sample} = -1$ V and $i_{tunnel} = 1$ pA. See text for details.

completely ordered regions. This qualitative information is sufficient in setting procedures that favor the formation of well-ordered decanthiolate SAMs on Au(111).

The acetyl-protected decanethiol was purified by simple bulb-to-bulb vacuum distillation. The purified sample used in these studies contained 0.04% decanethiol and 0.01% decanedisulfide as determined by GC-MS integration using total ion current. The solutions were prepared in absolute ethanol and were 2.5 mM in the thioacetate. If a thioacetyl cleaving agent was used, its concentration was also 2.5 mM, and a solution of the mixture was allowed to stand for 1 h prior to use allowing time for cleavage to occur. All solution work was carried out under benchtop (ambient) conditions, with no attempts to exclude oxygen. Freshly H_2 flame-annealed (cleaned) Au(111)/mica substrates were immersed in this solution for 16 h. They were then removed, rinsed in absolute EtOH, and blown dry with dry N_2. All sample preparation was performed at room temperature under ambient atmospheric conditions. Constant current STM imaging was performed in a dry N_2 purged atmosphere, under conditions known to routinely produce excellent molecularly resolved images of decanethiol/Au(111) SAMs.[24]

STM Studies of Direct Adsorption of C10SAc. SAMs prepared from C10SAc without a cleaving agent appeared to consist of high-density upright chains that exhibited almost no discernible molecular ordering by STM imaging. The Au substrate step edges and vacancy islands were observed (characteristic of alkanethiol SAMs). Very rarely observed were small islands of the expected $(\sqrt{3} \times \sqrt{3})$R30° crystalline-molecular order, which were higher than the surrounding monolayer. (Figure 1 and Supporting Information Figure S12). Deposition of decanethiol under identical conditions leads to well-ordered monolayers composed of $(\sqrt{3} \times \sqrt{3})$R30° domains. Attempts to backfill the decanethioacetate-produced high-density but molecularly disordered SAM with decanethiol by re-exposure of the SAM to decanethiol (vapor or in ethanol at 60 °C) did not increase the molecular ordering of the SAM; this result indicates that the originally formed disordered monolayer is kinetically stable as would be anticipated for high-coverage, standing-up monolayers. Repeating the SAM growth at higher temperature (60 °C) with a fresh substrate likewise did not improve the order.

Cleavage of C10SAc by NH_4OH. Following the literature precedent, we next added NH_4OH as the thioacetyl cleaving agent in an attempt to form decanethiol in situ, allowing 1 h for the cleavage reaction to proceed before the Au substrate was introduced.[14−16] The STM images show a SAM with generally poor, but improved order (Figure 2). The structure is manifested by two distinct types of regions with different heights. In the lower regions, generally no molecularly resolved imaging could be observed. In the higher regions, a $(\sqrt{3} \times \sqrt{3})$R30° molecular lattice was sometimes observed. The statistical percentage of molecularly ordered domains was not determined.

While these highly disordered SAMs are disappointing, our results are nevertheless consistent with the results of Tour and others who found near-monolayer coverages of high-density, standing-up molecules of undetermined molecular ordering. However, our results stand in contrast to the rigorously purified thioacetate in the work of Wöll et al., where highly ordered SAMs of the lying-down phase of decanethiolate are predominantly observed.[23] Our C10SAc samples, purified by bulb-to-bulb vacuum distillation and stored in glass vials, contained traces of decanethiol (0.04%) and decanedisulfide (0.01%). The trace thiol could be present through co-distillation or through trace hydrolysis on the glassware, and although it was below the detection limit of normal NMR measurements, its presence could be determined by GC-MS measurements. It seems reasonable that trace thiol, or perhaps even trace disulfide, could adsorb in preference to thioacetate. As discussed below, the extent of thioacetate cleavage by NH_4OH under our monolayer-forming conditions is perhaps too limited to provide a sufficiently high concentration of decanethiolate needed for the formation of a uniformly well-ordered monolayer. Therefore, we propose that either trace thiol or disulfide already present in our thioacetate samples is the principle component involved in formation of the monolayers. At the low

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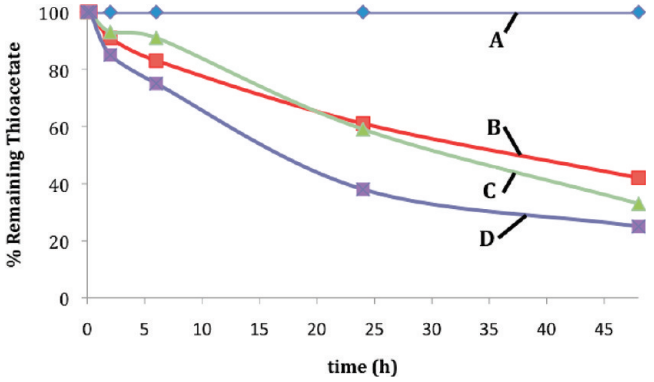

Figure 3. C10SAc (46 mM in CD_3OD) cleavage by NMR monitoring. A: no additive. B: NH_4OH (115 mM). C: HCl (250 mM). D: propylamine (70 mM).

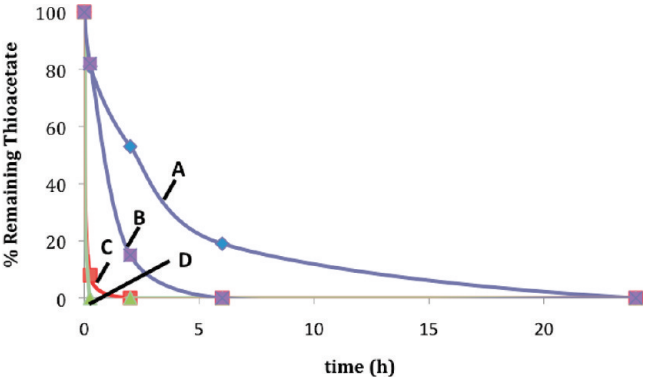

Figure 4. C10SAc (46 mM in CD_3OD) cleavage by NMR monitoring. A: K_2CO_3 (46 mM). B: NH_4OH (575 mM). C: DBU (58 mM). D: KOH (58 mM).

concentrations of decanethiol likely present in our samples, initially physisorbed thioacetate could inhibit formation of well-ordered crystalline regions, in a manner analogous to that reported for disulfides.

NMR Studies of C10SAc Cleavage. In order to gain insight into the extent of thioacetate cleavage, we examined NH_4OH for the cleavage of the thioacetate of decanethiol. In contrast to the report in the literature that NH_4OH completely cleaved arylthioacetates within 10 min in THF-d_8, we noted a slow cleavage of C10SAc (58 mM) and NH_4OH (115 mM) in CD_3OD at room temperature under air (58% cleavage after 48 h, Figure 3). During the time course of this reaction, the disulfide concentration also steadily increased to 31% after 48 h (Supporting Information Figure S4). The reaction course was monitored by ^{1}H NMR spectroscopy by integrating the methylene hydrogen atoms adjacent to the sulfur atom. These hydrogen atoms give characteristic and different signals in CD_3OD for the thioacetate (AcSCH_2−, 2.85 ppm), the thiol (HSCH_2−, 2.50 ppm) and the disulfide (−CH_2S−SCH_2−, 2.68 ppm) groups (see Supporting Information Figures S1−S3). The disappearance of the acetyl methyl group (2.30 ppm) can also be monitored for the extent of thioacetate cleavage. The detailed hydrolysis or methanolysis fate of the acetate group itself was not determined. When the NH_4OH concentration was increased to 575 mM, the cleavage was complete within 6 h (Figure 4). The extent of cleavage in the 2.5 mM solutions used to grow the SAMs will be considerably lower than observed in our NMR studies, where higher concentrations were used to improve NMR signal levels.

The low extent of thioacetate cleavage observed with NH_4OH in the methanol-d_4 correlates with a small fraction of the thioacetate converted to thiol in the SAM growth solution. Although more thiol (or disulfide) is present after treatment with NH_4OH, most of the thioacetate remains uncleaved. This supports our earlier speculation and explains why NH_4OH pretreatment is not dramatically different than no cleavage agent at all in the formation of large regions of molecularly ordered SAMs.

In order to facilitate the formation of not only high-density and well-defined, but also molecularly ordered decanethiolate monolayers on gold, we examined various exogenous bases for the in situ cleavage of the thioacetate moiety. Given the range of reagents and solvents reported for the thioacetate cleavage in the literature, we initially decided to screen, by NMR spectroscopy, the ability of several reagents to cleave C10SAc. Since our standard solvent for SAM formation of alkanethiolates on gold is absolute ethanol, we used methanol-d_4 as a suitable model solvent in these spectroscopic measurements. We hypothesized that reagents and conditions that led to faster and more complete cleavage of the thioacetate to form decanethiolate should be better for forming the well-ordered monolayers typically seen when decanethiol is used directly.

The cleavage of thioacetates under basic conditions has been studied mechanistically and was found to primarily occur by a slow addition of hydroxide (formed by the reaction of exogenous bases such as amines to water) to the thioacetate to form a tetrahedral intermediate that rapidly breaks down to form the cleavage products.[25,26] Similarly, protonation would activate the thioacetates toward addition of water or alcohols to form a tetrahedral intermediate that could decompose to liberate the thiol. We examined the use of aqueous concentrated HCl for acid-catalyzed cleavage in CD_3OD and *n*-propylamine as an additional amine base that could potentially react through acyl transfer to the amine as well as undergo the base-catalyzed cleavage. Although these reaction conditions led to some cleavage of the thioacetate, they also did not reach completion within 48 h even at these relatively high concentrations needed for the NMR measurements (Figure 3). In each case, the amount of disulfide steadily increased—to 11% after 48 h with HCl and 48% with propylamine (Supporting Information Figures S5 and S6). Since the weak base sodium citrate is often used in the production of gold nanoparticles,[27] we also examined its efficacy to cleave thioacetates. When sodium citrate (58 mM) and C10SAc (46 mM in CD_3OD) were reacted, no thioacetate cleavage was observed over 48 h—essentially the same result as obtained with methanol-d_4 alone.

Turning to stronger bases, thioacetate cleavage by K_2CO_3 in CD_3OD was studied; the NMR spectroscopic results indicated complete cleavage within 24 h with 19% disulfide after 48 h (Figure 4 and Supporting Information Figure S7). Presumably, carbonate is more effective at forming a higher concentration of the nucleophilic CD_3O^- K^+ species. The two strongest bases studied, KOH and DBU, led to complete cleavage of the thioester within minutes for KOH and within 2 h for DBU (Figure 4). In each case, disulfide continued to steadily form over the 48 h period studied to 30% and 46%, respectively (Supporting Information Figures S8 and S9). The rapid thioacetate cleavage by these two reagents can be readily understood in terms of their basicity (aqueous pK_a of conjugate acid is about 16 in each case), which would lead to the formation of a high concentration of CD_3O^- (K^+ or H-DBU$^+$).

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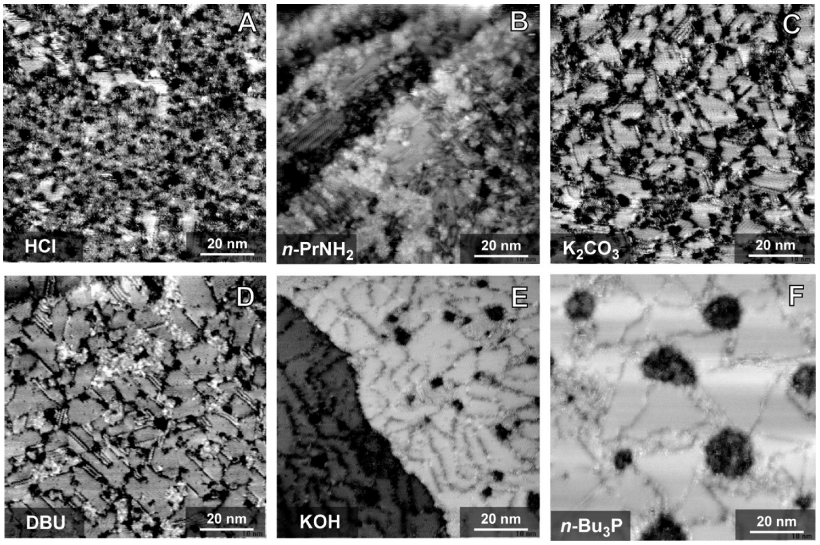

Figure 5. STM images SAMs on Au(111) grown for 16 h in 2.5 mM C10SAc in EtOH grown from a solution premixed for 1 h with 2.5 mM of (A) HCl, (B) $PrNH_2$, (C) K_2CO_3, (D) DBU, (E) KOH, and (F) Bu_3P. Each sample was grown from 2.5 mM each in ethanol (1 h premix, 16 h immersion of Au/mica). All STM images are 100 nm × 100 nm. Tunneling conditions are $V_{sample} = -1$ V and $i_{tunnel} = 1$ pA. See text for details.

Although we normally do not use THF solutions for alkanethiolate SAM formation on gold, we examined the extent of thioacetate cleavage by NMR spectroscopy in THF-d_8 by NH_4OH, Cs_2CO_3, and DBU in order to provide some additional comparison points to the literature. When no exogenous base was used or when Cs_2CO_3 (46 mM) or NH_4OH (58 mM) were reacted with C10SAc (46 mM), no cleavage was observed over 48 h. The use of more concentrated NH_4OH (173 mM) or DBU (58 mM) did cleave the thioacetate, albeit to a lower extent than when the reaction was studied in methanol-d_4 (29% and 72% cleavage at 24 h, respectively).

STM Imaging of in Situ Deprotected C10SAc. We prepared companion C10SAc samples to the NMR studies for STM imaging using different cleaving agents following the procedure described above for the NH_4OH cleaved SAMs. Figure 5 shows a resulting set of STM images and companion images at different scan sizes are given the Supporting Information (Figures S13−S17). These images were selected to be representative of the monolayer structure observed over many samples and hundreds of images. All samples showed Au(111) substrate steps and vacancy islands, typical of alkanethiol SAMs. The SAM produced by HCl-treated thioacetate (Figure 5A and Supporting Information Figure S13) exhibited the smallest fractional area of ordered regions of this set. The HCl result is very similar to that found for NH_4OH, which agrees with their similarly low extent of cleavage (Figure 3). As expected, *n*-$PrNH_2$ produced slightly better order (Figure 5B). In comparison, the SAM produced by K_2CO_3-treated thioacetate was significantly more ordered (Figure 5C and Supporting Information Figure S14). DBU and KOH are highly effective, showing a high degree of order (Figures 5D and E, respectively).

The molecular order can be qualitatively assessed visually from the definition of the structural domain boundaries, which appear between the crystalline domains of different orientation and substrate registration. The most prevalent domain boundaries are the missing zigzag row, which are observed as the straight lines between the different domains and run in the Au ⟨110⟩ crystallographic directions. When there are few ordered domains, there are no structural domain boundaries; the well-ordered regions are crystalline islands surrounded by lower disordered regions. As the crystalline order increases to an intermediate level, the structural domain boundaries appear between neighboring crystalline domains. The disordered regions appear interstitial to some ordered regions, existing as connected areas and expanded domain boundaries. Finally, very well-ordered SAMs have a high degree of crystalline order and the entire surface is composed of domains with crystalline order directly separated by domain boundaries, but with little or no disordered regions.

We note that, when there is a low to intermediate degree of order, the disordered regions image lower than the crystalline regions. However, when there is a high degree of order, the sparse, isolated disordered regions appear higher. This effect is seen dramatically in the DBU STM image in Figure 5D. Understanding the origin of this effect would require better characterization of the chemical composition of these dense-disordered regions that are higher than the ordered regions. .

Cleavage of Phenylthioacetates. Because most of the literature reports are for in situ cleavage of arylthioacetates, we extended our NMR study to the cleavage of phenylthioacetate by NH_4OH, HCl, KOH, and DBU, but did not attempt to form SAMs from these samples. In each case, we observed similar extents of cleavage as obtained with C10SAc (Supporting Information Figure S11). Our NMR results are consistent with other cleavage measurements in the literature.[26] Thioacetate cleavage followed using UV shows completion after 30 min (0.5 mM aryl SAc with 37.5 mM NH_4OH in acetone/MeOH).[16] When the levels of electrode passivation by adsorption were studied using cyclic voltammetry, it was found that more than an hour of precleavage was required for the adsorption rate to saturate when strong base at low concentrations (aryl thioacetate 0.1 mM with 0.27 mM NaOH in EtOH) was used.[17]

Effect of Added Tributylphosphine. An advantage of the in situ cleavage methods described here is that all experiments were run conveniently at ambient temperature with no efforts to exclude air or to limit the interaction of the cleavage reagent with the surface. A potential drawback of this approach is that significant amounts of disulfide can be formed, especially under prolonged employment of more basic conditions. In order to combat the disulfide formation, we examined the use of the sacrificial reductant tributylphosphine (Bu_3P) to convert disulfides to

thiols.[28] When the NMR-monitored thioacetate cleavage was performed with C10SAc (46 mM), DBU (58 mM), and Bu_3P (58 mM), cleavage was again almost complete within 15 min and was complete by 2 h. In the presence of Bu_3P, however, no disulfide was observed even after 48 h (Supporting Information Figure S10). The monolayer formed on gold/mica (C10SAc 2.5 mM, DBU 2.5 mM, Bu_3P 2.5 mM in ethanol, 1 h premixing, 16 h immersion) gave mostly well-ordered domains as was seen with DBU alone (Supporting Information Figure S17). Thus, neither the Bu_3P nor the DBU interfered with the formation of highly ordered monolayer.

When C10SAc in methanol-d_4 was reacted with just Bu_3P, no cleavage was observed by NMR spectroscopy through 48 h. The Bu_3P apparently did not produce enough methoxide through deprotonation of methanol, nor was it nucleophilic enough to directly cleave the thioacetate in methanol solution. Surprisingly, companion STM samples using the Bu_3P as the cleaving agent produced well-ordered SAMs (Figure 5F)—as good as those produced from the strong bases DBU and KOH (Figure 5D,E). Although the size of the vacancy islands in the Bu_3P SAM STM image are significantly larger than in the other images, this is not characteristic of the Bu_3P, but peculiar to this particular sample.

It is useful to speculate how addition of Bu_3P could lead to well-ordered SAMs without apparent prior cleavage of the thioacetates. Bu_3P is a weak base but a good nucleophile. Coordination of the thioacetate to the gold surface may activate the nucleophilic cleavage of the thioacetate bond through nucleophilic addition of the Bu_3P to the carbonyl and expulsion of an acetylphosphonium group. Bu_3P is also a reducing agent—and can convert all disulfides to thiols. The trace disulfide present in our C10SAc could lead to disordered monolayers that are a mixture of the disulfide and thioacetate or a mixture of thiol, disulfide, and thioacetate. Converting all the disulfide to thiol may allow the thiol to effectively displace any initially adsorbed thioacetate. Finally, phosphines are known to adsorb weakly on Au surfaces and can be readily displaced by more strongly binding thiols that form more ordered SAMs.[29] Whatever the mechanism, we observe that equimolar concentrations of Bu_3P can substantially improve the quality of our SAMs.

Summary. In conclusion, we can correlate the extent of cleavage of the thioacetate of decanethiol in methanol-d_4 as determined by NMR spectroscopy with the ability of in situ thioacetate deprotection schemes to produce larger fractions of well-ordered crystalline decanethiolate monolayers on Au(111). The conditions that produced most complete thioacetate cleavage within 2 h also produced the most ordered monolayers. Addition of Bu_3P as a sacrificial reductant was also helpful in this regard. Furthermore, based on our results presented here and the cited literature, we conclude that SAMs formed using thioacetates of ordinary purity grow from the thiol and/or disulfide impurities even in the presence of amines and alkali metal bases from the cleavage reagents. The poor SAM molecular order produced in the presence of a large excess of uncleaved thioacetate is likely caused by initial physisorption of the thioacetate onto the surface in a way that inhibits highly ordered phases from forming.

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Experimental Section

Preparation of C10SAc. Following literature precedent, potassium thioacetate (2.0 g, 17.5 mmol) was added to 1-bromodecane (2.0 g, 9.0 mmol) in absolute ethanol (50 mL) at room temperature under nitrogen. After stirring for 24 h, the solvent was removed in vacuo. The residue was partitioned between ice-cold water (100 mL) and diethyl ether (3×50 mL). The combined organic portion was washed with water (3×50 mL), dried ($MgSO_4$), and the solvent removed by rotary evaporation. The crude C10SAc containing decanethiol (0.6%) and decanedisulfide (2%) as determined by GC-MS measurements was purified through two bulb-to-bulb distillation cycles under vacuum (0.2 mm) to give 1-decanethioacetate as a pale yellow liquid (1.09 g, 56% yield). The ^{1}H NMR spectrum matched that reported in the literature.[21] GC-MS analysis of the purified decanethioacetate determined that trace decanethiol (0.04%) and decanedisulfide (0.01%) were present in the sample.

^{1}H NMR Spectroscopic Monitoring of Thioacetate Cleavage. Separate solutions of C10SAc (92 mM in methanol-d_4) and the reagent to be investigated (typically 116 mM in methanol-d_4) were mixed in equal portions to give final concentrations of 46 mM in C10SAc and typically 58 mM in reagent just prior to measuring the first NMR spectrum. These samples in methanol-d_4 were left in capped NMR tubes at room temperature and were periodically monitored by NMR spectroscopy. The ratios of thioacetate, thiol, and disulfide were based on the integration of the methylene signals at 2.85, 2.48, and 2.67 ppm for these three compounds in CD_3OD, respectively.

Preparation of Samples for STM. Separate solutions of C10SAc and the reagent to be investigated (KOH, DBU, K_2CO_3, aqueous conc. HCl, aqueous 30% NH_4OH, and DBU/Bu_3P) were freshly prepared in absolute ethanol with initial concentrations at 7.5 mM. The solutions of C10SAc and the reagent were mixed with additional ethanol to give final concentrations of 2.5 mM in each. The mixture was allowed to stand for 1 h prior to use allowing time for cleavage to occur. All solution work was carried out under benchtop (ambient) conditions, with no attempts to exclude oxygen. H_2 flame-annealed (cleaned) Au(111)/mica substrates were then immersed in this solution for 16 h. They were then removed, rinsed in absolute EtOH, and blown dry with dry N_2. All sample preparation was performed at room temperature under ambient atmospheric conditions.

STM Measurements. Constant-current STM imaging was performed in a dry N_2 purged atmosphere, under conditions known to routinely produce excellent molecularly resolved images of C10SH/Au(111) SAMs, $V_{sample} = -1$ V and $i_{tunnel} = 1$ pA.

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Supporting Information Available: Charts of cleavage progress, STM images for SAMs formed by in situ cleavage of C10SAc. This material is available free of charge via the Internet at http://pubs.acs.org.